Supporting Information for

Modular Design of Glyco-Microspheres via Mild Pericyclic Reactions and their Quantitative Analysis

Michael Kaupp,[a] Andrew P. Vogt,[a] Jens C. Natterodt,[a] Vanessa Trouillet,[b] Till Gruendling,[a] Thorsten Hofe,[c] Leonie Barner,[d] and Christopher Barner-Kowollik*[a,d]

[a]Preparative Macromolecular Chemistry, Institut für Technische Chemie und Polymerchemie,Karlsruhe Institute of Technology (KIT), Engesserstraße 18, 76128 Karlsruhe, Germany. E-mail: christopher.barner-kowollik@kit.edu

[b]Institute for Applied Materials (IAM-WPT), Karlsruhe Institute of Technology (KIT),Hermann-von-Helmholtz-Platz 1, 76344 Eggenstein-Leopoldshafen, Germany.

[c]Polymer Standards Service GmbH, In der Dalheimer Wiese 5, 55120 Mainz, Germany.

[d]Soft Matter Synthesis Laboratory, Institut für Biologische Grenzflächen I, Karlsruhe Institute of Technology (KIT), Hermann-von-Helmholtz-Platz 1, 76344 Eggenstein-Leopoldshafen, Germany.

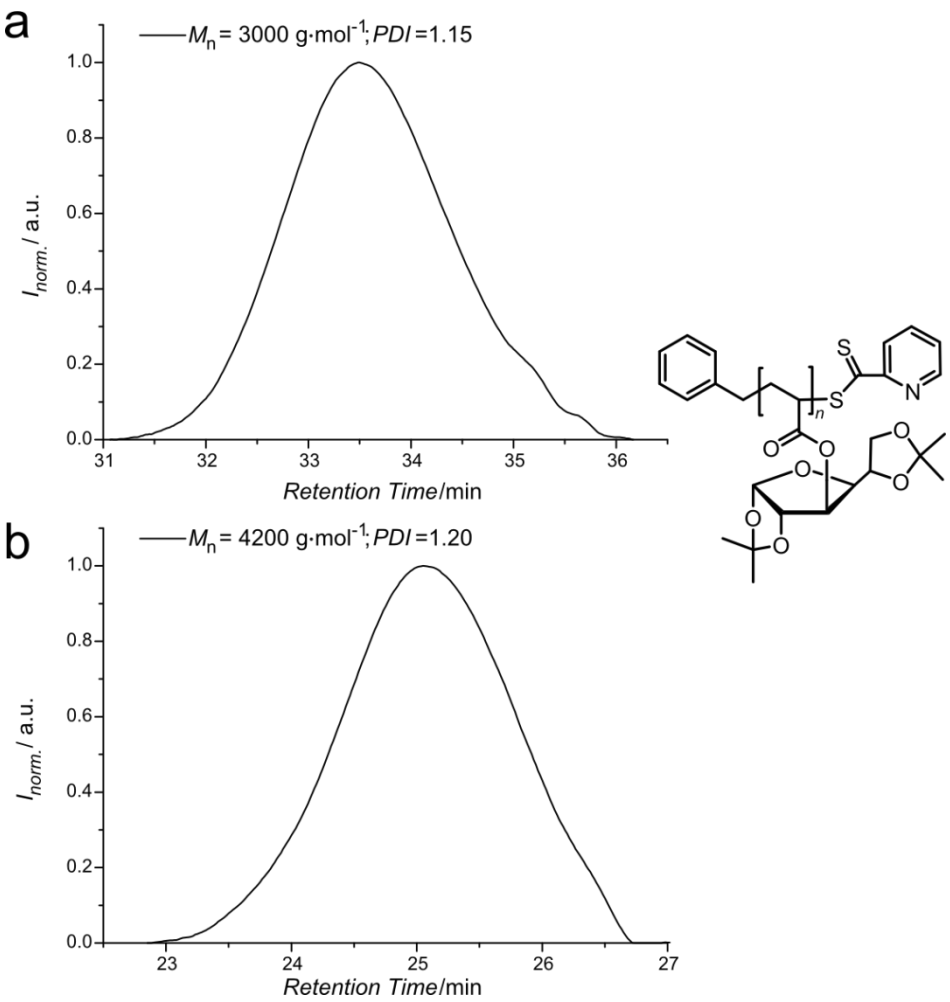

Fig. S1. Molecular weight distribution of the protected glycopolymer synthesized via RAFT-polymerization using BPDF as RAFT-agent and AIBN at 75°C in toluene for 4 h in THF (a) and DMAc (b) as eluent. The values for M_n and *PDI* correspond to polystyrene calibration.

