Electronic Supplementary Information for:

Construction and Morphology of Non-Covalently Double-Crosslinked Supramolecular Polymer Networks

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Experimental Section

Materials

All chemicals were purchased from Sigma-Aldrich, TCI or Alfa Aesar. n-Butyl acrylate (nBuA) was purified by passing through a column of basic aluminium oxide to remove inhibitors. 2,2'-Azobis(isobutyronitrile) (AIBN) was recrystallized twice from ethanol. Unless otherwise indicated, the other chemicals were used without further purification. The ATRP initiator, Ba-Br, was synthesized according to our previous report.\textsuperscript{1}

Characterization methods

\textsuperscript{1}H NMR spectra were recorded on Varian Gemini 2000 FT-NMR spectrometer (400 MHz) or Varian unity Inova 500 (500 MHz) NMR spectrometer, using CD\textsubscript{2}Cl\textsubscript{2} as solvent.

Polymers were analyzed by size exclusion chromatography (SEC) running in THF at 35°C (flow rate: 1 mL·min\textsuperscript{-1}) and recorded on GPCmax VE 2001 from Viscotek\textsuperscript{™}, which equipped with a column set of a H\textsubscript{HR}-H Guard-17369 column, a CLM30111 column and a G2500H\textsubscript{HR}-17354 column. The average molar masse of polymers was derived from refractive index signal based on polystyrene calibration curve.

Matrix-assisted laser desorption/ionization time of flight mass spectrometry (MALDI-TOF MS) measurements were performed on Bruker Autoflex III system (Bruker Daltonics) operating in linear mode. Data evaluation was carried out on DataAnalysis software. Ions were formed by laser desorption (smart beam laser at 355, 532, 808, and 1064±5 nm; up to 50 Hz repetition rate), accelerated by a voltage of 20 kV and detected as positive ions. Samples were prepared by mixing 50 μL of trans-3-indolacrylic acid (IAA) at 20 g·L\textsuperscript{-1} in THF with 10 μL of polymer solution at 20 g·L\textsuperscript{-1} in THF. To enhance cationization of polymers, 1 μL of sodium
trifluoroacetate (NaTFA) at 20 g·L⁻¹ in THF was added to solutions. Finally, 1 μL of resulting mixture was spotted on a MALDI sample plate and air-dried.

UV–visible (UV–vis) spectroscopic studies were performed on a Beijing Rayleigh Analytical Instrument Co., China using CHCl₃ as solvent.

Rheology experiments were carried out on a rheometer from Anton Paar (Physica) MCR 101/SN 80753612. A parallel plate system with a plate diameter of ~8 mm diameter was used. The sample temperature was controlled by thermoelectric heating/cooling in a Peltier-chamber under an atmosphere of dry oxygen. The samples were annealed at 50 °C for approximately 10 h prior the rheology experiments. All measurements were performed in a dynamic mode with an angular frequency ranging from 0.01 to 100 rad/s. Frequency sweep measurements were performed within the linear viscoelastic (LVE) region between 100 °C to 0 °C in 10 °C steps whereas samples were equilibrated at least 15 min at each temperature. For the evaluation of data the Rheoplus software and OriginPro 8G were used.

Transmission electron microscopy (TEM) analyses were conducted with an EM 900 transmission electron microscope (Carl Zeiss Microscopy GmbH, Oberkochen, Germany). The samples were dissolved in toluene with a concentration of 2 g/L and spread onto a Cu grid coated with a Carbon-film. After 1 min, excess solution was blotted off with filter paper. Subsequently, ~5 μL of 1 % aqueous uranyl acetate solution were deposited onto the grid and drained off after 1 min. TEM images were taken from theses negatively stained samples, using a SSCCD SM-1k-120 camera (TRS, Moerenweis, Germany).

Samples for atomic force microscopy (AFM) measurements were prepared by drop-casting polymer solutions in toluene (2 g/L) onto silicon wafers pre-cleaned via the piranha solution, followed by drying in air at room temperature. AFM images were obtained by a tapping mode with
a Digital Instruments Dimension 3100 Scanning Probe Microscope, performed at room temperature in air using standard silicon cantilevers with a nominal spring constant of 50 N/m and the resonance frequency of ~300 kHz.

