Supporting Information:

Quantifying Solvent Effects on Polymer Surface Grafting

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1 Experimental Procedures

1.1 Materials and Methods

4-Cyano-4-(phenylcarbonothioylthio)pentanoic acid (> 97%, Sigma Aldrich), 1-ethyl-3-(3-dimethylaminopropyl)carbodiimide (EDC, ≥98%, Sigma Aldrich), methanol (≥ 99.5%, analytical reagent, Ajax Finechem), ethanol (analytical reagent, Ajax Finechem), acetone (analytical reagent, Ajax Finechem), ethyl acetate (≥ 99.8%, Fisher Scientific), *N*,*N*-dimethylacetaminde (HPLC grade, Sigma Aldrich), tetraethyl orthosilicate (TEOS, 98% Sigma Aldrich), ammonia (28%, Thermo Fisher), lithium bromide (≥99%, Sigma Aldrich) and *n*-Pentane (analytical reagent, Ajax Finechem) were used as received. 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 (≥ 98%, Sigma Aldrich) was distilled prior to use. 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* SECurity^2 system consisting of a *PSS* SECurity Degasser, *PSS* SECurity TCC6000 Column Oven (35 °C), *PSS* SDV Column Set (8x150 mm 5 µm Precolumn, 8x300 mm 5 µm 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 2.52x10^6 g·mol^{-1}) and poly(methyl methacrylate) (M_n: 202 g·mol^{-1} to 2.2x10^6 g·mol^{-1}) standards (*PSS* ReadyCal) were used as calibrants. All samples were passed over 0.22 µm PTFE membrane filters prior to analysis. Molar mass and dispersity analysis was performed in *PSS* WinGPC UniChrom software (version 8.2).

Every sample was measured three times and the resulting, virtually identical, traces were averaged. All traces were referenced to an internal standard to correct for eventual changes in elution behavior.

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.

Dynamic Light Scattering (DLS)

Polymer hydrodynamic radii were obtained via DLS using a *Malvern* Zetasizer NanoZS with 4 mW He-Ne laser at 633 nm. Samples were filtered over 0.45 µm membranes and measured at 25 °C in quartz cuvettes. Data evaluation was performed in the *Malvern* Zetasizer software 7.11.

Nuclear magnetic resonance (NMR) spectroscopy

^{1}H NMR-spectra were recorded on a *Bruker* 600 Ascend LH, equipped with a BBO-Probe (5 mm) with z-gradient (^{1}H: 600 MHz,). The resonances are reported in chemical shift (δ = ppm, rounded to two decimals) relative to the solvent signal of $CHCl_3$ (7.26 ppm). Coupling constants (*J*) are reported in Hz. Spectra were processed using *Mestrelab Reasearch S.L.* MestReNova 11.

Transmission electron microscopy (TEM)

Transmission electron micrographs were recorded on a *JEOL* TEM1400 transmission electron microscope. Samples were prepared on 200 mesh copper grids with a *Formvar*/Carbon support film by dip coating of the grid with reaction mixtures or sonicated dispersions. Images were acquired at 80 kV in 4k by 4k using a *TVIPS* F416 CMOS camera.

Particle size analysis

TEM images were analyzed using *NIH* ImageJ2[1] in the Fiji[2] distribution package. The image was divided in equal areas containing about 100 particles per area. All unconcealed particles per area were outlined using the elliptical selection tool. This way a minimum of 100 particles per image was analyzed. The area of the selected outline was then converted to the diameter ($D = 2 \cdot \sqrt{\frac{A}{\pi}}$) thereby approximating elliptical shapes as circular. The arithmetic mean diameter ($\overline{D}$ (1)) as well as standard deviation (σ (2)) and standard error (*SE* (3)) were calculated in *Microsoft* Excel 2013.

