

Electronic Supplementary Material (ESI) for Polymer Chemistry
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Electronic Supplementary Information for:
The Long and the Short of Polymer Grafting

Lukas Michalek[†], Kai Mundsinger[†], Christopher Barner-Kowollik,^{} and Leonie Barner^{*}*

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1 Experimental Procedures

1.1 Materials and Methods

2,2-Azobisisobutyronitrile (AIBN, 12 wt.-% in acetone, Sigma Aldrich) was recrystallized twice from methanol prior to use. Methyl methacrylate (MMA, 99%, ≤ 30 ppm MEHQ as inhibitor, Sigma Aldrich) was passed over basic alumina. (3-amino-propyl)triethoxysilane ($\geq 98\%$, Sigma Aldrich) was distilled prior to use. 4-Cyano-4-(phenylcarbonothioylthio)pentanoic acid ($> 97\%$, Sigma Aldrich), 1-ethyl-3-(3-dimethylaminopropyl)carbodiimide (EDC, $\geq 98\%$, Sigma Aldrich), methanol ($\geq 99.5\%$, analytical reagent, Ajax Finechem), ethanol (analytical reagent, Ajax Finechem) and *n*-Pentane (analytical reagent, Ajax Finechem) were used as received. Dichloromethane (DCM, HPLC grade, Ajax Finechem), toluene (HPLC grade, Fisher Chemicals) and THF (HPLC grade, Fisher Chemicals) were dried over columns filled with aluminium oxide and molecular sieves in a LC Technology Solutions Inc. SP1 solvent purification system.

Size exclusion chromatography (SEC)

The molar masses and molar mass distributions of the prepared polymers were determined on a PSS SECurity² system consisting of a PSS SECurity Degasser, PSS SECurity TCC6000 Column Oven (35 °C), PSS SDV Column Set (8x150 mm 5 μ m Precolumn, 8x300 mm 5 μ m Analytical Columns, 100000 Å, 1000 Å and 100 Å) and an Agilent 1260 Infinity Isocratic Pump, Agilent 1260 Infinity Standard Autosampler, Agilent 1260 Infinity Diode Array and Multiple Wavelength Detector (A: 254 nm, B: 360 nm), Agilent 1260 Infinity Refractive Index Detector (35 °C). HPLC grade THF, stabilized with BHT, was used as eluent at a flow rate of 1 mL·min⁻¹. Narrow disperse linear poly(styrene) (M_n : 266 g·mol⁻¹ to 2.52x10⁶ g·mol⁻¹) and poly(methyl methacrylate) (M_n : 202 g·mol⁻¹ to 2.2x10⁶ g·mol⁻¹) standards (PSS ReadyCal) were used as calibrants. All samples were passed over 0.22 μ m PTFE membrane filters prior to analysis. Molar mass and dispersity analysis was performed in PSS WinGPC UniChrom software (version 8.2).

Number based molar mass distributions (MMD_n)

Depending on the employed detector, the MMD_n can be obtained directly or via a simple calculation. A UV detector can be tuned to the absorption wavelength of the polymer end group, which results in a directly recorded MMD_n. If, however, the end group is sensitive towards oxidation, like most RAFT derived end groups, this is unreliable. The refractive index signal instead is mass sensitive, implying it is proportional to the number of monomer units in the sample. Thus, RI detection returns the mass weighted concentration signal. If the ordinate values are divided by the respective molar mass of each slice concentration, a number (of polymer chains) weighted distribution is obtained.

Nuclear magnetic resonance (NMR) spectroscopy

¹H NMR-spectra were recorded on a Bruker 600 Ascend LH, equipped with a BBO-Probe (5 mm) with z-gradient (¹H: 600 MHz.). The resonances are reported in chemical shift (δ = ppm, rounded to two decimals) relative to the solvent signal of CHCl₃ (7.26 ppm). Coupling constants (*J*) are reported in Hz. Spectra were processed using Mestrelab Reasearch S.L. MestReNova 11.

Quartz microbalance measurements

Quartz microbalance measurements were performed using a Biolin Scientific QSense Explorer and flow module with 40 μ L volume above sensor and 250 μ L total volume. The temperature of the flow cell was kept at 50 °C and a flow rate of 15 μ L·min⁻¹ was employed. Qsense QSX 303 SiO₂ sensors were used after 30 min of plasma cleaning. The respective polymer samples **P1** to **P5** were dissolved in dry toluene to yield solutions containing 2 mg·mL⁻¹ polymer and degassed by argon purging for 20 min. The solutions were stored at 5 °C in air-tight amber glass bottles until used. For the mixed molar mass solutions, aliquots of the parent solutions were mixed, taking their respective $M_{n,GPC}$ into account, to obtain solutions with molar ratios of 1:1, 1:4 and 1:9. Each measurement was started flushing the flow cell with dry, degassed toluene to record a 30 min of a stable baseline for each measurement. Subsequently, the sample solution was introduced at approximately 10 mL·min⁻¹ to purge the system, then the flow rate was reduced to 15- μ L·min⁻¹. Frequency changes were recorded until a stable state was reached.

X-ray photoelectron spectroscopy (XPS)

Spectra were recorded on a Kratos Axis Supra photoelectron spectrometer. During analysis, the charge compensation system was employed to prevent any localised charge build-up. For each sample, wide spectra and high resolution spectra of individual peaks (C 1s, O 1s, N 1s, S 2s/2p and Si 2s/2p) were recorded. All spectra were calibrated by setting the C 1s peak to 285.00 eV. Evaluation, peak deconvolution and fitting was carried out in Casa Software Ltd CasaXPS 2.3.

