

Supporting information for:

Isophthalic acid – pyridine H-bonding: simplicity in the design of mechanically robust phase-segregated supramolecular polymers

Lucas Montero de Espinosa*, Sandor Balog and Christoph Weder*

Adolphe Merkle Institute, Polymer Chemistry and Materials, University of Fribourg, Rte de l'Ancienne Papeterie, CH-1723 Marly, Switzerland

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1. Materials

Dimethyl 5-hydroxyisophthalate (98%, Aldrich), *p*-toluenesulfonyl chloride ($\geq 99\%$, Aldrich), pyridine (anhydrous 99.8%, Aldrich), 4-dimethylaminopyridine (99%, Aldrich), tetrabutylammonium iodide (TBAI, $\geq 99\%$, Aldrich), K_2CO_3 (Aldrich), 4,4'-dipyridyl (98%, Aldrich), 1,2-bis(4-pyridyl)ethane (99%, Aldrich) and 4,4'-trimethylenedipyridine (98%, Aldrich) were used as received. Hydroxyl terminated hydrogenated poly(ethylene-*co*-butylene) was kindly donated by Cray Valley Company under the trade name Krasol HLBH-P 3000 ($M_n = 3100$ g/mol, functionalization degree 1.9). Anhydrous dichloromethane (DCM) was passed through an AlOx solvent purification system prior to use.

2. Characterization

1H -NMR spectra were recorded in $CDCl_3$ or $CDCl_3/TFA$ on a Bruker AVANCE 360 spectrometer operating at 360 MHz. Chemical shifts (δ) are reported in parts per million relative to the solvent signal ($CHCl_3$, $\delta = 7.26$ ppm). The relaxation time (d1) was set to 10 s. Size Exclusion Chromatography (SEC) analyses were performed with Wyatt Technology Corp. (Optilab REX interferometric refractometer, miniDawn TREOS laser photometer) and Agilent Technologies instrumentation (series 1200 HPLC). Columns: a

Polymer Laboratories 5 μm mixed-C guard column and two GPC columns. Eluent: THF at a flow rate of 1 $\text{mL}\cdot\text{min}^{-1}$ at 40 $^{\circ}\text{C}$. Detectors: multi-angle laser light scattering (MALLS) ($\lambda = 658\text{ nm}$, 25 $^{\circ}\text{C}$) and refractive index ($\lambda = 658\text{ nm}$, 40 $^{\circ}\text{C}$). Data analyses: Wyatt Technology software (ASTRA). The incremental refractive index (dn/dc) was obtained by a single-injection method assuming 100% mass recovery. Differential scanning calorimetry (DSC) studies were carried out with a Mettler-Toledo STAR system under nitrogen atmosphere, at a heating rate of 10 $^{\circ}\text{C min}^{-1}$ from -100 $^{\circ}\text{C}$ to 150 $^{\circ}\text{C}$ using a sample mass of approximately 5 mg. The glass transition temperature T_g is reported as the midpoint of the step change in the heat capacity and the melting temperature, T_m , was recorded as the minimum of the major endothermic melting peak. Dynamic mechanical thermal analyses (DMTA) were conducted with a TA Instruments DMA Q 800 under nitrogen atmosphere at a heating rate of 3 $^{\circ}\text{C min}^{-1}$, from -100 to 150 $^{\circ}\text{C}$ and at a frequency of 1 Hz using rectangular samples of the following approximate dimensions: 20 mm x 3.5 mm x 0.7 mm. Mechanical data are reported as the average of 3 independent tests. Tensile tests were performed in a TA Instruments DMA Q 800 at 25 $^{\circ}\text{C}$ with a strain rate of 1 %/min using rectangular samples of the following approximate dimensions: 20 mm x 3.5 mm x 0.7 mm. Mechanical data are reported as averages of 3 independent measurements. Young's moduli were calculated from the slope in the linear region between 0.3-0.5% strain. Small-Angle X-Ray Scattering (SAXS) was performed on a S-MAX3000 pinhole camera (Rigaku Innovative Technologies, Auburn Hills, MI). Measurements were performed at room temperature and raw data were processed according to standard procedures. Scattering spectra are presented as a function of the momentum transfer $q = 4\pi\lambda^{-1} \sin(\theta/2)$, where θ is the scattering angle and $\lambda = 0.1524\text{ nm}$ is the photon wavelength. Optical microscopy images were acquired with an Olympus BX51 microscope with a DP72 digital camera.

