Methacrylic Block Copolymers by Sulfur Free RAFT (SF RAFT) Free Radical Emulsion Polymerisation

Gabit Nurumbetov, †^a Nikolaos Engelis, †^a Jamie Godfrey, †^b Rachel Hand, ^a Athina Anastasaki, ^{ac} Alexandre Simula, ^a Vasiliki Nikolaou^a and David M. Haddleton. ^{ac*}

a - University of Warwick, Chemistry Department, Library road, CV4 7AL, Coventry, United Kingdom

b - ARC Centre of Excellence in Convergent Bio-Nano Science and Technology, Monash Institute of Pharmaceutical Sciences, Monash University (Parkville Campus), 399 Royal Parade, Parkville, Victoria 3152, Australia

†These authors contributed equally to this work

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1. Materials/Instrumentation

Materials:

All materials were obtained from Sigma-Aldrich UK or Fisher Scientific and used as received unless stated otherwise. Water used in all experiments was deionized. Cobaloxime boron fluoride (CoBF) was synthesized according to the method of Bakac and Espenson.¹ Tetra-phenyl-cobaloxime boron fluoride was obtained by the same procedure except that dimethyl glyoxime was replaced by diphenyl glyoxime.

Instrumentation:

¹H NMR spectra was recorded on a Bruker DPX-300 spectrometer using chloroform-d (CDCl₃, 99.8% atom D) as the solvent. Chemical shifts are given in ppm downfield from the internal standard tetramethylsilane (TMS).

Matrix-assisted laser desorption/ionization time of flight mass spectroscopy (MALDI-TOF-MS) was conducted employing a Bruker Daltonics Ultraflex II MALDI-TOF spectrometer, equipped with a nitrogen laser delivering 2 ns pulses (337 nm, 25 kV) with positive ion TOF detection. Solutions of trans-2-[3-(4-tert-butylphenyl)-2methyl- 2-propylidene] malonitrile (DCTB) as a matrix (saturated), sodium iodide as cationization agent (1.0 mg mL⁻¹) and sample (1.0 mg mL⁻¹) in tetrahydrofuran (THF) (50 mL) were mixed, and 0.7 mL of the mixture was applied to the target plate. Spectra were recorded in reflector mode calibrating PEG-Me 1100 kDa.

Size exclusion chromatography (SEC) was performed on an Agilent 1260 GPC-MDF instrument fitted with differential refractive index (RI), light scattering (LS) and viscometry (VS) detectors equipped with 2 × PLgel 5 mm mixed-C columns ($300 \times 7.5 \text{ mm}$), 1 × PLgel 5 mm guard column ($50 \times 7.5 \text{ mm}$) and autosampler. Narrow linear poly(methyl methacrylate) standards in range of 19600 to $5.0 \times 106 \text{ g mol}^{-1}$ were used to calibrate the system. All samples were filtered through 0.22 µm PTFE filter before analysis. THF containing 2% of trimethylamine and 0.01% of 2,6-di-*tert*-butyl-4-methylphenol was employed as the mobile phase at a flow rate of 1 mL min⁻¹. SEC data was analyzed using Cirrus v3.3 with calibration curves produced using Varian Polymer Laboratories Easi-Vials linear poly(methyl methacrylate) standards (19600-5.0 × 106 g mol⁻¹, intrinsic viscosity 0.483 dL g⁻¹).

Thermogravimetric analysis was performed (TGA) on a Mettler-Toledo STAR^e instrument under nitrogen flow (100 ml min⁻¹) at a heating rate of 10 °C per minute. The weight of samples was ~5 mg. Samples were compared to a baseline run without a polymer to confirm validity of TGA curves. The degradation temperature (T_d) was defined as the temperature of 50% loss of the total weight for all curves.

The partition ratio (K_D) of CoBF between monomers and water was determined on an Agilent Cary 60 UV-Vis spectrometer. CoBF dissolved in a monomer was added to water and equilibrated for 1 h at 25 °C. An aqueous phase was isolated and the concentration of CoBF was measured at absorption maxima at 453 nm.

The global and instantaneous conversion values were obtained by gravimetric analysis. All samples were cooled to 4 °C prior to measurements in order to reduce an error caused by evaporation.

