Amphiphilic Poly(ether urethanes) Carrying Associative Terpyridine Side Groups with Controlled Spacing

Katharina Breul, Sebastian Seiffert*

Department of Chemistry, Johannes Gutenberg University Mainz, Duesbergweg 10-14, 55128 Mainz, Germany

* Correspondence to Sebastian Seiffert (sebastian.seiffert@uni-mainz.de)

Suppporting Information

Materials

^{t}Butyl-dimethylsilyl chloride (TBDMS-Cl, 98%, Acros Organics), 1H-imidazole (99%, Acros Organics), triphenyl phosphine (PPh$_3$, > 99%, Alfa Aesar), diisopropyl azodicarboxylate (DIAD, 98% Sigma Aldrich), 2.6-bis(2-pyridyl)-4(1H)-pyridone (Tpy-OH, > 98%, TCI), ammonium hydrogen difluoride (NH$_4$HF$_2$, > 94%, Acros Organics), methanolic HCl (1.25M, Acros Organics), di-n-butyltin dilaurate (DBTDL, 98%, Alfa Aesar), copper(II) bromide (CuBr$_2$, 99%, Sigma Aldrich) and manganese(II) bis(trifluoromethanesulfonate) (MnOTf$_2$, Sigma Aldrich) are purchased from commercial resources and used without further purification. Isophorone diisocyanate (IPDI, mixture of cis/trans isomers (72:28), 98%, Acros Organics) is freshly vacuum distilled. Glycerol (Sigma Aldrich, > 99.5) is stirred over CaH$_2$ and vacuum distilled prior to use. The linear poly(ethylene glycol)s (Sigma Aldrich) are first purified by precipitation into diethyl ether, freeze dried from benzene containing 5vol% 1.25M methanolic HCl and further dried in high vacuum prior to polymerization. Cyclohexan (^{C}Hex), ethylacetate (EA), dichlormethane (DCM) and methanol (MeOH) are used as received. Anhydrous THF, DMF, DMSO, benzene, 1,4-dioxane and N,N-dimethylacetamide (DMA) are purchased from Acros Organics and used as received. Diethyl ether is dried over sodium and freshly distilled under nitrogen atmosphere. Uvasol® grade solvents (Sigma Aldrich) and Milli Q water are used for Light Scattering, UV-Vis and fluorescence spectroscopy.

Chromatography

Thin-layer chromatography is performed on F$_{254}$ silica gel 60 (Merck), silica gel 60 RP-18 (Merck) or aluminum oxide 60 (Merck) coated plates. Spots are detected with UV-light (λ = 254 nm) and immersion in KMnO$_4$ or iron(II)chloride solutions. Flash chromatography is performed on silica gel 60 (40–63 µm, Merck Millipore), LiChroprep® RP-18 (40–63 µm, Merck Millipore) or aluminum oxide (neutral, Brockmann I, 500–200 µm, Acros Organics). Analytical High Performance Liquid Chromatography at Critical Conditions (HPLC-CC) is performed with an Agilent Technologies 1260 Infinity system (1260 Quat pump, Softa 1300 evaporative light scattering detector). A Reprosil 100 (C$_{18}$, 5 µm particle size, 4.6 × 250 mm i.d.) column from Maisch GmbH is used. All data are analyzed with the PSS WinSEC Unity v7 software provided by Polymer Standards Service GmbH (PSS). The mobile phase consists of acetonitrile and water (v/v 44:56). Samples (1 g L^{-1}) are filtered through a Chromafil PET-45/15 MS syringe filter prior to injection. Size exclusion chromatography (SEC) measurements are performed at 60 °C in DMF (+ 1 g L^{-1} LiCl) using a 1260 Infinity GPC/SEC-system from Agilent (PSS SECcurity pump, VWR Elite Chrom RI detector) equipped with a PSS GRAM guard column, two PSS GRAM 1000Å and one PSS GRAM 100 Å columns at a flow rate of 1 mL min^{-1}. All data are analyzed with the software PSS WinSEC provided by PSS. The number- and

weight average molecular weight (M_n, M_w) and dispersity ($Đ$) are calculated with a pEG calibration (calibration standards provided by PSS). Samples (2 g L^{-1}) are filtered through a Chromafil PET-45/15 MS syringe filter prior to injection.

Instrumentation

NMR spectra are recorded on a Bruker Avance-III HD 300 or a Bruker Acance-II HD 400 instrument at 20 C. The chemical shift δ is given in ppm by using tetramethylsilane as internal standard (δ = 0 ppm) and deuterated solvents (CDCl$_3$, DMSO-d$_6$, CD$_3$CN) as internal reference. The reported signal splittings are abbreviated as follows: s = singlet, d = dublet, t = triplet, p = quintet. Coupling constants J are reported in Hz. High resolution electron spray mass spectra (HR-ESI MS) are measured with an Agilent 6545 QTOF-instrument. UV-Vis spectroscopy measurements are performed on a Jasco V-760-ST UV/Vis Spectrophotometer equipped with a magnetic stirrer and an external thermostat at 20 °C. Fourier transform infrared spectra (FT-IR) are measured on a JASCO FT/IR-4700 FTIR-instrument equipped with Attenuated Total Reflection (ATR) diamond. Fluorescence spectroscopy is performed on a spectrofluorometer FP-8200 by Jasco at room temperature. Dynamic light scattering measurements are performed using a ALV/SP-125 compact goniometer system equipped with a Uniphase He/Ne Laser (λ = 632.8 nm, 22 mW), ALV/High QE APD-Avalanche photo-diode (Excelitas Technologies SPCM CD3296H) and a ALV/LSE-5004 multiple-tau digital correlator (all components: ALV-Laser Vertriebsgesellschaft mbH, Langen, Germany). A constant temperature of 20 °C for all measurements is assured with an external thermostat (Lauda RC-6 CS). Thermal properties of polymers are studied by Differential Scanning Calorimetry (DSC) with a Mettler Toledo DSC 823. In the first cycle. samples are heated from −95 °C to 140 °C (20 °C min^{-1}), hold at 140 °C for 5 min and then cooled from 140 °C to −95 °C (10 °C min^{-1}). After holding the samples at −95 °C or 5 min, a second heating cycle (−95 °C to 140 °C, 10 °C min^{-1}) is applied which is used for further analysis. Linear shear rheology is performed on a stress-controlled modular compact rheometer of the type MCR 302 (Anton Paar, Graz, Austria) equipped with a stainless-steel cone–plate geometry (cone angle: 1°, cone diameter: 25 mm) and a solvent trap. The temperature is controlled by a Peltier plate. Motor adjustment and inertial calibration are performed before each measurement.

Synthesis

Compound 2

According to a modified procedure by Bunnelle et al.[1] Freshly distilled glycerol **1** (12.3 g, 134 mmol, 1.0 eq.) and 1H-imidazole (20.0 g, 294 mmol, 2.2 eq.) are dissolved in a mixture of anhydrous THF (60 mL) and DMF (40 mL) under inert atmosphere and cooled to 0 °C in an ice bath. A solution of ᵗbutyl-dimethylchlorsilane (27.8 g, 140 mmol, 4.9M, 1.05 eq) in anhydrous THF (60 mL) is added dropwise under vigorous stirring. After complete addition, the ice-bath is removed and the white suspension is stirred 16 h at rt, poured into water (600 mL) and extracted with diethyl ether (5 x 150 mL). The combined extracts are washed with brine (100 mL), dried over sodium sulfate and concentrated under reduced pressure. The alcohol **2** is purified via flash chromatography on silica gel (ᶜHex:EA = 4:1).
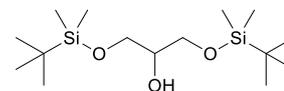
Yield: 36.4 g (114 mmol, 85%), colorless oil.

Molecular formula: $C_{15}H_{36}O_3Si_2$.

TLC: R_f = 0.70 (ᶜHex:EA = 4:1, SiO_2).

ESI-HRMS (m/z): Calculated for [M+Na]⁺: 343.2095, found: 343.2099.

¹H-NMR, COSY (300 MHz, DMSO-d₆): 4.60 (d, ^3J = 4.7 Hz, 1H, −OH), 3.54–3.47(m, 5H, OCH(CH₂O)₂), 0.86 (s, 18H, SiCCH₃), 0.03 (s, 12H, Si(CH₃)₂).

¹³C-NMR, HMBC, HSQC (75 MHz, DMSO-d₆): 71.76 (OCH), 63.96 (OCH₂), 25.84 (SiC), 18.05 (SiCCH₃), 5.29 (SiCH₃), −5.33 (SiCH₃).

The spectroscopic data is consistent with literature.[1]

Compound 2a

According to a modified procedure by Hovinen.[2] Compound **2** (2.00 g, 6.24 mmol, 1.0 eq.) and 2.6-bis(2-pyridyl)-4(1H)-pyridone **3** (1.87 g, 7.49 mmol, 1.2 eq.) are dissolved in anhydrous THF (20 mL) under inert atmosphere and cooled to 0 °C. After addition and complete dissolution of triphenyl phosphine (3.60 g, 13.7 mmol, 2.2 eq), a solution of diisopropyl azodicarboxylate (2.7 mL, 13.7 mmol, 2.2 eq.) in anhydrous THF (25 mL) is added dropwise. After complete addition, the ice-bath is removed and the yellow solution is stirred for 14 h at r.t..
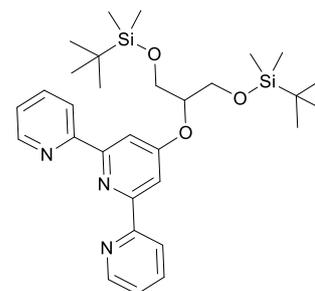
The reaction mixture is diluted with saturated NaHCO₃ solution (50 mL) and air is bubbled through the solution for 1 h to oxidize excess triphenyl phosphine. The solution is extracted with dichloromethane (3 x 100 mL) and the combined organic phases are washed with brine (50 mL), dried over sodium sulfate and concentrated under reduced pressure. The residue suspended in acetonitrile, heated to reflux for 15 min, cooled to 0 °C and insoluble triphenyl phosphine oxide is filtered off. This step is repeated twice. The product is then purified via flash chromatography on neutral Alox (ᶜHex:EA = 30:1).