Dynamic light scattering (DLS) measurement was conducted in toluene solution at a concentration of 2 g/L on a Viscotek 802 using OmniSIZE software.

**Polymerization of nBuA to afford Ba-PnBuA-Br**

The AGET ATRP polymerization of nBuA to afford Ba-PnBuA-Br is described in Figure 2. Typically, nBuA (0.36 mL, 2.5 mmol), CuBr₂ (1.1 mg, 0.005 mmol), and tris[2-(dimethylamino)ethyl]amine (Me₆TREN, 1.3 μL, 0.005 mmol) were dissolved in anisole (0.1 mL) in a Schlenk flask sealed with rubber septum and subsequently purged with argon for ~30 min. Tin(II) 2-ethylhexanoate (Sn(EH)₂, 10.1 mg, 0.025 mmol) and Ba-Br (23 mg, 0.05 mmol) were dissolved in anisole (0.2 mL) in a flask sealed with rubber septum and purged with argon for ~30 min. After removing oxygen, the initiator and reducing agent were transferred to the reaction Schlenk flask via a cannula, and then immersed in an oil bath thermostated at 65 °C. 40 min later, the reaction was stopped by plunging the flask into liquid nitrogen. The polymer was subsequently precipitated twice into cold MeOH/H₂O (1/1, v/v) in order to eliminate residual monomer. The polymer was dried under vacuum and characterized by ¹H NMR and SEC. The molar mass of pure poly(nBuA) was finally evaluated by ¹H NMR (CD₂Cl₂) from relative integration of the characteristic ester group protons of the PnBuA backbone (-O-CH₂-CH₂-, 2nH, δ = 4.05 ppm, with n being the degree of polymerization) and of the characteristic proton of Ba-Br (Br-CH-CH₃, 1H, δ = 4.20-4.28 ppm).
Synthesis of Ba-PnBuA-N₃

The synthesis of compound Ba-PnBuA-N₃ (Figure 2) was accomplished according to previous report with slight modification.² Ba-PnBuA-Br (\(M_n\) NMR = 4.4 kDa, \(M_n\) SEC = 4.7 kDa, \(D\) = 1.19, 0.32 g, 0.07 mmol) and NaN₃ (0.014 g, 0.22 mmol) were dissolved in 1.5 mL DMF, which was stirred overnight at 50 °C. Then, dichloromethane was added into the solution, which was successively washed with saturated sodium bicarbonate, brine and H₂O, respectively. The organic layer was dried over MgSO₄ and then the solvent was evaporated via rotavapor to afford Ba-PnBuA-N₃.

Synthesis of alkyne terminated 2,4,6-triaminopyrimidine, alkyne-TAP (Figure S1)

![Synthetic route to alkyne-TAP.](image)

Compound 1 was synthesized according to the previous report with slight modification.²

³Typically, to a stirred suspension of sodium hydride (60% in oil, 0.88 g, 22.0 mmol) in DMSO (20 mL), a solution of malononitrile (2.64 g, 40.0 mmol) in DMSO (5 mL) was added with cooling. After addition was complete, the mixture was stirred for 10 min; the temperature raised to 80 °C and 6-chloro-1-hexyne (2.33 g, 20.0 mmol) was added in one portion. The mixture was stirred for 3 h at 90 °C before being allowed to cool. The reaction mixture was poured into
water (50 mL) and extracted with dichloromethane (3 x 50 mL). The combined organic extract was washed with water (3 x 100 mL), saturated aqueous sodium chloride (2 x 100 mL), dried over magnesium sulfate and the solvent removed to give an orange oil. Chromatography on silica (eluent: ethyl acetate/hexane, 1/9, v/v) gave compound 1 (1.3 g, 45%, Figure S2) as a yellowish oil.