3. Experimental Procedures and characterization

Synthesis of *p*-toluenesulfonyl terminated hydrogenated poly(ethylene-*co*-butylene)
Krasol HLBH-P 3000 (5.00 g, 1.6 mmol), *p*-toluenesulfonyl chloride (1.53 g, 8.1 mmol, 5 eq. / end group) and DMAP (0.10 g, 0.8 mmol, 0.5 eq. / end group) were placed in a 100 mL round-bottomed flask equipped with a magnetic stirrer under nitrogen atmosphere. Anhydrous dichloromethane (20 mL) was added and the mixture was stirred at room temperature until all reagents completely dissolved. Anhydrous pyridine

(0.65 mL, 8.1 mmol, 5 eq. / end group) was subsequently added via a syringe and the reaction mixture was stirred for 48h at room temperature. Dichloromethane was then partially removed under reduced pressure until the reaction mixture became turbid and the concentrated dichloromethane solution was precipitated twice in 300 mL of ice-cold methanol. The product was dissolved in 200 mL of hexane, washed with 100 mL of brine, dried over Na₂SO₄ and directly filtered through 1 cm of silica with hexane as eluent (note that the use of a paper filter results in a hazy product). Removal of the solvent under reduced pressure afforded the tosylated product in 89% yield.

SEC data: $dn/dc = 0.0901$, $M_w = 3.7$ kDa, PDI = 1.05

¹H NMR (360 MHz, CDCl₃) δ = 7.79 (d, J = 8.1 Hz, CH_{Ar}), 7.34 (d, J = 8.1 Hz, CH_{Ar}), 4.07–4.00 (m, –CH₂–O–), 1.49–0.90 (m, CH₂ backbone), 0.90–0.73 (m, CH₃ backbone).

Synthesis of dimethyl isophthalate terminated hydrogenated poly(ethylene-*co*-butylene)

p-Toluenesulfonyl terminated hydrogenated poly(ethylene-*co*-butylene) (8.00 g, 2.2 mmol), dimethyl 5-hydroxyisophthalate (2.30 g, 10.8 mmol, 2.5 eq. / end group), tetrabutylammonium iodide (TBAI, 0.80 g, 2.2 mmol, 0.5 eq. / end group) and K₂CO₃ (1.50 g, 10.8 mmol, 2.5 eq. / end group) were mixed in a 100 mL round-bottomed flask equipped with a magnetic stirrer. Toluene (120 mL) was added, the flask was closed with a glass stopper, and the reaction mixture was stirred at 100 °C for 24 h. The reaction mixture was allowed to cool to room temperature and subsequently filtered to obtain a clear orange solution. Toluene was removed at reduced pressure and the crude product was precipitated twice in 500 mL of ice-cold methanol from a concentrated THF solution. The product was dissolved in 300 mL of hexane, washed with 150 mL of brine and dried over Na₂SO₄. The solvent was removed under reduced pressure and the resulting product was filtered through a short pad (1–2 cm) of silica using hexane/ethyl acetate 10:1 as eluent (removes colour) to obtain a colourless product in 72% yield.

SEC data: $dn/dc = 0.0861$, $M_w = 4.3$ kDa, PDI = 1.07

¹H NMR (360 MHz, CDCl₃) δ = 8.26 (s, CH_{Ar}), 7.74 (s, CH_{Ar}), 4.07–4.01 (m, –CH₂–O–), 3.93 (s, –OCH₃), 1.37–0.95 (m, CH₂ backbone), 0.89–0.80 (m, CH₃ backbone).

Synthesis of isophthalic acid terminated hydrogenated polybutadiene 2

Dimethyl isophthalate terminated Krasol (5.00 g, 1 mmol) and NaOH (0.40 g, 8 mmol, 4 eq. / end group) were dissolved in a mixture of THF (420 mL) and H₂O (42 mL) in a 1

L round-bottomed flask. The reaction mixture was heated under reflux for 5 h and then allowed to cool to room temperature. HCl (32 %) was added dropwise while stirring until a pH of 2 was reached and THF was removed under reduced pressure. The residue was dissolved in 300 mL of hexane, washed three times with 100 mL of brine and dried over Na₂SO₄. The solvent was removed under reduced pressure and the resulting sticky solid was precipitated in 400 mL of ice-cold methanol from a concentrated THF solution. The product was dried overnight at 50 °C under high vacuum. Yield 90%. No SEC data are available due to strong interactions with the column. M_n (¹H NMR): ca. 5000 g/mol as calculated by end-group integration (–CH₂–O– vs. aliphatic backbone) in the ¹H NMR spectrum.