Atomic force microscopy (AFM)

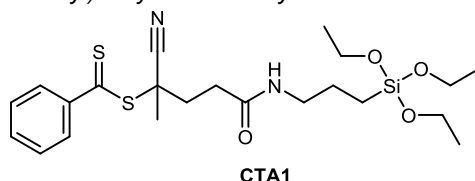
The AFM used for this measurements was an Asylum Research MFP-3D Bio. The cantilever which was used was an Olympus OMCL-TR400PB with the actual cantilever force constant of 0.11 N·m⁻¹. Force spectroscopy measurements were performed in a semi closed toluene solvent environment (Fluid Lite Cell, samples glued with epoxy resin on a glass cover slip) using a Z-sensor movement of 1 μ m, 0.5 μ m·s⁻¹ velocity correlating to a scan rate of 0.25 Hz per measurement, a trigger force of 1 nN and a dwell time of 1 s. The raw data recorded by the AFM was the Z-sensor position and the deflection of the cantilever. Calibration was performed against silicon (Si) wafers and thermal tuning was used to determine the actual cantilever force constant. Force mapping was performed on a 10 x 10 μ m sample area with 10 x 10 pixels, with an x-y velocity of 1 μ m·s⁻¹, generating 100 individual force-distance curves per measurement. For each sample, a minimum of five force maps at different positions were performed.

Ellipsometry

The ellipsometer used for this measurements was an J. A. Woollam M-2000UI with a wavelength range of 4245 – 1690 nm. The measurements were done with incidence angles from 60 to 80° (in 5° steps) and fitted by a Cauchy model using the CompleteEASE software.

1.2 Synthesis

Synthesis of 4-(3-(triethoxysilyl)propylcarbamoyl)-2-cyanobutan-2-yl benzodithioate **CTA1**

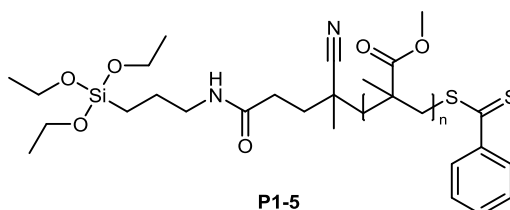


CTA1

The title compound was synthesized according to a literature procedure.^[1] 4-Cyano-4-(phenylcarbonothioylthio)pentanoic acid (757 mg, 2.7 mmol, 1.2 eq.) and EDC (649 mg, 3.4 mmol, 1.5 eq.) were dissolved in dry DCM (100 mL) under argon atmosphere using flame dried glassware. 3-Aminopropyltriethoxysilane (529 μ L, 2.3 mmol, 1 eq.) was added using a gas-tight syringe. The reaction was allowed to proceed for 3 h at ambient temperature. Subsequently, the reaction mixture was washed twice with saturated sodium hydrogen. The carbonate solution, twice with demineralized water, twice with brine and the organic phase was dried over magnesium sulfate. The solvent was removed under reduced pressure and the target compound **1** was obtained as red oil.

¹H-NMR (600 MHz, Chloroform-*d*, 25 °C): δ = 7.90 (d, ³J(H,H) = 7.3 Hz, 2 H, CH arom.), 7.56 (t, ³J(H,H) = 7.4 Hz, 1 H, CH arom.), 7.39 (t, ³J(H,H) = 7.9 Hz, 2 H, CH arom.), 5.96 (s, 1 H, NH), 3.82 (q, ³J(H,H) = 7.0 Hz, 6 H, CH₂), 3.27 (q, ³J(H,H) = 6.7 Hz, 2 H, CH₂), 2.65 – 2.38 (m, 4 H, CH₂), 1.93 (s, 3 H, CH₃), 1.64 (quin, ³J(H,H) = 7.0 Hz, 2 H, CH₂), 1.23 (t, ³J(H,H) = 7.0 Hz, 9 H, CH₃), 0.64 (t, ³J(H,H) = 8.0 Hz, 2 H, CH₂)

Synthesis of RAFT-PMMA **P1-5**



P1-5

The polymer samples were prepared according to literature known procedures.^[2] A stock solution of MMA (6.55 M) and AIBN (1.8 mM) in toluene was degassed by three freeze-pump-thaw cycles. The stock solution was then added to septum vials containing weighed amounts of RAFT chain transfer agent (RAFT CTA) **1** and purged with argon for 10 min. The vials were subsequently heated to 80 °C in an aluminium heating block and the polymerization was allowed to proceed for 16 h. The contents of each vial were dissolved in 4 mL THF and the polymers precipitated in methanol and subsequently in *n*-pentane. The polymers were dried in vacuo (≤ 0.002 mbar, 24 h) and stored under argon and exclusion of light.

¹H-NMR (**P1**) (600 MHz, Chloroform-*d*, 25 °C): δ = 7.90 (m, 2 H, CH arom.), 7.56 (m, 1 H, CH arom.), 7.39 (m, 2 H, CH arom.), 5.96 (s, 1 H, NH), 3.82 (q, ³J(H,H) = 7.0 Hz, 6 H, CH₂), 3.27 (q, ³J(H,H) = 6.7 Hz, 2 H, CH₂), 2.65 – 2.38 (m, 4 H, CH₂), 1.93 (s, 3 H, CH₃), 1.64 (quin, ³J(H,H) = 7.0 Hz, 2 H, CH₂), 1.23 (t, ³J(H,H) = 7.0 Hz, 9 H, CH₃), 0.64 (t, ³J(H,H) = 8.0 Hz, 2 H, CH₂)

Table S1 Molar masses and dispersities for PMMA via RAFT polymerization of MMA (6.55 M in toluene) with AIBN (1.8 mM) as initiator and **2** as RAFT CTA for 16 h at 80 °C.

Sample	$M_{n,theo.}^{[a]}$ g·mol ⁻¹	MMA M	AIBN mM	RAFT CTA mM	$M_{n,GPC}$ g·mol ⁻¹	$M_{w,GPC}$ g·mol ⁻¹	D_{GPC}
P1	10500	6.55	1.8	68.57	8200	8700	1.06
P2	44500	6.55	1.8	15.02	48000	50600	1.05
P3	85600	6.55	1.8	7.66	106000	116000	1.09
P4	176700	6.55	1.8	3.73	133900	158000	1.18
P5	396000	6.55	1.8	1.66	216100	289000	1.34

^[a] according to a simplified formula assuming quantitative conversion and full control: $M_{n,theo.} = \frac{[Monomer]}{[RAFT\ CTA]} \cdot M_{Monomer} + M_{RAFT\ CTA}$

Aminolysis of RAFT end-group P1, P3 and P5

Before performing force spectroscopic measurements (SMFS) on the PMMA polymer brushes, SI-RAFT agent end groups are removed by aminolysis (thiol end group for attachment to gold cantilever) by placing the polymer brush covered substrates in a solution of hexylamine (20 μ L, 0.153 mmol) and triethylamine (20 μ L, 0.153 mmol) in 5 mL toluene in a sample vial. These vials were shaken for 3 h and the substrates were subsequently rinsed with ethanol and acetone and dried in a N_2 stream.

