Electronic Supplementary Material (ESI) for Photochemical & Photobiological Sciences.

Self-Initiation of UV Photopolymerization Reactions Using Tetrahalogenated Bisphenol A (Meth)Acrylates

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Supplemental Information

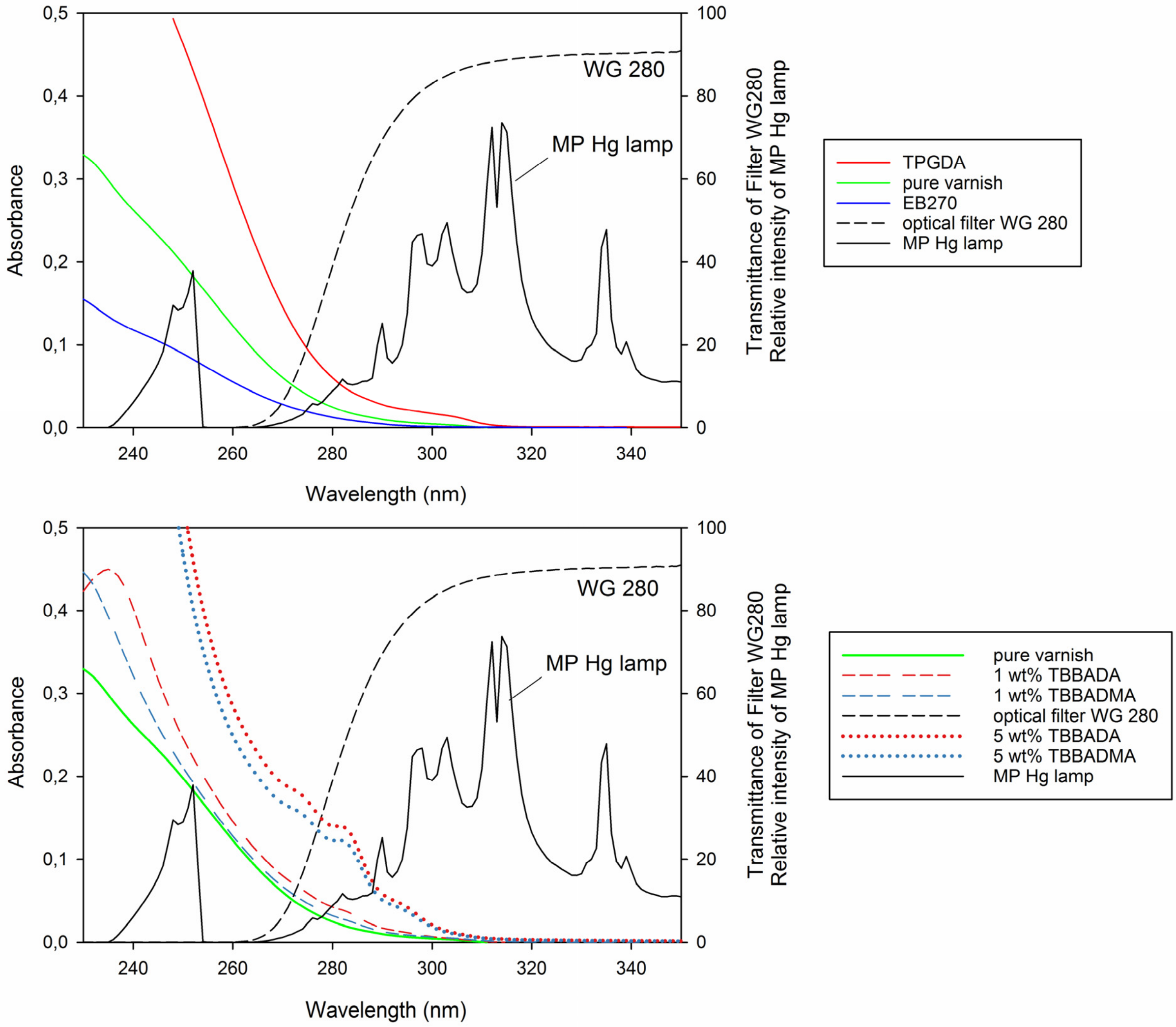

Fig. S1: Absorption spectra of thin layers (10 µm thick) of formulations in comparison to the emission spectrum of the medium-pressure mercury lamp and the transmission of a WG 280 edge filter.