$$\overline{D} = \frac{1}{n}\sum_{i=1}^{n} D_i \quad (1)$$

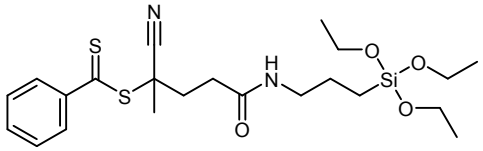
$$\sigma = \sqrt{\frac{1}{n}\sum_{i=1}^{n}(D_i - D_{mean})^2} \quad (2)$$

$$SE = \frac{\sigma}{\sqrt{n}} \quad (3)$$

$\overline{D}$ = arithmetic mean of the particle diameter
n = number of particles evaluated
D_i = diameter of the particle i.
σ = standard deviation
SE = standard error

1.2 Synthesis

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

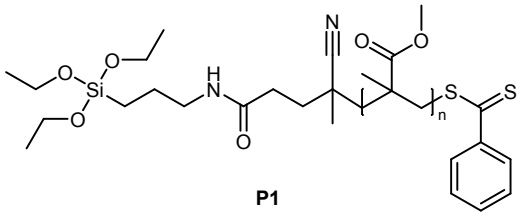


CTA1

The title compound was synthesized according to a literature procedure.[3] 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 µL, 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.

^{1}H-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, CH_2), 3.27 (q, ^3J(H,H) = 6.7 Hz, 2 H, CH_2), 2.65 – 2.38 (m, 4 H, CH_2), 1.93 (s, 3 H, CH_3), 1.64 (quin, ^3J(H,H) = 7.0 Hz, 2 H, CH_2), 1.23 (t, ^3J(H,H) = 7.0 Hz, 9 H, CH_3), 0.64 (t, ^3J(H,H) = 8.0 Hz, 2 H, CH_2)

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



P1

The polymer samples were prepared according to literature known procedures.[4] 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.

^{1}H-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, CH_2), 3.27 (q, ^3J(H,H) = 6.7 Hz, 2 H, CH_2), 2.65 – 2.38 (m, 4 H, CH_2), 1.93 (s, 3 H, CH_3), 1.64 (quin, ^3J(H,H) = 7.0 Hz, 2 H, CH_2), 1.23 (t, ^3J(H,H) = 7.0 Hz, 9 H, CH_3), 0.64 (t, ^3J(H,H) = 8.0 Hz, 2 H, CH_2)

Table S1 Molar mass and dispersity of 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]	MMA	AIBN	RAFT CTA	$M_{n,GPC}$	$M_{w,GPC}$	$Đ_{GPC}$
	g·mol^{-1}	M	mM	mM	g·mol^{-1}	g·mol^{-1}	
P1	396,000	6.55	1.8	1.66	216,100	289,000	1.34

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

Synthesis of silica nanoparticles

Silica nanoparticles were synthesized according to a procedure adopted from Carcouët[5]. A mixture of TEOS (100 mL), 2-propanol (75 mL) and methanol (25 mL) was added *via* a dropping funnel within 60 min under stirring (550 rpm, 3 cm elliptical stir bar) to a solution of ammonia (210 mL, 25 % in water) in isopropanol (750 mL) and methanol (250 mL) in a 3 L round bottom flask at 25 °C. The mixture was stirred overnight and particles were collected by centrifugation for 20 min at 9000 rpm. The particles **NP1** were washed twice with water and thrice with methanol *via* dispersion under sonication and subsequent centrifugation prior to drying *in vacuo* (<0.001 mbar) for 72 h.

*Grafting-to of **P1** on silica nanoparticles*

Solutions of 4 mg·mL^{-1} of **P5** in six different solvents (THF **S1**, Toluene **S2**, Acetone **S3**, Ethyl acetate (EA) **S4**, DMAc containing 0.08 wt.-% LiBr **S5**) were prepared by dissolving **P1** in the respective solvent overnight at 30 °C. Dispersions of silica nanoparticles containing 400 mg·mL^{-1} nanoparticles were prepared by sonicating the appropriate amount of SiO_2 NPs in the respective solvent (**S1-5**) two times for 5 min each. Subsequently 2.5 mL polymer solution and 2.5 mL nanoparticle dispersion of each solvent were combined in an enclosed septum vial and heated to 50 °C for 7 d under stirring. The particles were separated via centrifugation and washed twice with THF and Toluene. The supernatants were combined and the solvent evaporated under reduced pressure. The residue was taken up in THF and submitted to SEC analysis.