2 NMR Spectra

¹H-NMR (CDCl₃) Silane-RAFT-CTA **1**

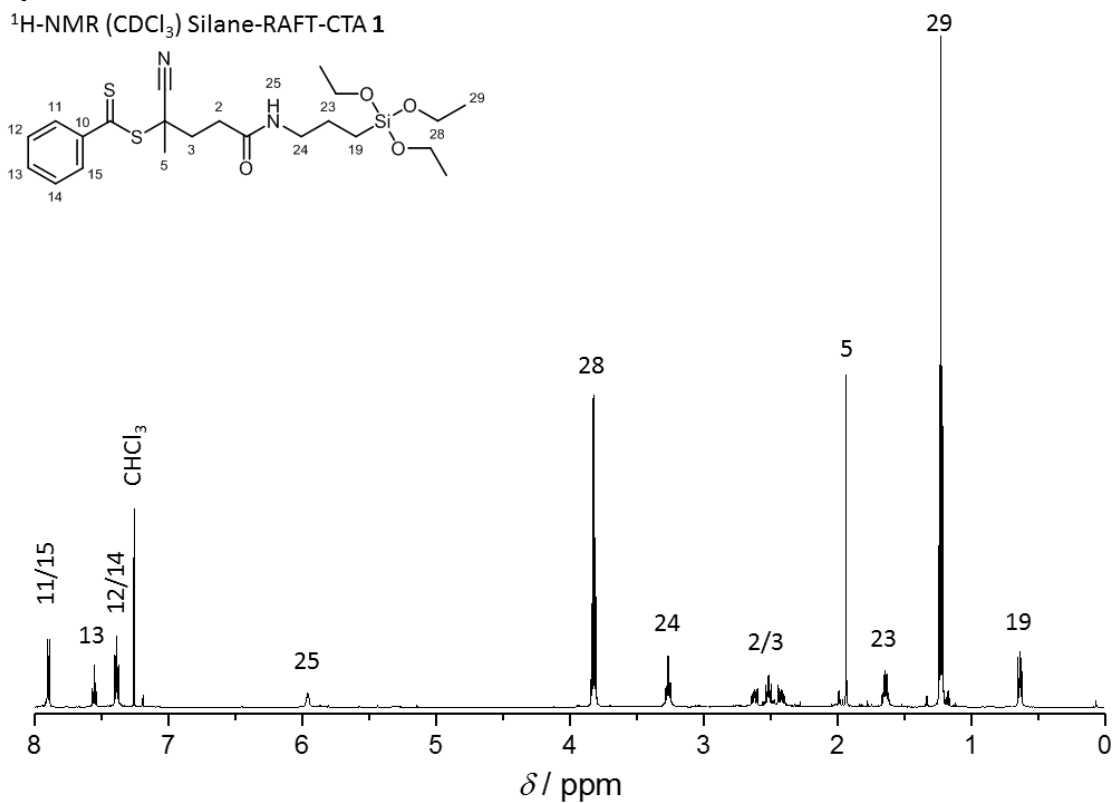


Figure S1 ¹H-NMR spectrum (CDCl₃) of CTA1.

¹H-NMR (CDCl₃) Silane-RAFT-PMMA **P1**

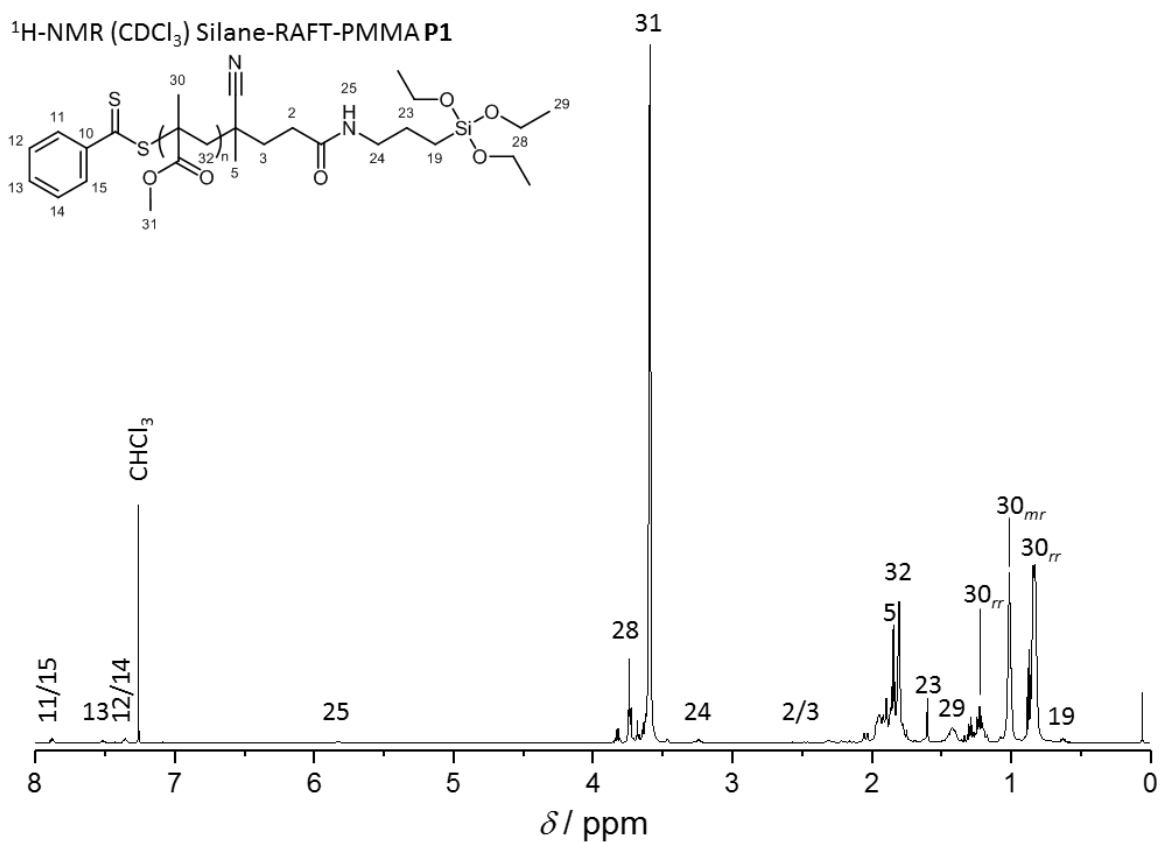


Figure S2 ¹H-NMR spectrum (CDCl₃) of P1.