¹H NMR (360 MHz, CDCl₃/TFA) δ = 8.41 (s, CH_{Ar}), 7.86 (s, CH_{Ar}), 4.12–4.05 (m, –CH₂–O–), 3.93 (s, –OCH₃), 1.40–0.95 (m, CH₂ backbone), 0.88–0.81 (m, CH₃ backbone).

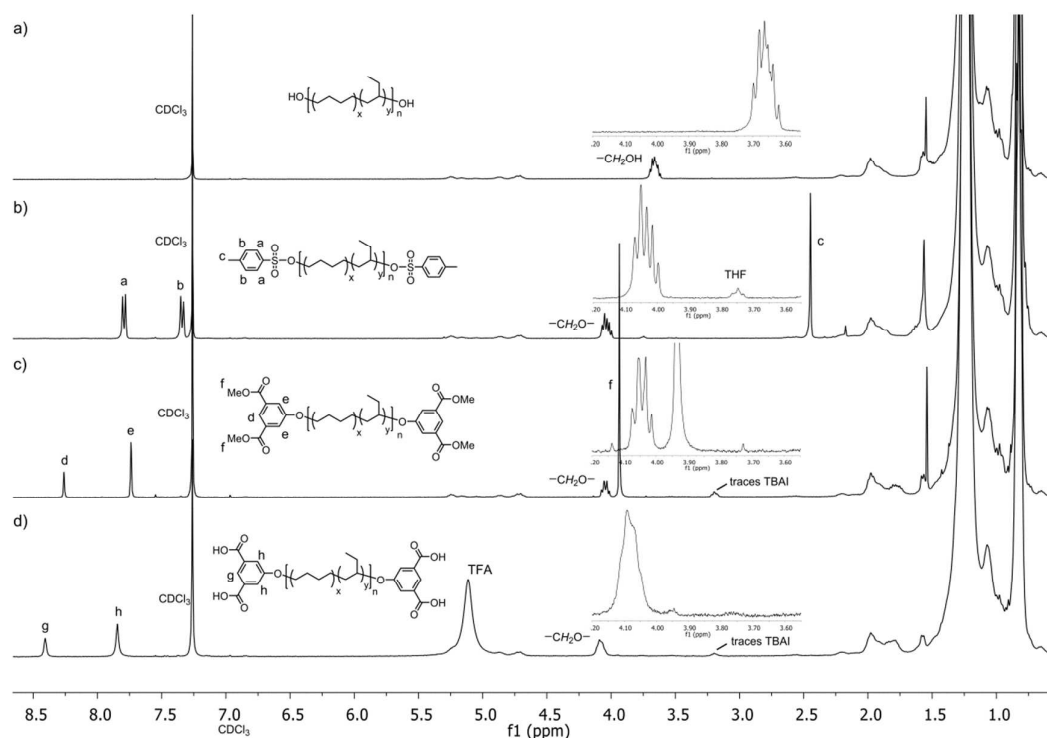


Figure S1. Assigned ¹H NMR spectra of a) Krasol HLBH-P 3000 (hydrogenated poly(ethylene-co-butylene)), b) *p*-toluenesulfonyl terminated hydrogenated poly(ethylene-co-butylene), c) dimethyl isophthalate terminated hydrogenated poly(ethylene-co-butylene) and d) isophthalic acid terminated hydrogenated poly(ethylene-co-butylene) in CDCl₃/TFA. The insets show the region of 4.20 – 3.55 ppm.