2. Experimental

Synthesis of macromonomers:

Macromonomers were synthesized employing a modified method reported by Haddleton and co-workers.^{2,3} The polymerization was carried out in a semi-batch mode employing 500 mL double-jacketed reactor equipped with a RTD temperature probe and an overhead stirrer. Sodium dodecyl sulfate (SDS) (0.3 g), 4,4'-azobis(4-cyanovaleric acid) (CVA) (0.5 g) and 130 mL of water were added to a reactor and purged with nitrogen for 30 min under vigorous stirring (325 rpm) prior to heating to 77 °C. CoBF (5 mg) was dissolved in deoxygenated methyl methacrylate (MMA) (20 mL) in a round bottom flask and kept under inert atmosphere. The solution of MMA/CoBF was fed into the reactor over 30 min (0.6667 mL min⁻¹) using a Harvard Apparatus PHD ULTRA syringe pump. The feeding started when the reactor contents reached the temperature of 70 °C. The reaction continued for another hour to completion. The conversion of monomer was >99%.

Synthesis of block and comb copolymers:

Block copolymers were obtained using a protocol originally reported by Moad and Rizzardo.^{4, 5} We implemented a continuous two-step procedure which includes the synthesis of macromonomer followed by the chain extension with a second methacrylic monomer. The first step includes the above mentioned synthesis of macromonomer with a modification. After 60 min of the reaction the temperature of reactor was increased to 86 °C and equilibrated for 30 min. Upon completion of the first step solutions of potassium persulfate (KPS) (0.2 g) in 40 mL of water and a monomer (40 mL) were fed into the reactor over 240 min (0.1667 mL min⁻¹) using a Harvard Apparatus PHD ULTRA syringe pump. Solutions were deoxygenated with for 30 min prior to use. Samples were taken after the first step (90 min) and every hour afterwards.

In case of comb-like polymers a methacrylic monomer was replaced with an acrylic monomer.

3. Supplementary tables and figures

Table S1. Solubility of monomers in water and distribution ratios of chain transfer agents between monomer-water and monomer.

СТА	Monomer [M]	[M] solubility in H₂O, wt%	KD
CoBF	MMA	~1.50	0.67
	EMA	~0.50	0.89
	BMA	~0.35	0.98
	EHMA	~0.31	1.00
	MMA	~1.50	0.00
CoPhBF	EMA	~0.50	0.00
	BMA	~0.35	0.00
	EHMA	~0.31	0.00



Figure S1. SEC trace of PMMA utilising 41.2 ppm of CoBF.



Figure S2. SEC trace of PMMA utilising 123.6 ppm of CoBF.



Figure S3. SEC trace of PMMA utilising 164.8 ppm of CoBF.



Figure S4. SEC trace of PMMA utilising 206 ppm of CoBF.



Figure S5. ¹H NMR spectrum of PMMA macromonomer (<u>M</u>_n=2900 g.mol⁻¹)



Figure S6. SEC chromatograms of the synthesised block copolymers PMMA-co-PMMA.



Figure S7. SEC chromatograms of the synthesised block copolymers PMMA-co-PEMA.



Figure S8. SEC chromatograms of the synthesised block copolymers PMMA-co-P/BMA.



Figure S9. SEC chromatograms of the synthesised block copolymers PMMA-co-PtBMA.



Figure S10. SEC chromatograms of the synthesised block copolymers PMMA-co-PEHMA.



Figure S11. SEC chromatograms of the synthesised block copolymers PMMA-co-PLMA.



Figure S12. SEC chromatograms of the synthesised block copolymers PMMA-co-PBzMA.



Figure S13. SEC chromatograms of the synthesised block copolymers PMMA-co-PIBMA.

Monomer	Solubility in H ₂ O,	Copolymer Đ
	wt%	
MMA	~1.50	1.28
EMA	~0.50	1.17
n-BMA	~0.35	1.14
<i>i</i> -BMA	~0.05	1.17
t-BMA	~0.05	1.42
EHMA	~0.31	1.15
LMA	insoluble	1.5
BzMA	~0.02	1.2
IBMA	insoluble	3.0
GMA	~5	1.5

Table S2. Solubility parameters of employed monomers and dispersity indices of the final block copolymers



Figure S14. ¹H NMR spectra of PMMA-PBA comb-like copolymer. Five molar equivalents of butyl acrylate were added. Further addition of the monomer led to the complete disappearance of vinyl and terminal methoxy groups signals.

4. Supplementary references

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