Supporting information

Impact of the Solvent Quality on the Local Dynamics of Soft and Swollen Polymer Nanoparticles Functionalized with Polymer Chains

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1. Synthesis of polymers and polymer nanoparticles

Chemicals
Styrene (St), divinylbenzene (DVB), hexadecane, 2,2'-Azobis(2-methylbutyronitrile) (V-59), sodium dodecyl sulfate (SDS) methyl acrylate (MA), dimethylformamide (DMF), dichloromethane (DCM), ethyl α-bromoisobutyrate, cyclohexane-d$_{12}$, acetone-d$_{6}$, DCM-d$_{2}$ were provided by Sigma-Aldrich. Anisole, n-hexane, tetrahydrofuran (THF), copper (II) bromide, ascorbic acid, N,N,N',N'',N'''-Pentamethyldiethylenetriamine (PMDETA) were purchased from Acros Organics. St, DVB, and MA were purified with a column of neutral alumina, and all other chemicals were used as received. Polymerizable macroinitiator (2-((2-((3-Methyl-2-oxobut-3-en-1yl)xy)ethyl)-disulfanyl)ethyl 2-Bromo-2-methyl propanoate) was synthesized according to the method previously reported. 1, 2

Synthesis of the ATRP inimer

2-((2-hydroxyethyl)disulfanyl)ethyl-2-bromo-2-methylpropanoate$^3$

(2-hydroxyethyl) disulfide (1.1 eq, 23.8 g) and trimethylamine (2.6 eq, 67.8 mL) were dissolved in cold DCM (600 mL) in a 1000 mL round-bottom flask. α-Bromoisobutyryl bromide was slowly added to the stirred solution using a dispensing pump (15mL h$^{-1}$). The reaction mixture was stirred overnight and the resulting mixture was filtered. The filtrate was mixed with 1M HCL (400 mL,
3x), sat. NaHCO₃ (600 mL, 3x) and sat. NaCl (600 mL, 3x) and extracted. The organic solution was dried over MgSO₄ and the solvent was evaporated. The product was purified by a silica filled column chromatography (hexane:ethyl acetate = 6:4, Rf = 0.56). ¹H-NMR spectroscopy (300 MHz, CDCl₃): chemical shift (δ/ppm) of 4.46 (t, 2H), 3.91 (t, 2H), 2.99 (t, 2H), 2.90 (t, 2H), 1.96 (s, 6H).

2-((2-(3-Methyl-2-oxobut-3-en-1-yl)xy)ethyl)disulfanyl)ethyl 2-bromo-2-methylpropanoate

2-((2-hydroxyethyl)disulfanyl)ethyl-2-bromo-2-methylpropanoate (1.0 eq, 16g) was dissolved in DCM (144 mL) and stirred in an ice bath. Trimethylamine (2.5 eq, 15 mL) was added to the solution and stirred. Freshly distilled methacryloyl chloride (3.0 eq, 14.26 mL) was added slowly to the solution and the reaction mixture was stirred overnight at room temperature. The resulting solution was filtered and extracted with 1 M HCl (360 mL, 3x) and sat. NaHCO₃ (430 mL, 3x). The organic phase was dried over MgSO₄. After evaporating the solvent, the product was purified by a silica filled column chromatography (hexane:ethyl acetate = 6:4, Rf = 0.2). To remove the remaining impurities, the mixture was purified with second column chromatography (hexane:diethyl ether = 9:1, Rf = 0.46) resulting in the pure product. ¹H-NMR spectroscopy (300 MHz, CDCl₃): δ/ppm of 6.07 (m, 1H), 5.53 (m, 1H), 4.36 (m, 4H), 2.91 (m, 4H), 1.87 (m, 9H).