The inaccuracy of the M_n does not affect the accuracy of the values for the loading capacity or grafting density, as only the sulfur in the chain end is needed for the calculation which is determined separately via elemental analysis. The values for M_n and *PDI* obtained from the analysis in DMAc are reported throughout this publication, as the M_n value is closer to the theoretical expected value for a controlled RAFT-polymerization at the conversion determined via ^{1}H-NMR (M_n of approximately 4000 g·mol^{-1} for a conversion of 25 %).

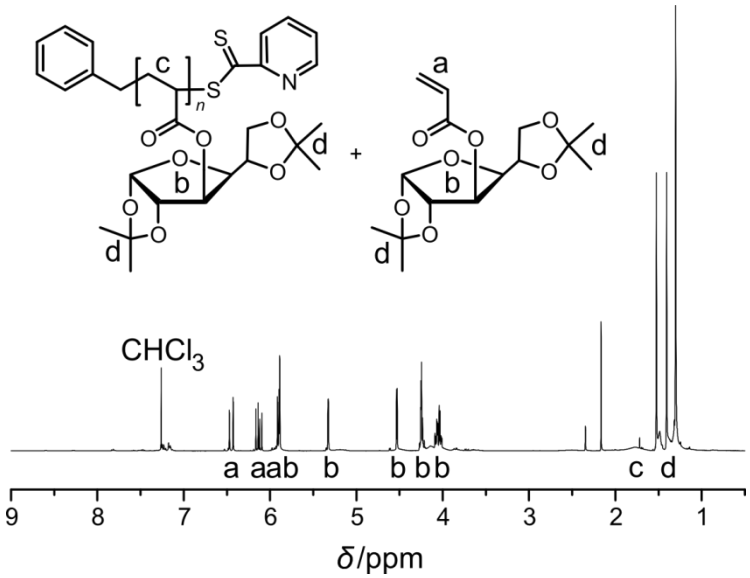

Fig. S2. ^{1}H-NMR spectrum in $CDCl_3$ of the protected glycopolymer synthesized via RAFT-polymerization using BPDF as RAFT-agent and AIBN at 75°C in toluene for 4 h after drying.

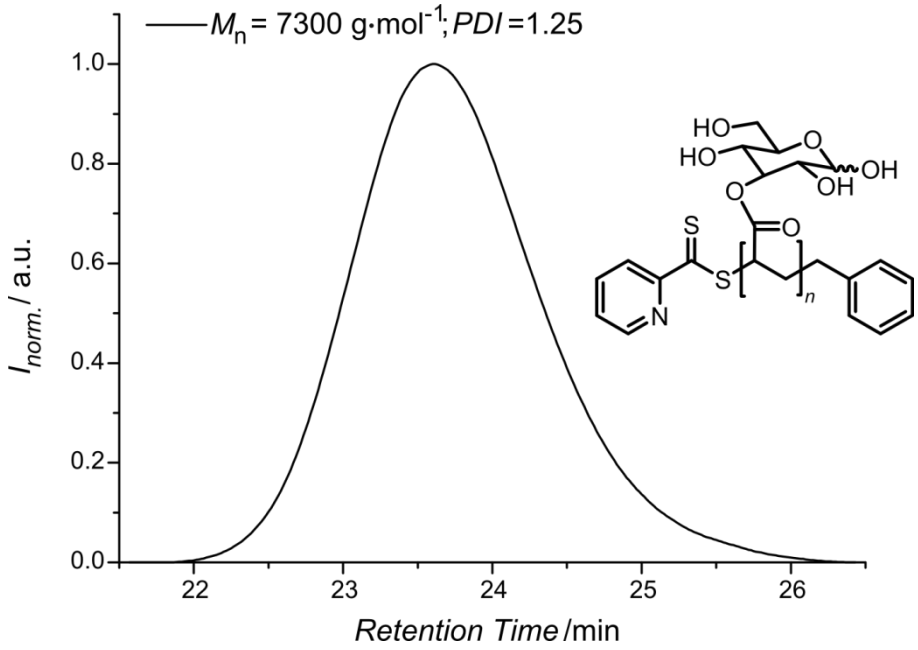

Fig. S3. Molecular weight distribution in DMAc of the deprotected glycopolymer recovered from the grafting reaction by dialyzing the filtrate and the first 50 mL of wash water against distilled water (utilizing a SpectraPor3 membrane (MWCO = 1000 Da)) and subsequent freeze drying. The values for M_n and *PDI* correspond to polystyrene calibration.

