Supporting Information

Photoswitchable Block Copolymers Based on Main Chain $\alpha\textsc{-}$ Bisimines

Linh Duy Thai,^{a,b,c} Thiago R. Guimaraes,^{*a,b} Sebastian Spann,^{e,f} Anja S. Goldmann,^{a,b} Dmitri Golberg,^{a,b} Hatice Mutlu,^{*c,d} Christopher Barner-Kowollik^{*a,b,c}

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Instruments and Characterization

Nuclear Magnetic Resonance (NMR) spectroscopy

¹H and ¹³C-NMR spectra were recorded on a Bruker System AM 500 spectrometer, equipped with a PABBO BB-Probe (5 mm), (¹H: 500 MHz, 32 scans for polymers and 16 scans for small molecules, ¹³C: 126 MHz). The δ -scale was normalized relative to the solvent signal of CHCl₃, THF or methanol for ¹H and ¹³C NMR spectra. The multiplicities were reported using the following abbreviations: s for singlet, d for doublet, t for triplet, q for quartet, p for pentet, m for multiplet and br for broad signal.

All DOSY experiments were performed at 300K on an Avance III HD Bruker 400MHz NMR spectrometer equipped with a BBI (Cohn) or a BBO (Babsi) probe. The Bruker pulse sequence *dstebppg3s* was used for all DOSY measurements to compensate the effect of convection. To gain adequate signal-to-noise ratio, all experiments were performed with 16 scans. To calculate the correct diffusion coefficient, 32 gradient points were recorded in linear manner ranging from 2% to 98%. The FID was recorded with 8192 points and a resulting acquisition time of 0.6815744 seconds. Before each DOSY measurement the gradient length (little delta) as well as the diffusion delay (big delta) were optimized individually to monitor the diffusional attenuation. The obtained data was processed with TopSpin 4.1.3 and Dynamics Center 2.8.0.1.

^a School of Chemistry and Physics, Queensland University of Technology (QUT), 2 George Street, Brisbane, QLD 4000, Australia. E-mail: christopher.barnerkowollik@qut.edu.au

^{b.}Centre for Materials Science, Queensland University of Technology (QUT), 2 George Street, Brisbane, QLD 4000, Australia. E-mail: thiago.rodriguesguimaraes@qut.edu.au

^c Institute of Nanotechnology, Karlsruhe Institute of Technology (KIT), Hermann-von-Helmholtz-Platz 1, 76344 Eggenstein-Leopoldshafen, Germany.

E-mail: hatice.mutlu@kit.edu

^d Soft Matter Synthesis Laboratory, Karlsruhe Institute of Technology (KIT), Hermann-von-Helmholtz-Platz 1, 76344 Eggenstein-Leopoldshafen, Germany

^{e.}.Institute for Biological Interfaces 4 (IBG-4), Karlsruhe Institute of Technology (KIT), Hermann-von-Helmholtz-Platz 1, 76344 Eggenstein-Leopoldshafen, Germany

^f Institute of Organic Chemistry, Karlsruhe Institute of Technology (KIT), Fritz-Haber-Weg 6, 76131 Karlsruhe

After Fourier transform of the 1D spectra, the signal decay along the gradients G was fitted to

$$f(G) = I_0 * e^{-D * G^2 * \gamma^2 * \delta^2 * \left(\Delta - \frac{\delta}{3}\right)} * 10^4$$

with the gyromagnetic ratio γ and the full signal intensity I_0 .

The stacked DOSY NMR spectra shown in Figure 4B, C in the article were obtained from MestRenova software (version 12.0.0-20080) using Bayesian method.