Top: Absorbance of pure varnish (30 wt% TPGDA / 70 wt% EB270) and its individual components. Please note that the absorption spectrum of the pure varnish extends up to 300 nm, thus direct excitation ist possible, even by the higher wavelength part of the medium-pressure mercury lamp when the WG280 edge filter is applied.

Bottom: Pure varnish and formulations containing 1 wt% or 5 wt% of brominated bisphenol di(meth)acrylates. A concentration of 1 wt% of the halogenated bisphenol acrylates does not increase significantly the absorbance properties (and thus the polymerization efficiency). At higher concentrations (≥ 5 wt%) a significant effect is expected for both irradiation with the high energy part at $\lambda \sim 250$ nm and with light with $\lambda > 270$ nm (using the WG 280 edge filter). The expected response to $\lambda > 270$ nm would allow the curing of thick layers.

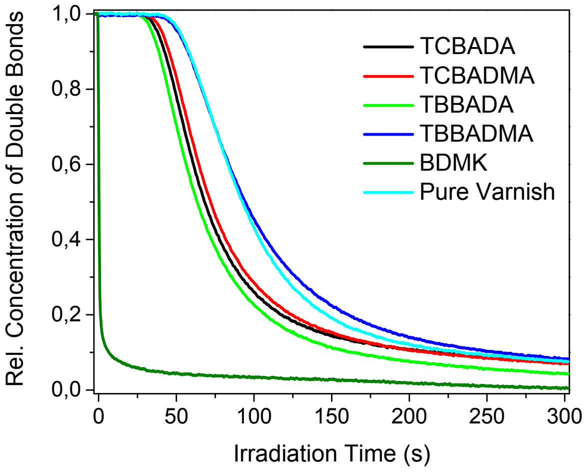

Fig. S2: Kinetics of the photopolymerization of the TPGDA/EB270 varnish with 1 wt% of tetra-halogenated bisphenol A di(meth)acrylates or BDMK, in nitrogen atmosphere with a 280 nm edge filter and a remaining light intensity of 124 mW cm^{-2}.

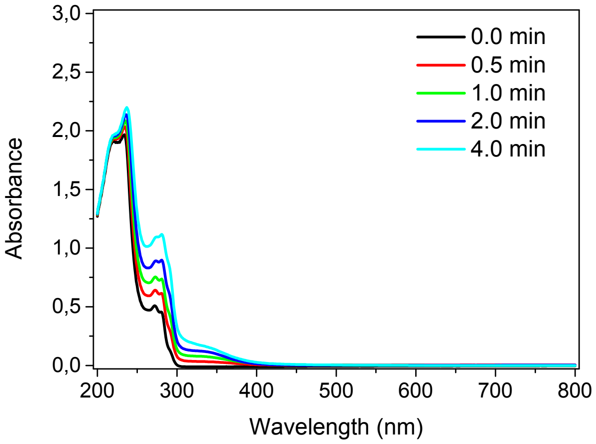

Fig. S3: UV-Vis spectra of solutions of tetrachlorinated bisphenol A diacrylate in acetonitrile ([c] = 10^{-3} mol L^{-1}) after various periods of irradiation with a 254 nm lamp (16 mW cm^{-2}).