3 Size Exclusion Chromatography

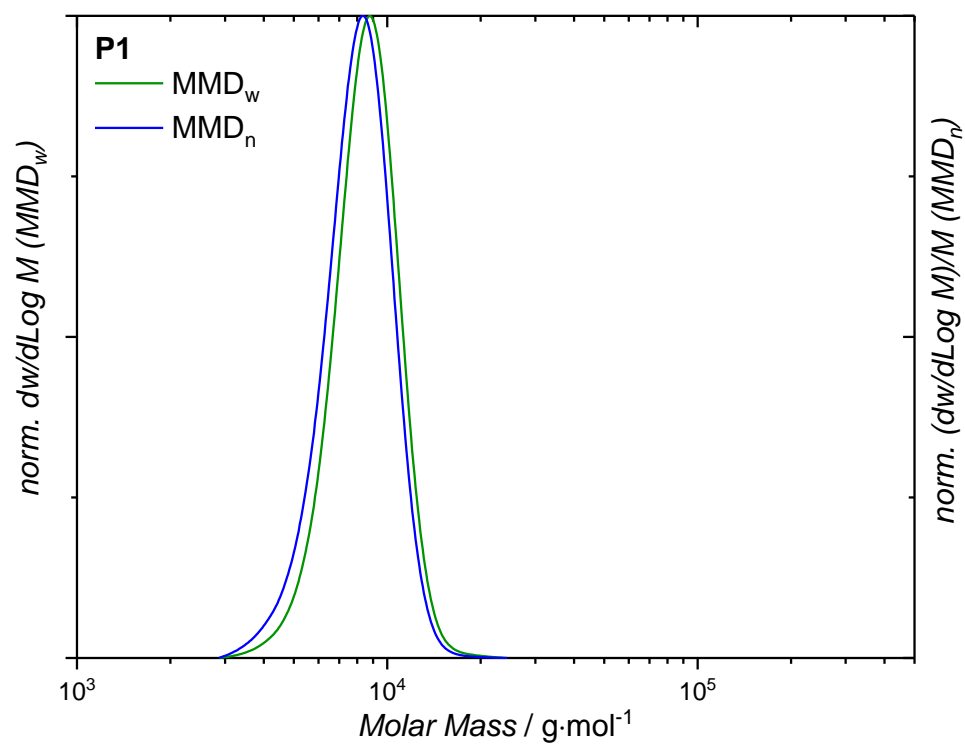


Figure S3 Mass (green) and number based (blue) MMD of **P1**. $M_n = 8200 \text{ g}\cdot\text{mol}^{-1}$, $M_w = 8700 \text{ g}\cdot\text{mol}^{-1}$, $\mathcal{D} = 1.06$.

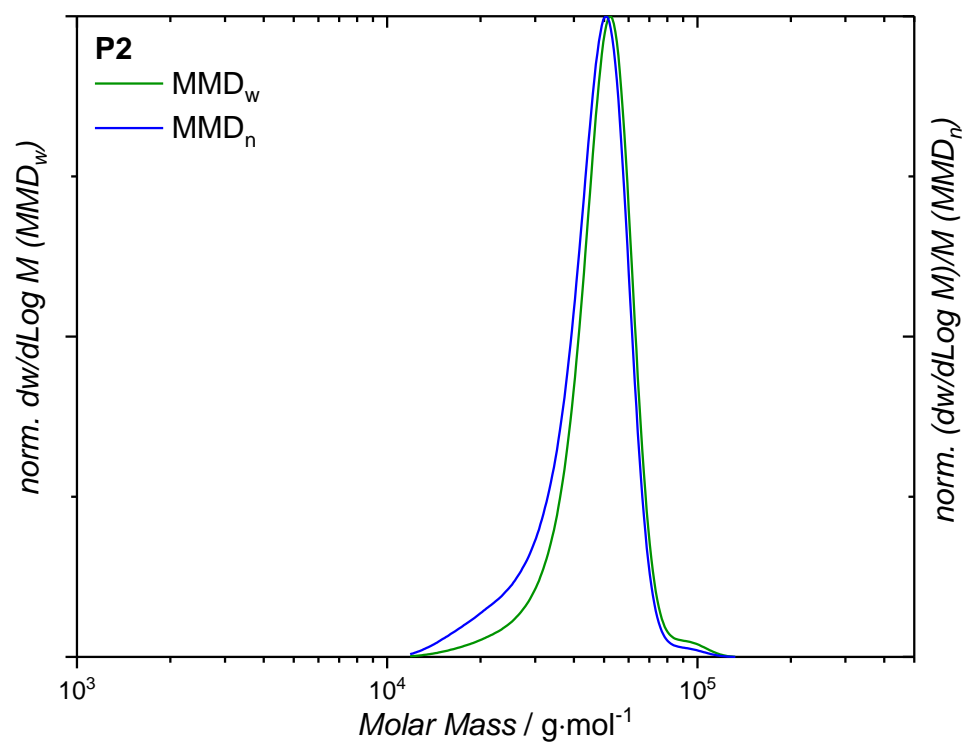


Figure S4 Mass (green) and number based (blue) MMD of **P2**. $M_n = 48000 \text{ g}\cdot\text{mol}^{-1}$, $M_w = 50600 \text{ g}\cdot\text{mol}^{-1}$, $\mathcal{D} = 1.05$.