Yield: 2.86 g (5.18 mmol, 83%), colorless solid.

Molecular formula: $C_{30}H_{45}N_3O_3Si_2$.

TLC: R_f = 0.18 (ACN/H₂O = 50:1, RP₁₈ silica gel); R_f = 0.20 (ᶜHex:EA = 30:1, Alox neutral).

ESI-HRMS (*m/z*): Calculated for [M+H]$^+$: 552.3072, found: 552.3081.

^{1}H-NMR, COSY (300 MHz, CDCl$_3$): 8.68 (ddd, ^3J = 4.8 Hz, ^4J = 1.7 Hz, ^5J = 0.9 Hz, 2H, Tpy:C$_{6'/6''}$*H*), 8.60 (ddd, ^3J = 7.8 Hz, ^4J = 1.1 Hz, ^5J = 0.9 Hz, 2H, Tpy:C$_{3'/3''}$*H*), 8.08 (s, 2H, Tpy:C$_{3/5}$*H*), 7.83 (atd, ^3J = 7.8 Hz, ^4J = 1.7 Hz, 2H, Tpy:C$_{4'/4''}$*H*), 7.31 (ddd, ^3J = 7.8 Hz, ^3J = 4.8 Hz, ^4J = 1.1 Hz, 2H, Tpy:C$_{5'/5''}$*H*), 4.78 (p, ^3J = 5.0 Hz, 1H, Tpy–O*CH*), 3.97–3.85 (m, 4H, O*CH*$_2$CH), 0.87 (s, 18H, SiCC*H*$_3$), 0.07 (s, 6H, SiC*H*$_3$), 0.04 (s, 6H, SiC*H*$_3$).

^{13}C-NMR, HMBC, HSQC (75 MHz, CDCl$_3$): 167.07 (Tpy:*C*$_4$), 157.22 (Tpy:*C*$_{2'/2''}$), 156.30 (Tpy:*C*$_{2/6}$), 149.14 (Tpy:*C*$_{6'/6''}$),, 136.83 (Tpy:*C*$_{4'/4''}$), 123.84 (Tpy:*C*$_{5'/5''}$), 121.39 (Tpy:*C*$_{3'/3''}$), 108.50 (Tpy:*C*$_{3/5}$), 79.06 (Tpy–O*C*H), 62.14 (O*C*H$_2$), 25.99 (Si*C*), 18.43 (Si*C*H$_3$), −5.22 (Si*C*H$_3$).

Terpyridine diol 4

According to a modified procedure by Seki *et al.*[3] Compound **2a** (2.74 g, 4.96 mmol, 1.0 eq.) is dissolved in anhydrous DMF (10 mL) in a Teflon flask and ammonium hydrogen fluoride (4.53 g, 80 mmol, 16 eq.) is added. After stirring for 72 h at r.t. (complete conversion indicated by TLC), the reaction mixture is neutralized with saturated NaHCO$_3$ solution and the solvents are removed under reduced pressure. The residue is suspended in water (30 mL) and extracted with dichloromethane (3 x 50 mL). The combined organic phases are washed with brine (30 mL), dried over sodium sulfate and concentrated under reduced pressure. A white solid is precipitated through the addition of diethyl ether.
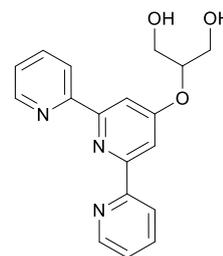
Yield: 1.28 g (3.97 mmol, 80%), colorless crystals.

Molecular formula: C$_{18}$H$_{17}$N$_3$O$_3$.

TLC: R_f = 0.14 (ACN/H$_2$O = 20:1, RP$_{18}$ silica gel)

ESI-HRMS (*m/z*): Calculated for [M+H]$^+$: 324.1343, found: 324.1347.

^{1}H-NMR, COSY (300 MHz, DMSO-d$_6$): 8.72 (dd, ^3J = 4.8 Hz, ^4J = 1.2 Hz, 2H, Tpy:C$_{6'/6''}$*H*), 8.61 (dd, ^3J = 7.8 Hz, ^4J = 1.1 Hz, 2H, Tpy:C$_{3'/3''}$*H*), 8.04 (s, 2H, Tpy:C$_{3/5}$*H*), 8.00 (atd, ^3J = 7.8 Hz, ^4J = 1.2 Hz, 2H, Tpy:C$_{4'/4''}$*H*), 7.49 (ddd, ^3J = 7.8 Hz, ^3J = 4.8 Hz, ^4J = 1.1 Hz, 2H, Tpy:C$_{5'/5''}$*H*), 4.97 (t, ^3J = 5.7 Hz, –O*H*) 4.65 (p, ^3J = 5.3 Hz, 1H, Tpy–O*CH*), 3.75–3.36 (m, 4H, O*CH*$_2$CH).

^{13}C-NMR, HMBC, HSQC (75 MHz, CDCl$_3$): 166.98 (Tpy:*C*$_4$), 156.59 (Tpy:*C*$_{2'/2''}$), 154.93 (Tpy:*C*$_{2/6}$), 149.23 (Tpy:*C*$_{6'/6''}$), 137.39 (Tpy:*C*$_{4'/4''}$), 124.47 (Tpy:*C*$_{5'/5''}$), 120.91 (Tpy:*C*$_{3'/3''}$), 107.78 (Tpy:*C*$_{3/5}$), 80.32 (Tpy–O*C*H), 60.28 (O*C*H$_2$).

Alternating (pEG-*alt*-Tpy)$_n$ Multiblock Copolymers

Alternating multiblock copolymers are synthesized in a two-step procedure according to the following Standard Procedures (SOP). Firstly, pEG with differing molecular weight (M_n = 1.95 (2k, n = 45), 4.22 (4k, n = 96) and 6.27 (6k, n = 143) kg mol^{-1}) is endcapped with isophorone diisocyanate, isolated and dried (SOP I.). Secondly, linear multiblock-polyurethanes (PU with *m* blocks) are obtained *via* chain extension with the terpyridine diol **4** (SOP II).
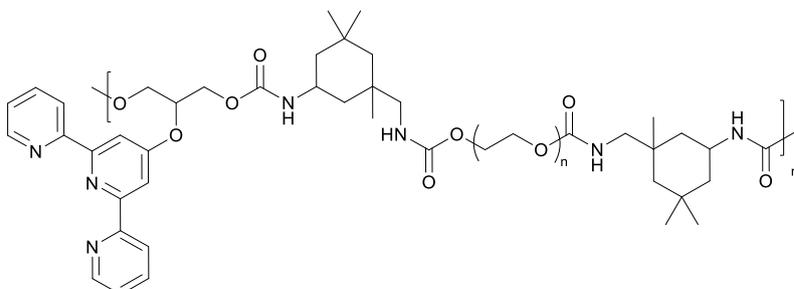
SOP I:. α,ω-Diisocyanato Poly(ethylene glycol):

All steps are carried out under argon atmosphere. IPDI **6** (30 eq. NCO to −OH) is dissolved in anhydrous DMA (2.0 g L^{-1}) in a flame-dried three-neck round bottom flask equipped with a dropping funnel. Freshly dried pEG (1 g, 1 eq/2 eq. −OH) is dissolved in anhydrous DMA (0.2 g L^{-1}) at 40 °C in a Schlenk-flask and transferred to the dropping funnel. After the addition of DBTDL (2 drops) to the IPDI mixture, the pEG solution is added dropwise under vigorous stirring over 10–30 min. Next, the clear solution is stirred for 2 h at r.t. and precipitated into anhydrous Et$_2$O (4 x 45 mL centrifuge tubes equipped with septum and argon balloon). After cooling the tubes to 0 °C for 30 min, the precipitate is centrifuged for 5 min at 10000 rpm. The ether is decanted in an argon counter flow and the polymer is re-precipitated analogously from benzene (2 mL/tube). After the second decanting, the polymer is dissolved in benzene, transferred to a flame-dried Schlenk-flask, freeze-dried and weighed.

SOP II: Chain extension of α,ω-Diisocyanato Poly(ethylene glycol) with Terpyridine Diol:

The prepolymer (1 eq.) is dissolved in anhydrous DMA (0.5 g L^{-1}) and heated to 50 °C under argon atmosphere. Then, DBTDL (2 drops) and the terpyridine diol **4** (0.8 eq., 0.2 mol L^{-1} solution in DMA) are added. Further equivalents of the terpyridine diol are added after 12 and 24 h (0.2 eq. respectively, 0.2 mol L^{-1} solution in DMA). After 48 h, the reaction mixture is cooled to r.t., diluted with MeOH (2–5 mL) and the polymer is precipitated in ice-cold Et$_2$O. After a further re-precipitation into Et$_2$O., the polymer is obtained as colorless solid by lyophilization.