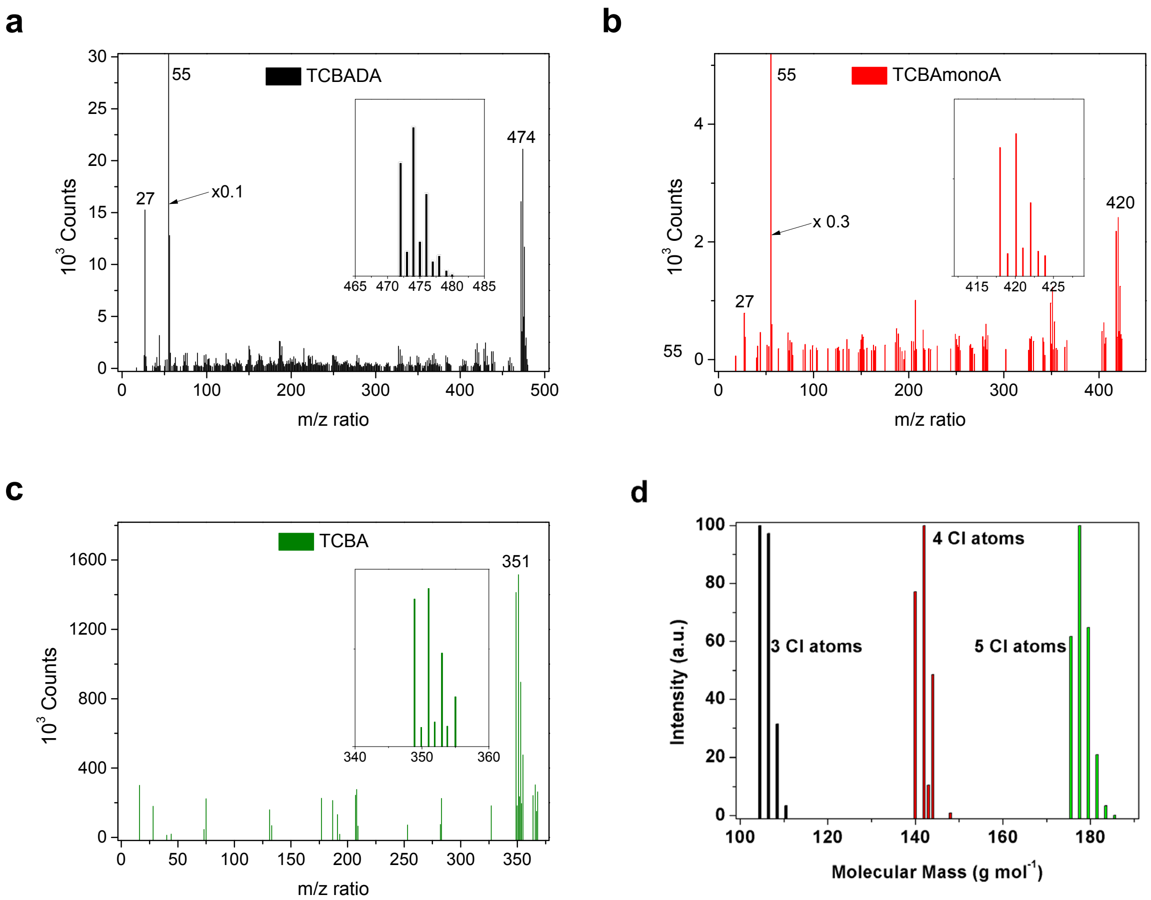

Fig. S4: Mass spectra and isotopic splitting patterns of the molecular ion peaks of TCBADA (a), TBBAmonoA (b) and TCBA (c) obtained during the GC-MC analysis of TCBADA solutions and theoretical isotopic splitting patterns for a polychlorinated molecule (d).

