## **Electronic Supplementary Information**

## One pot synthesis of high order quasi-block copolymer libraries via sequential RAFT polymerization in an automated synthesizer<sup>†</sup>

Joris J. Haven,<sup>*a,b*</sup> Carlos Guerrero-Sanchez,<sup>*\*a,c*</sup> Daniel J. Keddie,<sup>*a,d*</sup> Graeme Moad,<sup>*\*a*</sup> San H. Thang<sup>*a*</sup> and Ulrich S. Schubert<sup>*c*</sup>

## Experimental

Characterization methods

Proton nuclear magnetic resonance (<sup>1</sup>H-NMR) (400 MHz) spectra were recorded using a Bruker AV400 spectrometer at 25 °C in deuterated chloroform (CDCl<sub>3</sub>) to determine monomer to polymer conversions and copolymer compositions. The following method is typical. Figure S1 in the Electronic Supporting Information (ESI) displays representative <sup>1</sup>H-NMR spectra and their analysis for the four different monomers investigated in this work.

The monomer to polymer conversion for the polymerizations of BMA was determined by comparing the integration of peaks using the following equation: % BMA conversion =  $[\int 3.8 / (\int 4.0 + \int 3.8)] \times 100$ ; where  $\int 4.0$  and  $\int 3.8$  are the integral values for the O–CH<sub>2</sub> protons of the BMA and of the PBMA polymer, respectively.

The monomer to polymer conversion for the polymerizations of MMA using the following equation: % MMA conversion =  $[J_{3.5} / (J_{3.6} + J_{3.5})] \times 100$ ; where  $J_{3.6}$  and  $J_{3.5}$  are the integral values for the O–CH<sub>3</sub> protons of the MMA monomer and of the PMMA polymer, respectively.

The monomer to polymer conversion for the polymerization of DEGMA was determined by comparing the integration of resonance peaks in the  $\delta$  4.1 ppm region, corresponding to the O–CH<sub>2</sub> protons of the DEGMA monomer, with that of the peaks in the  $\delta$  3.9 ppm region, pertaining to the O–CH<sub>2</sub> protons of the repeat units of the poly(2-(hydroxyethoxy)ethyl methacrylate) (PDEGMA) polymer.

The monomer to polymer conversion for the polymerization of BzMA was determined by comparing the integration of resonance peaks in the  $\delta$  5.0 ppm region, corresponding to the O–CH<sub>2</sub> protons of the BzMA monomer, with that of the peaks in the  $\delta$  4.7 ppm region, pertaining to the O–CH<sub>2</sub> protons of the repeat units of the poly(benzyl methacrylate) (PBzMA) polymer.

The "impurity" levels of a specific monomer in the subsequent blocks of the quasi-multiblock copolymer materials were also determined by <sup>1</sup>H-NMR. The complexity of <sup>1</sup>H-NMR spectra increases with increasing the order of blocks. A variety of <sup>1</sup>H-NMR integration methods were applied for the determination of these defects derived from monomer "impurity" and as a consequence of not reaching full conversion in previous polymerization steps. The amount of BMA monomer "impurity" in quasi-tri- (ABC), tetra- (ABCD) and penta- (CBABC) block copolymers was assumed to be 0% in