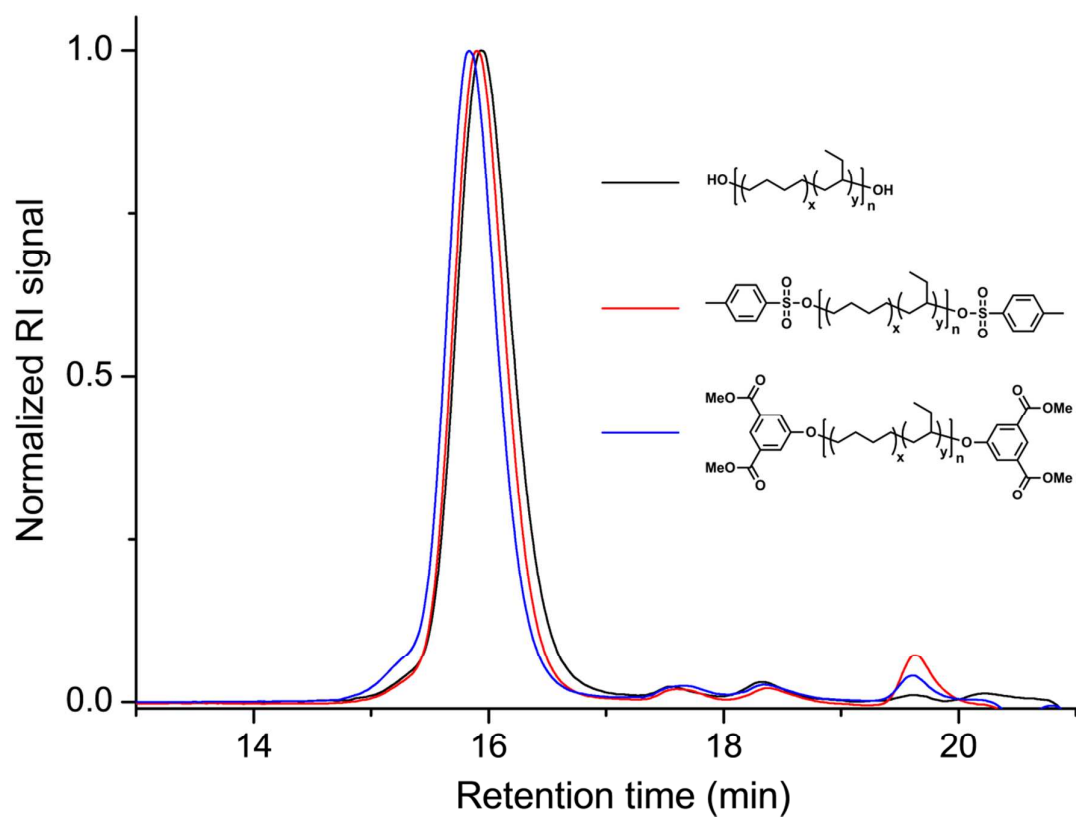


Figure S2. SEC traces of Krasol HLBH-P 3000 (black), *p*-toluenesulfonyl terminated hydrogenated poly(ethylene-*co*-butylene) (red) and dimethyl isophthalate terminated hydrogenated poly(ethylene-*co*-butylene) (blue).

