Supporting Information

RAFT iniferter polymerization in miniemulsion using visible light

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Experimental Section

Materials

Butyl methacrylate (BuMA, Sigma-Aldrich) was deinhibited by passing through a column of basic alumina. 4-Cyano-4-[(dodecylsulfanylthiocarbonyl)sulfanyl] pentanoic acid (CDTPA, Boron Molecular) was used as received. Hexadecane (HD, Sigma-Aldrich) and sodium dodecyl sulfate (SDS, Sigma-Aldrich) was used as received. MilliQ water was used for miniemulsion experiments.

Characterizations

Conversion was measured using gravimetry by drying samples in a vacuum oven at 40 °C. The molecular weight and molecular weight distribution was measured by gel permeation chromatography (GPC). Tetrahydrofuran (HPLC grade, 0.05% w/v 2,6-dibutyl-4-methylphenol (BHT)) was used as the eluent at 40 °C and at a flow rate of 1 mL/min. The GPC system was comprised of a Shimadzu SIL-10AD auto-injector, a Polymer Laboratories 5.0 μ m bead-size guard column (50x7.5 mm²), 4 linear PL (Styragel) columns (10⁵, 10⁴, 10³ and 500 Å) and an RID-10A differential refractive index (RI) detector and UV-Vis detector.

Droplet/particle diameters and their distributions were characterized by dynamic light scattering (DLS) via a Malvern Zetasizer Nano running DTS software. The instrument was comprised of a 4 mW He-Ne laser operating at a wavelength of 633 nm and an avalanche photodiode (APD) detector with the angle set at 173 °.

Bulk polymerizations

In a typical procedure, CDTPA (0.2539 g, 6.29 x 10^{-4} mol) was added to a 21 mL (d = 2 cm) borosilicate glass vial equipped with a magnetic stirrer. Butyl methacrylate (8.4909 g, 6.29 x 10^{-2} mol) was then added to the vial and the vial was subsequently sealed with a rubber septum and bubbled with N₂ gas in an ice bath for 30 mins. Following the deoxygenation process, the reaction vessel was placed into the visible light reactor setup shown below and polymerization was started by turning on the light (stirred at 400 rpm).

For batch reactions, the polymerization was stopped by turning the light off and exposing the reaction mixture to oxygen after the predetermined exposure time. For kinetic experiments, sampling was performed at predetermined exposure times using a gas-tight syringe, filled with N_2 , directly from the reaction vessel without switching the light off. The aliquots were first dried in a vacuum oven (40°C, 48 h) for gravimetric analysis. The dried samples were further analysed by GPC.

Miniemulsion polymerizations

For the preparation of miniemulsions, the organic and aqueous phases were first prepared separately. For all miniemulsion reactions presented in this work, the monomer was fixed at 0.5 g (5 wt% relative to the aqueous phase which was fixed at 10 g). The hydrophobe hexadecane and the RAFT agent, CDTPA were also fixed at 0.04 g (8 wt% relative to the monomer) and 0.014 g (for DP_{target} = 100) respectively. The aqueous phase was prepared by adding the surfactant, SDS (which ranged from 0.02 g (4 wt%) to 0.06 g (12 wt%), to a Cospak bottle, followed by the addition of deionized milliQ water (10g). In a separate glass vial, CDTPA (0.014 g, 3.52×10^{-5} mol), hexadecane (0.04 g) and butyl methacrylate (0.5 g, 3.52×10^{-3} mol) were mixed and then added to the aqueous phase. The 2 phase mixture was subsequently homogenized using an ultrasonic probe (Branson 450) for 10 mins at an amplitude of 50 % whilst being cooled by an ice bath. The miniemulsion was allowed to mature for 30 mins before an aliquot was removed for DLS analysis. Thereafter, 10 mL of the miniemulsion was transferred to a 21 mL glass vial equipped with a magnetic stirrer bar and then sealed with a septum and subsequently bubbled with N₂ for 30 mins in an ice bath. The deoxygenated reaction vessel was then placed in the visible light reactor and polymerization was started by turning on the light.

For batch reactions, the polymerization was stopped by switching off the light and exposing the miniemulsion to air. Kinetic sampling was performed using a gas-tight syringe filled with N_2 , and samples were removed directly from the reaction vessel without turning the light source off.

Samples were first analysed by DLS and then dried in a vacuum oven (40 °C, 48 h) for gravimetric analysis. The dried samples were further analysed by GPC.

Reactor Setup

The reactor setup shown below consists of an LED strip (2.5 m, 14.4 W/m, 25 leds, $\lambda_{max} = 530$ nm) wrapped on the inside of an oil bath. The reaction vessel was placed in the center of the reactor (c.a. 6 cm from the LED strip).