2 NMR Spectra

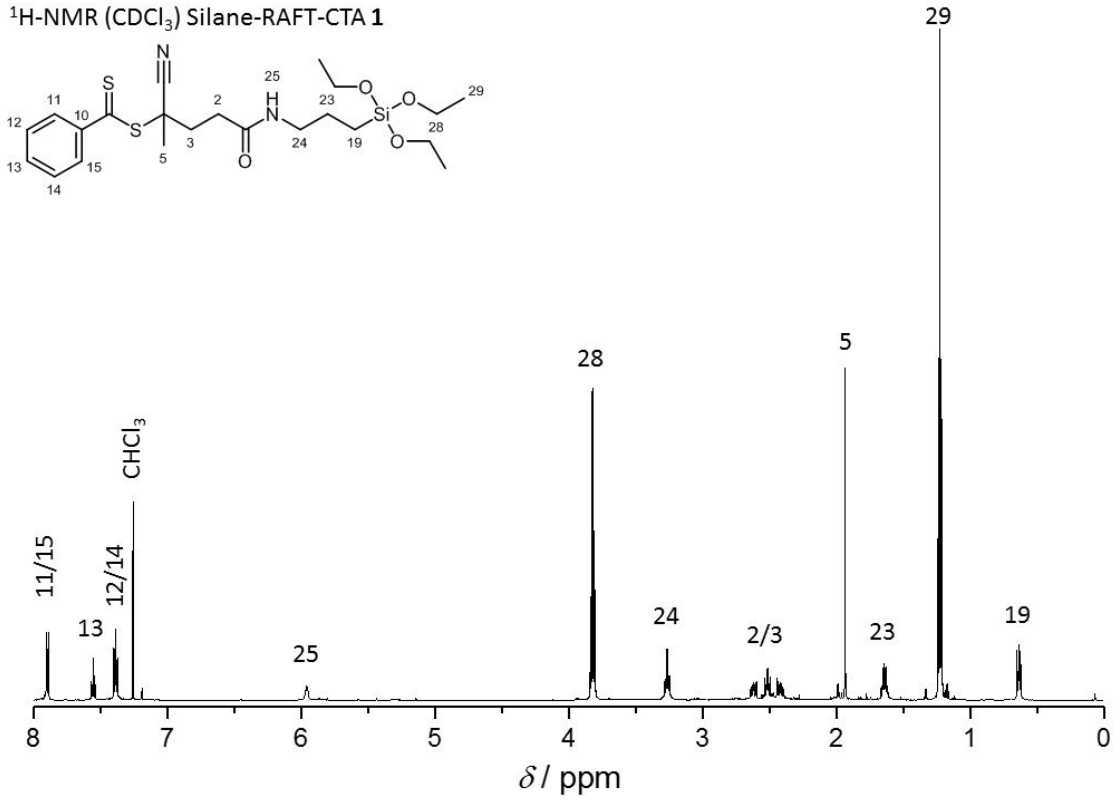


Figure S1 ^{1}H-NMR spectrum ($CDCl_3$) of **CTA1**.