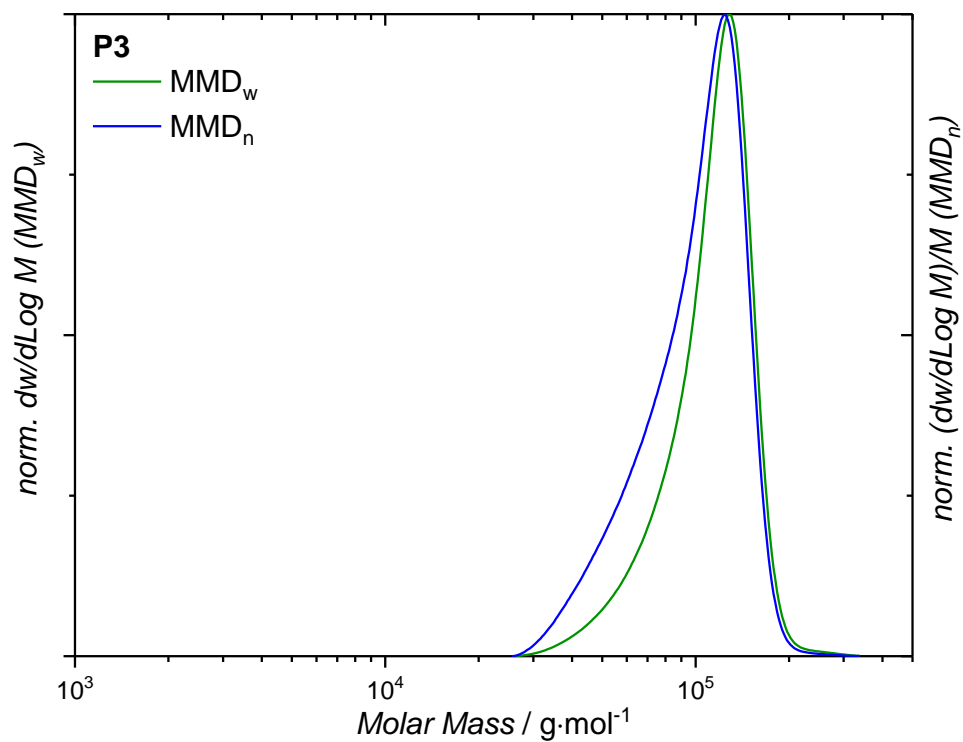


Figure S5 Mass (green) and number based (blue) MMD of **P3**. $M_n = 106000 \text{ g}\cdot\text{mol}^{-1}$, $M_w = 116000 \text{ g}\cdot\text{mol}^{-1}$, $D = 1.09$.

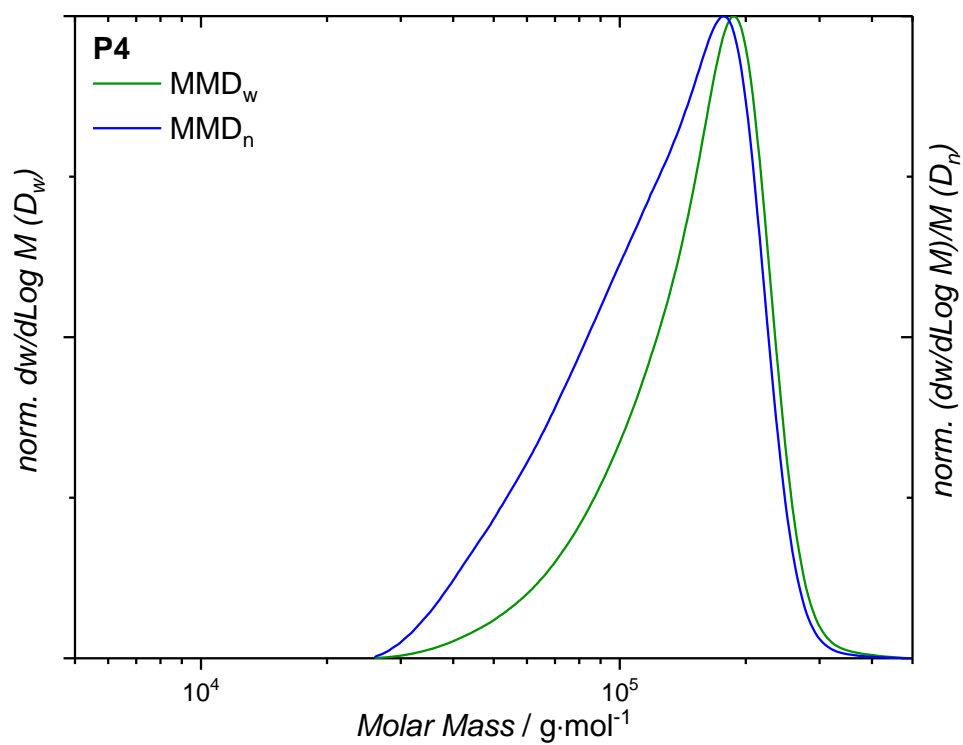


Figure S6 Mass (green) and number based (blue) MMD of **P4**. $M_n = 133900 \text{ g}\cdot\text{mol}^{-1}$, $M_w = 158000 \text{ g}\cdot\text{mol}^{-1}$, $D = 1.18$.

