Supporting Information for:

**Supramolecular Polymer Brushes: Influence of Molecular Weight and Crosslinking on Linear Viscoelastic Behavior**

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1. Experimental Section

1.1. Materials.

Methyl acrylate was purchased from Aldrich and passed through neutral alumina column before use. α,α’-Azobis-(isobutyronitrile) (AIBN, Fluka, 99%) was recrystallized from methanol. N,N-dimethylformamide (DMF, anhydrous) was purchased from Fisher Scientific and used as received. Chloroform (anhydrous), 4-cyano-4-[(dodecylsulfanylthiocarbonyl)sulfanyl]pentanol (CTA), dibutyltin dilaurate, poly(ethylene glycol)s (PEGs), malic acid, 2,6-diaminopyridine were purchased from Aldrich and used without further purification. Hexamethylene diisocyanate (HDI) was purchased from TCI. Amino-1,8-naphthyridin-2(1H)-one was synthesized by previously published method*.

1.2. Characterization

$^1$H NMR spectra were recorded at room temperature on a Varian VXR 400 MHz (1H: 400 MHz) spectrometer using deuterated solvents. Chemical shifts (δ) are reported in ppm, whereas the chemical shifts are calibrated to the solvent residual peaks. Tetramethylsilane (TMS) was used for calibration of chemical shifts. Gel permeation chromatography (GPC) measurements were performed in THF at 25 °C (1 mL/min) on a Spectra-Physics AS 1000, equipped with PLGel 5 μm x 30 cm mixed-C columns. Universal calibration was applied using a Viscotek H502 viscometer and a Shodex RI-71 refractive index detector. The GPC was calibrated using narrow disperse polystyrene standards (Polymer Laboratories).
Melt rheology was carried out via a TA Instruments, AR 1000 under nitrogen flow and 8 mm parallel plate geometries and interplate gap of 0.8-1 mm were used in all cases. Samples were vacuum dried overnight before use. All measurements were performed in the linear viscoelastic regime, determined via torque sweep measurements. Frequency sweeps 0.01-10 or 0.01-100 Hz (depending on the viscosity) were carried out in different temperatures between 20-160 °C for PmA based polymers and 50-70 °C for PEGs. Mastercurves were constructed using TA rheology advantage data analysis software. Temperature sweeps were carried out also within linear regimes in a temperature range between 20-170 °C depending on the sample stability and viscosity. The temperature was kept constant for one minute at each temperature to ensure the equilibrium within the sample.

For the temperature sweep measurement for PmA based samples: samples were first left to equilibrate at \( T = T_g + 40 \) °C between the plates and then, the temperature was increased in a step-wise fashion. The heating rate between each temperature was 1 °C/min and 30 seconds equilibration time at each temperature.

For the frequency sweep measurements for PmA based samples: samples similarly were equilibrated at each temperature for 10 minute and the frequency sweep measurements were performed.

For the frequency/temperature sweep measurement for PEG based samples: samples were heated to above \( T_m \) to avoid crystallization effect on the measurements and the gap between the plates were closed to ensure no sample breakage / slippage. and after 10 minutes equilibrium the frequency/temperature sweeps were performed. For annealing experiments, the samples were left at 65 °C in vacuum oven and later placed between the plates at 55 °C. Subsequently, left for equilibrium for 30 minutes and then, the temperature sweeps were carried out.

Differential scanning calorimetric (DSC) measurements were done on a TA-Instruments Q1000. For PEGs, the samples were heated from room temperature
to 80 °C and kept there for 15 minutes to remove the thermal history. Then, they were cooled down to -50 °C with a rate of 2 °C min⁻¹, equilibrated for 15 minutes and heated (10 °C min⁻¹) to 80 °C. The data was obtained from the cooling and the second heating scans. For PmAs the heating was up to 130 °C and cooling down to -40 °C.

SAXS experiments were performed at the MINA instrument in Groningen. The MINA instrument is equipped with a rotating Cu anode operating at 45 kV and 60 mA (x-ray wavelength λ = 1.54 Å). SAXS patterns were recorded using Vantec Bruker detectors with a 10min exposure time. The beam size on the sample was 0.25 mm. The sample temperature was controlled using a Linkam TMS600 hot stage. Two different sample-to-detector distances of 24 cm and 200 cm were used to cover an extended angular range. The beam center position at the detector and the exact sample-to-detector position (i.e. the scattering angles) were determined using the diffraction rings from a standard Silver Behenate powder. The data were radially integrated and merged into a single curve using a Matlab code. The sample were annealed before the measurements similar to rheology experiments.