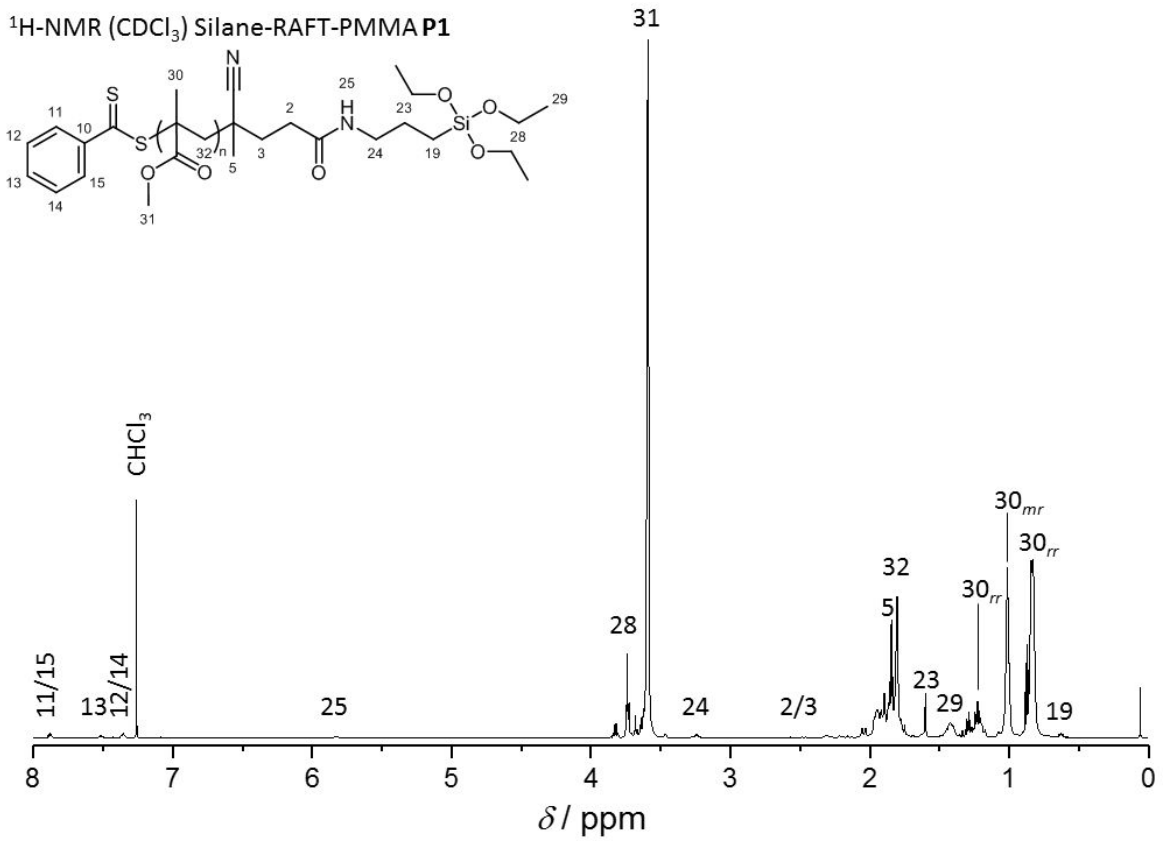


Figure S2 ^{1}H-NMR spectrum ($CDCl_3$) of **P1**.

