

# **Blue Light-Initiated Alcoholic RAFT Dispersion Polymerization of Benzyl Methacrylate: A Detailed Study**

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## EXPERIMENTAL SECTION

**Materials.** Benzyl methacrylate (BzMA, Aladdin), hydroxypropyl methacrylate (HPMA, Aladdin), monomethoxy poly(ethylene glycol) (mPEG<sub>45</sub>, 2000 g/mol, Sigma-Aldrich), dicyclohexylcarbodiimide (DCC, Aladdin), 4-dimethylaminopyridine (DMAP, Aladdin), hydroquinone (Aladdin), sodium 2,2-dimethyl-2-silapentane-5-sulfonate (DSS, Aladdin), and phenylbis(2,4,6-trimethylbenzoyl)phosphine oxide (BAPO, Tianjin Jiuri) were used without further purification. 2, 2-Azobisisobutyronitrile (AIBN, Aladdin) was recrystallized from ethanol prior to storage under refrigeration at 4 °C. 4-Cyano-4-(dodecylsulfanylthiocarbonyl)sulfanylpentanoic acid (CDPA) was synthesized according to a published procedure.<sup>1</sup>

**Synthesis of mPEG<sub>45</sub>-CDPA.** A solution of CDPA (8.07 g, 20 mmol) in 40 mL of anhydrous dichloromethane (DCM) was introduced in a dry flask under nitrogen atmosphere containing mPEG<sub>45</sub> (20.0 g, 10 mmol). Then a solution of DCC (4.12 g, 20 mmol) and DMAP (0.244 g, 2 mmol) in 10 mL of anhydrous dichloromethane was added dropwise to the reaction mixture at 0 °C. The esterification reaction proceeded under stirring at room temperature for 48 h. The polymer was collected by precipitation of the reaction mixture in cold diethyl ether, passing through a column, and finally dried at 45 °C under vacuum to obtain a yellow powder.

**Synthesis of PHPMA macro-RAFT agent.** HPMA (40.0 g, 277 mmol), AIBN (0.456 g, 2.77 mmol), and CDPA (5.60 g, 13.9 mmol) were added into a 250 mL round-bottom flask, and then dissolved with dioxane (60.0 g, 40% w/w) to form a homogeneous solution. 1,3,5-Trioxacyclohexane (2.5 g, 27.7 mmol) was added to the reaction mixture as an internal standard. The reaction mixture was then purged with nitrogen for 1 h, sealed, and then immersed in a 70 °C pre-heated oil bath for

120 min. The polymerization was quenched by immersion in ice-water and exposure to air. The polymer was precipitated by adding excess hexane (600 mL) and washed several times with additional hexane. The obtained product was then dried at 45 °C under vacuum overnight, and then analyzed by <sup>1</sup>H NMR spectroscopy and THF gel permeation chromatography (GPC). <sup>1</sup>H NMR measurement indicated a mean degree of polymerization of 18 for this macro-RAFT agent (denoted as PHPMA<sub>18</sub>-CDPA), and THF GPC measurement confirmed its  $M_n = 4200 \text{ g mol}^{-1}$  and  $M_w/M_n = 1.15$ .

**Blue light-initiated alcoholic RAFT dispersion polymerization.** In a typical experiment for the synthesis of mPEG<sub>45</sub>-PBzBA<sub>100</sub> (20% w/w): BzMA (1.5 g, 8.5 mmol), mPEG<sub>45</sub>-CDPA (0.20 g, 0.085 mmol), and BAPO (0.0119 g, 0.028 mmol) were weighed into a 25 mL round bottom flask. Then an isopropanol/water mixture (4.8 g/1.2 g, 80/20, w/w) was added into the flask to dissolve all reagents. The reaction mixture was purged with nitrogen for 20 min, and then irradiated by a visible light LED lamp (465 nm, 4.2 mW/cm<sup>2</sup>) for 3 h. The reaction was quenched by exposure to air and the addition of a small amount of hydroquinone.

