ELECTRONIC SUPPORTING INFORMATION

Probing the first steps of photoinduced free radical polymerization at water-oil interfaces.

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Experimental procedures.

Materials. Dioctyl sulfosuccinate sodium salt (AOT, 96%, Sigma-Aldrich), octane (anhydrous, Sigma-Aldrich), 4-acryloylmorpholine (NAM, 97% Sigma-Aldrich) and styrene (ST, ReagentPlus, Sigma-Aldrich) were used as purchased without further purification. Photoinitiators (PI) bis(2,4,6-trimethylbenzoyl)-phenylphosphaneoxide, Irgacure 819[®] (BAPO) and 2,4,6-trimethylbenzoyldiphenylphosphane oxide, Lucirin-TPO[®] (MAPO) were obtained from CIBA Geige (currently part of BASF). Double distilled water was used for all experiments.

TR-EPR Spectroscopy. Continuous-wave time-resolved (TR) EPR experiments were performed on a Bruker ESP 300E X- band spectrometer (without magnetic field modulation) equipped with a 125 MHz dual channel digital oscilloscope (Le Croy 9400). The frequency tripled Nd:YAG laser light (InnoLas Spitlight 400, 355 nm, operating at 20 Hz, ca. 7 mJ/pulse, 8 ns) was used for irradiation. The setup is controlled by the fsc2 software developed by Dr. J. T. Toerring (Berlin). Spectra were recorded by acquiring the accumulated (50 accumulations) time responses to the incident laser pulses at each magnetic field value of the chosen field range (field steps: 0.1 mT). Argon-saturated solutions in octane with 0.7 M AOT (saturated photoinitiator concentration <10 mM) or AOT/octane/water micro-emulsion (with 0.7 M AOT in 2:1 v.v., sat. PI <10mM) were pumped through a quartz 1 mm i.d. tube positioned in the cavity of the EPR spectrometer using a flow system (flow rate: 2-3 mL min⁻¹). Experiments with the addition of 0.12 M of monomers (NAM, ST), were performed in the same system. The EPR spectra were analyzed and simulated with the Easyspin toolbox.¹

1 S. Stoll, A.Schweiger, J. Magn. Reson. 2006, **178**, 42–55.

³¹**P** NMR. ³¹P NMR spectra were recorded on Bruker AVANCE DPX 200MHz NMR spectrometer using H_3PO_4 as external reference (δ =0.00 ppm).



Figure S1. TR EPR spectra of BAPO (left) in octane/AOT solution, (right) in water/octane/AOT microemulsion, after laser flash photolysis at 355 nm. Time profiles of the EPR signal (normalized amplitude) for **P1**• (red), **M**• (green) and **X**• (blue) are shown in the top panels.



Figure S2. TR EPR spectra of BAPO in water/octane/AOT microemulsion with addition of (left) ST or (right) NAM after laser flash photolysis at 355 nm. Time profiles of the EPR signal (normalized amplitude) for **P1**• (red), **M**• (green), **X**• (blue), **P1-ST**• (magenta) and **P1-NAM**• (cyan) are shown in the top panels.



octane/AOT solution, (right) in water/octane/AOT microemulsion, after laser flash photolysis at 355 nm. Time profiles of the EPR signal (normalized amplitude) for **P2**• (orange) and **M**• (green) are shown in the top panels.



Figure S4. TR EPR spectra of MAPO in water/octane/AOT microemulsion with addition of (left) ST or (right) NAM after laser flash photolysis at 355 nm. Time profiles of the EPR signal (normalized amplitude) for **P2**• (orange), **M**• (green), **P2-ST**• (magenta) and **P2-NAM**• (cyan) are shown in the top panels.

Shake-flask determination of the distribution between oil and water phases

Photoinitiator/monomer were placed in a flask containing equal volumes of water and octane. The proper amount of photoinitiator/monomer was chosen so that final nominal molar concentration in the flask exceeded working molar concentrations by factor of 10. The flask with all the components were shacked for 10 min and then rested for 30 min to allow phase separation. Organic and water phases were taken separately and put into NMR tube. Concentration of dissolved components were measured by ¹H NMR spectroscopy.

Table S01. Water/octane solubility matrix of photoinitiators and monomers as determined by shake-flask NMR experiments.