1.3. Synthesis of poly(methyl acrylate)s (PmA)

A general procedure is as follows: to a Schlenk tube containing a magnetic stirrer, CTA, and AIBN ([CTA/AIBN]:10/1) in DMF (3 mL), methyl acrylate (2g, 23 mmol) was added followed by four times free-pump-thaw cycles. Then, the reaction mixture was inserted in a pre-heated oil bath of 75 °C and stirred for 6 hours. Subsequently the reaction mixture was precipitated in a methanol water mixture and recovered via centrifugation. The polymers were dried under vacuum and yielded the desired product.

1.4. Synthesis of ((1-(6-Isocyanatohexyl)-3-(7-oxo-7,8-dihydro-1,8-naphthyridin-2-yl)urea) (ODIN))

4g (0.025 mol) 7-amino-1,8-naphthyridin-2(1H)-one was added to a 100 mL three-necked round bottom flask equipped with an egg-shaped magnetic stirrer. The solids were allowed to dry for one hour under vacuum. The flask was kept under nitrogen atmosphere by 3 consequent vacuum/nitrogen cycles. 60 mL HDI (0.37 mol) was added to the reaction flask. The reaction mixture
was heated to 110 °C while stirring. After 19h the reaction mixture was cooled down to room temperature. Then, it was precipitated in 500 mL hexane. The precipitate was filtered off and the traces of HDI was removed by distillation under reduced pressure (0.01 mbar) at 130 °C. (84% yield)

\[ ^1H \text{ NMR (400 MHz, DMSO-}d_6\text{) } \delta: 12.15 \text{ (s, 1H}_1\text{), 9.63 \text{ (s, 1H}_2\text{), 8.98 \text{ (t, 1H}_7\text{), 7.88 \text{ (d, } J = 8.5 \text{ Hz, 1H}_4\text{), 7.75 \text{ (d, } J = 9.4 \text{ Hz, 1H}_5\text{), 6.83 \text{ (d, } J = 8.5 \text{ Hz, 1H}_3\text{), 6.31 \text{ (dd, } J = 9.3, 1.9 \text{ Hz, 1H}_6\text{), 3-3.3 \text{ (m, 4H}_8\text{), 1.1-1.6 \text{ (m, 8H}_9\text{).}} \]

\[ ^1H \text{ NMR (400 MHz, Chloroform-}d\text{) } \delta: 12.75 \text{ (s, 1H}_1\text{), 11.22 \text{ (s, 1H}_2\text{), 8.19 \text{ (d, } J = 8.8 \text{ Hz, 1H}_3\text{), 7.80 \text{ (d, } J = 8.8 \text{ Hz, 1H}_4\text{), 7.70 \text{ (d, } J = 9.3 \text{ Hz, 1H}_5\text{), 6.45 \text{ (d, } J = 9.3 \text{ Hz, 1H}_6\text{), 5.93 \text{ (s, 1H}_7\text{), 3.05-3.45 \text{ (m, 4H}_8\text{), 1.25-1.75 \text{ (m, 8H}_9\text{).}} \]

1.5. Synthesis of PmA-ODINs

A 100 mL three necked round bottom flask was equipped with a reflux condenser and an egg-shaped magnetic stirrer and put under nitrogen atmosphere. 300 mg PmA and 3 equivalent of ODIN was added to the reaction flask under nitrogen atmosphere. Then, 10 mL of anhydrous chloroform and 2 droplets of DBTDL was added to the reaction mixture. The reaction mixture was refluxed overnight and then, hexane was added (3 mL) and the unreacted extra ODIN was isolated by centrifugation at 4500 rpm for 30 minutes. The solution was collected and the solvent was removed under reduced pressure. A yellow solid was obtained.

\[ ^1H \text{ NMR (400 MHz, chloroform-}d\text{) } \delta: 12.89 \text{ (s, 1H}_1\text{), 11.25 \text{ (s, 1H}_2\text{), 8.19 \text{ (d, 1H}_3\text{), 7.83 \text{ (d, } J = 8.6 \text{ Hz, 1H}_4\text{), 7.72 \text{ (d, } J = 9.4 \text{ Hz, 1H}_5\text{), 6.54 \text{ (d, } J = 9.5 \text{ Hz, 1H}_6\text{), 5.99 \text{ (s, 1H}_7\text{), 4.87 \text{ (s, 1H}_8\text{), 1.10-4.10 \text{ (m, 320H}_9\text{-12).}} \]

1.6. Synthesis of PEG-ODINs

The same procedure as 1.5. was used for PEGs except that methanol as non-solvent for centrifugation was used instead of hexane.

2. Supplementary Figures
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