# SUPPORTING INFORMATION

# Microwave-Assisted Synthesis of Block Copolymer Nanoparticles via RAFT with Polymerization-Induced Self-Assembly in Methanol

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# **Experimental**

#### Materials

All reagents were purchased from the Sigma-Aldrich Chemical Co. at the highest available purity and utilized as received unless noted otherwise. 2-Phenylethyl methacrylate (PEMA) was purchased from Monomer-Polymer and Dajac Labs. 2,2'-Azobis(isobutyronitrile) (AIBN) was purified by recrystallization twice from methanol and stored in a freezer until needed. Oligo(ethylene glycol) methyl ether methacrylate (OEGMA) (average  $M_n = 300$ ), benzyl methacrylate (BzMA), and PEMA were purified by passing through a basic Al<sub>2</sub>O<sub>3</sub> column to remove inhibitor prior to use.

# Synthesis of Poly[oligo(ethylene glycol) methyl ether methacrylate] (pOEGMA) *via* RAFT homopolymerization

Below is a general procedure for the RAFT homopolymerization of OEGMA mediated by 2cyanopropan-2-yl dithiobenzoate (CPDB).

A solution containing OEGMA (13.5 g,  $4.5 \times 10^{-2}$  mol), CPDB ( $1.99 \times 10^{-1}$  g,  $5.38 \times 10^{-4}$  mol), AIBN ( $2.93 \times 10^{-2}$  g,  $1.08 \times 10^{-4}$  mol), and acetonitrile (56 mL) was added to a reaction vial equipped with a magnetic stir bar. The reaction vessel was sealed and the reaction mixture purged with argon for 1 hour prior to being placed in a preheated oil bath at 70 °C. Polymerization was allowed to proceed for 4 h after which it was halted by exposure to air while cooling in an ice/water bath. The pOEGMA homopolymer(s) were isolated by precipitation into a mixture of diethyl ether and petroleum spirits (1:1, v/v) dried over several days under N<sub>2</sub> gas prior to NMR spectroscopic and SEC analysis.

## RAFT dispersion polymerization in alcoholic media by conventional heating

Below is a general procedure for the RAFT dispersion polymerization (RAFTDP) of benzyl methacrylate (BzMA) or 2-phenylethyl methacrylate (PEMA) with a pOEGMA<sub>22</sub> macro-CTA in anhydrous methanol by conventional heating. All RAFTDPs by conventional heating were performed in a similar fashion.

A solution containing BzMA  $(2.41 \times 10^{-1} \text{ g}, 1.37 \times 10^{-3} \text{ mol})$ , POEGMA<sub>22</sub> macro-CTA  $(1.10 \times 10^{-1} \text{ g}, 1.61 \times 10^{-5} \text{ mol})$ , AIBN  $(5.27 \times 10^{-4} \text{ g}, 1.57 \times 10^{-6} \text{ mol})$  and anhydrous methanol (1.77 mL) was added to a 10 mL glass vial (G10 reaction vial, Anton Paar) equipped with a magnetic stir bar. This corresponds to a molar ratio of [BzMA]:[macro-CTA]:[AIBN] of 85:1:0.2. The reaction vessel was sealed with a silicone septum and the solution purged with Argon for 1 hour prior to being placed in a preheated oil bath at 70 °C. Polymerization was allowed to proceed for 15 h after which it was halted by exposure to air while cooling in an ice/water bath. Kinetic samples were removed from reaction mixture periodically by a nitrogen-purged syringe to determine monomer conversion and polymer molecular weight via <sup>1</sup>H NMR spectroscopy and SEC analysis. Block copolymer samples were isolated by precipitation into a large excess of diethyl ether and petroleum spirits mixture (1:1, v/v) followed by filtration and dried overnight prior to NMR spectroscopic and SEC analysis.

## Microwave-assisted RAFT dispersion polymerizations

Microwave-assisted synthesis were performed in a single-mode microwave reactor (MONOWAVE 300, Anton Paar) equipped with an infrared temperature sensor (maximum pressure = 32 bar, maximum power = 50 W). All the polymerizations were conducted with simultaneous cooling by compressed air flow. The approximate ramping time varied between 30 seconds and 1 minute depending on the temperature setup and the polar nature of the species in the polymerization.

#### Microwave-Assisted RAFT dispersion polymerization in methanol

Below is a general procedure for the microwave-assisted RAFTDP of BzMA or PEMA with a pOEGMA<sub>22</sub> macro-CTA in anhydrous methanol. All microwave-assisted RAFTDPs were performed in a similar fashion.

