Supporting Information

Photoswitchable Block Copolymers Based on Main Chain α-Bisimines

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Contents

Instruments and Characterization .............................................................................................................1
1H and 13C NMR spectra and MS data .....................................................................................................3
COSY NMR SPECTRA ..............................................................................................................................22
DOSY NMR spectra .................................................................................................................................24
SEC traces .............................................................................................................................................32

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

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

with the gyromagnetic ratio $\gamma$ 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 SECurity$^2$ 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, 10000 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 mL min$^{-1}$. Narrow disperse linear poly(styrene) ($M_n$: 266 g mol$^{-1}$ to $2.52 \times 10^6$ g mol$^{-1}$) (PSS ReadyCal) or poly(methyl methacrylate) ($M_p$: 800 – $2.20 \times 10^6$ g mol$^{-1}$) 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 Al 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.
**$^1$H and $^{13}$C NMR spectra and MS data**

α-Bisimine diol 1

![NMR Spectrum](image)

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

$^1$H 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, -CH$_2$cyclic-OH), 3.23 – 3.12 (m, 2H, -CH$_2$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 $^{13}$C NMR spectrum of bisimine diol 1 in MeOD.

$^{13}$C NMR (126 MHz, Methanol-$d_4$) $\delta$/ppm: 165.2 (C=N-C, 2C), 138.0 (C$_{Ar}$-C=N, 2C), 132.2 (CH$_{Ar}$, 2C), 129.8 (4CH$_{Ar}$), 128.8 (CH$_{Ar}$, 4C), 70.3 (CH$_{cyclic}$-OH, 2C), 63.8 (CH$_{cyclic}$-N=C-, 2C), 34 (CH$_2_{cyclic}$, 2C), 33.9 (CH$_2_{cyclic}$, 2C), 33.0 (CH$_2_{cyclic}$, 2C), 31.7 (CH$_2_{cyclic}$, 2C)

HRMS (ESI): calculated $m/z$ for C$_{26}$H$_{33}$N$_2$O$_2$ [M+H$^+$] = 405.2537, found: 405.2531
Figure S3 $^1$H NMR spectrum of mono-ol 2 in CDCl$_3$

$^1$H NMR (500 MHz, chloroform-$d$) $\delta$ 7.82 – 7.68 (m, 4H, HAr), 7.45 – 7.28 (m, 6H, HAr), 5.87 – 5.72 (m, 1H, CH$\equiv$CH-), 5.02 – 4.87 (m, 2H, CH$\equiv$CH-), 4.85 – 4.73 (m, 1H, CH$_{\text{cyclic}}$C(O)O-), 3.71 – 3.60 (m, 1H, CH$_{\text{cyclic}}$-OH), 3.28 – 3.13 (m, 2H, CH$_{\text{cyclic}}$N=C-), 2.22 (t, $J = 7.6$ Hz, 2H, -CH$_2$ -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 $^{13}$C NMR spectrum of mono-ol 2 in CDCl$_3$

$^{13}$C NMR (126 MHz, CDCl$_3$) δ/ppm: 173.43 (C(O)O-, 1C), 163.22&163.17 (C=N, 2C), 139.24 (-CH=CH$_2$, 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=CH$_2$, 1C), 71.83 (CH-OC(O), 1C), 69.89 (-CH-OH, 1C), 62.00 & 61.50 (-CH-N=C, 2C), 34.75 (C$_{a}$H$_2$-C(O)-O-, 1C), 33.86 (CH$_2$-CH=CH$_2$, 1C), 33.30&33.20 (CH$_2$$_{cyclic}$, 2C), 31.96&31.46 (CH$_2$$_{cyclic}$, 2C), 30.78&30.35 (CH$_2$$_{cyclic}$, 2C), 29.34&29.25 (CH$_2$$_{cyclic}$, 2C), 29.13&29.11 (CH$_2$$_{aliphatic}$, 4C), 28.94 (CH$_2$$_{aliphatic}$, 1C), 25.12 (C$_{b}$H$_2$, 1C).

HRMS (ESI): calculated $m/z$ for C$_{37}$H$_{51}$N$_2$O$_3$ [M+H$^+$] = 571.3895, found: 571.3887
Figure S5 $^1$H NMR spectrum of (Z,Z)-ADMET monomer 3 in CDCl$_3$

$^1$H NMR (500 MHz, Chloroform-$d$) $\delta$ 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, CH$_2$=CH-COO), 6.05 (dd, $J = 17.3, 10.5$ Hz, 1H, CH$_2$=CH-COO), 5.85 – 5.73 (m, 2H, CH$_2$=CH-C(O)O & CH$_2$=CH-CH$_2$-), 5.01 – 4.84 (m, 3H, CH$_2$=CH-CH$_2$- & 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, -CH$_2$$_{cyclic}$ COO), 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 $^{13}$C NMR spectrum of (Z,Z)-ADMET monomer 3 in CDCl$_3$

