

Supplementary information for “High-resolution in-situ photo-irradiation MAS NMR: Application to the UV-polymerization of n-butyl acrylate”

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Solid-state NMR experimental details

The bespoke system was demonstrated on an Oxford wide-bore 11.7 T magnet controlled by a Bruker Avance spectrometer and a Varian MAS control system. All spectra were processed using the Topspin software package and referenced to the unified scale using IUPAC recommended frequency ratios relative to the ^{13}C adamantane(s) methylene resonance ($\delta = 37.77$ ppm).^{1,2} The ^1H NMR ($\nu_0 = 499.80$ MHz) one-pulse experiments were acquired with a $\pi/2$ pulse of $5.65 \mu\text{s}$ (determined on adamantane(s)) and recycle delays of 20 s. The ^1H T_1 relaxation measurements were performed via saturation recovery experiments with a 200 pulse saturation train. The ^{13}C ($\nu_0 = 125.68$ MHz) decoupled one-pulse experiments were acquired with a $\pi/2$ pulse of $5.25 \mu\text{s}$ (determined on adamantane(s)), high power proton decoupling, and recycle delays of 15 s. The ^{79}Br ($\nu_0 = 125.23$ MHz) one-pulse experiments were acquired with a $\pi/2$ pulse of $4 \mu\text{s}$ (determined on KBr(s)) and recycle delays of 0.5 s.

Light-irradiation equipment

The bespoke system utilized the following Thorlabs equipment: USB LED driver (UPLD); 3 m long custom high-OH multi-mode SMA to flat-cleave 0.4 mm diameter fiber optic cable (FT200UMT); and 365 nm mid-power fiber-coupled LED (M365FP1). The USB LED driver allows driver current control from 0 – 1200 mA resulting in a linearly related output power of 0 – 13.3 mW at the output of the fiber optic. Photometer power measurements were performed to ensure the linearity of the current/power relationship. Fiber-coupled LEDs with alternative wavelengths or higher powers can be easily interchanged for future experiments.

Monomer conversion simulation parameters

Table S1. Parameters for the calculation of the polymerization reaction curves (Figure 5(a)) at different radiant powers using the mechanistically derived analytical equation 3 from K.V.K. Boodhoo, *et al.*³

Parameter	Symbol (units)	Value	Source
polymerization propagation rate	k_p ($\text{Lmol}^{-1}\text{s}^{-1}$)	1.63×10^4	literature ⁴
termination rate	k_t ($\text{Lmol}^{-1}\text{s}^{-1}$)	6×10^7	literature ⁴
average thin film thickness	L (cm)	0.05	measurement ^a
sample surface area	S (cm^2)	1.5	measurement ^a
initial photo-initiator concentration	P_0 (molL^{-1})	0.02	measurement
quantum yield of initiation	ϕ	0.6	literature ⁵
absorption coefficient	α ($\text{Lmol}^{-1}\text{cm}^{-1}$)	215	literature ⁶
wavelength	λ (m)	365×10^{-9}	measurement
speed of light	c (ms^{-1})	2.998×10^8	
Avogadro's constant	N_a (mol^{-1})	6.022×10^{23}	
Planks constant	h (Js)	6.626×10^{-34}	
incident light power	I (mW)	13.3; 6.7; 3.3; 1.7	measurement ^b

^a Calculated by modelling the tapered glass rod as a perfect cone.

^b Calculated by assuming that 100 % of the fiber optic radiant power is incident on the sample

Additional static ^1H NMR spectra

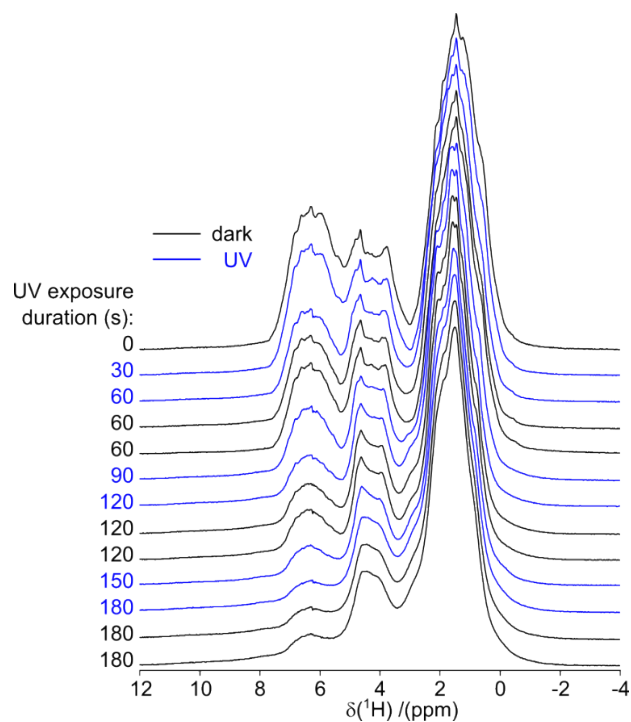


Figure S1. Static ^1H NMR spectra of *n*BA polymerization after variable durations of UV exposure (365 nm at 13.3 mW fiber optic output power). Black spectra were taken under dark conditions pre/post UV exposure, while blue lines were taken while under irradiation. Post-UV exposure spectra under dark conditions are very similar to the spectra taken under UV irradiation just before the light is turned off. This demonstrates that the reaction terminates rapidly once the UV irradiation is stopped.

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