Reaction Control

NCO-Endcapping: Liquid Chromatography at Critical Conditions

To follow the hydroxyl group conversion by LC-CC, α,ω-diisocyanato poly(ethylene glycol)-2k is prepared according to SOP I. The addition of the pEG solution is finished after 10 min. Aliquots are taken from the reaction mixture after 10, 12.5, 15, 17.5, 20, 22.5, 25, 27.5, 30, 40, 50, 60 min (with respect to the beginning of the pEG addition) and quenched with a 100-fold excess of benzyl alcohol under inert atmosphere. The aliquots are precipitated into diethyl ether, centrifuged and dried in vacuo prior to LC-CC analysis. The aliquot taken after 60 min is also analyzed by ESI-MS (Figure S1) and ^{1}H-NMR (Figure S2) to confirm the formation of the IPDI-endcapped pEG.
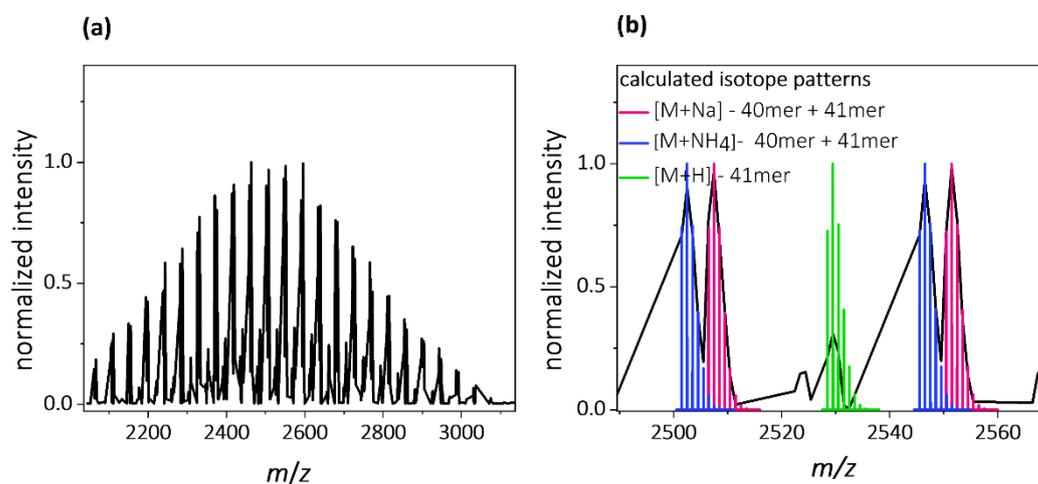
Figure S1. (a) Part of the ESI-MS spectrum of the benzyl alcohol quenched aliquot of isophorone diisocyanate endcapped pEG-2k **7a** and (b) overlay of spectrum and calculated isotope pattern of pEG-40/41-mer provided by https://www.envipat.eawag.ch/index.php.
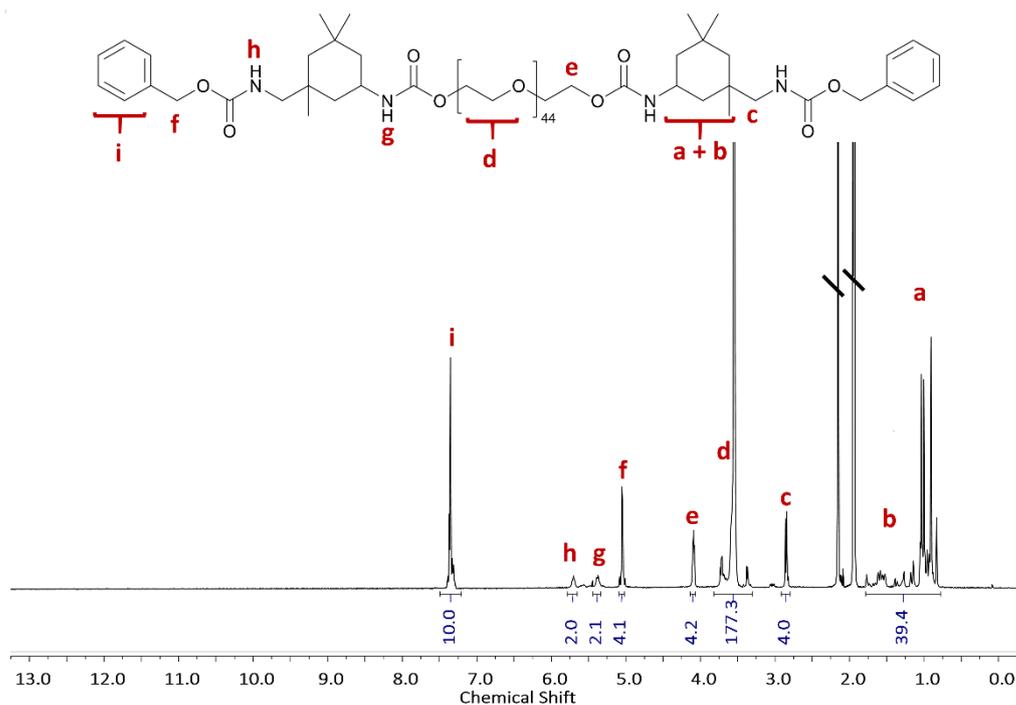
Figure S2. ^{1}H-NMR (CD$_3$CN) of the benzyl alcohol quenched aliquot of isophorone diisocyanate endcapped pEG-2k **7a**.

Chain Elongation

Due to the high dependency on stoichiometry accuracy, the chain elongation step is carried out with different amounts of initially added Tpy diol **4**. The reactions are performed according to SOP II with an initial addition of 1, 0.9 and 0.8 eq. of the Tpy diol **4**, followed by further Tpy additions in 0.2 eq. portions until 1.2 eq have been added in each case. The molar mass distribution of the obtained PUs is analyzed by SEC as summarized in Figure S3.
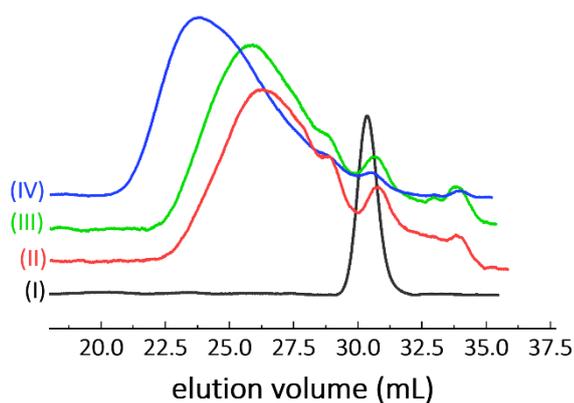
Figure S3. SEC traces of (I) pEG-2k **5a** (black) and PU_2k-alt with an initial addition of (II) 1, (III) 0.9 and (IV) 0.8 equivalents of terpyridine diol **4** (RI signal).

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Polymer Characterization

PU_2k-alt

Yield: 0.72 mg (71%).

SEC: M_n = 14.2 kg mol^{-1}, M_w = 27.0 kg mol^{-1}, Đ = 2.0.

^{1}H-NMR (400 MHz, DMSO-d$_6$): 8.69 (m, 1.3H, Tpy:C$_{6'/6''}H$), 8.65 (m, 1.3H, Tpy:C$_{3'/3''}H$), 8.05 (m, 2.6H, Tpy:C$_{3/5}H$, C$_{4'/4''}H$), 7.49 (m, 1.3H, Tpy:C$_{5'/5''}H$), 7.25–7.03 (m, 2.6H, NH), 5.61–5.92 (m, 1.7H, NH), 5.27 (s, 0.7H, TpyOCH), 4.1–4.39 (m, 2.8H, TpyOCHCH_2), 4.06 (m, 4H, NHC(=O)OCH_2CH$_2$O), 3.88–3.45 (m, 180H, (CH_2CH_2O)$_n$), 2.86 (m, 4.1H, IPDI:OC(=O)NHCH_2), 1.36–0.68 (m, 32H, IPDI).

Peak assignment accoring to literature reports.[4]

PU_4k -alt

Yield: 0.41 mg (65%).

SEC: M_n = 31.8 kg mol^{-1}, M_w = 61.8 kg mol^{-1}, Đ = 1.9.

^{1}H-NMR (400 MHz, DMSO-d$_6$): 8.75 (m, 1.4H, Tpy:C$_{6'/6''}H$), 8.68 (m, 1.4H, Tpy:C$_{3'/3''}H$), 8.12 (m, 2.7H, Tpy:C$_{3/5}H$, C$_{4'/4''}H$), 7.53 (m, 1.3H, Tpy:C$_{5'/5''}H$), 7.26–6.96 (m, 2.7H, NH), 5.91–5.66 (m, 1.9H, NH), 5.37 (s, 0.7H, TpyOCH), 4.25 (m, 2.3H, TpyOCHCH_2), 4.05 (m, 4H, NHC(=O)OCH_2CH$_2$O), 3.91–3.43 (m, 364H, (CH_2CH_2O)$_n$), 2.91 (m, 4.4H, IPDI:OC(=O)NHCH_2), 1.76–0.67 (m, 32H, IPDI).

PU_6k-alt

Yield: 0.54 mg (64%).

SEC: M_n = 33.2 kg mol^{-1}, M_w = 63.7 kg mol^{-1}, Đ = 1.9.