Size Exclusion Chromatography (SEC)

SEC measurements were conducted on a PSS SECurity² system consisting of a PSS SECurity Degasser, PSS SECurity TCC6000 Column Oven (35 °C), PSS SDV Column Set (8x50 mm 5 µm Precolumn, 8x300 mm 5 µm Analytical Columns, 100000 Å, 1000 Å) and an Agilent 1260 Infinity II Isocratic Pump, Agilent 1260 Infinity II Standard Autosampler, Agilent 1260 Infinity II Diode Array and Multiple Wavelength Detector (A: 254 nm, B: 360 nm), Agilent 1260 Infinity II Refractive Index Detector (35 °C). HPLC grade THF, stabilized with BHT, is used as eluent at a flow rate of 1 mLmin⁻¹. Narrow disperse linear poly(styrene) (M_n : 266 gmol⁻¹ to 2.52x10⁶ gmol⁻¹) (PSS ReadyCal) or poly(methyl methacrylate) (Mp: 800 – 2.20x10⁶ gmol⁻¹) was used as calibrant. All samples were passed through 0.22 µm PTFE membrane filters. Molecular weight and dispersity analysis was performed in PSS WinGPC UniChrom software (version 8.2).

Differential Scanning Calorimetry (DSC)

DSC measurements was conducted using a Netzsch DSC 204 F1 Phoenix. Samples were sealed into Netzsch AI sample capsules. 3 cycles of heating/cooling ramps at scanning speed of 10 °C·min⁻¹ were used over the temperature range from 0 °C to 200 °C with isothermal exposures (2 min) at 0°C and 200°C. A nitrogen sample purge flow of 20 mL·min⁻¹ was employed. Glass transition temperatures were determined from the 2nd heating ramp. The data was analysed using the TA Instruments Universal Analysis 2000 software (version 4.2E).

Thermogravimetric Analysis (TGA)

TGA was performed on a STA 449 F3 Jupiter from Netzsch. Samples were analyzed in aluminum oxide pans at a heating rate of 20 °C·min⁻¹ from 30 °C to 800 °C under nitrogen atmosphere. The data was analysed using TA Instruments Universal Analysis 2000 software (version 4.2E).

Mass Spectrometry (MS)

Fast-atom-bombardment (FAB) and electron ionization (EI) spectra were recorded on a Finnigan MAT 95 mass spectrometer. A Q Exactive (Orbitrap) mass spectrometer (Thermo Fisher Scientific, San Jose, CA, USA) equipped with a HESI II probe was employed to record high resolution electrospray ionization–MS (ESI-MS). Calibration was carried out in the m/z range of (74–1822) using premixed calibration solutions (Thermo Fisher Scientific). A constant spray voltage of 4.7 kV and a dimensionless sheath gas of 5 were employed. The S-lens RF level was set to 62.0, while the capillary temperature was set to 250 °C.

¹H and ¹³C NMR spectra and MS data

α -Bisimine diol 1



Figure S1 ¹H NMR spectrum of bisimine diol 1 in MeOD.

¹H NMR (500 MHz, methanol-*d*₄) δ/ppm: 7.76 – 7.70 (m, 4H, H_{Ar}), 7.49 – 7.36 (m, 6H, H_{Ar}), 3.63 – 3.52 (m, 2H, -C**H**_{cyclic}-OH), 3.23 – 3.12 (m, 2H, -C**H**_{cyclic}-N=C), 2.07 – 1.96 (m, 2H), 1.85 – 1.71 (m, 4H), 1.66 – 1.52 (m, 4H), 1.41 – 1.30 (m, 2H), 1.28 – 1.16 (m, 2H), 1.04 – 0.90 (m, 2H).



Figure S2 ¹³C NMR spectrum of bisimine diol 1 in MeOD.

¹³C NMR (126 MHz, Methanol- d_4) δ/ppm: 165.2 (**<u>C</u>=N-C**, 2C), 138.0 (**<u>C</u>_{Ar}-C=N</u>, 2C), 132.2 (CH_{Ar}, 2C), 129.8 (4CH_{Ar}), 128.8 (CH_{Ar}, 4C), 70.3 (CH_{cyclic}-OH, 2C), 63.8 (<u>C</u>H_{cyclic}-N=C-**, 2C), 34 (CH_{2cyclic}, 2C), 33.9 (CH_{2cyclic}, 2C), 33.0 (CH_{2cyclic}, 2C), 31.7 (CH_{2cyclic}, 2C)