$^{13}$C NMR (126 MHz, CDCl$_3$) δ/ppm: 173.47 (-CH2-N=C(O)O, 1C), 165.77 (CH2=CH-N=C(O)O, 1C), 163.28 & 163.23 (C=N, 2C), 139.30 (-CH2-CH=CH2, 1C), 136.95 (-N=C-CH$_2$Ar, 2C), 130.85 (CH$_2$Ar, 2C), 130.48 ((-CH2=CH-C(O)O, 1C), 129.05 (CH2=CH-C(O)O-, 1C), 128.74 (CH$_2$Ar, 4C), 127.76 (CH$_2$Ar, 4C), 114.28 (CH2=CH-CH2-, 1C), 72.27 & 71.82 (-CH$_2$Cyclic-C(O)OR, 2C), 61.53 & 61.45 (-CH$_2$Cyclic-N=C, 2C), 54.79 (-CH$_2$Cyclic-C(O)O-, 1C), 33.91 (-CH2-CH=CH2, 1C), 31.54 & 31.48 (CH2Cyclic, 2C), 30.40 & 30.35 (CH2Cyclic, 2C), 29.39 (CH2Cyclic, 2C), 29.30 (CH2Cyclic, 2C), 29.18 & 29.16 (CH2Aliphatic, 4C), 29.00 (CH2Aliphatic, 1C), 25.17 (-CH$_2$H2, Aliphatic, 1C).

HRMS (ESI): calculated $m/z$ for C$_{46}$H$_{53}$N$_2$O$_4$ [M+H$^+$] = 625.4000, found: 625.3991
**PS$_{70}$Br**

Figure S7 $^1$H NMR spectrum of PS$_{70}$Br in CDCl$_3$
Figure S8 \(^1\)H NMR spectrum of PS\(_{70}A2\) in CDCl\(_3\)
Figure S9 $^1$H NMR spectrum of $\text{PS}_{115}\text{Br}$ in CDCl$_3$
Figure S10 $^1$H NMR spectrum of $\text{PS}_{115}\text{A2}$ in CDCl$_3$
Figure S11 $^1\text{H}$ NMR spectrum of $\text{PS}_{230}\text{Br}$ in CDCl$_3$
Figure S12 $^1$H NMR spectrum of $\text{PS}_{230}\text{A2}$ in CDCl$_3$
$\text{PS}_{70}\text{ADMET}_5$

Figure S13 $^1\text{H}$ NMR spectrum of $\text{PS}_{70}\text{ADMET}_5$ in CDCl$_3$
Figure S14 $^1$H NMR spectrum of PS$_{70}$ADMET$_8$ in CDCl$_3$
Figure S15 $^1$H NMR spectrum of PS$_{70}$ADMET$_{34}$ in CDCl$_3$
Figure S16 $^1$H NMR spectrum of PS$_{115}$ADMET$_{10}$ in CDCl$_3$
Figure S17 $^1$H NMR spectrum of PS$_{115}$ADMET$_{36}$ in CDCl$_3$
Figure S18 $^1$H NMR spectrum of PEG$_{46}$A1 in CDCl$_3$
Figure S19 $^1$H NMR spectrum of PEG$_{46}$ADMET$_{20}$ in CDCl$_3$
**COSY NMR SPECTRA**

**ADMET monomer 3**

*Figure S20* COSY NMR spectrum of (Z,Z) – ADMET monomer 3 in CDCl$_3$
Figure S21 COSY NMR spectrum of $\text{PS}_{115}\text{ADMET}_{36}$ in CDCl$_3$
**DOSY NMR spectra**

**PS$_{70}$A2**

--- **Diffusion Analysis**

*Figure S22* DOSY NMR spectrum of PS$_{70}$A2 in CDCl$_3$
Figure S23 DOSY NMR spectrum of PS$_{70}$ADMET$_5$ in CDCl$_3$
Figure S24 DOSY NMR spectrum of PS$_{70}$ADMET$_8$ in CDCl$_3$
Figure S25 DOSY NMR spectrum of PS$_{70}$ADMET$_{34}$ in CDCl$_3$
**Figure S26** DOSY NMR spectrum of PS$_{115}$A2 in CDCl$_3$
Figure S27 DOSY NMR spectrum of $\text{PS}_{115}\text{ADMET}_{10}$ in CDCl$_3$
Figure S28 DOSY NMR spectrum of PS$_{115}$ADMET$_{36}$ in CDCl$_3$
Figure S29 DOSY NMR spectrum of PEG$_{46}$ADMET$_{20}$ in CDCl$_3$
Figure S30 THF-SEC traces from block copolymer synthesis experiment using $\text{PS}_{230}\text{A2}$ as macro-chain stopper