Supporting Information

Efficient Multiblock Starpolymer Synthesis from Photo-Induced Copper-Mediated Polymerization with up to 21 Arms

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Materials and Methods

Copper(II) bromide (CuBr₂, Sigma-Aldrich, 99%), β -cyclodextrin (98%, Acros Organics), triethylamine (99%, Acros Organics), 2-bromopropionyl bromide (97%, Alfa Aesar), trifluoroacetic acid (TFA, 99% Acros Organics), dichloromethane (DCM, VWR Prolabo Chemicals), diethyl ether (VWR Prolabo Chemicals), chloroform (CHCl₃, VWR Prolabo Chemicals), *n*-hexane (VWR Prolabo Chemicals), tetrahydrofuran (THF, VWR Prolabo Chemicals) and dimethyl sulfoxide (DMSO, Merck, pro analysis) were all used as received. Tris(2-(dimethylamino)ethyl)amine (Me₆TREN)¹, pentaerythritol tetrakis (2-bromoisobutyrate) (4BrⁱBu)², dipentaerythritol hexakis (2-bromoisobutyrate) (6BrⁱBu)² and 2,3,6-tri-O-(2-bromo-2-methylpropionyl]-β-cyclodextrin)³ were synthesized according to literature procedures. Methyl acrylate (MA, Acros, 99%), *n*-butyl acrylate (*n*BA, Acros, 99%), *tert*-butyl acrylate (*t*BA, Alfa Aesar, 99%) and di(ethylene glycol) ethyl ether acrylate (DEGA, Acros, 99%) were deinhibited over columns of activated basic alumina, prior to use.

A 400 MHz Oxford Istruments Ltd. NMR spectrometer was used to record the ¹H NMR spectra in deuterated chloroform with a pulse delay of 12 s.

The analytical size exclusion chromatography (SEC) measurements were performed on a Tosoh EcoSEC HLC-8230GPC, equipped with an autosampler and a Tosoh EcoSEC RI differential refractive index detector. The SEC was equipped with a PSS guard SVD (50 x 7.5 mm) and three PSS SDV analytical linear XL (5 μ m, 300 x 7.5 mm) columns. The columns were thermostated at 40 °C and had a molecular weight range between 1 x 10² to 1 x 10⁶ g · mol⁻¹. THF with toluene as flow marker was used as eluent with a flow rate of 1 mL·min⁻¹. For calibration PSS Laboratories linear narrow polystyrene standards with a range of 470 - 7.5 x 10⁶ g · mol⁻¹ were used. MHKS parameters ($\alpha = 0.74$, K = 10.2 x 10⁻⁵ dL · g⁻¹, THF 30 °C)⁴ were applied for analysis.

To determine the average size of the star block copolymers, dynamic light scattering (DLS) was employed, using a Brookhaven Instruments ZetaPALS. For all DLS measurements 100

mg of the polymer was dissolved in 1 mL ethanol which was then diluted with 9 mL water. Before measuring the solution was ultrasonicated for 15 seconds.

For the reactions performed in the flow microreactor a Labtrix Start R2.2 (Chemtrix BV) system was used. The system was equipped with a glass microcreactor (3227) with an internal volume of 19.5 μ L (width channel = 300 μ m, depth channel = 120 μ m). A Fusion 100 classic syringe pump (Chemyx Inc.) with two gas-tight 1 mL SGE syringes (Trajan Scientific Australia Pty Ltd.) was used for reaction solution delivery. Via controlling the delivery rate of the syringes the residence time (reaction time) can be varied. As a UV light source an OmniCure S1000 system with a 100 W high pressure mercury vapor short arc lamp (spectral emission: 320-500 nm, peak at 365 nm) was used. The identical setup was used for previous studies.^{5, 6}

Experimental Procedures

4-arm star block copolymer synthesis with IR probe. $43.5 \text{ mg} (5.9 \cdot 10^{-2} \text{ mmol}, 1 \text{ eq.})$ $4\text{Br}^{i}\text{Bu}$ (macro)initiator, 0.5 mg ($2.4 \cdot 10^{-3}$ mmol, 0.04 eq.) CuBr₂, 4.1 mg ($1.8 \cdot 10^{-2}$ mmol, 0.30 eq.) Me₆TREN and 475 mg (5.5 mmol, 93 eq.) MA are weight into a 5 mL volumetric flask. The flask is filled with DMSO and the reaction mixture is transferred into a 100 mL three-neck round bottom flask. Through one neck a Mettler Toledo TM15 in-situ FTIR probe is introduced into the reaction mixture. After sealing the flask the solution is purged with nitrogen for 5 minutes. The reaction is started by switching on the Omnicure S1000 system (spectral emission: 320-500 nm, peak at 365 nm) at an iris opening of 100%. After reaching a monomer conversion of 95% the lamp is switched off and a sample for analysis is taken before 437.6 mg (5.5 mmol, 93 eq.) *t*BA is added. The solution is purged again with nitrogen for 5 minutes and the reaction reinitiated by switching on the UV lamp. The same experimental setup was used by Chuang et al. and more detailed information can be found there.⁷

General polymerization procedure in the flow reactor. Reactions were carried out in a Labtrix Start microflow reactor (Chemtrix, Geleen, NL) Before filling a 10 mL volumetric flask with DMSO 1 eq. 4BrⁱBu, 0.30 eq. Me₆TREN and 93 eq. MA are added. CuBr₂ is added accordingly to

the different tested concentration (0.02, 0.04, 0.08 and 0.20 eq.). Before filling the gas tight 1 mL glass syringes the solution was purged with nitrogen for 5 minutes. Via the flow rate the reaction time (residence time) in the reactor is controlled and changed. Two times the residence time was waited to stabilize the reaction conditions before the samples were taken.