In a typical experiment for the synthesis of PHPMA<sub>18</sub>-PBzBA<sub>100</sub> (20% w/w), BzMA (1.5 g, 8.5 mmol), PHPMA<sub>18</sub>-CDPA (0.26 g, 0.085 mmol), and BAPO (0.0119 g, 0.028 mmol) were weighed into a 25 mL round bottom flask. Then an isopropanol/water mixture (5.4 g/0.6 g, 90/10, w/w) was added into the flask to dissolve all reagents. The reaction mixture was purged with nitrogen for 20 min, and then irradiated by a visible light LED lamp (465 nm, 4.2 mW/cm<sup>2</sup>) for 3 h. The reaction was quenched by exposure to air and the addition of a small amount of hydroquinone.

**Kinetic study of blue light-initiated alcoholic RAFT dispersion polymerization.** BzMA (2.5 g, 14.2 mmol), mPEG<sub>45</sub>-CDPA (0.34 g, 0.142 mmol), sodium 2,2-dimethyl-2-silapentane-5-sulfonate

(DSS, 80 mg) and BAPO (0.0198 g, 0.047 mmol) were weighed into a 25 mL round bottom flask. Then an isopropanol/water mixture (8.0 g/2.0 g, 80/20, w/w) was added into the flask to dissolve all reagents. The reaction mixture was purged with nitrogen for 20 min, and then irradiated by a visible light LED lamp (465 nm, 4.2 mW/cm<sup>2</sup>). Samples were withdrawn at predetermined time intervals by syringes under nitrogen, and the reaction was quenched by exposure to air and the addition of a small amount of hydroquinone. The samples were then analyzed by <sup>1</sup>H NMR spectroscopy and gel permeation chromatography (GPC).

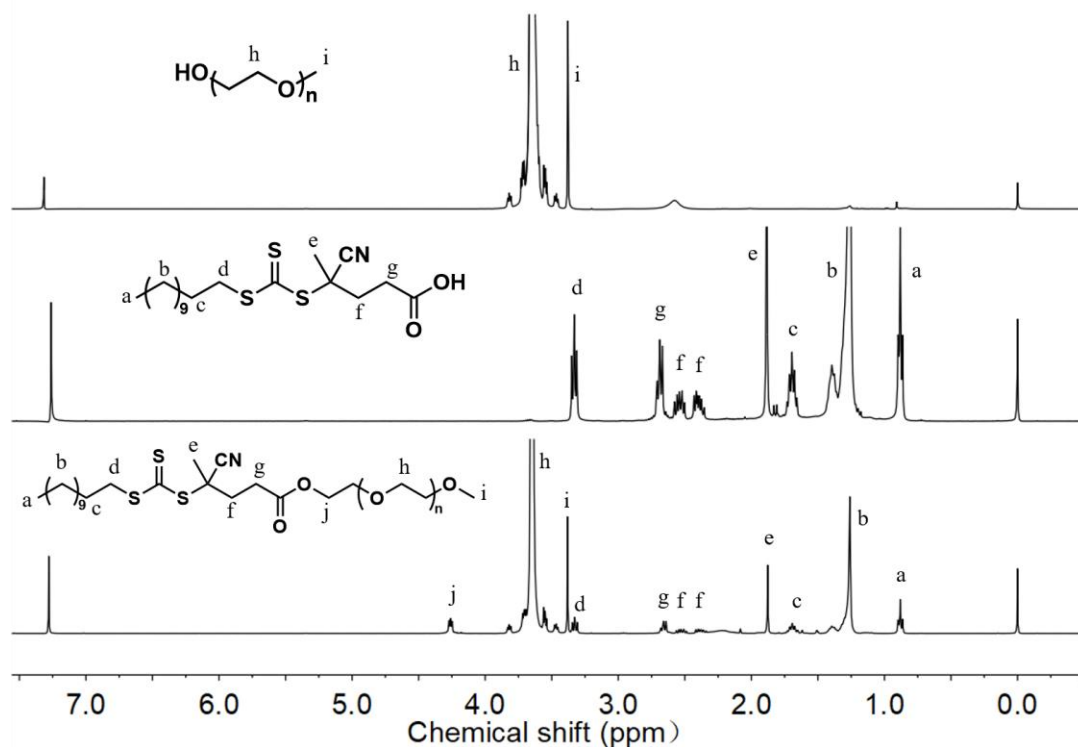
**Characterization.** The obtained dispersions were diluted 100-fold with isopropanol-water mixtures. A drop of the solution was placed on the copper grid for 1 min and then blotted with filter paper to remove excess solution. A drop of uranyl acetate solution (0.5 wt %) was soaked on the same copper grid for 1.5 min, and then blotted with filter paper to remove excess stain. Transmission electron microscope (TEM) observations were carried out on a Hitachi 7700 instrument operated at 120 kV.