A solution containing BzMA ( $2.41 \times 10^{-1}$  g,  $1.37 \times 10^{-3}$  mol), POEGMA<sub>22</sub> macro-CTA ( $1.10 \times 10^{-1}$  g,  $1.61 \times 10^{-5}$  mol), AIBN ( $5.27 \times 10^{-4}$  g,  $1.57 \times 10^{-6}$  mol) and anhydrous methanol (1.77 mL) was added to a 10 mL glass vial (G10 reaction vial, Anton Paar) equipped with a magnetic stir bar. This corresponds to a molar ratio of [BzMA]:[Macro-CTA]:[AIBN] of 85:1:0.2. The reaction vessel was sealed with a silicone septum and the solution purged with Argon for 1 hour prior to being placed in a

MONOWAVE 300 monomodal microwave reactor. The reaction temperature was programmed to 70 °C that is constantly monitored utilizing an infrared sensor. Kinetic samples were removed from reaction mixture periodically by a nitrogen-purged syringe to determine monomer conversion and polymer molecular weight via <sup>1</sup>H NMR spectroscopy and SEC analysis. Block copolymer was isolated by precipitation into a large excess of petroleum spirits followed by filtration and dried overnight prior to NMR spectroscopic and SEC analysis.

## Nuclear magnetic resonance (NMR) Spectroscopy

NMR spectra were recorded on a Bruker 400 MHz spectrometer. <sup>1</sup>H NMR spectra were recorded in deuterated chloroform (CDCl<sub>3</sub>). Residual CHCl<sub>3</sub> ( $\delta$  = 7.26 ppm) was utilized as the internal reference signal.

## Size exclusion chromatography (SEC)

SEC analysis was performed on a Shimadzu modular system consisting of a 4.0 mm  $\times$  3.0 mm Phenomenex Security Guard<sup>TM</sup> Cartridge, two linear phenogel columns (10<sup>3</sup> and 10<sup>4</sup> Å pore size) in tetrahydrofuran (THF) operating at a flow rate of 1.0 mL/min at 40 °C using a RID-20A refractive index detector, a SPD-M20A prominence diode array detector and a miniDAWN TREOS multi-angle static light scattering (MALS) detector. The system was calibrated with a series of narrow molecular weight distribution poly(methyl methacrylate) standards with molecular weights ranging from 2.8 to 220 kg mol<sup>-1</sup>. Chromatograms were analysed using LabSolutions SEC software. Homopolymer samples were prepared at 5 g L<sup>-1</sup> and filtered twice through a 0.22 µm nylon filter prior to analysis. Copolymer samples

# **Dynamic light scattering (DLS)**

DLS measurements were performed utilizing a Malvern Instrument Zetasizer Nano Series instrument (laser power = 4 mW, wavelength = 633 nm, detection angle =  $173^{\circ}$ ) at 25 °C. For sample preparation, 70 µL of the parent RAFTDP solution was diluted with 1.93 mL of methanol and the solution was then stirred for 10 min prior to filtration through 0.45 µm PTFE filters.

#### Transmission electron microscopy (TEM)

TEM analyses were conducted on a JEOL 2100 transmission electron microscope operated at 120 kV. Samples for analysis were prepared by slowly adding 70  $\mu$ L of the parent RAFTDP solution to 1.93 mL of methanol under stirring. The copolymer solution (0.7 wt%) was dropped onto the top of a carbon-coated copper grid (SPI Supplier) and allowed to contact for 1 min. Excess solution was wicked off using a filter paper. To stain the nano-objects, uranyl acetate (0.2 wt%) solution was soaked on the sample-loaded grid for 30 s and then carefully blotted to remove excess stain.

# Results

Sample	Reaction Time (hours)	Mn	$\mathcal{D}_M$
MW 10 wt %	10h	9400	1.19
CH 10 wt %	10h	6900	1.12
MW 20 wt %	10h	13800	1.18
CH 20 wt %	10h	11200	1.22
MW 30 wt %	10h	14500	1.26
CH 30 wt %	10h	14500	1.21
MW 40 wt %	7h	15900	1.21
CH 40 wt %	7h	15600	1.21

Table S1. Final SEC measured Mn's and dispersities for the  $p(OEGMA_{22}-b-BzMA_x)$  block copolymers prepared under MA and CH conditions at 10, 20, 30 and 40% w/w in MeOH.

Below are given representative examples of the series of SEC traces obtained in the kinetic experiments for the above series of eight  $p(OEGMA_{22}-b-BzMA_x)$  copolymerizations.



Below are given representative <sup>1</sup>H NMR spectra of a pOEGMA macro-CTA, a p(OEGMA-*b*-BzMA) copolymer and a p(OEGMA-*b*-PEMA) block copolymer



Chemical shift (d, ppm)