Figure S1. Reactor setup



Figure S2. Kinetic results of RAFT iniferter polymerization of butyl methacrylate conducted under bulk conditions using green light ($\lambda_{max} = 530 \text{ nm}$, DP_{target} = 100). **A**) Evolution of conversion and ln([M]₀/[M]_t) versus exposure time. **B**) Evolution of the molecular weight distribution with increasing conversion.

Exp.	Exposure time (h)	SDS Conc. (wt%)	Conversion (%)	M _{n,theo} (g/mol)	M _{n,GPC} (g/mol)	M_w/M_n	D _{h,pre} (nm)	PDI (post)	D _{h,post} (nm)	PDI (post)
Α	6	-	82	12000	12700	1.14	-	-	-	-
В	20	10	neg.	-	-	-	61	0.149	71	0.126
С	20	10	76	11400	9800	2.62	62	0.153	110	0.097
D	20	12	53	8000	8700	3.54	77	0.143	106	0.110
Е	20	8	78	11600	11700	1.60	75	0.143	118	0.087
F	20	6	88	13200	13100	1.31	71	0.153	136	0.091
G	20	4	95	14200	13900	1.35	89	0.159	149	0.073

Table S1. Results of RAFT iniferter polymerization of butyl methacrylate in miniemulsion using green light ($\lambda_{max} = 530$ nm, DP_{target} = 100)

A. Bulk experiment

B. Miniemulsion experiment with no RAFT agent added



Figure S3. Molecular weight distributions (normalized to peak height) of batch RAFT iniferter polymerizations of butyl methacrylate in miniemulsion using green light ($\lambda_{max} = 530$ nm, DP_{target} = 100, 20 h exposure time).



Figure S4. Evolution of average hydrodynamic diameter by intensity measured by DLS at the investigated SDS concentrations for RAFT iniferter polymerization of butyl methacrylate in miniemulsion using green light ($\lambda_{max} = 530$ nm).



Figure S5. Comparison of RI and UV GPC chromatograms at various surfactant concentrations of RAFT iniferter polymerization of butyl methacrylate in miniemulsion using green light ($\lambda_{max} = 530$ nm, DP_{target} = 100) at low conversion. **A)** 4 wt% surfactant, 17 % conversion, **B)** 6 wt% surfactant, 21 % conversion, **C)** 8 wt% surfactant, 16 % conversion, **D)** 10 wt% surfactant, 14 % conversion & **E)** 12 wt% surfactant, 12 % conversion.



Figure S6. Free SDS concentration relative to initial droplet diameters for RAFT iniferter polymerization of butyl methacrylate in miniemulsion using green light ($\lambda_{max} = 530$ nm). See below for calculation method.

Calculation of free surfactant concentration

Method

- 1. For each surfactant concentration studied, the total interfacial area was calculated based on arbitrary initial droplet diameters using the following formulae:
- $A (interfacial area) = n_d \cdot \pi \cdot D^2$

$$n_d$$
 (number of monomer droplets) = $\frac{(total volume)}{\frac{4}{3} \cdot \pi \cdot r^3}$ and D = avg. droplet diameter

Where,

2. From the obtained interfacial area (A), the number of SDS molecules at the interface was calculated using:

$$N \ (mol \ of \ SDS \ at \ interface) = A \cdot \Gamma_{cmc}$$

Where, $\Gamma_{cmc}(surface \ conc. \ of \ SDS \ at \ interface) = 4.17 \ x \ 10^{-10} \ mol \cdot cm^{-2}$

3. To obtain the amount of free surfactant, the value obtained from step 2 was subtracted from the actual surfactant amount used.

Comments

The above calculations are based on a surface concentration of SDS at a styrene water interface as reported by Chang et al.¹ Figure S5 presents the results of these calculations. The DLS results (Figure 4, main text) indicate that the initial droplet diameters are below 100 nm at surfactant concentrations used in the study. At or below this diameter, there are significant amounts of free surfactant at surfactant concentrations of 12 and 10 wt%. However, the calculated surfactant concentration is below the cmc of SDS (8 mM).² It is important to note that these calculations do not take into account the surface activity of the RAFT agent and its impact on the SDS concentration at the interface.

1. Chang, H.-C.; Lin, Y.-Y.; Chern, C.-S.; Lin, S.-Y., Determination of Critical Micelle Concentration of Macroemulsions and Miniemulsions. *Langmuir* **1998**, *14* (23), 6632-6638.

2. Dominguez, A.; Fernandez, A.; Gonzalez, N.; Iglesias, E.; Montenegro, L., Determination of Critical Micelle Concentration of Some Surfactants by Three Techniques. *Journal of Chemical Education* **1997**, *74* (10), 1227.