The molecular weight and polydispersity of the block copolymers were measured by gel permeation chromatography (GPC) at 40 °C using a Waters 1515 GPC instrument with tetrahydrofuran (THF) as the mobile phase and Waters styragel HR1, HR4 columns. The flow rate of THF was 1 mL/min. Linear poly (methyl methacrylate) polymers with narrow molecular weight distributions were used as the standards to calibrate the apparatus.

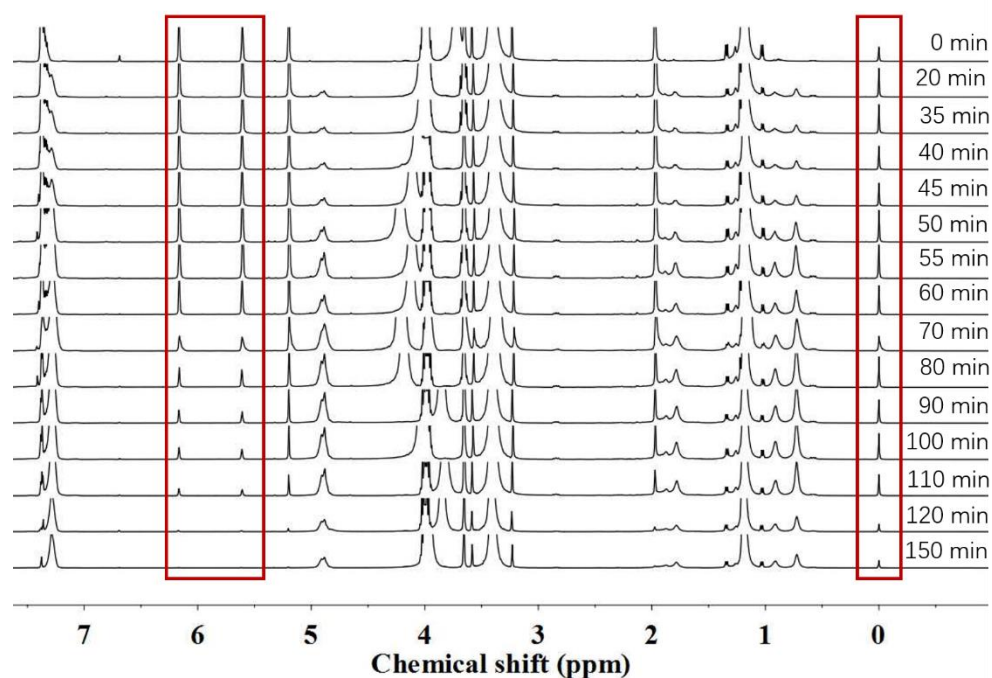
<sup>1</sup>H NMR spectra were recorded in CDCl<sub>3</sub> using a Bruker Avance III 400 MHz NMR spectrometer at a temperature of 25 °C. Note: The samples prepared by PISA were first diluted with methanol, and then dissolved in CDCl<sub>3</sub>.

UV-vis spectra were recorded with a 1.0 cm quartz cuvette using a UV2450 spectrometer.