**Synthesis of polystyrene core (PS NPs)**

For the preparation of PS NPs, an organic phase containing 28.6 mmol of St, 0.1 mmol of DVB, 0.1 mmol of V-59 and 1.1 mmol of hexadecane was mixed with 24 mL of 0.3 wt% aqueous solution of SDS. The mixture was pre-emulsified by mechanical agitation for 10 min and then emulsified by ultrasonication (Branson Sonifier W 450 Digital equipped with a titanium solid extender tip, diameter of 1/2"). The solution was sonicated in an ice bath at 70% amplitude for 2 minutes with a sequence of 10-seconds pulse-on and 2-seconds pulse-off. The emulsified mixture was placed in an oil bath at 80 °C to initiate free radical polymerization. When the double-bond conversion reached 90%, 2 mL of 7.6 wt% SDS aqueous solution was added in order to increase the SDS concentration to 0.5 wt%. Afterward, a mixture of 5.8 mmol of St, 0.06 mmol of DVB and 0.03 mmol of V-59 and 0.3 mmol of ATRP inimer was added to the reaction vessel at a rate of 1.5 mL/h. The reaction continued overnight under argon. The resulting macronitiasator-functionalized NPs were purified by precipitation (3X in methanol) followed by redispersion in THF and by (3X in n-hexane) followed by redispersion in THF and finally dried.
Synthesis of polystyrene nanoparticles functionalized with a canopy of poly(methyl acrylate) chains (PS-PMA NPs)

A stock solution of Cu(II)/PMDETA was prepared by mixing CuBr₂ (5 mg, 0.022 mmol) and PMDETA (48 μL, 0.22 mmol) with DMF (2.5 mL); a stock solution of ascorbic acid was made by dissolving 0.23 mmol of ascorbic acid in DMF. A suspension of initiator functionalized PS NPs (0.1 g, 0.0078 mmol of initiator) in anisole (2 mL) was placed in a Schlenk tube with methyl acrylate (0.5 mL, 5.5 mmol). The mixture was purged with argon for 20 min. Then, 87.6 μL and 42.6 μL of Cu(II)/PMDETA and ascorbic acid stock solution were added to the Schlenk tube and the reaction was carried out in an oil bath at 70 °C. After different polymerization times, the polymerization was quenched, and the polymer functionalized PS nanoparticles were precipitated in hexane and washed by centrifugation followed by redispersion in DCM (3X).

Synthesis of free poly(methyl acrylate) (PMA)

Free PMA chains were synthesized in a free initiator (ethyl α-bromoisobutyrate). The initiator (15.3 mg, 0.07 mmol) was dissolved in anisole (20 mL) and injected into a Schlenk tube with methyl acrylate (1.05 mL, 0.01 mol). The mixed solution was degassed with argon for 20 min, and the stock solutions of Cu(II)/PMDETA (0.88 mL) and of ascorbic acid (0.43 mL) were added. The reaction mixture was placed in an oil bath at 70 °C and stirred for 1 hour. The reaction was cooled down, exposed to the air, and washed with hexane and DCM 3 times.

Table S1. Library of PMA and PS-PMA NPs analyzed

| Sample         | Initiator/MA/Cu(II)/PMDETA | Reaction time (h) | N₀ | Mₙ, NMRb (kg mol⁻¹) | Mₙ, GPC (kg mol⁻¹) | Dₙ, DCM (nm) | PDI  |
|----------------|---------------------------|-------------------|----|---------------------|--------------------|--------------|------|
| PS             | --                        | --                | 0  | --                  | --                 | 179 ± 2      | 0.04 ± 0.02 |
| PS-PMA₄k       | 1/249/0.1/1               | 1.5               | 50 | 4.3                 | --                 | 192 ± 2      | 0.02 ± 0.01 |
| PS-PMA₂₂k      | 1/702/0.1/1               | 1                 | 257| 22.1                | --                 | 248 ± 2      | 0.06 ± 0.02 |
| PS-PMA₂₈k      | 1/766/0.1/1               | 1                 | 320| 27.5                | 21.3               | 307 ± 2      | 0.05 ± 0.02 |
| PS-PMA₄₂k      | 1/991/0.1/1               | 1                 | 487| 42.0                | 33.1               | 379 ± 2      | 0.04 ± 0.02 |
| PS-PMA₅₂k      | 1/1404/0.1/1              | 1                 | 600| 51.7                | 47.2               | 407 ± 4      | 0.05 ± 0.02 |
| Free PMA₄k     | 1/148/0.1/1               | 1                 | 43 | 3.7                 | 4.0                | --           | --            |
| Free PMA₂₂k    | 1/702/0.1/1               | 1                 | 264| 22.7                | 22.6               | --           | --            |
| Free PMA₁₁₆k   | 1/1685/0.1/1              | 6                 | 1312| 113                 | 116                | --           | --            |