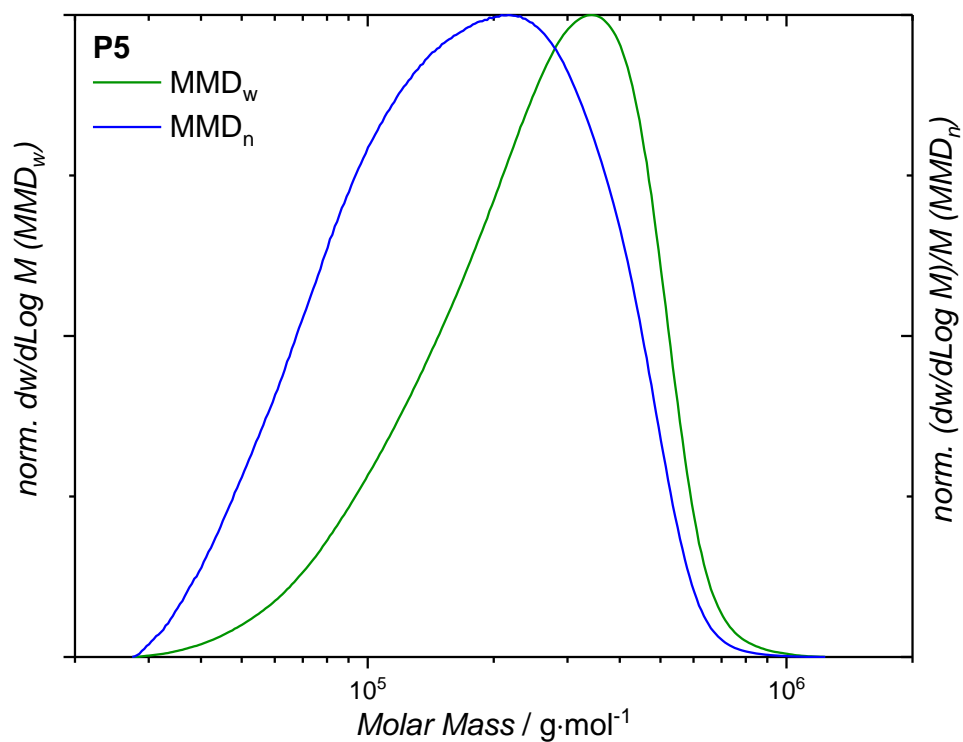


Figure S7 Mass (green) and number based (blue) MMD of **P5**. $M_n = 216100 \text{ g}\cdot\text{mol}^{-1}$, $M_w = 289000 \text{ g}\cdot\text{mol}^{-1}$, $D = 1.34$.

4 X-ray Photoelectron Spectroscopy

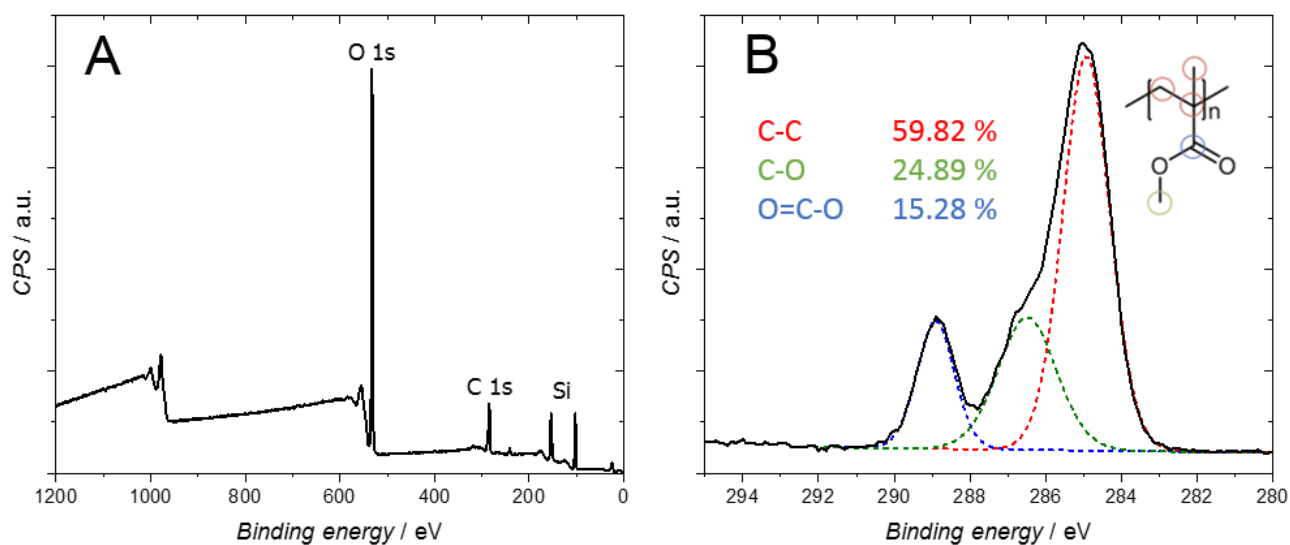


Figure S8 Wide spectra (A) and high resolution spectrum of the C1s peak (B) of **P3** on a QCM sensor, ratios matching expected ratios for PMMA (C-C 60%, C-O 20% and O=C-O 20%).

5 Quartz Microbalance Data

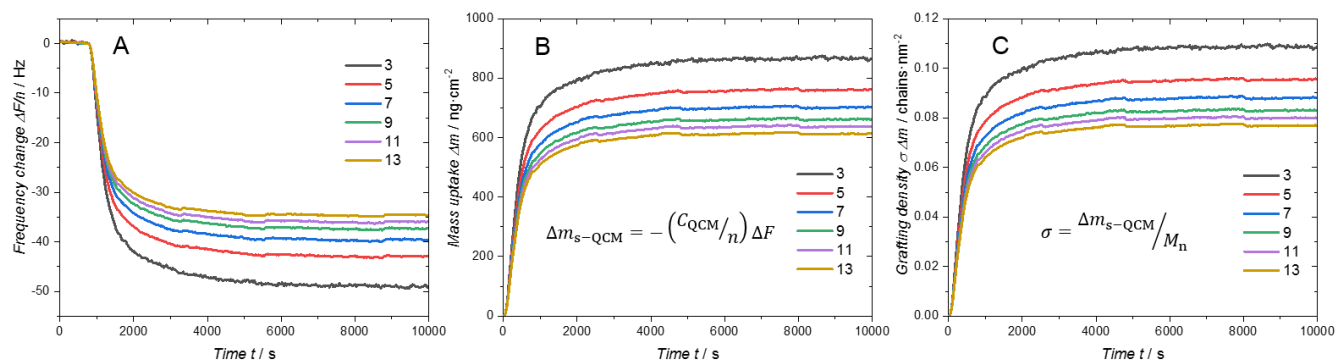


Figure S9 Evaluation procedure for all overtone numbers n . **A)** Time dependent frequency change. **B)** Time dependent mass uptake. **C)** Time dependent grafting density.