^{1}H-NMR (400 MHz, DMSO-d$_6$): 8.71 (m, 1.3H, Tpy:C$_{6'/6''}H$), 8.61 (m, 1.3H, Tpy:C$_{3'/3''}H$), 8.01 (m, 2.6H, Tpy:C$_{3/5}H$, C$_{4'/4''}H$), 7.50 (m, 1.3H, Tpy:C$_{5'/5''}H$), 7.22–7.01 (m, 2.3H, NH), 5.92–5.62 (m, 1.6H, NH), 5.13 (s, 0.6H, TpyOCH), 4.37–4.19 (m, 2.2H, TpyOCHCH_2), 4.05 (m, 4.6H, NHC(=O)OCH_2CH$_2$O), 3.67–3.39 (m, 528H, (CH_2CH_2O)$_n$), 2.68 (m, 4H, IPDI: OC(=O)NHCH_2)), 1.59–0.63 (m, 35H, IPDI).

Random pEG-Polyurethanes

SOP III

Freshly dried pEG (1 eq) is dissolved in anhydrous DMA (0.5 g L^{-1}) in a 50 mL Schlenk flask and heated to 50 °C under argon atmosphere. After the addition of Tpy diol **4** (1 eq.), IPDI (2 eq.) and DBTDL (2 drops) the reaction mixture is stirred 50 °C until complete conversion of the isocyanate is indicated by the disappearance of the NCO band in the FT-IR spectrum (Figure S4). The reaction times vary between 48 and 72 h.
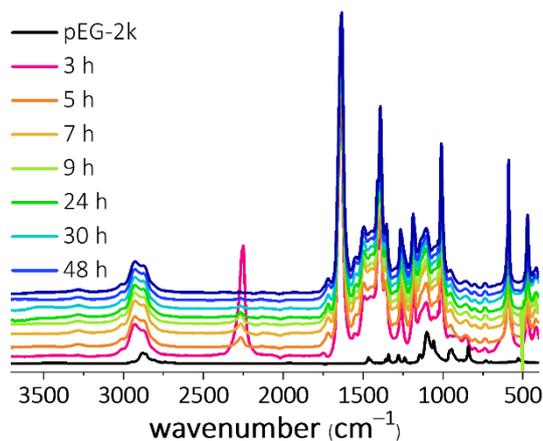
Figure S4. FT-IR spectra of films drop-cast onto the ATR crystal from the reaction mixture of PU_2k-ran under nitrogen atmosphere after different reaction times.

Polymer Characterization

PU_2k-ran

Yield: 0.48 mg (90%).

SEC: M_n = 22.2 kg mol^{-1}, M_w = 45.9 kg mol^{-1}, $Đ$ = 2.1.

^{1}H-NMR (400 MHz, DMSO-d$_6$): 8.71 (m, 1.7H, Tpy:C$_{6'/6''}H$), 8.63 (m, 1.7H, Tpy:C$_{3'/3''}H$), 7.98 (m, 3.4H, Tpy:C$_{3/5}H$, C$_{4'/4''}H$), 7.49 (m, 1.6H, Tpy:C$_{5'/5''}H$), 7.32–6.95 (m, 2.6H, NH), 5.92–5.41 (m, 2.7H, NH), 5.18 (s, 0.8H, TpyOCH), 4.45–4.13 (m, 3.3H, TpyOCHCH_2), 4.03 (m, 4.5H, NHC(=O)OCH_2CH$_2$O), 3.67–3.36 (m, 180H, (CH_2CH$_2$O)$_n$), 2.71 (m, 4H, IPDI:OC(=O)NHCH_2), 1.61–0.73 (m, 40H, IPDI).

Peak assignment accoring to literature reports.[4]

PU_4k-ran

Yield: 0.86 mg (94%).

SEC: M_n = 33.8 kg mol^{-1}, M_w = 64.8 kg mol^{-1}, $Đ$ = 1.9.

^{1}H-NMR (400 MHz, DMSO-d$_6$): 8.71 (m, 1.5H, Tpy:C$_{6'/6''}H$), 8.62 (m, 1.6H, Tpy:C$_{3'/3''}H$), 7.98 (m, 3H, Tpy:C$_{3/5}H$, C$_{4'/4''}H$), 7.49 (m, 1.5H, Tpy:C$_{5'/5''}H$), 7.36–7.02 (m, 3.1H, NH), 6.03–5.52 (m, 3.0H, NH), 5.19 (s, 0.9H, TpyOCH), 4.48–4.23 (m, 2.5H, TpyOCHCH_2), 4.06 (m, 4H, NHC(=O)OCH_2CH$_2$O), 3.95–3.39 (m, 364H, (CH_2CH$_2$O)$_n$), 2.73 (m, 5H, IPDI:OC(=O)NHCH_2), 1.67–0.55 (m, 35H, IPDI).

PU_6k-ran

Yield: 0.89 mg (89%).

SEC: M_n = 43.0 kg mol^{-1}, M_w = 77.9 kg mol^{-1}, $Đ$ = 1.8.

^{1}H-NMR (400 MHz, DMSO-d$_6$): 8.70 (m, 1.5H, Tpy:C$_{6'/6''}H$), 8.58 (m, 1.5H, Tpy:C$_{3'/3''}H$), 7.99 (m, 3H, Tpy:C$_{3/5}H$, C$_{4'/4''}H$), 7.49 (m, 1.5H, Tpy:C$_{5'/5''}H$), 7.20–7.03 (m, 2.8H, NH), 5.92–5.46 (m, 3H, NH), 5.15 (s, 0.9H, TpyOCH), 4.4–4.2 (m, 3H, TpyOCHCH_2), 4.03 (m, 3.9H, NHC(=O)OCH_2CH$_2$O), 3.67–3.36 (m, 528H, (CH_2CH$_2$O)$_n$), 2.71 (m, 4H, IPDI:OC(=O)NHCH_2)), 1.64–0.67 (m, 40H, IPDI).

UV-Vis Measurements

Spectrometric Titration

PU_6k-alt (19.5 mg) is dissolved MeOH in a volumetric flask (100 mL). After measuring an initial spectrum (260–450 nm), 25 µL of a CuBr$_2$ solution (2.1 mM in MeOH) are added and the mixture is stirred for 5 min before taking an aliquot and measuring another spectrum. Afterwards, the aliquot is transferred back to the volumetric flask before the titration was continued analogously with 5 µL portions of the CuBr$_2$ solution (Figure S5 a). The relative intensity increase at the absorption maximum of the CuTpy$_2$ complex at (λ_{max} = 313.5 nm) shows two regimes which are separately fitted (Figure S5 b). The equivalence point is determined from the intersection point of these linear fits (n_{CuBr2} = 1.1 µmol). A terpyridine content of 113 µmol g^{-1} is calculated under the assumption $n_{Tpy} = 2n_{Cu(II),equivalence\ point}$.
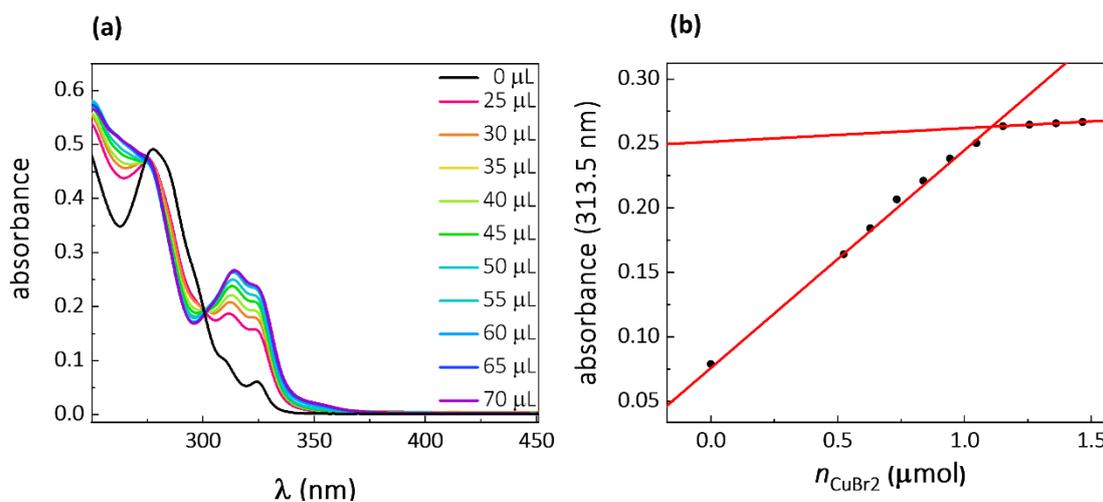
Figure S5. (a) UV-Vis spectra of PU_6k-alt in methanol upon the stepwise addition of CuBr$_2$ (2.1 mM solution). (b) Absorbance at the absorption maximum of the CuTpy$_2$ complex (λ_{max} = 313.5 nm) as function of the amount of added CuBr$_2$ and determination of the equivalence point *via* linear fitting.

Molar Extinction Coefficient and Terpyridine Content

The molar decadic extinction coefficient of Tpy diol **4** in methanol is determined from the calibration shown in Figure S6 as ε = (22.6 ± 1)·10^2 L mol^{-1} cm^{-1}. For the terpyridine content determination, the PUs (10–20 mg) are dissolved in methanol in volumetric flasks (25 mL). These stock solutions are diluted with methanol (1:5) prior to the UV-Vis measurements.
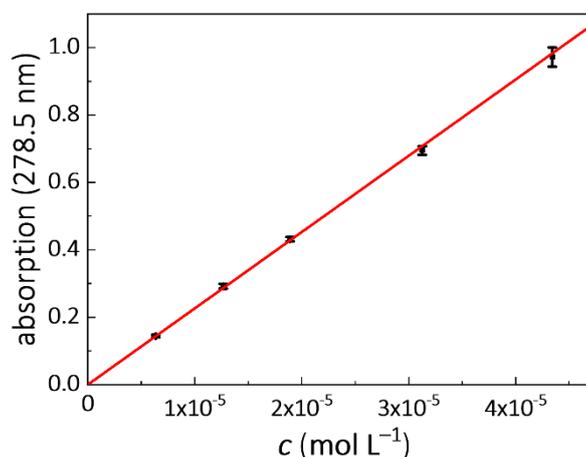
Figure S6. Absorption of Tpy diol **4** at λ = 278.5 nm in methanol as a function of the molar concentration with linear fit.