a: degree of polymerization
b: \[\frac{[\Delta \delta]_{T=25}}{[\Delta \delta]_{T=0}} \times \text{molar ratio of MA to Initiator}
2. Control of the solvent quality

The Flory-Huggins polymer-solvent interaction parameters ($\chi_{12}$) were calculated using the Hansen solubility parameters (Eq. S1).\(^4\)

$$\chi_{12} = \frac{\alpha v_1}{RT} \left( (\delta_{1,d} - \delta_{2,d})^2 + 0.25(\delta_{1,p} - \delta_{2,p})^2 + 0.25(\delta_{1,hb} - \delta_{2,hb})^2 \right)$$  \hspace{1cm} (eq. S1)

where, $\alpha$ is a constant, $v_1$ is the molar volume of solvent, $R$ is the universal gas constant, $T$ is absolute temperature, $\delta_{1,d}$ is the Hansen dispersion parameter for the solvent, $\delta_{2,d}$ is the Hansen dispersion parameter for the polymer, $\delta_{1,p}$ is the Hansen polarity parameter for the solvent, $\delta_{2,p}$ is the Hansen polarity parameter for the polymer, $\delta_{1,hb}$ is the Hansen hydrogen bonding parameter for the solvent, $\delta_{2,hb}$ is the Hansen hydrogen-bonding parameter for the polymer.

**Table S2.** Molar volume and Hansen solubility parameter of polymers and solvents.\(^4,5\)

| Polymer or solvent composition | Molar volume / (cm\(^3\) mol\(^{-1}\)) | $\delta_d$ (MPa)\(^{1/2}\) | $\delta_p$ (MPa)\(^{1/2}\) | $\delta_{hb}$ (MPa)\(^{1/2}\) |
|-------------------------------|----------------------------------------|----------------|----------------|----------------|
| PS                            | -                                      | 18.5          | 4.5            | 2.9            |
| PMA                           | -                                      | 18.6          | 10.5           | 7.5            |
| $x_{DCM}$ 1.00                 | 63.9                                   | 17            | 7.3            | 7.1            |
| $x_{Acetone}$ 1.00             | 74.1                                   | 15.5          | 10.4           | 7.0            |
| $x_{Cyclohexane}$ 1.00         | 108.0                                  | 16.8          | 0              | 0.2            |
| $x_{Acetone}$ 0.09 + $x_{DCM}$ 0.91 | 64.8                               | 16.9          | 7.6            | 7.1            |
| $x_{Acetone}$ 0.18 + $x_{DCM}$ 0.82 | 65.7                              | 16.7          | 7.9            | 7.1            |
| $x_{Acetone}$ 0.27 + $x_{DCM}$ 0.73 | 66.6                              | 16.5          | 8.2            | 7.1            |
| $x_{Acetone}$ 0.36 + $x_{DCM}$ 0.64 | 67.6                              | 16.4          | 8.5            | 7.1            |
| $x_{Cyclohexane}$ 0.06 + $x_{DCM}$ 0.94 | 66.6                              | 17.0          | 6.6            | 6.4            |
| $x_{Cyclohexane}$ 0.13 + $x_{DCM}$ 0.87 | 69.5                              | 17.0          | 5.8            | 5.7            |
| $x_{Cyclohexane}$ 0.20 + $x_{DCM}$ 0.80 | 72.8                              | 16.9          | 5.1            | 5.0            |
| $x_{Cyclohexane}$ 0.28 + $x_{DCM}$ 0.72 | 76.3                              | 16.9          | 4.4            | 4.3            |
**Table S3.** Flory-Huggins interaction parameters of the solvent mixtures