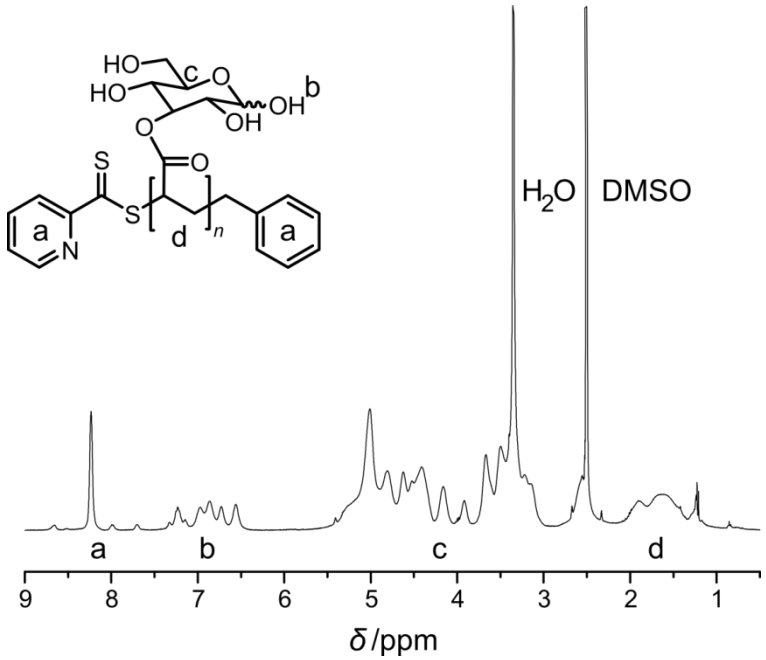

Figure S4. ^{1}H-NMR spectrum in DMSO-d_6 of the deprotected glycopolymer after deprotection in 80 % formic acid at ambient temperature for 48 h, dialysis against distilled water (utilizing a SpectraPor3 membrane (MWCO = 1000 Da)) and subsequent freeze drying.

Table S1. Collected data from the inverse size exclusion chromatography of the non-modified microspheres employed in this work under the assumption of cylindrical pores by the method described by Gorbunov:[1, 2]

Sample	Average pore dimension [nm]	Width of pore size distribution [nm]	Surface area [m^2/cm^3]
pGMA 30 Å	3.33 ± 0.06	11.9 ± 0.1	601.3 ± 11.4
pGMA 100 Å	6.29 ± 0.09	8.5 ± 0.1	318.0 ± 4.5
pGMA 1000 Å	8.87 ± 1.27	29.8 ± 1.5	225.4 ± 34.6
pGMA 3000 Å	24.37 ± 2.06	57.9 ± 2.6	82.1 ± 7.4
pGMA 10000 Å	15.13 ± 1.42	67.7 ± 2.4	132.2 ± 13.1
pGMA 30000 Å	8.55 ± 0.76	108.4 ± 3.0	234.0 ± 21.8

1 A. A. Gorbunov and A. M. Skvortsov, *Polymer*, 1991, **32**, 3001.
2 A. A. Gorbunov, L. Y. Solovyova and V. A. Pasechnik, *J. Chromatogr. A*, 1988, **448**, 307.

Table S2. Collected data from elemental analysis of all samples described in this work:

Sample	N [wt%] [a]	C [wt%]	H [wt%]	S [wt%] [b]	O [wt%] [b]
pGMA 30 Å	0.27	55.68	6.90	0.00	32.60
Cp-functionalized	0.28	54.65	6.80	0.00	31.23
24 h HDA	0.31	51.11	6.29	0.57	34.45
48 h HDA	0.38	50.87	6.20	0.65	34.02
96 h HDA	0.36	50.40	6.02	0.67	33.31
pGMA 100 Å	0.00	58.66	7.41	0.00	33.89
Cp-functionalized	0.00	57.98	7.23	0.00	33.46
24 h HDA	0.22	52.77	6.53	0.70	33.71
48 h HDA	0.21	52.07	6.40	0.79	33.82
96 h HDA	0.21	51.50	6.23	0.94	34.30
pGMA 1000 Å	0.19	55.77	6.88	0.00	32.84
Cp-functionalized	0.00	57.59	7.24	0.00	31.88
24 h HDA	0.23	58.28	7.08	0.62	34.25
48 h HDA	0.30	52.51	6.39	0.63	33.94
96 h HDA	0.33	52.01	6.19	1.09	33.63
90 h HDA[c]	0.39	51.75	6.26	1.34	32.75
HDA with glycopolymer	0.37	51.90	6.57	0.24	35.11
HDA with glycopolymer (repeated)	0.45	51.41	6.13	0.31	35.67