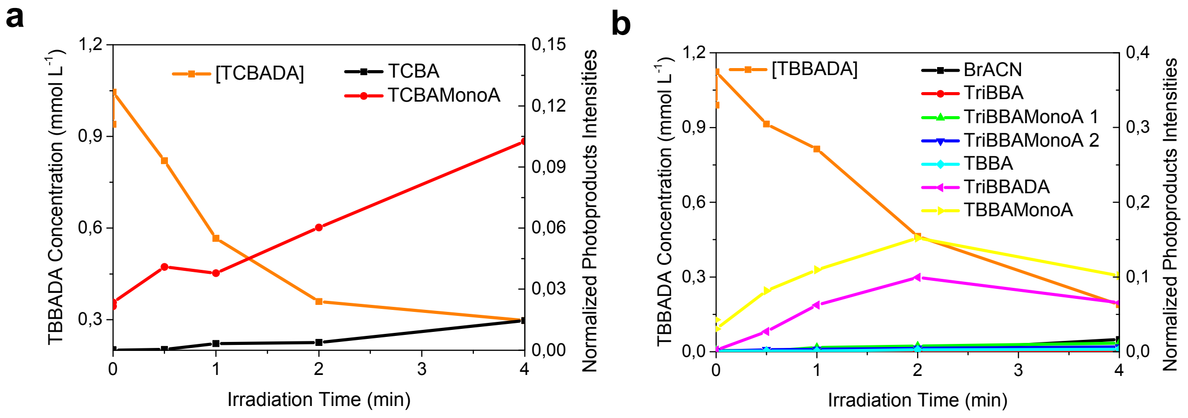

Fig. S5: Time dependence of the TCBADA (a) and TBBADA (b) consumption and corresponding photoproducts formation vs. irradiation time. The tiny decrease at t = 0 min is due to the degassing of the solution via a bubbling and thus increase of the concentration.

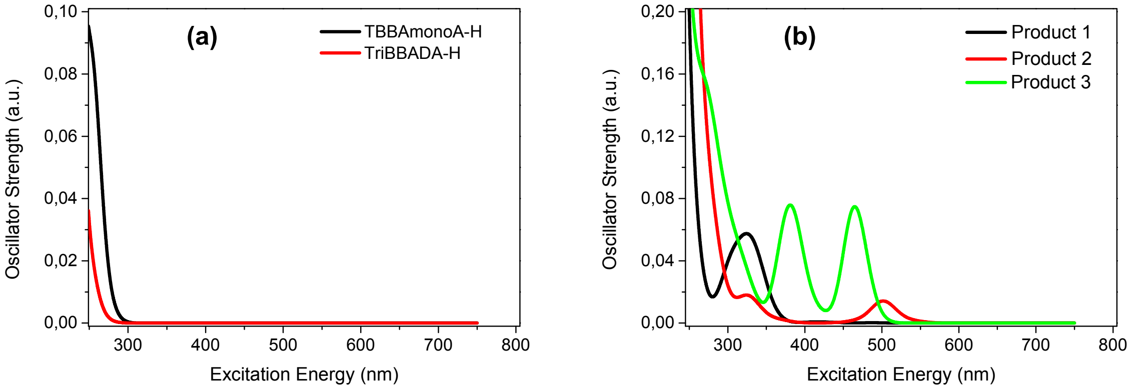

Fig. S6: Calculated UV-Vis spectra of TBBAmonoA (i.e. TBBAmonoA• after H-abstraction from the solvent) and TriBBADA (i.e. TriBBADA• after H-abstraction from the solvent) ground state molecules (a) and transients after addition of radicals to the double bond of another ground state molecule (product 1: model case of addition of Br• on (3-methyl-2,5-bromobenzene) acrylate; product 2: addition of Br• to another TBBADA; product 3: addition of an acrolein radical to another TBBADA) (b).

