Supporting Information for

Processing and Adjusting the Hydrophilicity of Poly(oxymethylene) (Co)polymers: Nanoparticle Preparation and Film Formation

Markus B. Bannwarth,[1,3,‡] Rebecca Klein,[2,3,‡] Sven Kurch,[2] Holger Frey,[2] Katharina Landfester,[1] Frederik R. Wurm [1,]*

[1]Max Planck Institute for Polymer Research, Ackermannweg 10, D-55128 Mainz, Germany

[2]Institute of Organic Chemistry, Johannes Gutenberg-University Mainz, Duesbergweg 10-14, D-55099 Mainz, Germany

[3]Graduate School "Material Science in Mainz", Staudingerweg 9, D-55099 Mainz, Germany

wurm@mpip-mainz.mpg.de

‡ These authors contributed equally.

Synthesis of poly(oxymethylene) (POM) and the ABA triblock copolymers (*hb*PG-*b*-POM-*b*-*hb*PG)

For the synthesis of the linear poly(oxymethylene) block, trioxane (100 g, 1.11 mol) was preheated to 80 °C and dioxolane (10 g, 0.13 mol) and formic acid (1.8 g, 0.04 mol) added and stirred vigorously. Triflic acid was added and the resulting polymer dissolved in NMP (1.5 L) at 150-160 °C, triethylamine (1.5 mL) and water (1.0 mL) were added and heated to 100 °C. After 30 min the water was removed by distillation and the solution was again heated to 140 °C for 2 h. Then the mixture was allowed to cool down to 65 °C and filtrated to

remove low molecular weight side-products. The filter cake was diluted in methanol and again heated to 70 °C for 1 h. After filtration of the mixture, the filter cake was dried *in vacuo* (yield: 53%). SEC (HFIP, PMMA standard): M_n = 10,700 g mol^{-1}; PDI = 2.09. ^{1}H NMR (HFIP-d_2, 600 MHz): δ [ppm] = 5.20-5.00 (-CH_2- polymer main chain); 5.00-4.95 (-CH_2- dioxolane); 3.95-3.90 (-CH_2- dioxolane).

Acid-catalyzed degradation of the nanoparticles

1 mL of the nanoparticles dispersion in water was combined with 1 mL hydrochloric acid (5 mol L^{-1}) or 1 mL acetic acid and 1 mL DMF and stirred at 80 °C for 1 h. Then, the solution was centrifuged at 4500 rpm for 5 min.

Additional Figures and Tables:

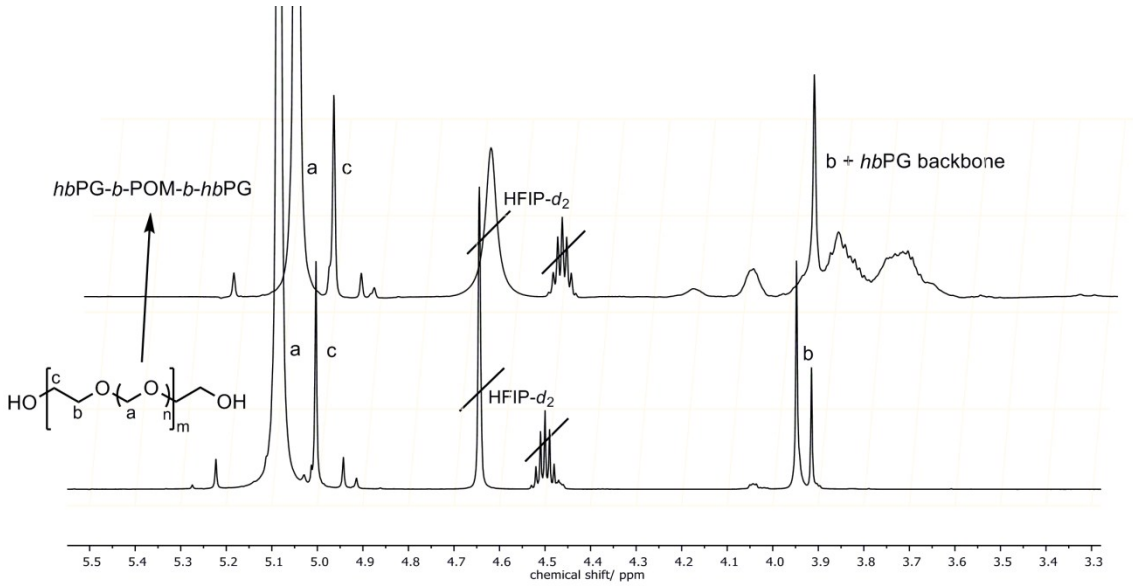

Figure S1. ^{1}H NMR spectra (600 MHz, HFIP-d_2, 37 °C) of POM_{120} (bottom) and *hb*PG_7-*b*-POM_{120}-*b*-*hb*PG_7 (top).