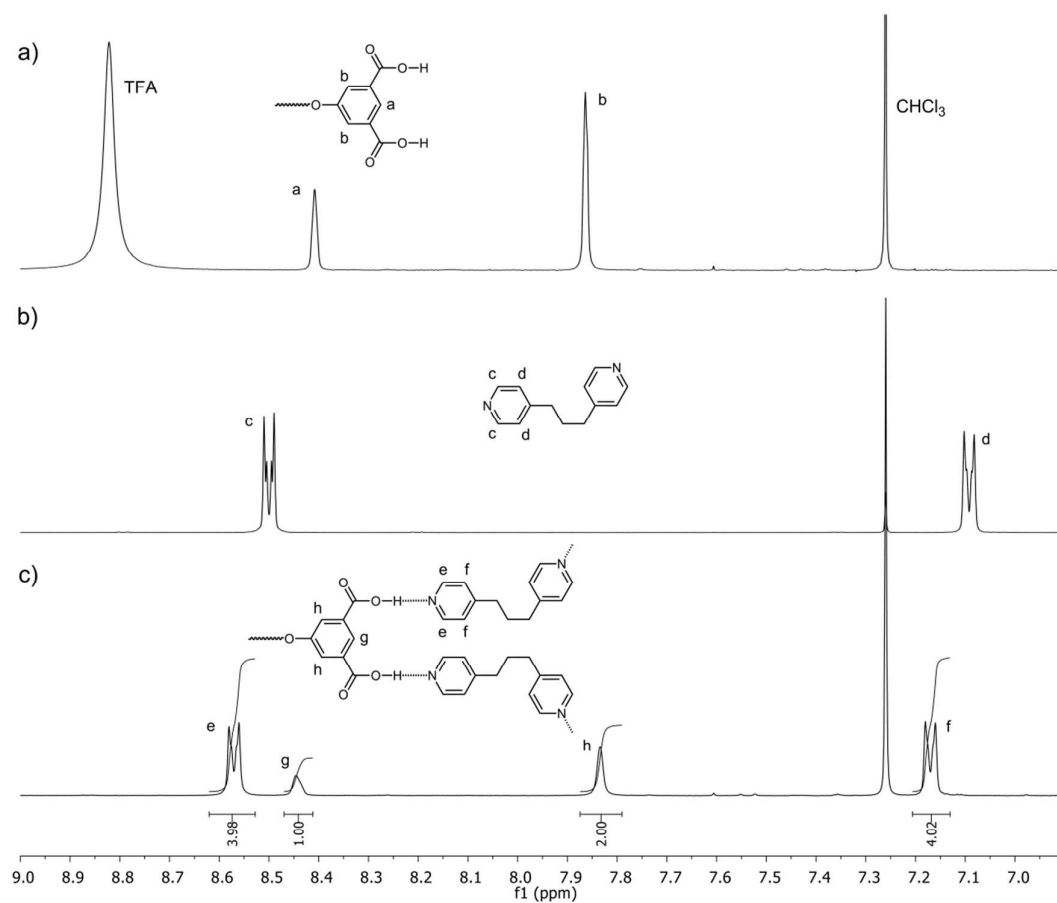


Figure S3. Aromatic region of the ^1H NMR spectra of a) isophthalic acid terminated hydro-generated poly(ethylene-*co*-butylene) in CDCl_3/TFA , b) 4,4'-trimethylenedipyridine and c) $\text{P}_{2,3}$.

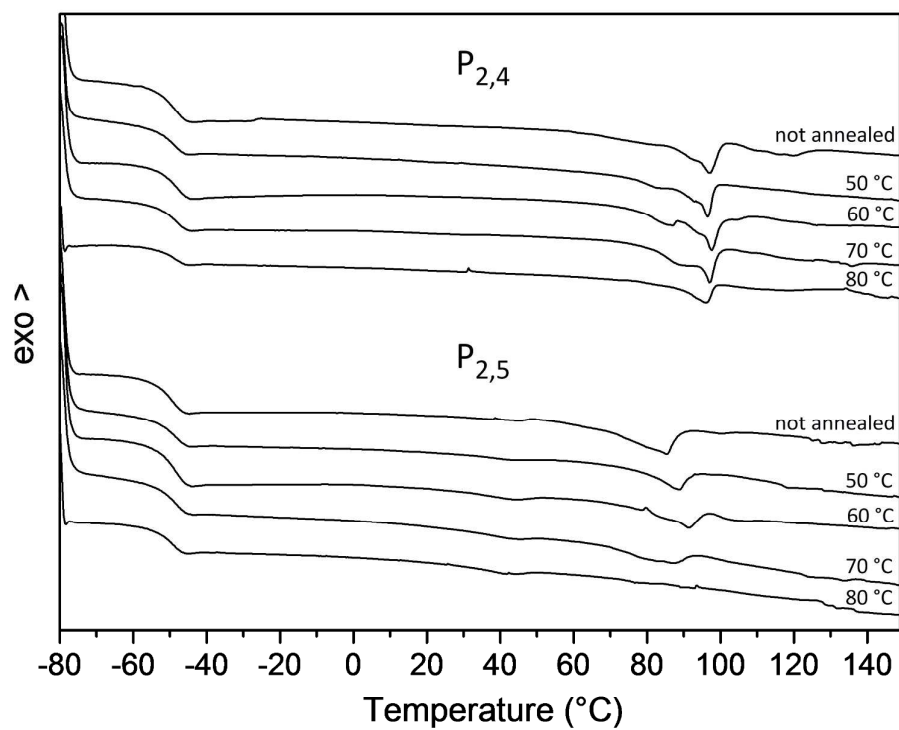


Figure S4. DSC traces of $P_{2,4}$ and $P_{2,5}$ in the not annealed state as well as after 24 h of annealing at 50, 60, 70, or 80 °C.