| Solvent composition | Flory-Huggins interaction parameter, $\chi_{12}$ |
|---------------------|-----------------------------------------------|
| $x_{\text{DCM}} 1.00$ | 0.22 0.13 |
| $x_{\text{Acetone}} 1.00$ | 0.65 0.29 |
| $x_{\text{Cyclohexane}} 1.00$ | 0.43 1.92 |
| $x_{\text{Acetone}} 0.09 + x_{\text{DCM}} 0.91$ | 0.24 0.13 |
| $x_{\text{Acetone}} 0.18 + x_{\text{DCM}} 0.82$ | 0.28 0.14 |
| $x_{\text{Acetone}} 0.27 + x_{\text{DCM}} 0.73$ | 0.32 0.16 |
| $x_{\text{Acetone}} 0.36 + x_{\text{DCM}} 0.64$ | 0.35 0.16 |
| $x_{\text{Cyclohexane}} 0.06 + x_{\text{DCM}} 0.94$ | 0.17 0.18 |
| $x_{\text{Cyclohexane}} 0.13 + x_{\text{DCM}} 0.87$ | 0.13 0.25 |
| $x_{\text{Cyclohexane}} 0.20 + x_{\text{DCM}} 0.80$ | 0.11 0.34 |
| $x_{\text{Cyclohexane}} 0.28 + x_{\text{DCM}} 0.72$ | 0.09 0.45 |
3. Characterizations

**Determination of the molecular weight of the PMA chains.**

The monomer conversion was followed by NMR spectroscopy (Bruker Avance 300) and used to calculate the degree of polymerization and the molecular weight ($M_{n,NMR}$) (Table S1). Furthermore, the molecular weight of the PMA chains was also confirmed by GPC ($M_{n,GPC}$) (Table S1). To characterize the end-tethered PMA, the disulfide bonds present in the ATRP initiator and tethering the PMA chains to the PS NPs were cleaved by reduction with dithiothreitol. A suspension of 0.1 g of NPs was in 10 mL of DCM was mixed with 10 mg of DL-dithiothreitol and ca. 20 mg of 1,8-diazabicyclo[5.4.0]undec-7-ene and stirred for 24 h. The reaction mixture was dried and redissolved in 10 mL of THF with an additional 5 mg of DL-dithiothreitol and let to react for an additional 24 h. The suspension was filtered and centrifuged at 29 068 g for 20 min to eliminate the residual PS core. The resulting PMA solution was diluted to ca. 1 mg·mL$^{-1}$ of PMA in THF and analyzed by GPC. The GPC was performed at a flow rate of 1 mL·min$^{-1}$ on an Agilent Technologies 1260 Infinity equipped with three SDV columns and a refractive index detector SECcurity RID (Polymer Standards Service). The GPC was calibrated with a series of poly(methyl methacrylate) standards from Polymer Standards Service.

**Determination of the grafting density of the PMA chains.**

To determine the number of initiating sites at the surface of the NP, the sulfur content in the NPs was analyzed. The NPs were dispersed in water and stabilized with cetyltrimethylammonium chloride prepared by the dropwise addition of the NPs suspension in DCM to 10 mL of an aqueous solution containing 5.0 mg of CTAC. The resulting suspension was sonicated, and then the DCM was evaporated. The sulfur content in the resulting aqueous suspension of PS NPs was measured by inductively coupled plasma atomic emission spectrometry (ICP-AES) with an ACTIVA M spectrometer (Horiba). The grafting density measured in water decreased upon swelling in the different solvent used. The effective grafting density of the NPs samples studied by NMR spectroscopy was between 0.19 to 0.24 chains·nm$^{-2}$ (Table S4).
Table S4. Grafting density of PS-PMA NPs in different solvent mixtures.