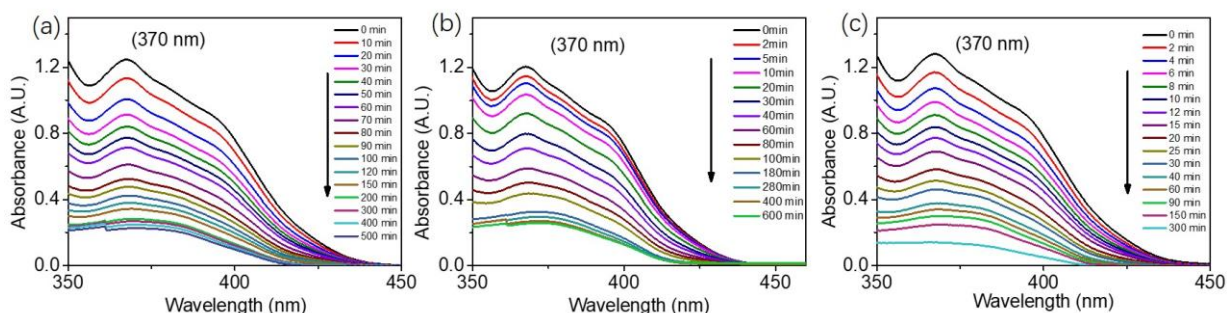
## ADDITIONAL RESULTS



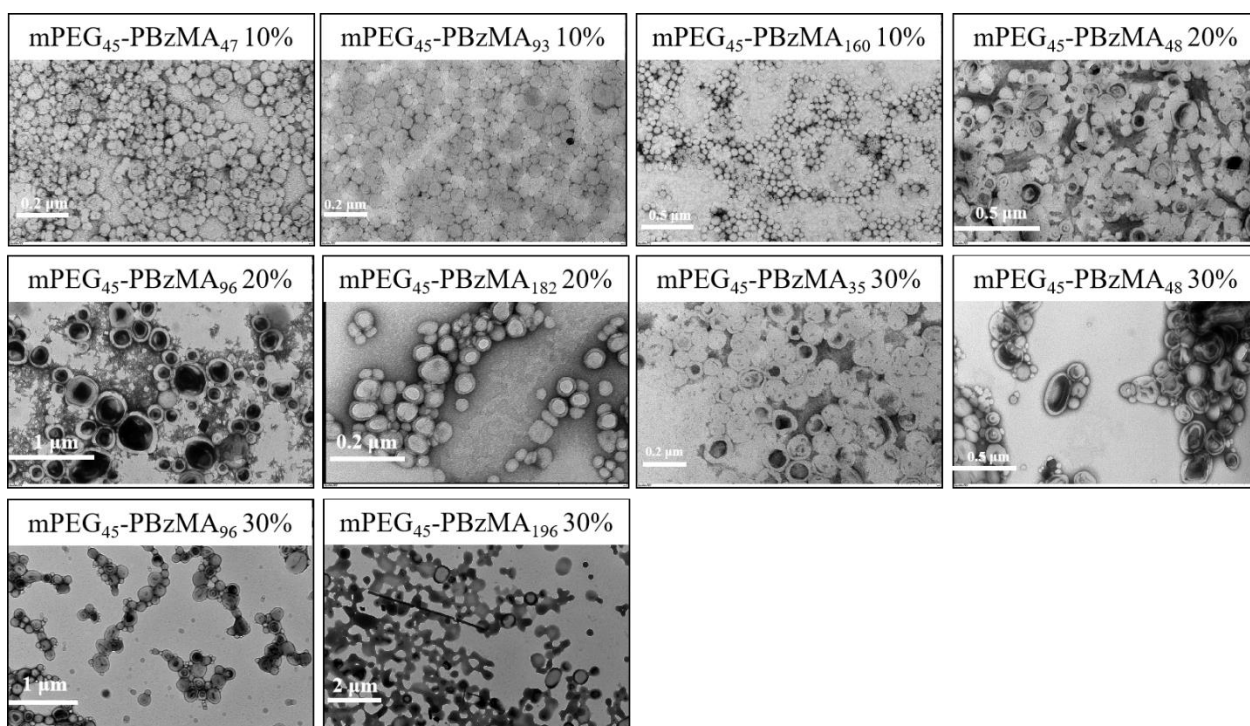
**Figure S1.**  $^1\text{H}$  NMR spectra of mPEG<sub>45</sub>, CDPA and mPEG<sub>45</sub>-CDPA.



**Figure S2.**  $^1\text{H}$  NMR spectra ( $\text{CDCl}_3$ ) recorded during the blue light-initiated RAFT dispersion polymerization of BzMA using a mPEG<sub>45</sub>-CDPA macro-CTA in an isopropanol/water (80/20, w/w) mixture (BzMA concentration of 20% w/w, target DP of 100). Sodium 2,2-dimethyl-2-silapentane-5-sulfonate (DSS) was used as the internal  $^1\text{H}$  NMR standard.