3 Size Exclusion Chromatography

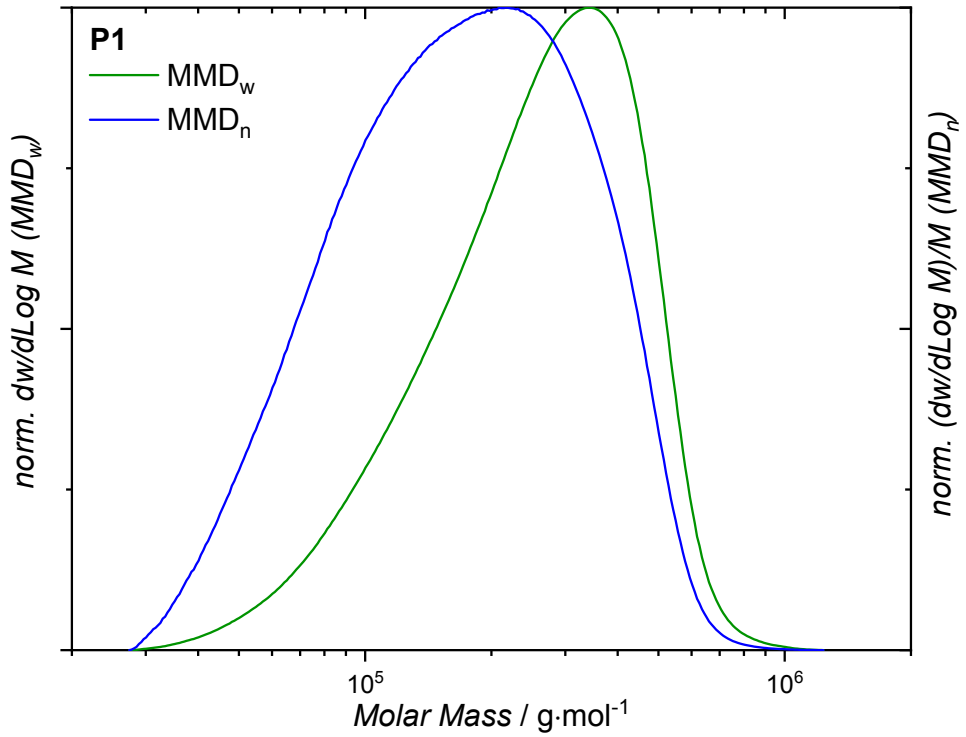


Figure S3 Mass (green) and number based (blue) MMD of **P1**. M_n = 216,100 g·mol^{-1}, M_w = 289,000 g·mol^{-1}, $Đ$ = 1.34.

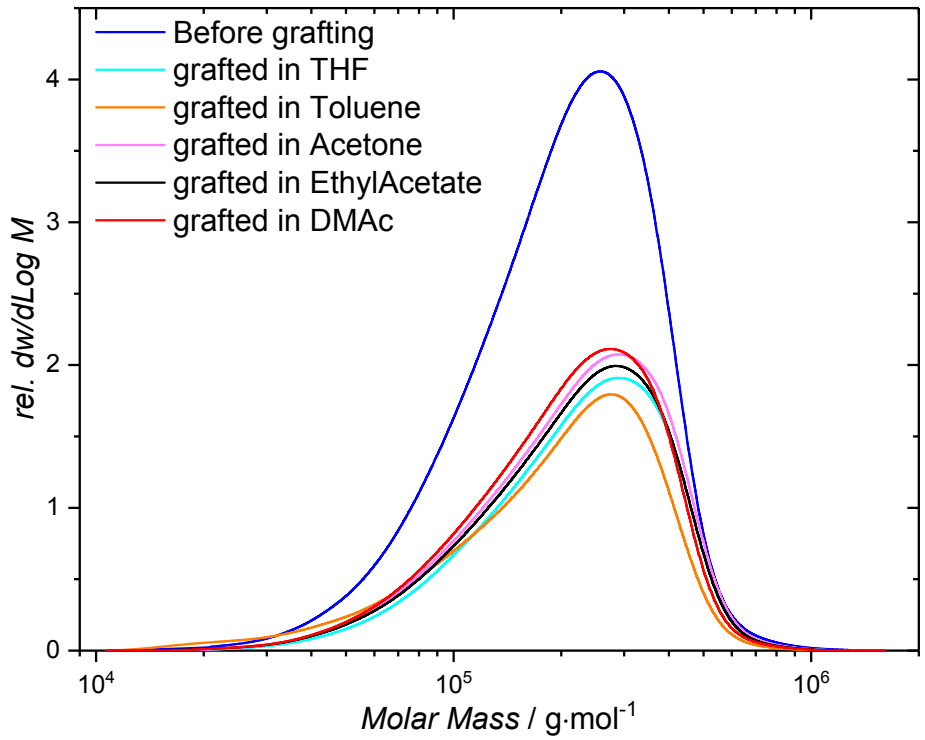


Figure S4 Relative molar mass distributions of all samples illustrating a grafting percentage of 50.4±1.5 %.

Table S2 Percentage of **P5** grafted onto **NP1**.

Grafting solvent	Concentration change / %
THF	52
Toluene	56
Acetone	47
Ethyl acetate	50
DMAc/LiBr	47