| Solvent composition       | Grafting density (chains·nm⁻²) | Radius of the PS core (nm) |
|---------------------------|--------------------------------|---------------------------|
| X_water 1.00              | 0.81±0.06                      | 45                        |
| X_DCM 1.00                | 0.20±0.02                      | 90                        |
| X_Acetone 0.09+X_DCM 0.91| 0.21±0.02                      | 88                        |
| X_Acetone 0.18+X_DCM 0.82| 0.22±0.02                      | 87                        |
| X_Acetone 0.27+X_DCM 0.73| 0.23±0.02                      | 85                        |
| X_Acetone 0.36+X_DCM 0.64| 0.24±0.02                      | 83                        |
| X_Cyclohexane 0.06+X_DCM 0.94 | 0.20±0.01                  | 91                        |
| X_Cyclohexane 0.13+X_DCM 0.87 | 0.19±0.01                  | 93                        |
| X_Cyclohexane 0.20+X_DCM 0.80 | 0.19±0.01                  | 93                        |
| X_Cyclohexane 0.28+X_DCM 0.72 | 0.19±0.01                  | 93                        |

Determination of the size of the particles

The size of the NPs was determined by dynamic light scattering (DLS) measured with a Malvern Instruments Zetasizer Nano S90 at a fixed angle of 90°. The NPs were dispersed either in DCM, anisole, or mixtures of DCM/acetone or DCM/cyclohexane. All the measurements were carried out at 25 °C. The sizes reported are the Z-average; the Z-average and the polydispersity index (PDI) (PDI=(σ_c/D_c)^2) were obtained from the cumulant analysis. The errors in the graphs represent the standard deviation of 3 independent size measurements. The sizes of the free PMA chains were analyzed with static light scattering by using ALV spectrometer (ALV-GmbH, Germany) equipped with a goniometer and an ALV/LSE-5004 multiple-tau full-digital correlator with 320 channels.

The NPs were also analyzed by transmission electron microscopy (TEM) using an FEI Tecnai F20 operated with an accelerating voltage of 200 kV.
Figure S1. (a) Solvodynamic size distribution of PS NPs (black line), PS-PMA_{4k} NPs (green line) and PS-PMA_{28k} NPs (red line) in DCM measured by DLS and transmission electron microscopy image of (b) PS NPs and (c) PS-PMA_{28k} NPs.

Figure S2. Hydrodynamic radii of free PMA_{116k} measured by static light scattering in solvent mixtures at 298k. Normalized by $D_s$ in DCM. For solvent mixtures of DCM with cyclohexane (▼), and with acetone (□).
Figure S3. Normalized solvodynamic diameter of PS of PS NPs (▼), PS-PMA$_{4k}$ (■), PS-PMA$_{22k}$ (○), PS-PMA$_{28k}$ (♦) in the solvent mixture of (a) DCM/acetone and (b) DCM/cyclohexane measured by light scattering in solvent mixtures at 298k.

The variation in the size of the swollen NPs functionalized with the different PMA chain length was used to calculate the stretching factors of the grafted chains in the different solvent mixture used according to:

\[ T \sim N^v \]  

(eq. S2)

where \( T \) is the thickness of grafted chains \((T=(D_{PS-PMA}-D_{PS})/2)\), \( N \) is the degree of polymerization of the PMA chains, and \( v \) is the stretching parameter. When \( v \) is equal to 1, the chains are in a completely stretched conformation. As \( v \) decreases, the chains are adopting a more and more collapsed conformation.
Figure S4. (a) Thickness of PMA canopy measured with DLS and scaling fitting with Eq. S2 in DCM$_{0.6}$+cyclohexane$_{0.4}$ (■), and in DCM$_{0.6}$+acetone$_{0.4}$ (□). (b) Stretching parameter of grafted PMA chains in PS-PMA in solvent mixtures. For solvent mixtures of DCM (●) with cyclohexane (▼), and with acetone (■).