Phase/Compound	BAPO	ΜΑΡΟ	ST	NAM	
Octane	yes	yes	yes	no	
Water	no	no	no	yes	

Laser flash photolysis. The stock solution of photoinitiators (BAPO 1.05 mg/ml, MAPO 1 mg/ml) in microemulsion (octane (1 ml) + water (0.5 ml) + AOT (300 mg)) were prepared and stored in the dark. The samples for laser flash photolysis experiment were further diluted to achieve optical density of 0.3 at 340 nm in a 1 cm cell, corresponding to the actual concentration of the phototiniator $c_{(MAPO)} = 0.5$ mg/ml and $c_{(BAPO)} = 0.37$ mg/ml. Microemulsions were deoxygenated by purging with argon for 10 min before the measurement. The experiments were performed with a LKS80 Laser Flash Photolysis Spectrometer (Applied Photophysics, UK). Samples were excited with the frequency tripled light from the Spitlight Compact 100 (InnoLas, Germany) solid-state Nd:YAG laser at 355 nm (pulse duration: 8 ns, energy: 10 mJ/pulse). The decay of the phosphanoyl radicals was recorded at the absorption maximum determined from the transient absorption spectra (340 nm and 460 nm with BAPO, and 340 nm with MAPO).

The second order rate constant for the guenching of the phospanoyl radicals in photoinitiator/microemulsion system were obtained in a pseudo-first order experiment performed in an excess of monomers. The decay of the absorbance, in microemulsions with different concentration of monomers (styrene (ST) or 4-acryloylmorpholine (NAM)), was fit with the mono-exponential function to obtain the pseudo-first-order rate constant (k). The experimental pseudo-first-order rate constant (k) is related to the second-order addition rate constant (k_m) by eq. 1:

$$k = k_0 + k_m \cdot c \tag{1}$$

where c represents the monomer concentration and k_0 is the estimated rate constant for the decay of the radicals in the absence of a quencher. The k_m values were obtained from the linear fits of concentration dependence of the k values.

The rate constants for the quenching of the phosphanoyl radical(s) with water were obtained in analogous manner. The reference value in homogenous solution was determined in acetonitrile solutions.

Table	S02.	The	pseudo-first-order	rate	constant	for	quenching	of	P1•	from	BAPO	in
micro	emuls	ion										

ST (340 nm))	ST (460 nm)		NAM (340 n	m)
c / M	k / 10 ⁷ s ⁻¹	с/М	k / 10 ⁷ s ⁻¹	c / M	k / 10 ⁷ s ⁻¹
0.05	1.65	0.05	2.47	0.03	1.15
0.1	2.61	0.1	3.79	0.04	1.23
0.15	3.47	0.15	4.63	0.045	1.27
0.2	4.89	0.2	6.09	0.05	1.33
0.3	6.91	0.3	8.35		

Table	S03.	The	pseudo-first-order	rate	constant	for	quenching	of	P2•	from	MAPO	in
micro	emuls	ion										

ST (340 nm)		NAM (340 nm)		
c / M	k / 10 ⁷ s ⁻¹	c / M	k / 10 ⁷ s ⁻¹	
0.05	0.58	0.03	0.78	
0.1	1.01	0.04	1.07	
0.15	1.50	0.05	1.40	
0.2	2.03	0.06	1.65	
0.3	3.41			



Figure S05. The experimental pseudo-first-order rate constant (k) for quenching of **P1**• from BAPO (determined at 340 nm detection wavelength) versus ST concentrations. The second-order rate constants k_m are obtained from the slopes.



Figure S06. The experimental pseudo-first-order rate constant (k) for quenching of **P1**• from BAPO (determined at 460 nm detection wavelength) versus ST concentrations. The second-order rate constants k_m are obtained from the slopes.



Figure S07. The experimental pseudo-first-order rate constant (k) for quenching of **P1**• from BAPO (determined at 340 nm detection wavelength) versus NAM concentrations. The second-order rate constants k_m are obtained from the slopes.



Figure S08. The experimental pseudo-first-order rate constant (k) for quenching of **P2**• from MAPO (determined at 340 nm detection wavelength) versus ST concentrations. The second-order rate constants k_m are obtained from the slopes.

Table S04. The second-order rate constant for quenching of P1• and P2•	by monomers in
microemulsion	

	k _m (340 nm) / 10 ⁸ dm ³ mol ⁻¹ s ⁻¹	k _m (460 nm)/ 10 ⁸ dm ³ mol ⁻¹ s ⁻¹
ST / P1•	2.14	2.34
NAM / P1•	0.89	
ST/ P2 •	1.13	
NAM/ P2 •	2.95	



Quenching of P1• by water in homogeneous solution (Acetonitrile/Water)

Figure S09. The experimental pseudo-first-order rate constant (k) for quenching of **P1**• (determined at 340 nm detection wavelength) versus water concentrations in Acetonitrile. The second-order rate constant k_w is obtained from the slopes.



Figure S10. The experimental pseudo-first-order rate constant (k) for quenching of **P1**• (determined at 340 nm detection wavelength) versus water concentrations in microemulsion. The second-order rate constant k_w is obtained from the slopes.



Figure S11. The absorbance decays of **P1**• in microemulsion, together with the corresponding mono-exponential function fits.

NMR.



Figure S12. ³¹P NMR spectra of BAPO in octane (upper trace) and in microemulsion (lower trace) recorded with the external reference.