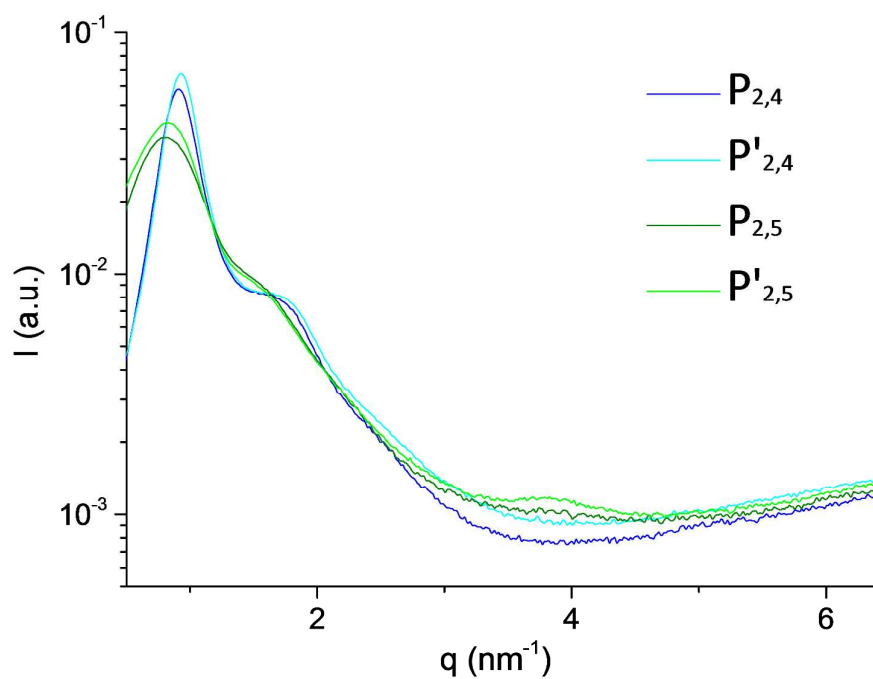


Figure S5. Azimuthally integrated small-angle x-ray scattering (SAXS) spectra of supramolecular polymers $P_{2,4}$, $P'_{2,4}$ (annealed), $P_{2,5}$ and $P'_{2,5}$ (annealed).

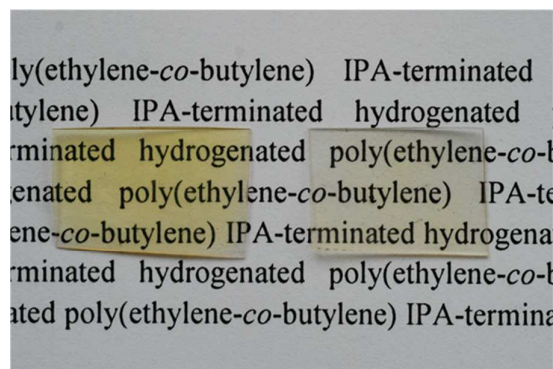


Figure S6. Photograph of films of $P_{2,4}$ and $P_{2,5}$.



Figure S7. Picture demonstrating the mechanical flexibility of a film of $P_{2,3}$.