FT-IR Spectroscopy

The PUs are dissolved in DCM, dropped onto the ATR crystal and left to dry under nitrogen atmosphere for 30 min. Afterwards, an IR spectrum is recorded at room temperature which is then normalized to the C-O-C stretching vibration at 1100 cm^{-1}. The peak deconvolution of the carbonyl region is performed with the Software OriginPro 2019. The area between 1800 –1620 cm^{-1} is separately normalized and baseline-subtracted before a peak fitting of Gaussian shape is conducted assuming the presence of two (alt) or three (ran) individual peaks. The spectra, and corresponding fits are summarized in Figure S7 .
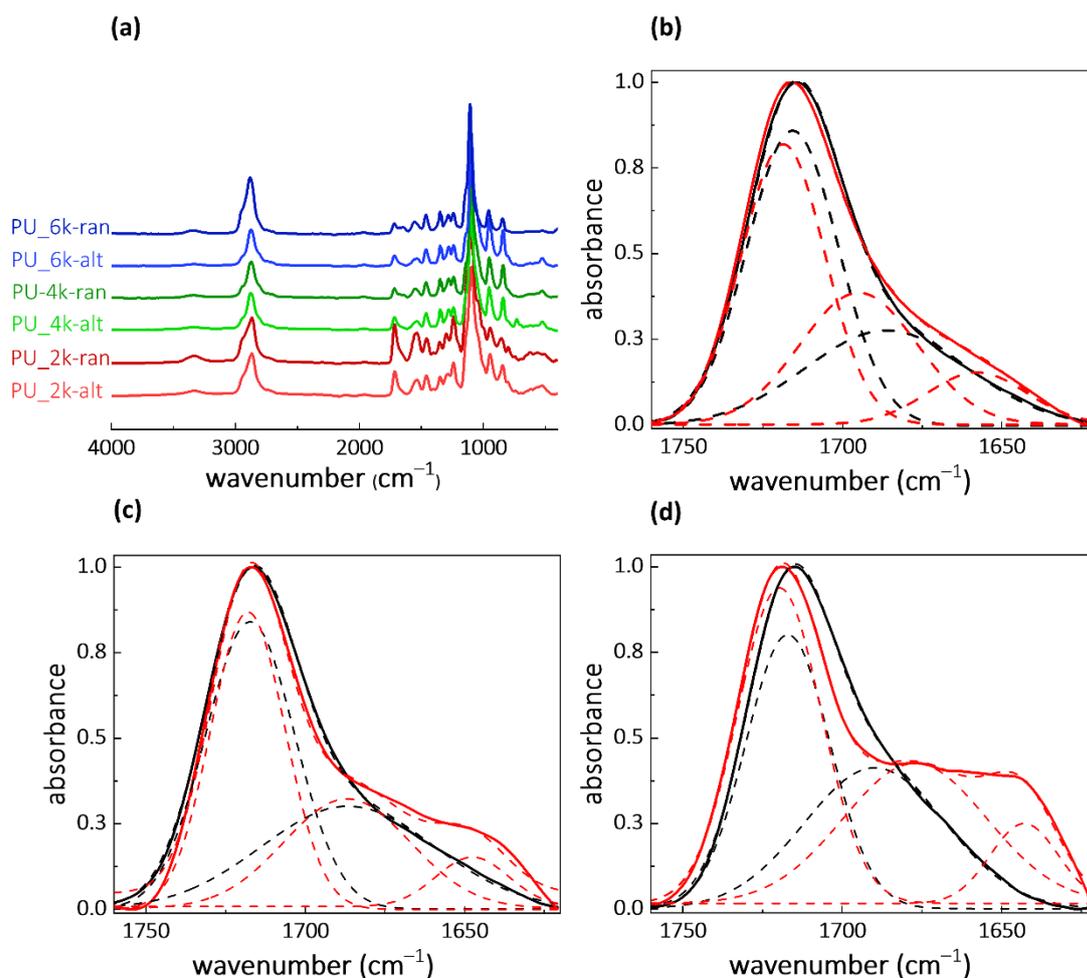
Figure S7. (a) Normalized FT-IR spectra of drop-cast PU films. Baseline subtracted, normalized carbonyl region of (b) PU_2k-alt (black line)/-ran (red line), (c) PU_4k-alt (black line)/-ran (red line) and (d) PU_6k-alt (black line)/-ran (red line) with Gaussian curve fitting (dashed lines in corresponding color) performed for peak deconvolution.

Differential Scanning Calorimetry

The thermal properties of pEG-2k/-4k and -6k applied for the synthesis, the IPDI-endcapped pEG prepolymers and the random and alternating PUs are investigated via DSC. In a first cycle. samples are heated from –95 °C to 140 °C (20 °C·min^{-1}), hold at 140 °C for 5 min and then cooled from 140 °C to –95 °C (10 °C·min^{-1}). After holding the samples at –95 °C or 5 min, a second heating cycle (–95 °C to 140 °C, 10 °C·min^{-1}) is applied which is depicted in Figure S8 and used for further analysis.
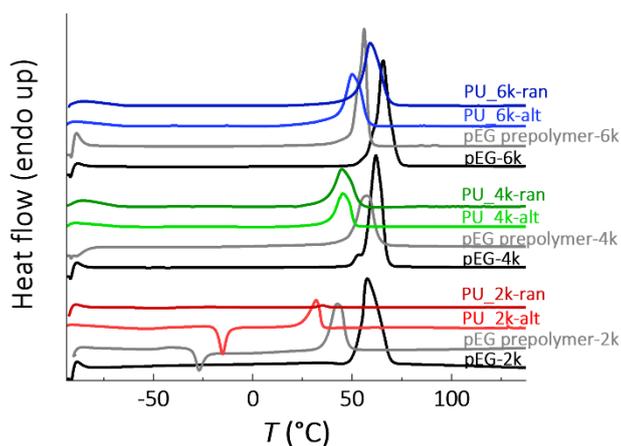
Figure S8. DSC thermograms of the 2nd heating run (rate: 10.0 °C min^{−1}) of pEG-2k/4k/-6, the IPDI-endcapped the random and alternating PUs (baseline corrected).

Fluorescence Spectroscopy

The fluorometric determination of the critical aggregation concentration (cac) with pyrene as hydrophobic probe is conducted according to a standard procedure by Zhu and co-workers.[5] A stock solution of pyrene (9.9 mg) in ethanol is prepared in a volumetric flask (100 mL, $c_{pyrene,EtOH}$ = 0.49 mM). The ethanolic pyrene solution is further diluted to a concentration of $c_{pyrene,H2O}$ = 2µM in Milli-Q water (100 mL volumetric flask). To prepare a polymer-pyrene stock solution, PU_6k-alt (50 mg), 20 µL of the ethanolic pyrene stock solution and Milli-Q water (around 3 mL) are added to a volumetric flask (5 mL) and gently shaken at 35 °C for 60 min before filling the flask to the mark. Next, the PU-pyrene stock solution is diluted to polymer concentrations of c_{PU} = 10, 5, 2.5, 1, 0.5, 0.25, 0.1, 0.05, and 0.025 g L^{−1} (1 mL of each) with the aqueous pyrene stock solution and shaken for 30 min. Finally, the emission spectra of all solutions are recorded (excitation wavelength λ_{ex} = 334 nm). Accordingly, a stock solution of PU_6k-alt is prepared in pure Milli-Q water and diluted analogously. The emission spectra of the pure PU solutions are recorded and subtracted from the PU-pyrene emission spectra before the I_1/I_3 intensity ration is analyzed (Figure 6) to determine the cac.

Dynamic Light Scattering Measurements

Prior to all DLS measurements, the polymers are filtered through a combination of a Whatman Anotop filter (20 nm pore size) and a Millex-LG® filter (200 nm pore size) in methanol at a concentration of 1 g·L^{−1} to remove impurities. After freeze drying from an acetonitrile/water mixture, the PUs are dissolved in Milli-Q water or methanol to the required concentration. Dust particles are removed from the light scattering quartz cuvettes by rinsing them with hot acetone before the polymer solutions are filtered into the cuvettes (syringe filter: Millex-LG®, 200 nm pore size) inside a dust-free laminar flow box. Angular dependent DLS measurements are performed at 20 °C with a successively increasing scattering angle of 30 to 120° (10° steps). At each angle, ten runs with a correlation time of 60 s are recorded. For data evaluation, the experimental intensity autocorrelation functions $g^{(2)}(q, \tau) = (<I(q, t)> \cdot <I(q, t+ \tau)>) \cdot (<I(q, t)>)^{−2}$ are converted to the amplitude autocorrelation function $g^{(1)}(q, \tau)$ by applying the Siegert relation. Herein, $I(q, \tau)$ denotes the angular- and time dependent intensity with the lag time