control	0.00	55.73	6.88	0.00	34.91
pGMA 3000 Å	0.00	58.63	7.27	0.00	32.93
Cp-functionalized	0.00	58.34	7.23	0.00	31.92
24 h HDA	0.00	53.04	6.36	0.66	34.03
48 h HDA	0.00	52.41	6.26	0.76	33.81
96 h HDA	0.10	51.94	6.12	0.88	33.61
pGMA 10000 Å	0.00	58.37	7.35	0.00	32.75
Cp-functionalized	0.00	57.67	7.10	0.00	31.16
24 h HDA	0.00	53.47	6.38	0.72	33.21
48 h HDA	0.00	53.31	6.33	0.75	32.80
96 h HDA	0.22	52.76	6.26	0.90	32.85
pGMA 30000 Å	0.00	59.70	7.41	0.00	32.89
Cp-functionalized	0.00	58.37	7.21	0.00	32.41
24 h HDA	0.00	54.26	6.47	0.60	32.03
48 h HDA	0.09	53.50	6.37	0.62	33.63
96 h HDA	0.09	52.81	6.25	0.67	33.29

[a] The nitrogen found in the untreated and Cp-functionalized microspheres can be explained by fragments from the nitrogen containing initiator, stabilizer or gaseous nitrogen trapped in the porous surface morphology of the microspheres. Since the nitrogen value is not used for any further calculations, this does not lead to an error for the calculated loading capacity or grafting density values. [b] The sulfur and oxygen contents were each measured independently. [c] The reaction was performed separately. Why a higher loading capacity was reached is still under investigation.

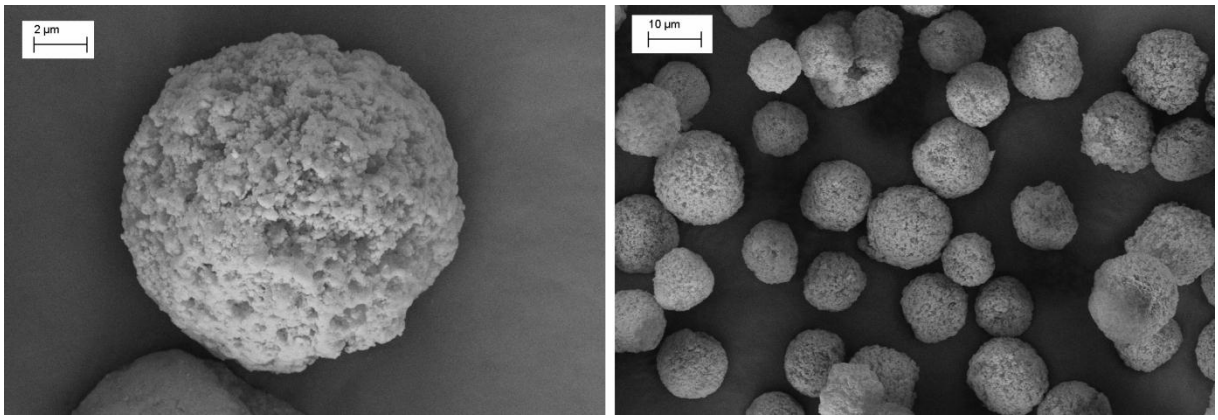

Fig. S5. SEM images of the non-modified pGMA microspheres with an average pore size of 10000 Å.

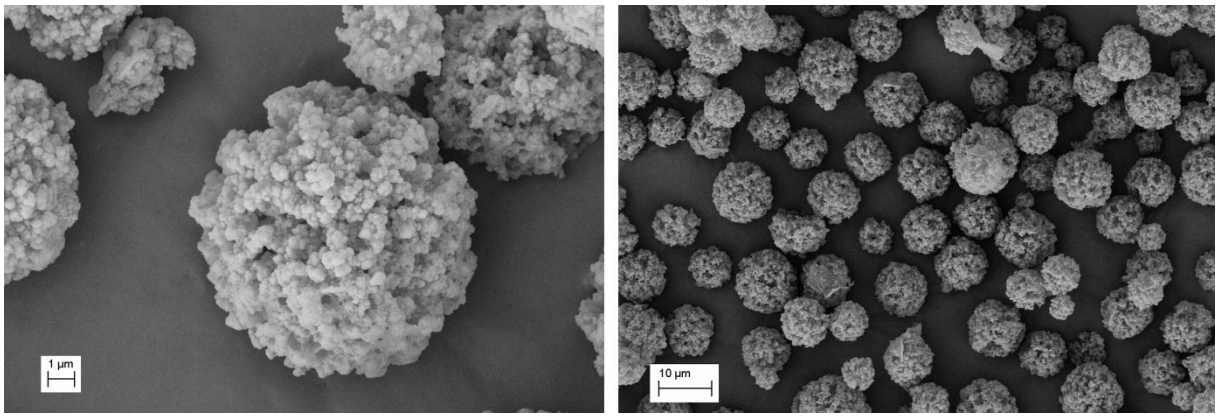

Fig. S6. SEM images of the non-modified pGMA microspheres with an average pore size of 30000 Å.