Table S2 Measured frequency change and calculated grafting density after reaching the plateau for **P1-P5** and all overtone frequencies

n	P1		P2		P3		P4		P5	
	ΔF [Hz]	σ [nm^{-2}]	ΔF [Hz]	σ [nm^{-2}]	ΔF [Hz]	σ [nm^{-2}]	ΔF [Hz]	σ [nm^{-2}]	ΔF [Hz]	σ [nm^{-2}]
3	-111	0.476	-146	0.108	-160	0.054	-156	0.041	-148	0.024
5	-164	0.424	-213	0.094	-229	0.046	-223	0.035	-193	0.019
7	-217	0.400	-275	0.087	-283	0.041	-174	0.020	-262	0.018
9	-264	0.380	-334	0.082	-356	0.040	-332	0.029	-310	0.017
11	-317	0.373	-393	0.079	-394	0.036	-382	0.027	-374	0.017
13	-309	0.308	-448	0.076	-422	0.033	-427	0.026	-398	0.015
avg.	-205	0.394	-269	0.088	-274	0.041	-250	0.030	-251	0.018
SD	93	0.052	123	0.011	119	0.007	123	0.007	110	0.003

The grafting density is monotonically decreasing for increasing overtone numbers which suggests that there is a slight dissipation in the measurements. Nevertheless the scaling behavior in all overtone numbers is the same for the different polymer samples. Therefore, the solvent interaction parameter for each overtone number is in the range of the determined one $n^* = 0.47 \pm 0.02$ (by the average of all overtone numbers) and is not changing.

Table S3 Samples **R1-R5** used to investigate grafting bias, theoretical normalization with M_n^{sol} in solution for all overtone numbers.

n	R1 $M_n^{\text{sol}} = 8.24$ kDa	R2 $M_n^{\text{sol}} = 57.12$ kDa	R3 $M_n^{\text{sol}} = 86.45$ kDa	R4 $M_n^{\text{sol}} = 96.22$ kDa	R5 $M_n^{\text{sol}} = 106$ kDa
	$\Delta F/nM_n$ [$\text{Hz} \cdot \text{kDa}^{-1}$]	$\Delta F/nM_n$ [$\text{Hz} \cdot \text{kDa}^{-1}$]	$\Delta F/nM_n$ [$\text{Hz} \cdot \text{kDa}^{-1}$]	$\Delta F/nM_n$ [$\text{Hz} \cdot \text{kDa}^{-1}$]	$\Delta F/nM_n$ [$\text{Hz} \cdot \text{kDa}^{-1}$]
3	-4.47	-0.78	-0.33	-0.36	-0.67
5	-3.98	-0.66		-0.31	-0.50
7	-3.75	-0.60	-0.25	-0.28	-0.43
9	-3.56	-0.59		-0.26	-0.38
11	-3.50	-0.57	-0.21	-0.25	-0.34
13	-2.89	-0.56	-0.19	-0.24	-0.31
avg.	-3.69	-0.63	-0.24	-0.28	-0.39
SD	0.48	0.07	0.05	0.04	0.06

Table S4 Samples **R2-R4** used to investigate grafting bias, theoretical normalization with M_n^{sol} in solution and expected M_n^{sur} on surface for all overtone numbers

Ratio	Reality	Expected from solution ratio	Adjustment factor κ
	$\Delta F/nM_n^{\text{sol}}$ [$\text{Hz} \cdot \text{kDa}^{-1}$]	$\Delta F/nM_n^{\text{sur}}$ [$\text{Hz} \cdot \text{kDa}^{-1}$]	
R2	-0.63 ± 0.07	-2.04	3.26 ± 0.39
R3	-0.24 ± 0.05	-1.05	4.29 ± 0.96
R4	-0.28 ± 0.04	-0.72	2.54 ± 0.38
		avg.	3.36 ± 0.58

Table S5 Samples used to investigate grafting bias R1*-R3*, theoretical normalization with M_n^{sol} in solution for all overtone numbers.

n	R1* $M_n^{\text{sol}} = 48$ kDa	R2* $M_n^{\text{sol}} = 77$ kDa	R3* $M_n^{\text{sol}} = 106$ kDa
	$\Delta F/nM_n$ [Hz·kDa ⁻¹]	$\Delta F/nM_n$ [Hz·kDa ⁻¹]	$\Delta F/nM_n$ [Hz·kDa ⁻¹]
3	-1.01	-0.55	-0.67
5	-0.89	-0.48	-0.50
7	-0.82	-0.43	-0.43
9	-0.77	-0.40	-0.38
11	-0.74	-0.38	-0.34
13	-0.72	-0.36	-0.31
avg.	-0.83	-0.43	-0.39
SD	0.48	0.06	0.06

Table S6 Samples used to investigate grafting bias R2*, theoretical normalization with M_n^{sol} in solution and expected M_n^{sur} on surface for all overtone numbers

Ratio	Reality $\Delta F/nM_n^{\text{sol}}$ [Hz·kDa ⁻¹]	Expected from solution ratio $\Delta F/nM_n^{\text{sur}}$ [Hz·kDa ⁻¹]	Adjustment factor κ
R2*	-0.43 ± 0.06	-0.61	1.40 ± 0.10

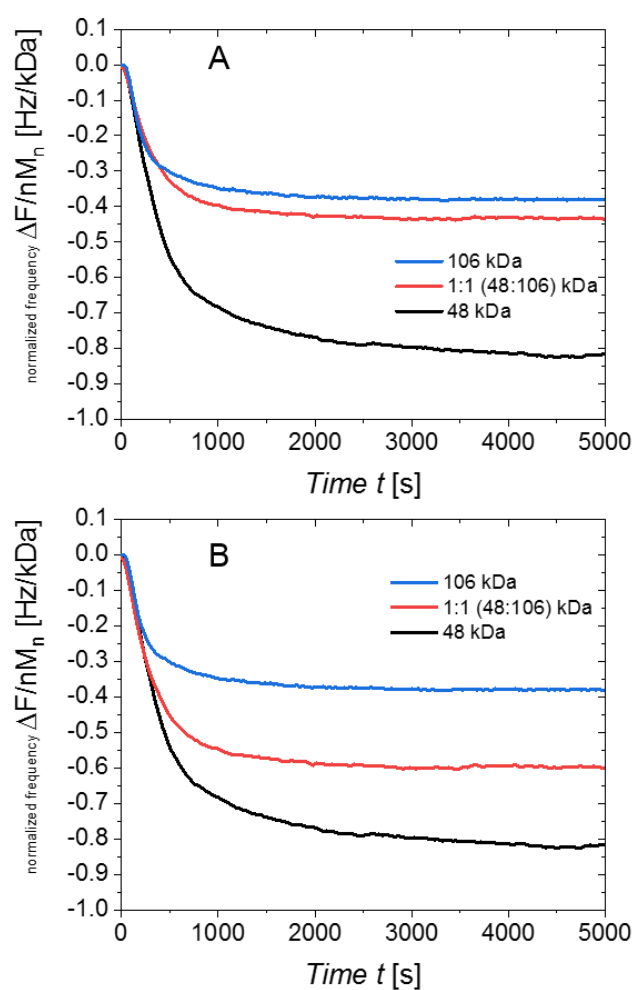


Figure S10 A) Time dependent frequency change for polymer mixtures R1* to R3* normalized by their average molar mass in solution M_n^{sol} . **B)** Time dependent frequency change for R1* to R3* normalized by M_n^{sur} to match expected frequency behavior of sample P2 and P3