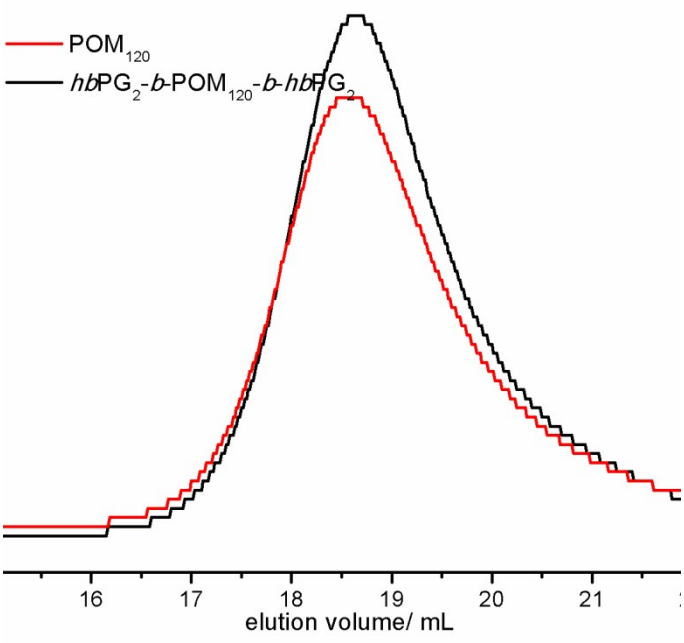

Figure S2. SEC (HFIP, RI-detector, PMMA standards) traces of the POM_{120} macroinitiator (red) and *hb*PG_2-*b*-POM_{120}-*b*-*hb*PG_2 (black).

Table S1. Hydrodynamic diameter and standard deviation of different POM nanoparticles in water as determined via DLS measurements.

no.	composition (NMR)	Hydrodynamic diameter/ nm	Standard deviation
1	**POM_{120}**	**320**	**41%**
2	*hb*PG_2-*b*-POM_{120}-*b*-*hb*PG_2	310	41%
3	*hb*PG_3-*b*-POM_{120}-*b*-*hb*PG_3	310	42%
4	*hb*PG_5-*b*-POM_{120}-*b*-*hb*PG_5	310	46%
5	*hb*PG_7-*b*-POM_{120}-*b*-*hb*PG_7	300	39%