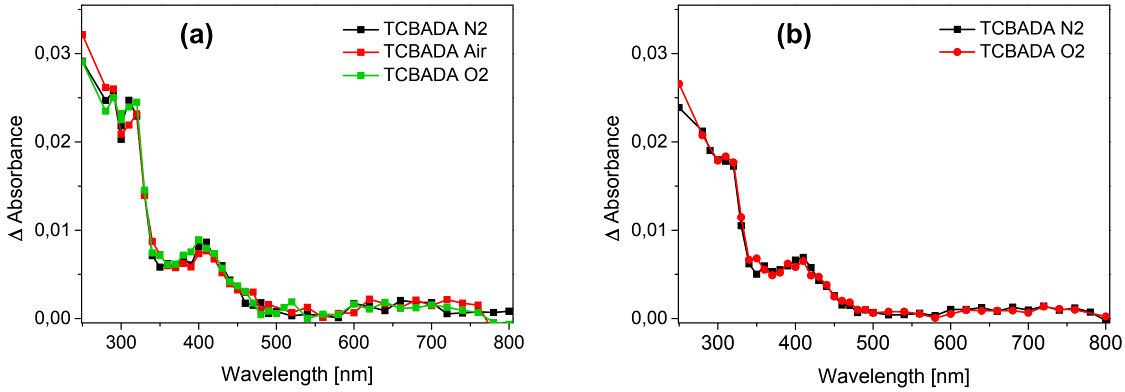

Fig. S7: UV-Vis spectra of the transients formed after photolysis with 266 nm / 6 mJ pulses of the TCBADA solutions at 5×10^{-4} mol L^{-1} in acetonitrile under various gas-saturated conditions 100 ns (a) and 100 µs (b) after the laser pulse.

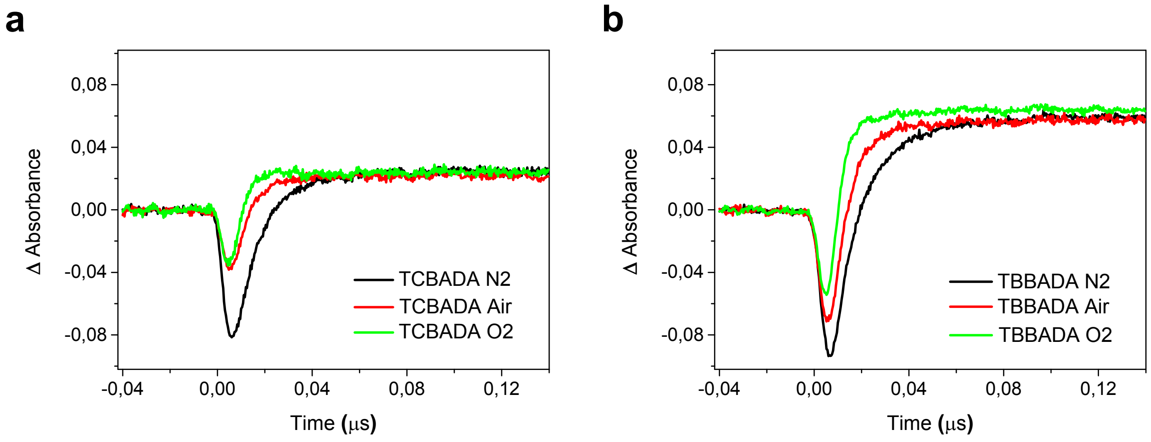

Fig S8: Transient absorbance observed at 300 nm after laser flash photolysis with 266 nm / 6 mJ pulses of (a) TCBADA and (b) TBBADA solutions at 5×10^{-4} mol L^{-1} in acetonitrile under various gas-saturated conditions.