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τ and the scattering vector $q = 4\pi \cdot n_D \cdot \lambda^{-1} \cdot \sin(\vartheta/2)$ depending on the refractive index of the solvent n_D (n_D(MeOH) = 0.583 mPa·s, n_D(H$_2$O) = 0.988 mPa·s), the scattering angle ϑ and the laser wavelength λ= 632.8 nm. The amplitude autocorrelation functions $g^{(1)}(q, \tau)$ are fitted with a sum of (stretched) exponentials as detailed in the main text. The normalized amplitude correlation functions measured at 30°, the applied fits and corresponding residuals of concentration dependent measurements of PU_6k-alt and -ran in methanol are shown in and Figure S9 a) and Figure 8 a) respectively. In Figure S9 b), the normalized amplitudes of the fast and slow mode from the fitting is shown as a function of the PU concentration.
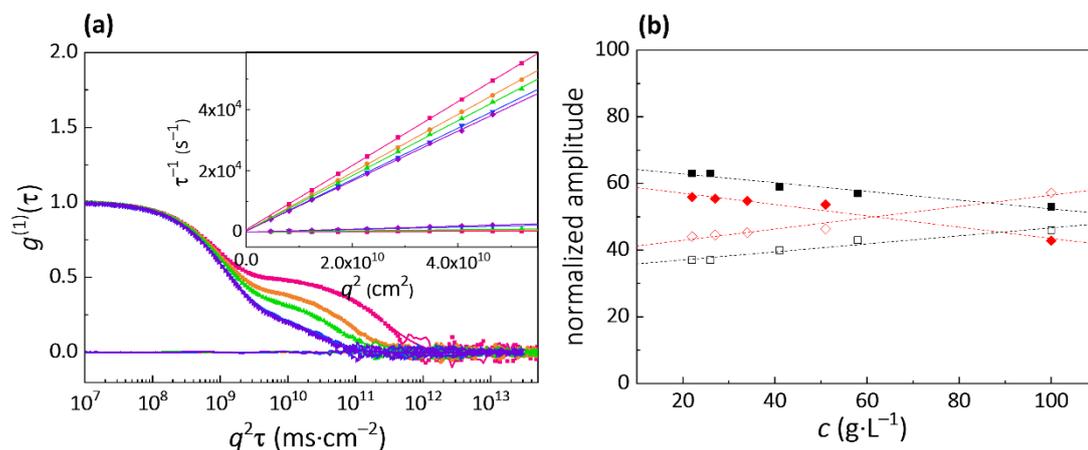
Figure S9. (a) Normalized DLS autocorrelation function $g^{(1)}(\tau)$ of PU_6k-alt in methanol (pink: c_1 = 100 g L^{-1}, orange: c_2 = 58 g L^{-1}, green: c_3 = 41 g L^{-1}, blue: c_4 = 26 g L^{-1} and purple: c_5 = 22 g L^{-1}) along with fits to a double exponential decay and corresponding residuals measured at a scattering angle of 30° at 20 °C. Insert: Inverse relaxation times τ as a function of the square of the scattering vector q^2 (same color code as before) with linear fits. (b) Concentration dependence of the relative amplitudes of the fast (open symbols) and slow mode (closed symbols) in the fit function (PU_6k-alt: black squares and PU_6k-ran: red diamonds).

Gel Preparation and Rheological Measurements

All gels are prepared in a total volume of 250 µL and a terpyridine concentration of 20 µM. The respective amount of the PU is dissolved in 150 µL methanol before an appropriately concentrated manganese (II) triflate solution (100 µL, n_{Mn2+} = 0.5n_{Tpy}) is added which is followed by immediate vortexing for 10–20 s. Afterwards, the samples are sealed and equilibrated for 24 h at 35 °C. Before the measurement, all samples are centrifuged for 10 min to remove air bubbles. The gels are further equilibrated for 15 min after application onto the rheometer and between different at constant shear amplitude and frequency (γ = 0.1%; ω = 1 rad·s^{-1}). Frequency sweeps are measured between ω = 100–00.01 rad·s^{-1} with a logarithmic increasing shear amplitude from γ = 1–10% which is well within the viscoelastic regime of all gels.

¹H- and ¹³C-NMR spectra

Compound **2**
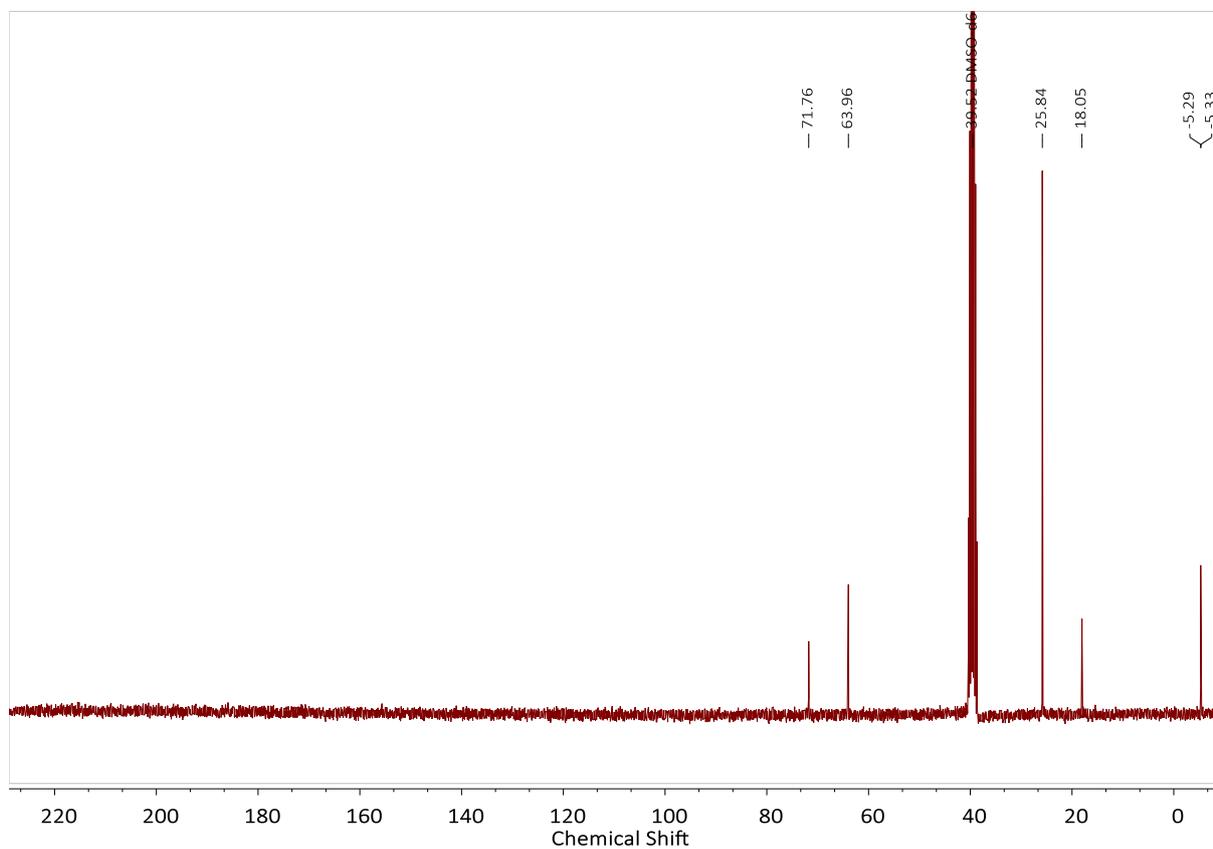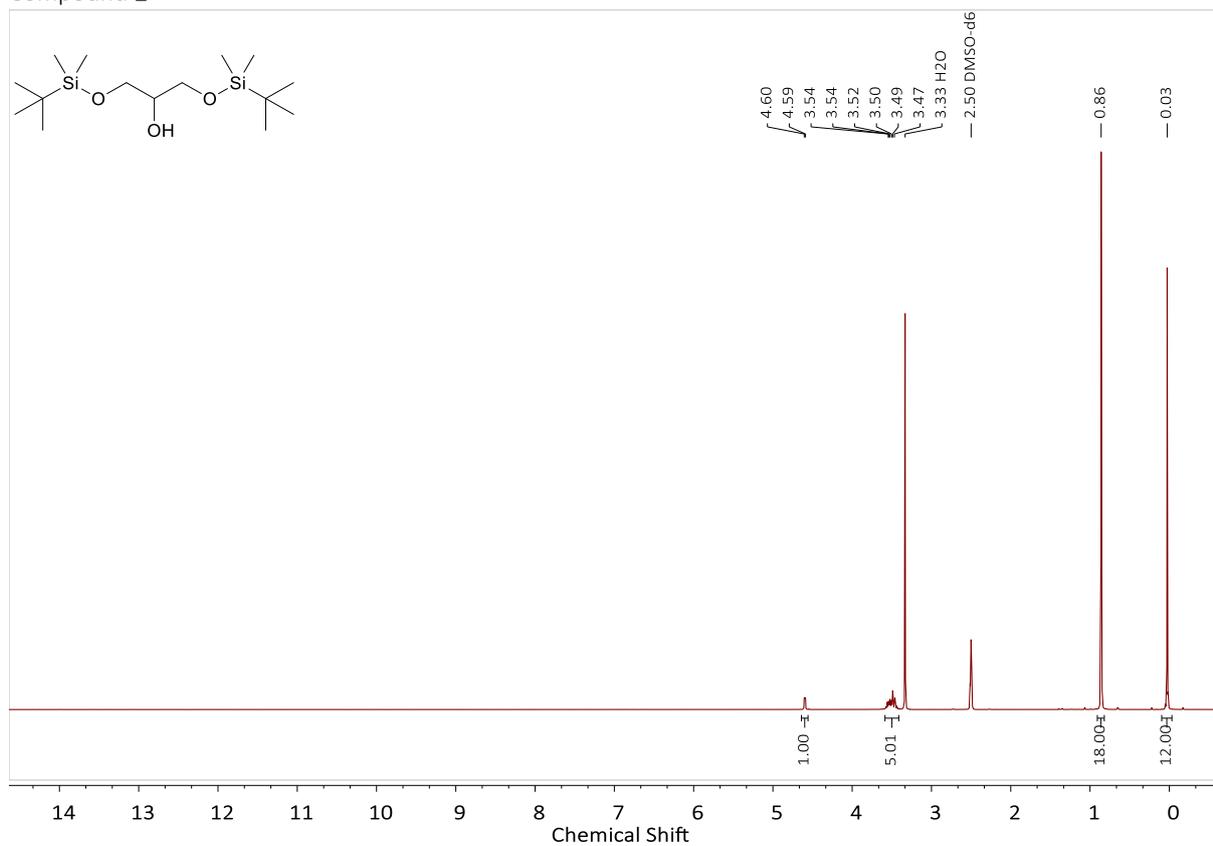
Figure S10: ¹H- and ¹³C-NMR of Compound **2** (300 MHz, 75MHz, DMSO-d₆).