Table S5. Stretching parameter of the PMA canopy of PS-PMA NPs in solvent mixtures.

| Solvent composition | Stretching parameter |
|---------------------|----------------------|
| $x_{\text{DCM}}$ 1.00 | 0.89±0.05            |
| $x_{\text{Acetone}}$ 0.09 + $x_{\text{DCM}}$ 0.91 | 0.88±0.01            |
| $x_{\text{Acetone}}$ 0.18 + $x_{\text{DCM}}$ 0.82 | 0.88±0.01            |
| $x_{\text{Acetone}}$ 0.27 + $x_{\text{DCM}}$ 0.73 | 0.89±0.01            |
| $x_{\text{Acetone}}$ 0.36 + $x_{\text{DCM}}$ 0.64 | 0.89±0.01            |
| $x_{\text{Cyclohexane}}$ 0.06 + $x_{\text{DCM}}$ 0.94 | 0.89±0.02            |
| $x_{\text{Cyclohexane}}$ 0.13 + $x_{\text{DCM}}$ 0.87 | 0.86±0.02            |
| $x_{\text{Cyclohexane}}$ 0.20 + $x_{\text{DCM}}$ 0.80 | 0.88±0.01            |
| $x_{\text{Cyclohexane}}$ 0.28 + $x_{\text{DCM}}$ 0.72 | 0.85±0.02            |
Measurement of the Spin-Spin relaxation ($T_2$)

The PS NPs, PS-PMA NPs and PMA free chain were dispersed in deuterated solvent mixtures at a concentration of 16.7 mg mL$^{-1}$. The relaxation experiments were performed on NMR AVANCE spectrometers (Bruker), working at a nominal frequency of 300.13 MHz. The spin-spin relaxation time constants ($T_2$) were measured using the Carr-Purcell-Meiboom-Gill (CPMG) pulse sequence using 16 spin-echo times ($\tau$). The $\tau$ was varied from 4 ms to 8.3 s and the temperature was set at 298 K. The protons in the aromatic ring of PS (7.1 to 6.6 ppm) and in the methoxy group (3.7 ppm) were chosen for the analysis. The area of the NMR peak at each spin-echo time ($M$) was fitted with a stretched exponential function (Eq. S3) to calculate the apparent relaxation constant $T_{2,\text{App}}$. The average relaxation $T_{2,\text{Ave}}$ was obtained from the Eq. S4.6

\[
M(\tau) = A_0 \times \exp\left(-\frac{\tau}{T_{2,\text{App}}}\right)^{\beta} \tag{eq. S3}
\]

\[
T_{2,\text{Ave}} = \frac{T_{2,\text{App}}}{\beta} \times \Gamma\left(\frac{1}{\beta}\right) \tag{eq. S4}
\]

where $\beta$ represents the width of the distribution and $\Gamma$ is the gamma function.

**Figure S5.** Influence of the molecular weight on the mobility of free PMA chain. $T_2$ relaxation of $^1$H of methoxy group of free PMA4k (empty symbol) and PMA22k (filled symbol) in DCM/cyclohexane (▼) and DCM/acetone (■) mixtures measured at a Larmor frequency of 300.13 MHz at 298K.
Figure S6. Variation of the $T_2$ relaxation time of (a) PS NPs and (b) free PMA chains in different binary solvent mixtures.

Figure S7. Flory-Huggins interaction parameter of PS as a function of that of PMA with DCM/cyclohexane (▽), DCM/acetone (□), and DCM (○).
Figure S8. Normalized $T_2$ relaxation of $^1$H of the aromatic ring of (a) PS NPs (■), (b) PS-PMA$_{4k}$ (■), (c) PS-PMA$_{22k}$ (■), (d) PS-PMA$_{28k}$ (■), (e) PS-PMA$_{48k}$ (■), (f) PS-PMA$_{52k}$ (■) and methoxy group of (g) free PMA$_{22k}$ (▲), (h) PS-PMA$_{4k}$ (▲), (i) PS-PMA$_{22k}$ (▲), (j) PS-PMA$_{28k}$ (▲), (k) PS-PMA$_{48k}$ (▲), (l) PS-PMA$_{52k}$ (▲) as a function of $\chi_{12}$ of PS and PMA. $T_2$ normalized to the $T_2$ of the pure PS NPs or free PMA chains in pure DCM. Black, blue, and red in x-z and y-z planes indicate the solvents with DCM, DCM/acetone, and DCM/cyclohexane, respectively.
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