Average = 50.4±1.5 % σ = 3.4

4 Preferential grafting factor *κ*

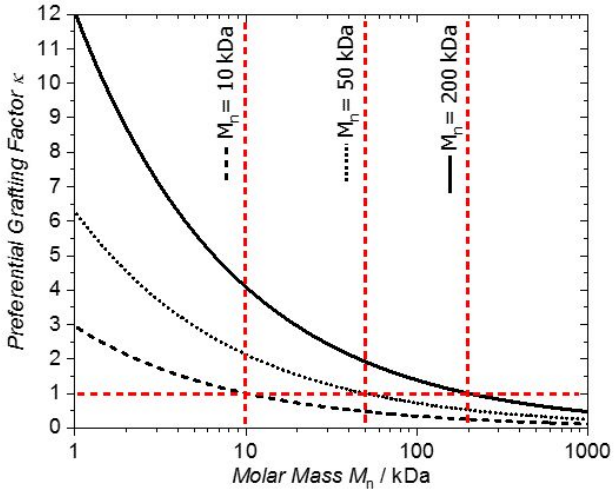


Figure S5 Preferential grafting factor *κ* for three different number average molar masses M_n = 10, 50 and 200 kDa (dashed, dotted and solid line), calculated via Eq. (1). The intersection of the red dashed lines mark the points where κ = 1 for each sample, which is the number average molar mass of the sample. A larger value for κ implies a stronger bias towards grafting of the particular molar mass.

5 Transmission electron microscopy

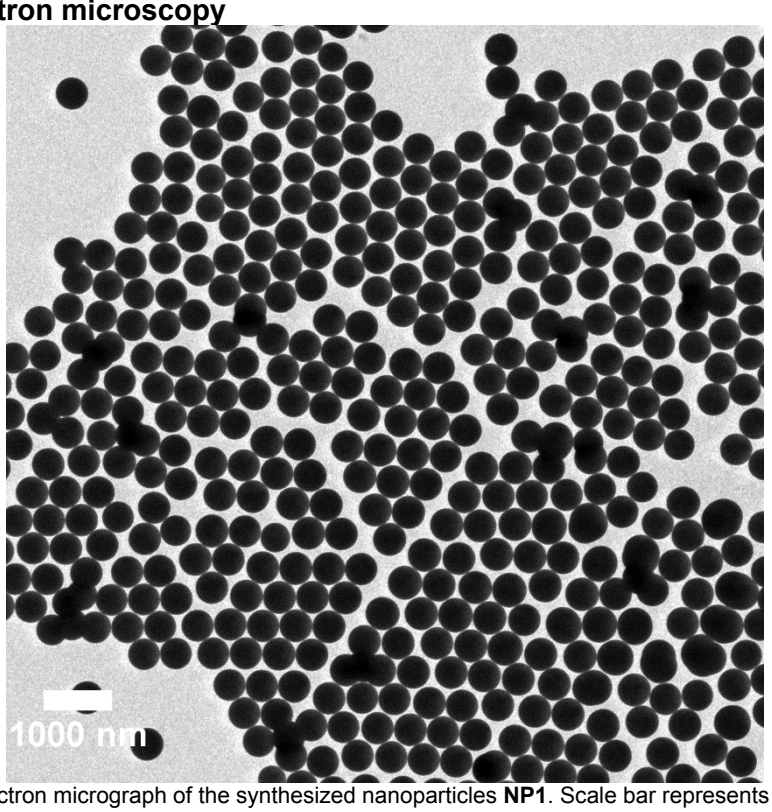


Figure S6 Transmission electron micrograph of the synthesized nanoparticles **NP1**. Scale bar represents 1000 nm.