Compound **2a**
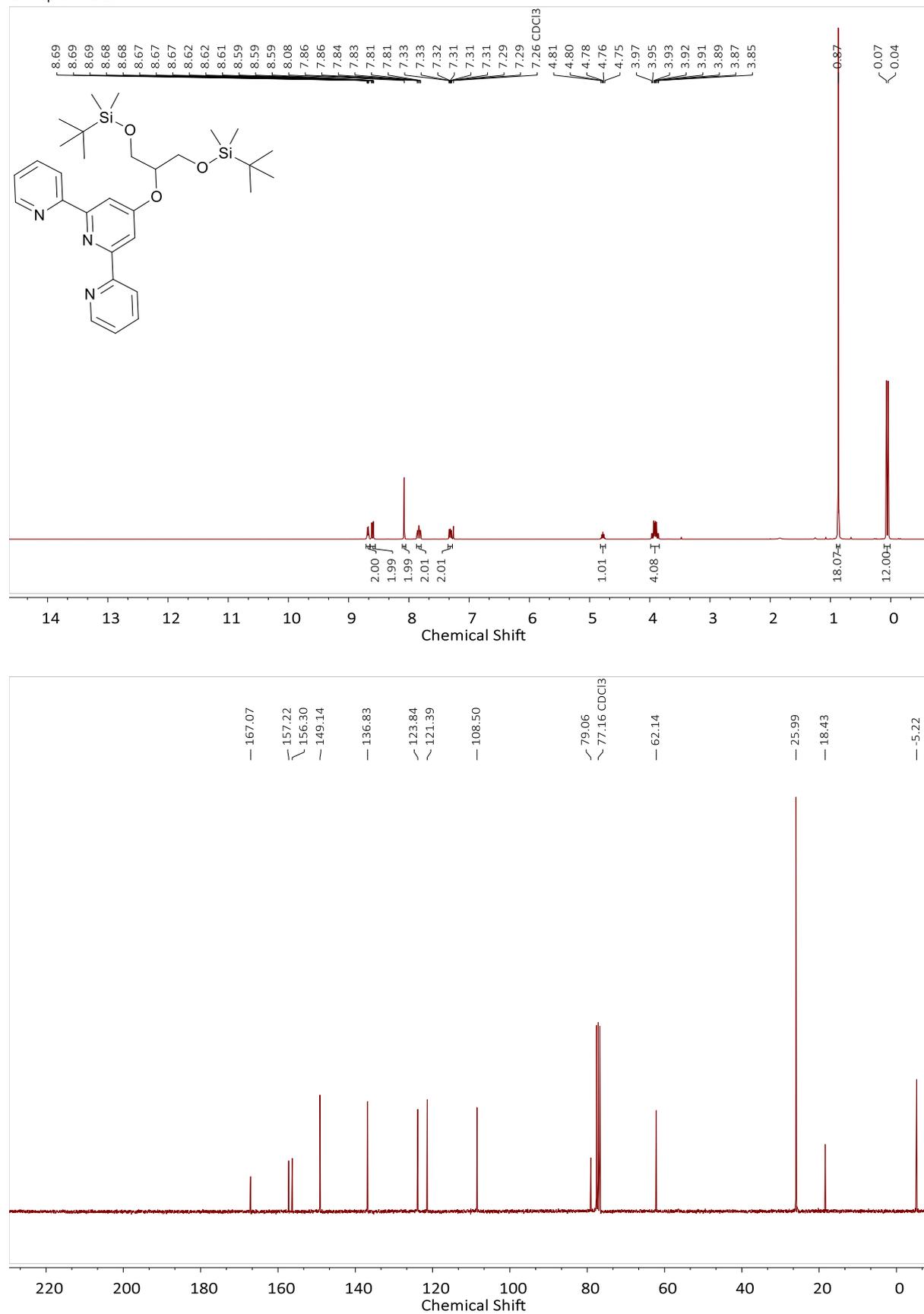
Figure S11: ^{1}H- and ^{13}C-NMR of Compound **2a** (300 MHz, 75 MHz, CDCl$_3$).

Compound **4**
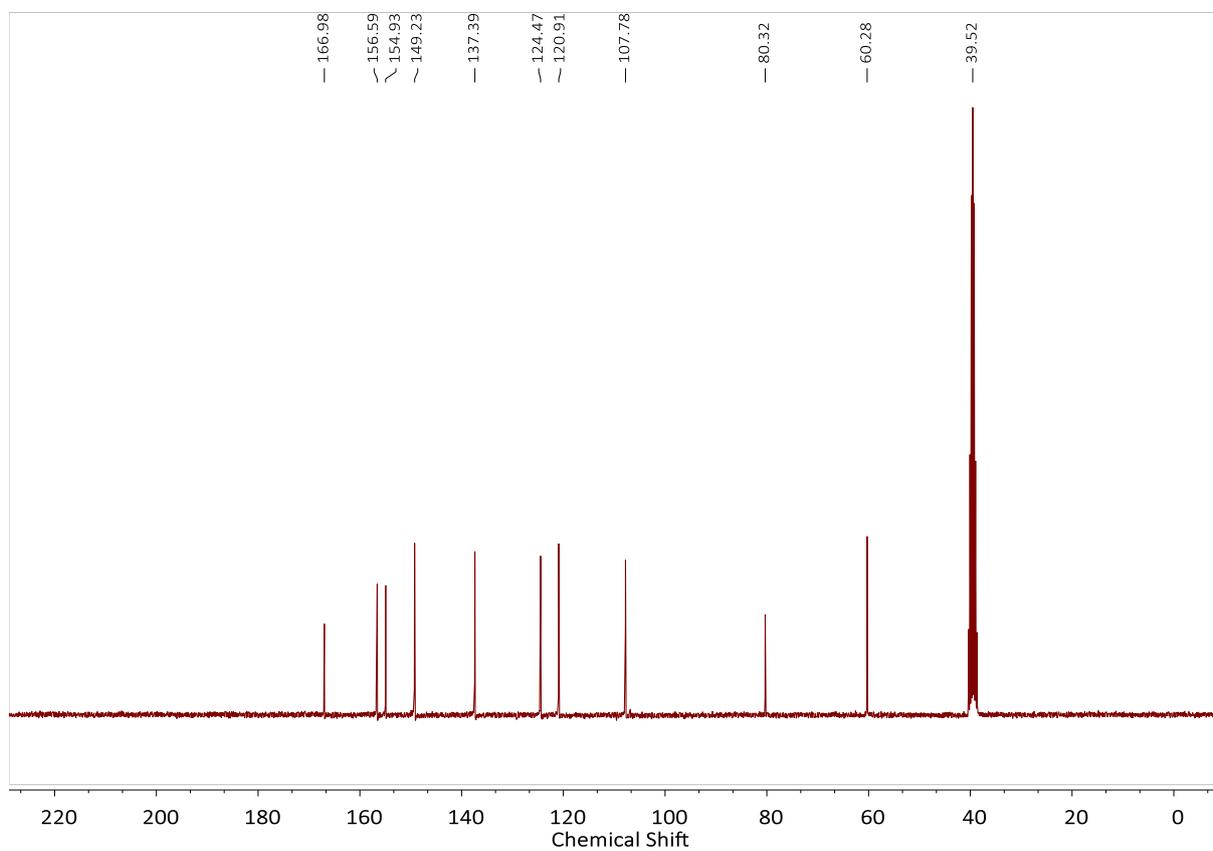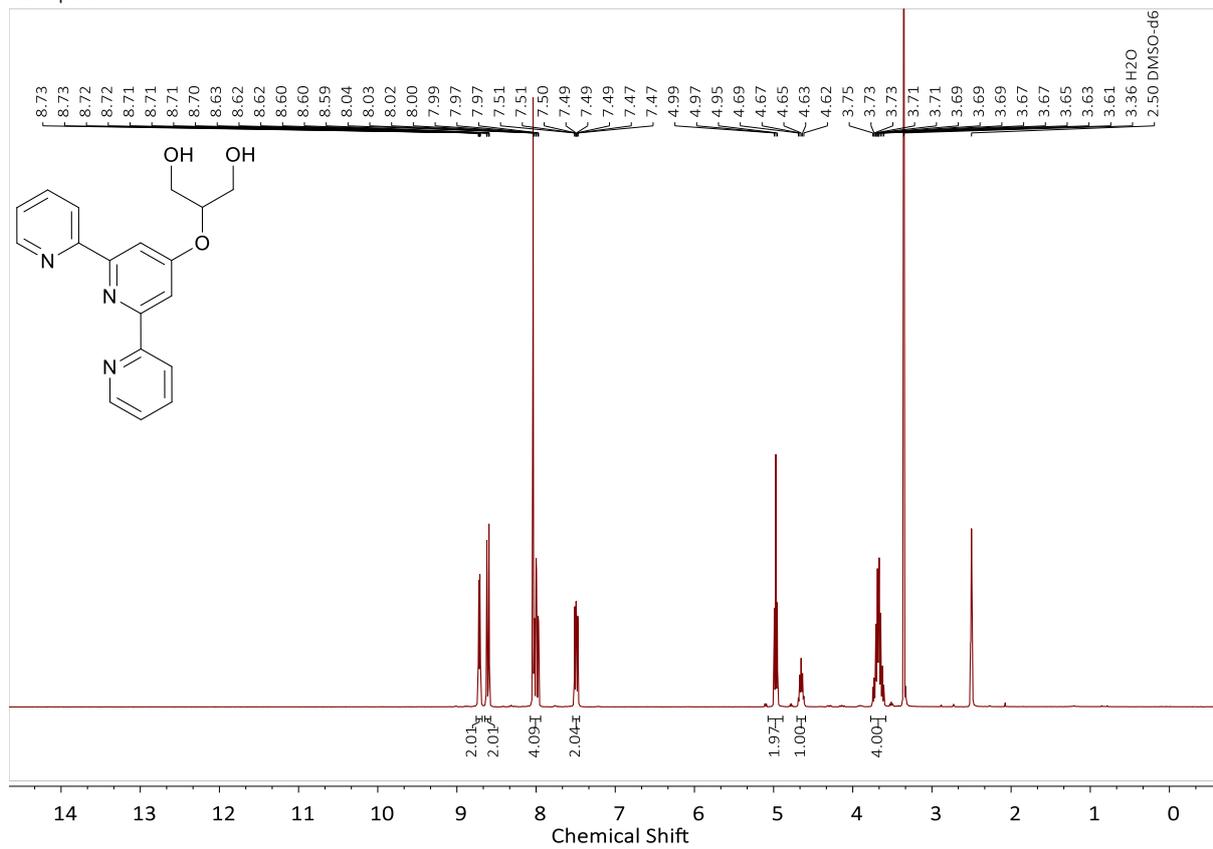
Figure S12: ^{1}H- and ^{13}C-NMR of Compound **4** (300 MHz, 75 MHz, DMSO-d$_6$).