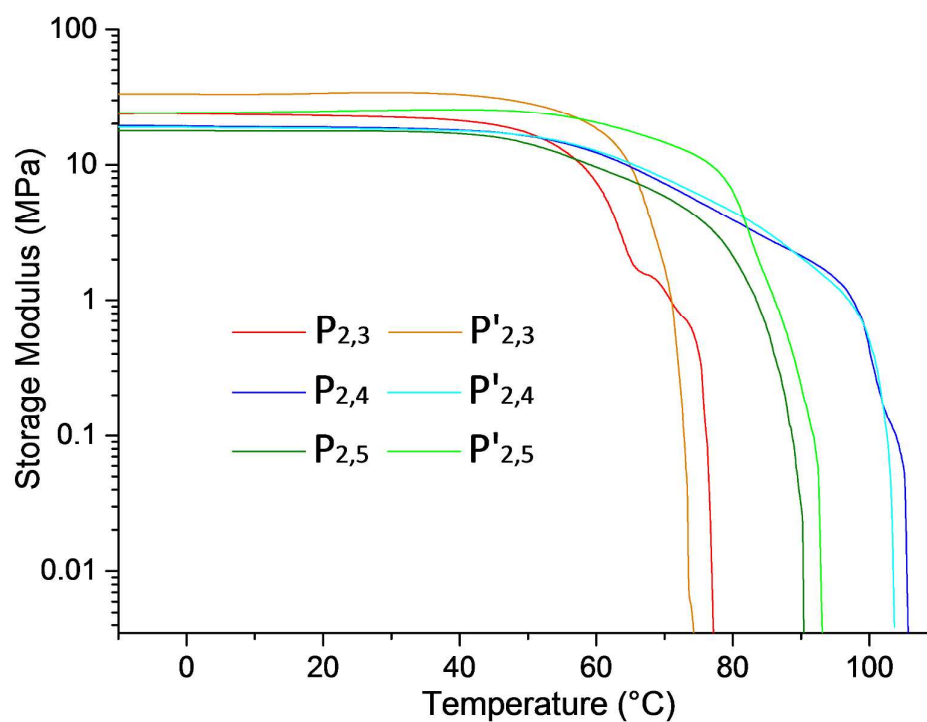


Figure S8. Storage modulus as a function of temperature: comparison of supramolecular polymers $P_{2,3}$, $P_{2,4}$ and $P_{2,5}$ with annealed samples $P'_{2,3}$, $P'_{2,4}$, and $P'_{2,5}$.

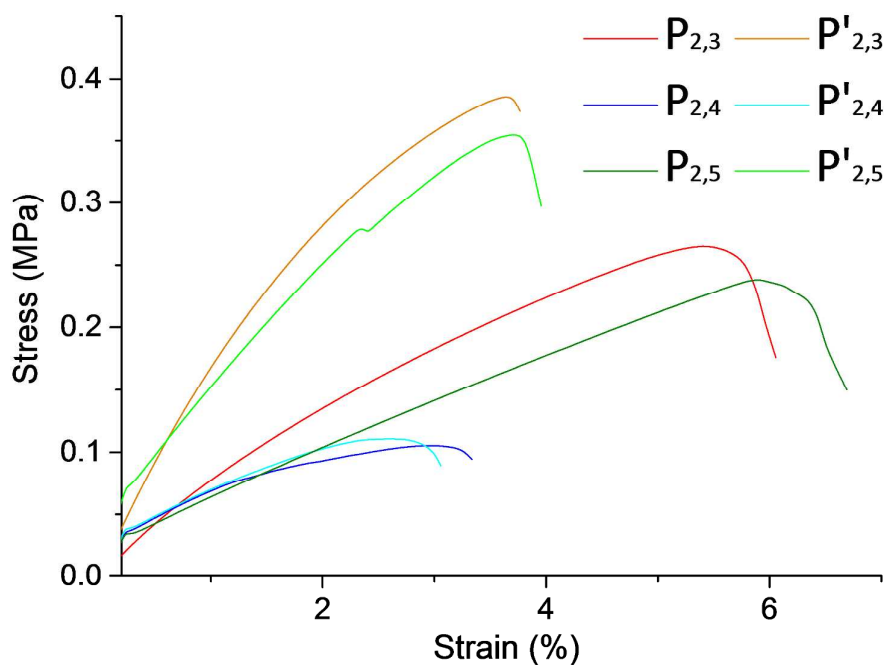


Figure S9. Tensile tests of supramolecular polymers $P_{2,3}$, $P_{2,4}$ and $P_{2,5}$ and of annealed samples $P'_{2,3}$, $P'_{2,4}$ and $P'_{2,5}$ at 25 °C. Initial strain: 0.2%, strain rate: 1 %/min. Representative curves are shown, the characteristic parameters provided in Table S1 and in the main text are average values of three independent measurements.

Table S1. Mechanical properties of IPA-Py based supramolecular polymers.

Polymer	T_m (°C)	T_g (°C)	E' at 25°C (MPa)	Young modulus (MPa)	Strain at break (%)	Tensile strength (MPa)
$P_{2,3}$	55	-49	23 ± 1	7.9 ± 1.7	6.6 ± 0.4	0.26 ± 0.01
$P'_{2,3}$	65	-49	34 ± 2	18.0 ± 1.5	4.7 ± 0.8	0.44 ± 0.05
$P_{2,4}$	97	-49	18 ± 1	4.3 ± 0.5	3.7 ± 0.3	0.11 ± 0.01
$P'_{2,4}$	96	-49	18 ± 2	4.0 ± 0.4	3.4 ± 0.3	0.12 ± 0.01
$P_{2,5}$	85	-49	17 ± 2	4.3 ± 0.6	7.1 ± 0.9	0.23 ± 0.02
$P'_{2,5}$	91	-49	26 ± 2	10.3 ± 2.2	3.7 ± 0.2	0.34 ± 0.02