HRMS (ESI): calculated m/z for C₂₆H₃₃N₂O₂ [M+H⁺] = 405.2537, found: 405.2531



Figure S3 ¹H NMR spectrum of mono-ol 2 in CDCl₃

¹H NMR (500 MHz, chloroform-*d*) δ 7.82 – 7.68 (m, 4H, HAr), 7.45 – 7.28 (m, 6H, HAr), 5.87 – 5.72 (m, 1H, CH2=CH-), 5.02 – 4.87 (m, 2H, CH2=CH-), 4.85 – 4.73 (m, 1H, CH_{cyclic}-C(O)O-), 3.71 – 3.60 (m, 1H, CH_{cyclic}-OH), 3.28 – 3.13 (m, 2H, CH_{cyclic}-N=C-), 2.22 (t, *J* = 7.6 Hz, 2H, -CH2_α-C(O)O-), 2.13 – 1.99 (m, 4H), 1.95 – 1.82 (m, 2H), 1.82 – 1.70 (m, 2H), 1.64 – 1.51 (m, 6H), 1.46 – 1.02 (m, 16H).



Figure S4 ¹³C NMR spectrum of mono-ol 2 in CDCl₃

¹³C NMR (126 MHz, CDCl₃) δ/ppm: 173.43 (C(O)O-, 1C), 163.22&163.17 (C=N, 2C), 139.24 (-CH=CH2, 1C), 136.97 & 136.91 (C_{Ar} -C=N-, 2C), 130.79&130.74 (CH_{Ar}, 2C) 128.68 (CH_{Ar}, 4C), 127.73 &127.68 (CH_{Ar}, 4C), 114.25 (-CH=CH2, 1C), 71.83 (CH-OC(O), 1C), 69.89 (-CH-OH, 1C), 62.00 & 61.50 (-CH-N=C, 2C), 34.75 (C_{α} H2-C(O)-O-, 1C), 33.86 (CH2-CH=CH2, 1C), 33.30&33.20 (CH2_{cyclic}, 2C), 31.96&31.46 (CH2_{cyclic}, 2C), 30.78&30.35 (CH2_{cyclic}, 2C), 29.34&29.25 (CH2_{cyclic}, 2C), 29.13&29.11 (CH2_{aliphatic}, 4C), 28.94 (CH2_{aliphatic}, 1C), 25.12 (C_βH2, 1C).

HRMS (ESI): calculated m/z for $C_{37}H_{51}N_2O_3$ [M+H⁺] = 571.3895, found: 571.3887

(Z,Z)-ADMET monomer 3



Figure S5 ³H NMR spectrum of (Z,Z)-ADMET monomer 3 in CDCl₃

¹H NMR (500 MHz, Chloroform-*d*) δ 7.81 – 7.71 (m, 4H, H_{Ar}), 7.44 – 7.30 (m, 6H, H_{Ar}), 6.34 (dd, J = 17.3, 1.6 Hz, 1H, CH2=CH-COO), 6.05 (dd, J = 17.3, 10.5 Hz, 1H, CH2=CH-COO), 5.85 – 5.73 (m, 2H, CH2=CH-C(O)O & CH2=CH-CH2-), 5.01 – 4.84 (m, 3H, CH2=CH-CH2- & CH_{cyclic}-acrylate), 4.79 (m, 1H, CH_{cyclic}-OC(O)R), 3.30 – 3.19 (m, 2H, CH_{cyclic}-N=C-), 2.22 (t, J = 7.6 Hz, 2H, -CH2_α C(O)O), 2.18 – 1.86 (m, 6H), 1.84 – 1.72 (m, 2H), 1.70 – 1.51 (m, 6H), 1.51 – 1.15 (m, 16H).