6 Dynamic light scattering

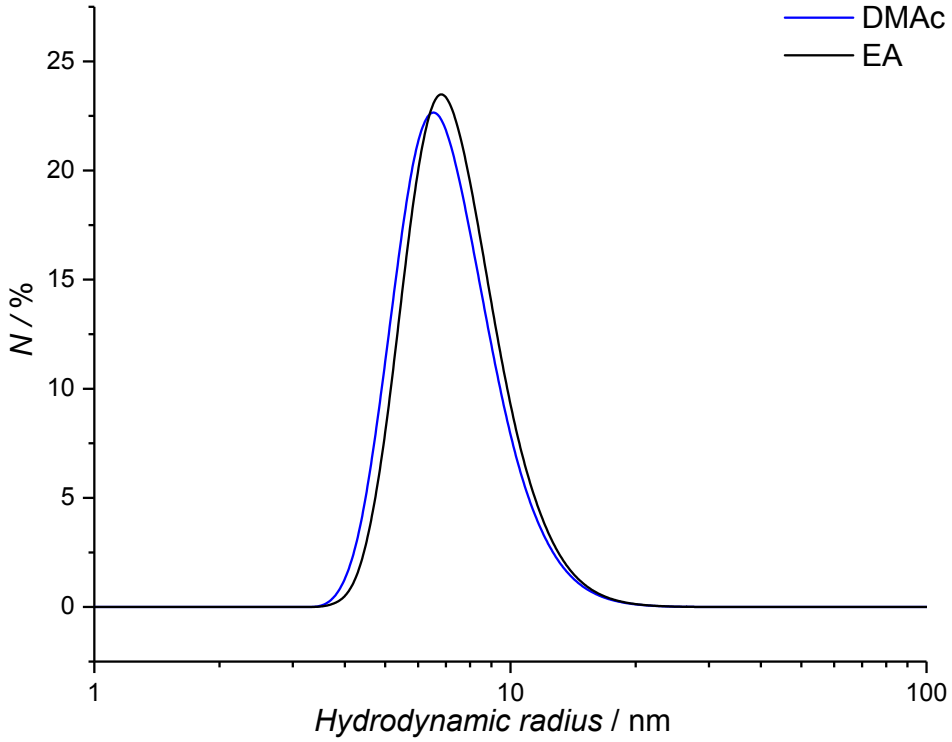


Figure S7 Hydrodynamic radii of **P1** in DMAc (7.3 nm, black) and ethyl acetate (7.6 nm, blue) obtained via DLS.

7 Calculations

7.1 Radius of gyration

$$R_g = bN^n = 0.153\ \text{nm} \cdot 2157^{0.5} \approx 7.1\ \text{nm}$$

With *b* = 0.153 nm for the smallest freely rotating unit (in this case a C-C bond was used for calculation), *N* the degree of polymerization and *n* = 0.5 the solvent interaction parameter (here used for θ-conditions).[6]

7.2 *MMD* calculation

For the calculations of the *MMD* a symmetrical Gaussian distribution with following shape was used:

$$MMD = A \cdot \frac{\sqrt{2/\pi}}{w} \exp\left(-2 \cdot \frac{(x - x_c)^2}{w}\right)$$

$$\rightarrow MMD_{sur} = \kappa \cdot MMD \cdot f \text{ with the condition } \int MMD_{sur} = \frac{1}{2}\int MMD \rightarrow MMD_{sol} = MMD - MMD_{sur}$$

With *A* =2,000,000 [g/mol], w = 220,000 and xc = 500,000. The shifted surface distributions MMD_{sur} where calculated by multiplying the starting *MMD* with κ (from Equation 1 in the main paper), with the condition (as a correction factor) that the resulting graph area must be 50% of the starting graph area. The solution distribution after grafting, MMD_{sol}, was calculated subtracting the surface distribution MMD_{sur} from the starting distribution *MMD*. All *MMD*s where normalized before plotting. To investigate various solvent interaction parameters *n*, the following values were used for the Gaussian distributions.

Table S3 Gaussian distribution parameters used in the calculations.

n	*A* surf.	*w* surf.	x_c surf.	*A* sol.	*w* sol.	x_c sol.
0.1	999,834	220,571	497,503	1,000,221	219,333	502,475
0.2	999,640	221,159	494,978	1,000,620	218,467	504,923
0.3	999,419	221,764	492,425	1,001,259	217,420	507,333
0.4	999,166	222,387	489,842	1,002,218	216,217	509,692
0.5	998,872	223,029	487,227	1,003,583	214,882	511,989
0.6	998,527	223,690	484,581	1,005,443	213,444	514,213
0.7	998,115	224,370	481,901	1,007,894	211,931	516,354
0.8	997,613	225,068	479,186	1,011,031	210,372	518,404
0.9	996,984	225,785	476,435	1,014,954	208,797	520,354

1	996,168	226,514	473,645	1,019,774	207,234	522,198

7.3 Normalization of *MMD*

For the normalization of all *MMD, OriginLab* OriginPro's 2017 normalize to [0, 1] function was used (which represents a common way of normalization and can be performed by any calculation program). Suppose Y is the y values of input curve, then the normalized curve Y' is:

$$Y' = \frac{Y - Y_{min}}{Y_{max} - Y_{min}}$$

8 References

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