General polymerization procedure. Initiator (4BrⁱBu, 6BrⁱBu or 21BrCD), Me₆TREN, monomer and CuBr₂ were added to an amber volumetric flask which was then filled with DMSO. The ratios are 0.04 eq CuBr₂, 0.075 eq Me₆TREN and 23 eq monomer per initiating group CH-Br. The mixture was ultrasonicated until a homogeneous solution was obtained before being transferred to an erlenmeyer flask of the appropriate volume. The solution was shielded from light and purged with N₂-gas for 15-45 minutes, depending on the volume of the solution. Afterwards it was placed in a Multilamp Reactor MLU 18 (Photochemical Reactor Ltd.) equipped with ten 15 Watt lamps (Vilber Lourmat) with a peak emission of 365 nm. Before extracting the polymer solution 3 times with 25 mL CHCl₃, 25 mL H₂O was added. Afterwards the organic phase was washed twice with 25 mL H₂O and the solvent was removed under reduced pressure. The polymer product was then filtered through a silica filter into an amber glass vial. Next, the vial was placed in the vacuum oven overnight for drying.

4-arm star block copolymer synthesis. The general polymerization procedure was carried out with the following equivalence ratios: 1 eq. $4Br^{i}Bu$ (macro)initiator, 0.04 eq. CuBr₂ and 0.30 eq. Me₆TREN. MA, *t*BA, *n*BA and DEGA equivalence ratios were appropriately adjusted in order to obtain varying target molecular weights per arm. The received products were each time used as macroinitiator for further block synthesis.

6-arm star block copolymer synthesis. The general polymerization procedure was carried out using the following equivalence ratios: 1 eq. $6Br^{i}Bu$ (macro)initiator, 0.06 eq. CuBr₂, 0.45 eq. Me₆TREN. The equivalence ratios of MA and *t*BA were adjusted in order to obtain different arm lengths. The received products were each time utilized as macroinitiator for further block synthesis.

21-arm star block copolymer synthesis. The following equivalence ratios were used for each reaction: 1 eq. 21BrCD (macro)initiator, 0.21 eq. CuBr₂, 1.58 eq. Me₆TREN. Different arm lengths were obtained by varying the equivalence ratios of MA and *t*BA. The received products were each time used as macroinitiator for further block synthesis.

General procedure for the degradation of *t***BA to acrylic acid.** After dissolving around 100 mg of each polymer containing *t*BA in roughly 2 mL DCM and 2 mL TFA, they were stirred overnight. The DCM and TFA were removed under reduced pressure.



Figure S 1 SEC traces from the synthesis of a pMA-*b*-p*t*BA blockcopolymer in a one-pot process with the 4-arm initiator (4BrⁱBu). The graph shows for the second block a clear shift to a higher molecular weight. But for both blocks a high molecular weight shoulder can be seen which originates from star-star coupling. The reaction was carried out in a batch reactor equipped with a FTIR-probe for live monitoring of the conversion. The monomer for the second block was added after a monomer conversion of 95% was reached. After 4h and 75% monomer conversion the addition of the second block was stopped. The reaction mixture had a [CH-BR] : [Cu(II)] : [Me₆TREN] : [MA] ratio of 1 : 0.01 : 0.075 : 23 and was diluted with DSMO (10 vol% reaction mixture to 90 vol% DMSO).



Figure S 2 Comparison of the SEC traces of a 4-arm pMA star polymer synthesized via photoinduced copper-mediated polymerization in a microflow reactor with different CH-Br to Cu(II) concentrations. All samples had a monomer conversion around 90 % and as CH-Br to Cu(II) concentration 1 : 0.01, 0 02, 0.05 were used. Ratios of 1 : 0.01 : 0.075 : 23 [CH-BR] : [Cu(II)] : [Me₆TREN] : [MA] were used for the reaction mixture. DMSO was used as solvent in a ratio of 7 : 1 with respect to monomer volume.



Figure S 3 Decrease of star-star coupling with increasing dilutions of 4-arm pMA star polymers synthesized via photo-induced copper-mediated polymerization. All shown samples had a monomer conversion between 88 and 92 %. The reactants were used in the following ratios $[CH-Br]: [CuBr_2]: [Me_6TREN]: [MA] - 1: 0.01: 0.075: 23$. Dilutions of 1:7 and 1:10 monomer with respect to DMSO were used.



Figure S 4 SEC trace of the 4-arm star shaped octa block copolymer synthesized via photo-induced copper-mediated polymerization. As block builder MA and *t*BA were used in an alternating order.



Figure S 5 ¹H NMR spectrum before and after the hydrolysis of a pMA-*b*-p*t*BA 4-arm star shaped polymer with TFA. The characteristic broad tert-butyl peak around 1.4 ppm is not present after the hydrolysis with TFA.



Figure S 6 SEC traces before and after the TFA treatment of a pMA 4-arm star shaped polymer. The polymer was dissolved in DCM and TFA and stirred overnight. No shift in the molar mass is observed which proves that the acid treatment has no effect at the core ester-groups.



Figure S 7 Cumulative number weighted size distribution for a 21 arm star polymer containing a pMA and pDEGA block with a corrected number average molecular weight per arm of 6200 g \cdot mol⁻¹. The sizes were measured with a Brookhaven ZetaPals at 10, 25 and 35 °C in EtOH/H2O (10/90 v/v%) solution with a polymer concentration of 0.01 g \cdot mL⁻¹.

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