the blocks obtained in second and third chain extension reactions. Similarly, the amount of MMA "impurity" in quasi-tetrablock copolymers (ABCD) was assumed to be 0% in the block obtained in the third chain extension reaction (PBZMA block). The MMA "impurity" in blocks derived from a second or third chain extension reaction (*i.e.*, in quasi-tri- (ABC), tetra- (ABCD) and penta- (CBABC) block copolymers) was determined by integration of the MMA methacrylate peak  $\delta$  5.9 ppm region (relative to the constant PBMA peak in the  $\delta$  3.8 ppm region) using t=0 (the onset of the corresponding chain extension reaction) as a reference spectra. The integration method utilizes the following equation: mol % of MMA monomer in the quasi-block copolymer = [(ref]5.9 - ]5.9) / ref[5.9] × 100; where ref ]5.9 and ]5.9 are the integral values of the C=CH<sub>2</sub> methacrylate protons of the MMA monomer. The DEGMA monomer "impurity" in the block derived from a third chain extension reaction (*i.e.*, PBZMA block in the quasi-tetrablock copolymers (ABCD)) was estimated by the following equation: mol % of DEGMA in the quasi-tetrablock copolymer = [([3.9 / 2) / (j3.9 / 2 + ]4.7 / 2)] × 100; where ]3.9 and ]4.7 are the integral values of the O–CH<sub>2</sub> protons of the repeat units of the PDEGMA and PBZMA, respectively.

SEC was performed on a Shimadzu system equipped with a CMB-20A controller system, a SIL-20A HT autosampler, a LC-20AT tandem pump system, a DGU-20A degasser unit, a CTO-20AC column oven, a RDI-10A refractive index detector and 4 × Waters Styragel columns (HT2, HT3, HT4, HT5 each 300 mm × 7.8 mm providing an effective molar mass range of  $100 - 4 \times 106$ ). This SEC system uses *N*,*N*-dimethylacetamide (DMAc) (with 2.1 g L<sup>-1</sup> of lithium chloride (LiCl)) as eluent with a flow rate of 1 mL min<sup>-1</sup> at 80 °C. The molar mass of the samples was obtained from a calibration curve constructed with PMMA standards (Polymer Laboratories) of low molar mass dispersity (*Đ*). A 3<sup>rd</sup> order polynomial was used to fit the log  $M_p$  vs. time calibration curve, which was linear across the molar mass ranges.



Figure S1. <sup>1</sup>H-NMR spectra of the final reaction mixture of the synthesis of macro-RAFT agent for determination of the conversion of the copolymer blocks in the synthesis of PBMA-qb-PMMA-qb-PDEGMAqb-PBzMA (Scheme 1). A) PBMA, B) PBMA-qb-PMMA, C) PBMA-qb-PMMA-qb-PEGMA and D) PBMA*qb*-PMMA-*qb*-PDEGMA-*qb*-PBzMA.



**Figure S2.** Kinetic plots of the synthesized PMMA-*qb*-PBMA-*qb*-PMMA quasi-triblock copolymer materials derived from *bis*-macro-RAFT (Table 1) A) precursor agent **1** and B) precursor agent **2**.  $M_n$  and dispersity (*D*) as a function of the MMA conversion (left) and MMA conversion as a function of reaction time (right).



**Figure S3.** Kinetic plots of the synthesized PDEGMA-*qb*-PMMA-*qb*-PBMA-*qb*-PMMA-*qb*-PDEGMA quasipentablock copolymer materials derived from *bis*-macro-RAFT (Table 2) A) precursor agent **5** and B) precursor agent **6**.  $M_n$  and dispersity (*D*) as a function of the DEGMA conversion (left) and DEGMA conversion as a function of reaction time (right).



**Figure S4.** Kinetic plot of the synthesized PBMA-*qb*-PMMA-*qb*-PDEGMA quasi-triblock copolymer materials derived from macro-RAFT (Table 3) A) precursor agent **7** and B) precursor agent **8**.  $M_n$  and dispersity (D) as a function of the DEGMA conversion (left) and DEGMA conversion as a function of reaction time (right).



**Figure S5.** Appearance of shoulders and tailings during the second chain extension when bringing to higher conversion. SEC trace of a chain extension RAFT polymerization of the previously synthesized PBMA-*qb*-PMMA-*qb*-PDEGMA quasi-triblock.



**Figure S6.** SEC trace of the chain extension RAFT polymerization (Table 4) of the synthesized PBMA-*qb*-PMMA-*qb*-PDEGMA-*qb*-PBzMA quasi-tetrablock copolymer materials derived from macro-RAFT precursor agent **9**.