Figure S6 ¹³C NMR spectrum of (Z,Z)-ADMET monomer 3 in CDCl₃

¹³**C** NMR (126 MHz, CDCl₃) δ/ppm: 173.47 (-CH2- \underline{C} (O)O, 1C), 165.77 (CH2=CH- \underline{C} (O)O, 1C), 163.28 &163.23 (C=N, 2C), 139.30 (-CH2-CH=CH2, 1C), 136.95 (-N=C- \underline{C}_{Ar} , 2C), 130.85 (CH_{Ar}, 2C), 130.48 ((- \underline{C} H2=CH-C(O)O, 1C), 129.05 (CH2= \underline{C} H-C(O)O-, 1C), 128.74 (CH_{Ar}, 4C), 127.76 (CH_{Ar}, 4C), 114.28 (\underline{C} H2=CH-CH2-, 1C), 72.27 & 71.82 (- \underline{C} H_{cyclic}-C(O)OR, 2C), 61.53& 61.45 (- \underline{C} H_{cyclic}-N=C, 2C), 34.79 (- \underline{C}_{α} H2-C(O)O-, 1C), 33.91 (- \underline{C} H2-CH=CH2, 1C), 31.54 & 31.48 (CH2_{cyclic}, 2C), 30.40 & 30.35 (CH2_{cyclic}, 2C), 29.39 (CH2_{cyclic}, 2C), 29.30 (CH2_{cyclic}, 2C), 29.18 & 29.16 (CH2_{aliphatic}, 4C), 29.00 (CH2_{aliphatic}, 1C), 25.17 (- \underline{C}_{β} H2, aliphatic, 1C).

HRMS (ESI): calculated m/z for $C_{40}H_{53}N_2O_4$ [M+H⁺] = 625.4000, found: 625.3991



Figure S7 ¹H NMR spectrum of PS₇₀Br in CDCl₃



Figure S8 ¹H NMR spectrum of PS₇₀A2 in CDCI₃

PS ₁₁	₀₅Br
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Figure S9 ¹H NMR spectrum of PS₁₁₅Br in CDCI₃



Figure S10 ¹H NMR spectrum of PS₁₁₅A2 in CDCI₃

PS230B	r
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Figure S11 ¹H NMR spectrum of PS₂₃₀Br in CDCI₃

PS₂₃₀A2



Figure S12 ¹H NMR spectrum of PS₂₃₀A2 in CDCI₃

PS₇₀ADMET₅



Figure S13 ¹H NMR spectrum of PS₇₀ADMET₅ in CDCI₃

PS₇₀ADMET₈



Figure S14 ¹H NMR spectrum of PS₇₀ADMET₈ in CDCI₃

PS₇₀ADMET₃₄



Figure S15 ¹H NMR spectrum of PS₇₀ADMET₃₄ in CDCl₃



Figure S16 ¹H NMR spectrum of PS₁₁₅ADMET₁₀in CDCI₃



Figure S17 ¹H NMR spectrum of PS₁₁₅ADMET₃₆in CDCI₃



Figure S18 ¹H NMR spectrum of $PEG_{46}A1$ in $CDCI_3$

PEG₄₆ADMET₂₀



Figure S19 ¹H NMR spectrum of PEG₄₆ADMET₂₀ in CDCI₃

COSY NMR SPECTRA

ADMET monomer 3



Figure S20 COSY NMR spectrum of (Z,Z) – ADMET monomer 3 in CDCI₃



Figure S21 COSY NMR spectrum of PS₁₁₅AMET₃₆ in CDCI₃

DOSY NMR spectra

PS₇₀A2



Figure S22 DOSY NMR spectrum of PS₇₀A2 in CDCI₃



Figure S23 DOSY NMR spectrum of PS₇₀ADMET₅ in CDCI₃



Figure S24 DOSY NMR spectrum of $PS_{70}ADMET_8$ in CDCl₃



Figure S25 DOSY NMR spectrum of PS₇₀ADMET₃₄ in CDCI₃



Figure S26 DOSY NMR spectrum of PS₁₁₅A2 in CDCl₃



Figure S27 DOSY NMR spectrum of PS₁₁₅ADMET₁₀ in CDCI₃



Figure S28 DOSY NMR spectrum of PS₁₁₅ADMET₃₆ in CDCI₃



Figure S29 DOSY NMR spectrum of PEG₄₆ADMET₂₀ in CDCI₃



Figure S30 THF-SEC traces from block copolymer synthesis experiment using $PS_{230}A2$ as macro-chain stopper