Although UV-Vis absorption spectra were very similar for different oxygen concentrations, kinetic curves at 300 nm (i.e. assumed to be attributed partially to the triplet state signal) displayed in Fig S8a and S8b are evidence of a small influence of the oxygen concentration. In case of chlorinated samples, the kinetics in nitrogen-saturated atmosphere is composed of a drop and then a “recovery” of the signal. This behavior was attributed to the overlap of (1) the bleaching of the (meth)acrylates at the ground state and concomitant formation of the excited state (probably triplet) with a lower absorption coefficient – responsible for the drop –, (2) the decay of the triplet state (back to ground state) – inducing a fast increase of the signal and (3) the formation of transients due to the cleavage. The presence of oxygen in the solution led to a rapid deactivation of the triplet state molecules and thus a faster recovery of the signal. As the product spectra are not affected (see Fig S7a+b), the formation of products is likely not to arise from the triplet state T_1, but rather the excited singlet state S_1. The apparent smaller drop in case of air- and oxygen-saturated measurements was due to the limited time resolution of the LFP setup unable to record the sharp signal drop. Similar influence of the atmosphere was monitored during the measurement of brominated samples. In the latter case the competitive formation of TriBBADA-OO$^{\bullet}$ radicals (see main paper) is additionally overlapping the transient spectra, making decisive conclusions more difficult.

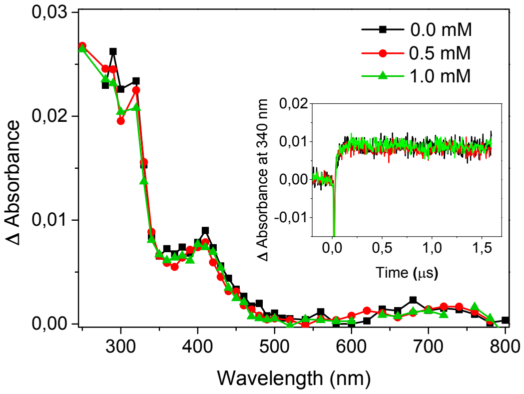

Fig. S9: UV-Vis spectra of the transients (main figure) and transient absorbance observed at 300 nm (inset) formed after photolysis of TCBADA solutions (5×10^{-4} mol L^{-1} in acetonitrile) containing different scavenger concentrations with 266 nm / 6 mJ pulses.

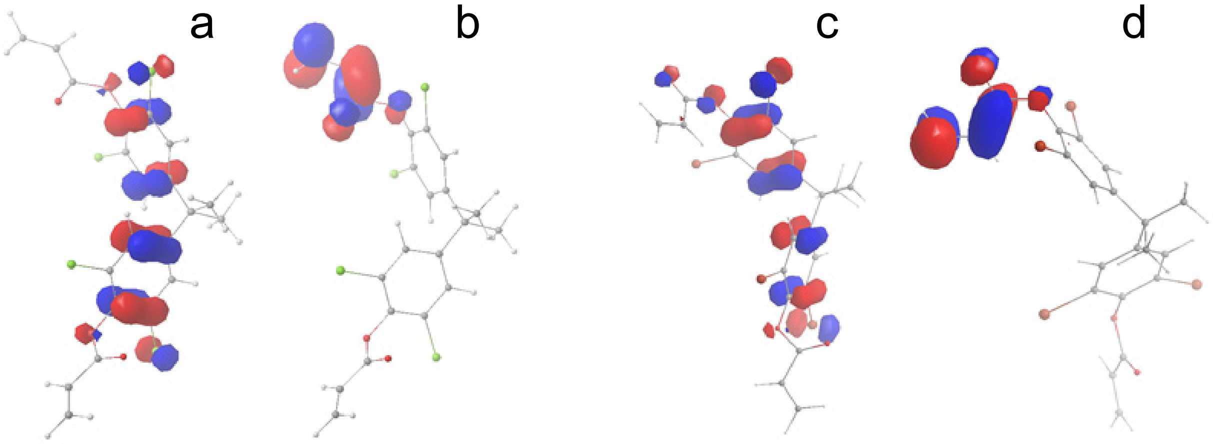

Fig. S10: HOMO and LUMO orbitals obtained by quantum chemical modeling of the tetrahalogenated bisphenol A diacrylates: (a) TCBADA HOMO (-6.769 eV), (b) TCBADA LUMO (-1.562 eV), (c) TBBADA HOMO (-7.891 eV), (d) TBBADA LUMO (-1.662 eV).