7 Preferential grafting factor κ

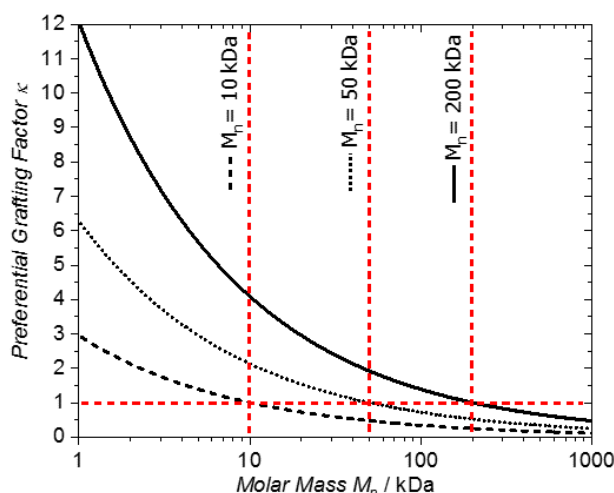


Figure S11 Preferential grafting factor κ for three different number average molar masses $M_n = 10, 50$ and 200 kDa (dashed, dotted and solid line), calculated via Eq. (4). The intersection of the red dashed lines mark the points where $\kappa = 1$ for each sample, which is the number average molar mass of the sample. A larger value for κ implies a stronger bias towards grafting of the particular molar mass.

8 Single-molecule force spectroscopy (SMFS)

The rupture length l_R of the samples **P1**, **P3** and **P5** was determined from the force – distance curves of the recorded force maps. We want to point out that only a small fraction of the individual force curves has an actual rupture event due to the low grafting density. Nevertheless, for each sample at least 50 clear rupture events were found. The individual rupture lengths for all three samples can be found in **Table S7-S9** and the corresponding histograms with matching Gaussian fits (using the average and the standard deviation as fitting parameters) in **Figure S11**.

Table S7 Individual rupture lengths for sample **P1** with average (AV), standard deviation (SD) and standard error (SE).

Rupture length l_R [nm]				
8	10	14	24	44
8	11	14	29	45
9	11	15	31	47
9	12	15	33	51
9	12	15	37	53
10	12	17	38	56
10	12	17	39	58
10	12	19	41	64
10	13	19	42	70
10	14	21	43	74
AV = 26 SD = 18 SE = 3				

Table S8 Individual rupture lengths for sample **P3** with average (AV), standard deviation (SD) and standard error (SE).

Rupture length l_R [nm]					
67	85	112	132	171	232
67	86	113	138	176	251
68	88	114	138	183	252
69	88	120	138	190	258
71	91	121	140	192	260
73	91	123	147	196	265
73	92	123	148	221	271
76	100	125	149	225	276
77	103	127	160	228	305
84	104	130	164	229	312
AV = 150 SD = 68 SE = 9					

Table S9 Individual rupture lengths for sample **P5** with average (AV), standard deviation (SD) and standard error (SE).

Rupture length l_R [nm]					
34	68	83	125	168	222
40	69	87	126	168	248
44	72	93	127	172	259
49	72	98	129	176	278
57	72	99	133	180	333
62	73	100	138	197	340
64	75	112	146	203	412
65	81	115	151	204	414
66	81	118	160	209	446
67	83	118	162	219	659

AV = 154 SD = 115 SE = 15

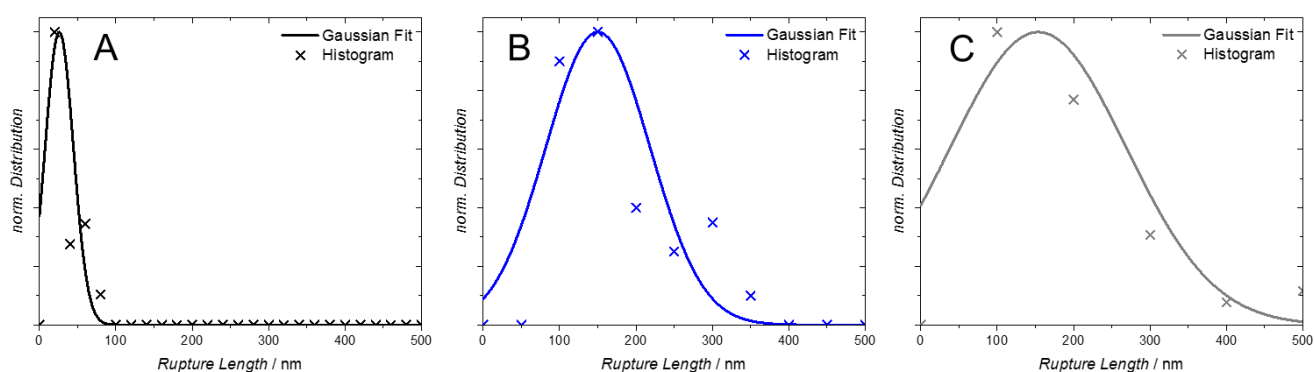


Figure S12 Histograms (experimental values) with matching Gaussian fits (using the average and the standard deviation as fitting parameters) for sample **P1** (in panel **A**), **P3** (in panel **B**) and **P5** (in panel **C**).

9 Ellipsometry

Table S10 Film thickness for sample **P5** with average (AV), standard deviation (SD) and standard error (SE).

P1 thickness [nm]	P3 thickness [nm]	P5 thickness [nm]
7.70	8.73	8.85
6.04	7.14	8.63
7.06	7.20	8.01
AV = 6.93±0.68	AV = 7.69±0.74	AV = 8.50±0.34

10 References

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