**Figure S3.** UV-vis absorbance spectra recorded for the decomposition of BAPO in isopropanol/water (80/20, w/w) under blue light irradiation ( $\lambda_{\max} = 465 \text{ nm}$ ) with different light intensities. (a)  $2.0 \text{ mW/cm}^2$ ; (b)  $4.2 \text{ mW/cm}^2$ ; (c)  $8.0 \text{ mW/cm}^2$ .



**Figure S4.** TEM images of  $\text{mPEG}_{45}\text{-PBzMA}_n$  diblock copolymer nano-objects prepared via alcoholic blue light-initiated RAFT dispersion polymerization of BzMA in isopropanol/water (80/20, w/w) at  $25 \text{ }^\circ\text{C}$ .

**Table S1.** Summary of GPC data obtained for a series of  $\text{PHPMA}_{18}\text{-PBzMA}_{100}$  diblock copolymers prepared by blue light-initiated RAFT dispersion polymerization of BzMA in an isopropanol/water (90/10, w/w) mixture at a BzMA concentration of 25% w/w under different light intensities.<sup>a</sup>

Light intensity	Target composition	BzMA conversion	GPC	
			$M_n \text{ (g mol}^{-1}\text{)}$	$M_w/M_n$
$2.0 \text{ mW/cm}^2$	$\text{mPEG}_{45}\text{-PBzMA}_{100}$	93	13275	1.24
$4.2 \text{ mW/cm}^2$	$\text{mPEG}_{45}\text{-PBzMA}_{100}$	95	13520	1.28
$8.0 \text{ mW/cm}^2$	$\text{mPEG}_{45}\text{-PBzMA}_{100}$	88	12758	1.28

<sup>a</sup> All polymerizations were conducted using a macro-CTA/photoinitiator molar ratio of 3.0. Monomer conversions were measured using  $^1\text{H}$  NMR spectroscopy, and GPC data were recorded via THF GPC.

**Table S2.** Summary of reaction temperature, synthesis conditions, monomer conversions, GPC data, and TEM characterization obtained for a series of PHPMA<sub>18</sub>-PBzMA<sub>n</sub> diblock copolymers prepared by blue light-initiated RAFT dispersion polymerization (light intensity of 4.2 mW/cm<sup>2</sup>) of BzMA in an isopropanol/water (90/10, w/w) mixture at a BzMA concentration of 25% w/w.<sup>a</sup>

Reaction temperature (°C)	Target composition	BzMA conversion (%)	Actual PBzMA DP	GPC		TEM
				M <sub>n</sub> (kg/mol)	M <sub>w</sub> /M <sub>n</sub>	morphology
	PHPMA <sub>18</sub> -CDPA	-	-	4.2	1.15	
25	PHPMA <sub>18</sub> -PBzMA <sub>50</sub>	98	49	11.2	1.25	spheres + worms
25	PHPMA <sub>18</sub> -PBzMA <sub>100</sub>	92	92	15.9	1.48	spheres + worms + vesicles
25	PHPMA <sub>18</sub> -PBzMA <sub>150</sub>	91	137	23.0	1.65	spheres + vesicles
25	PHPMA <sub>18</sub> -PBzMA <sub>200</sub>	86	172	38.5	1.65	spheres + vesicles
70	PHPMA <sub>18</sub> -PBzMA <sub>50</sub>	98	49	10.2	1.41	Spheres + worms
70	PHPMA <sub>18</sub> -PBzMA <sub>100</sub>	97	97	17.1	1.42	vesicles
70	PHPMA <sub>18</sub> -PBzMA <sub>150</sub>	97	146	20.3	1.60	vesicles
70	PHPMA <sub>18</sub> -PBzMA <sub>200</sub>	97	194	25.4	1.64	vesicles

<sup>a</sup> All polymerizations were conducted using a macro-CTA/photoinitiator molar ratio of 3.0. Monomer conversions were measured using <sup>1</sup>H NMR spectroscopy, and GPC data were recorded via THF GPC.

## REFERENCES

- (1) Moad, G.; Chong, Y. K.; Postma, A.; Rizzardo, E.; Thang, S. H. *Polymer* **2005**, *46* (19), 8458–8468.