\[ \text{\textsuperscript{1}H NMR (CDCl}_3\text{) } \delta \text{ (ppm): 1.65 (quint, 2H), 1.77 (quint, 2H), 1.99 (t, 1H), 2.06 (quart, 1H), 2.26 (sext, 2H), 3.74 (t, 1H).} \]

![Figure S2: \textsuperscript{1}H NMR spectrum of compound 1 recorded in CDCl\textsubscript{3} at 27 °C.](image)

Alkyne-TAP was synthesized according to the published methods with slight modifications.\textsuperscript{2} Typically, to a stirred solution of sodium ethoxide (782 mg, 11.5 mmol) in
ethanol (12 mL) was added guanidine hydrochloride (742 mg, 7.77 mmol). The mixture was stirred for 5 min and filtered to remove the precipitated sodium chloride. To the resulting solution compound 1 (1.02 g, 6.98 mmol) was added and the mixture was heated at 85 °C refluxing for 3 h. The reaction was allowed to cool; the solution was then filtered, and the residue was washed with cold ethanol and dried to give alkyne-TAP (0.8 g, 56%, Figure S3 and Figure S4) as white solid.

$^1$H NMR (DMSO-$d_6$) δ (ppm): 1.38 (quint, 2H), 1.47 (quint, 2H), 2.16 (m, 4H), 2.70 (t, 1H), 5.12 (s, 2H), 5.39 (s, 1H).

$^{13}$C NMR (DMSO-$d_6$) δ (ppm): 17.86, 22.46, 27.29, 27.77, 70.98, 84.93, 85.65, 160.69, 162.04.

Figure S3. $^1$H NMR spectrum of alkyne-TAP recorded in DMSO-$d_6$ at 27 °C.
Synthesis of Ba-PnBuA-TAP

Ba-PnBuA-TAP (Figure 2) was prepared according to the reported method with modification.² Ba-PnBuA-N₃ (0.27 g, 0.06 mmol) and alkyne-TAP (0.011 g, 0.054 mmol) were added to a round-bottomed flask and dissolved in DMF (1 mL). Sodium L-ascorbate (0.0048 g, 0.024 mmol) was added, and the mixture was degassed by bubbling N₂ for ~30 min. CuSO₄·5H₂O (0.0015 g, 0.006 mmol) was added; the flask was degassed again by bubbling N₂ for ~30 min, and then allowed to stir at 60 °C for 15 h. The mixture was cooled, concentrated, dissolved in CH₂Cl₂, and filtered to remove CuSO₄·5H₂O and sodium L-ascorbate, and then the filtrate was purified by column chromatography (eluent: CH₂Cl₂/MeOH, 30/1, v/v) to give Ba-PnBuA-TAP as a yellowish solid (0.22 g, yield 80%). Subsequently, the obtained product Ba-
PnBuA-TAP was analyzed by $^1$H NMR (Figure 3, top), and MALDI-TOF MS (Figure 4A, B, and Table S2).

**MALDI-TOF MS results**

**Table S1.** MALDI-TOF MS results of Ba-PnBuA-Br.

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<th>$m/z$ measured</th>
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**Table S2.** MALDI-TOF MS results of Ba-PnBuA-TAP.

<table>
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<td>3551.2697</td>
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</table>
**UV/Vis spectra**

![UV/Vis spectra](image)

*Figure S5*: UV−vis spectra recorded from the samples Ba-PnBuA-TAP (blue) and Ba-PnBuA-TAP with 0.5 equiv. of [PdCl₂(PhCN)₂] (red) using CHCl₃ as solvent.

**Rheological results**

![Rheological results](image)

*Figure S6*: logarithmic plot of the zero shear viscosity $\eta_0$ vs. temperature.
TEM results

Figure S7. TEM images of (A) Ba-PnBuA-Br, and (B) Ba-PnBuA-Br with 0.5 equiv. of [PdCl₂(PhCN)₂].

AFM results

Figure S8: AFM height image (A), and cross-section (B) of Ba-PnBuA-TAP.
DLS results

Figure S9. DLS results of Ba-PnBuA-TAP (black), and Ba-PnBuA-TAP + Pd(II) (blue) in toluene at 2 g/L.

References