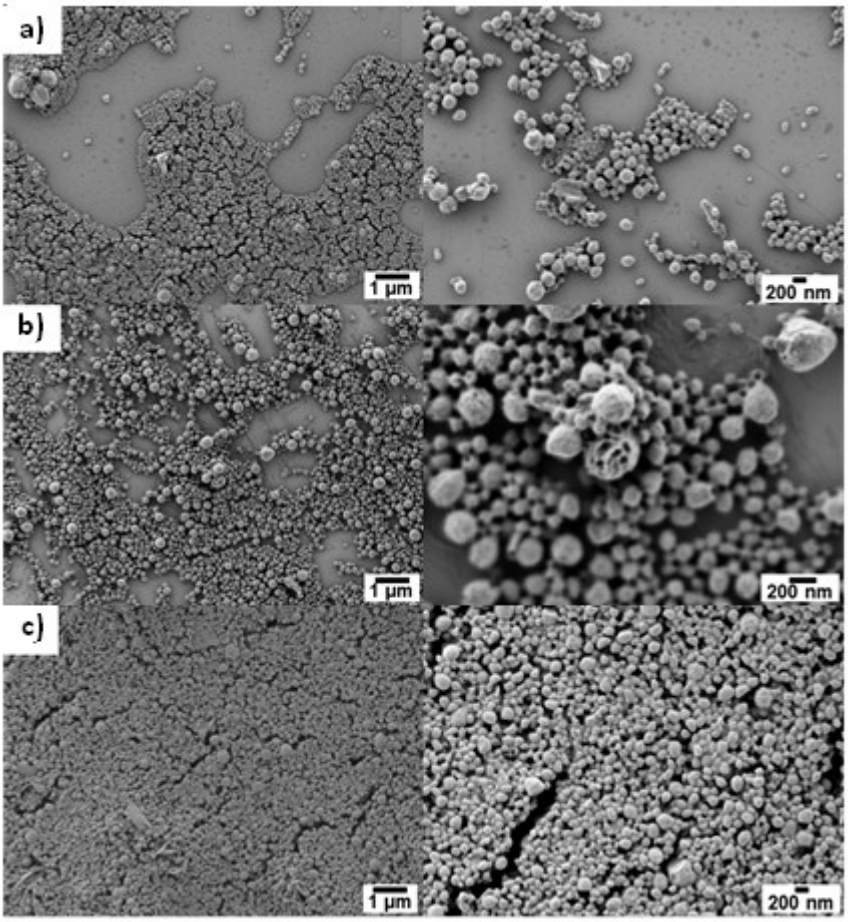

Figure S3. SEM images of POM nanoparticles composed of POM chains with different end-group functionalization: a) *hb*PG_2-*b*-POM_{120}-*b*-*hb*PG_2, b) *hb*PG_3-*b*-POM_{120}-*b*-*hb*PG_3, c) *hb*PG_7-*b*-POM_{120}-*b*-*hb*PG_7.

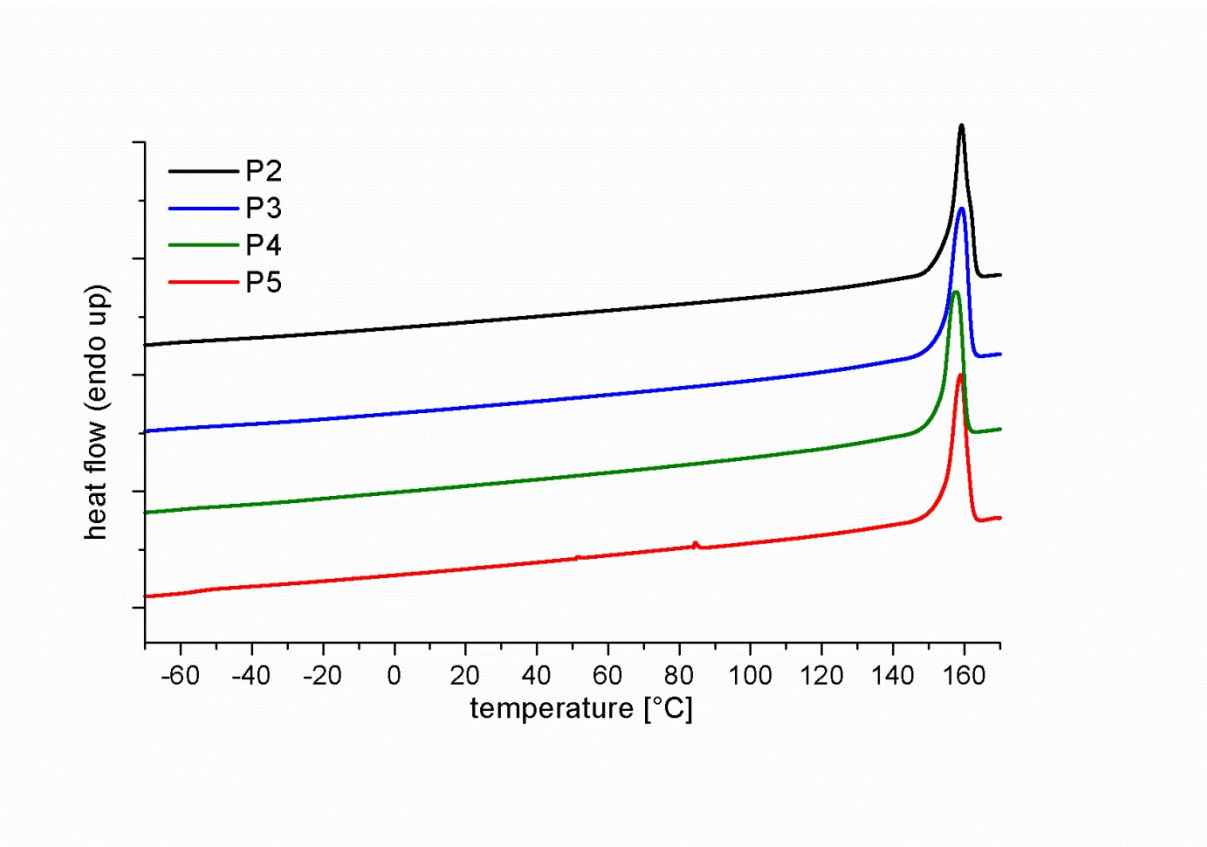

Figure S4. DSC curves of block copolymers used in this study.