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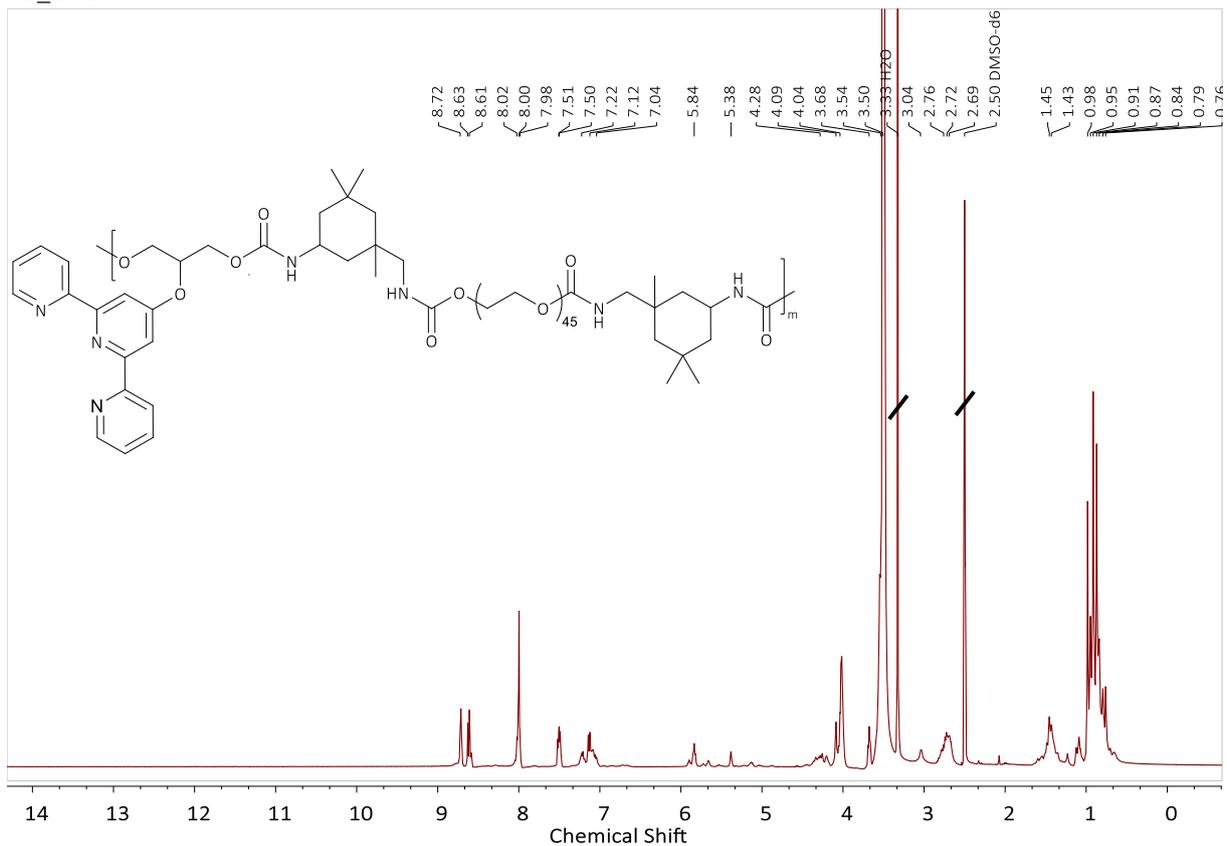
PU_2k-alt

Figure S13: ^{1}H-NMR of PU_2k-alt (400 MHz, DMSO-d$_6$).

PU_2k-ran
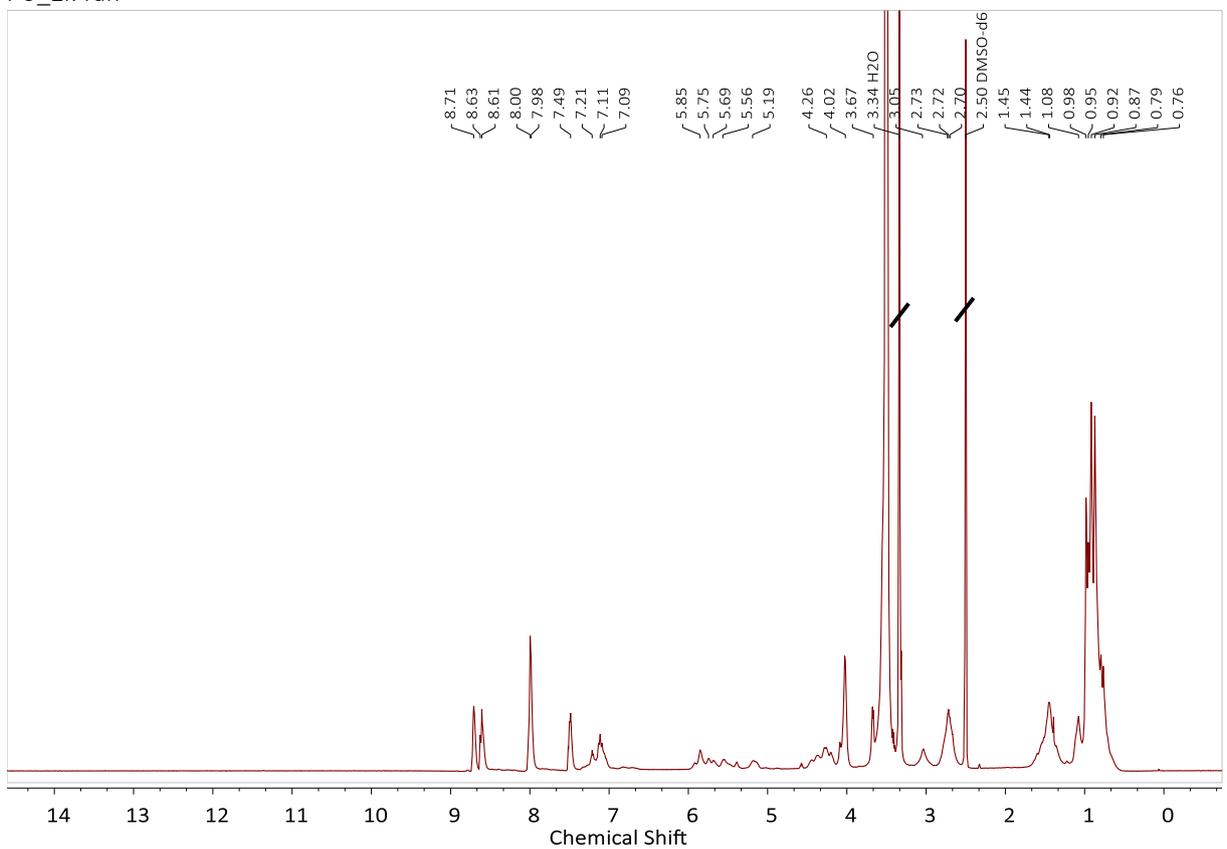
Figure S14: ^{1}H-NMR of PU_2k-ran (400 MHz, DMSO-d$_6$).

PU_4k-alt
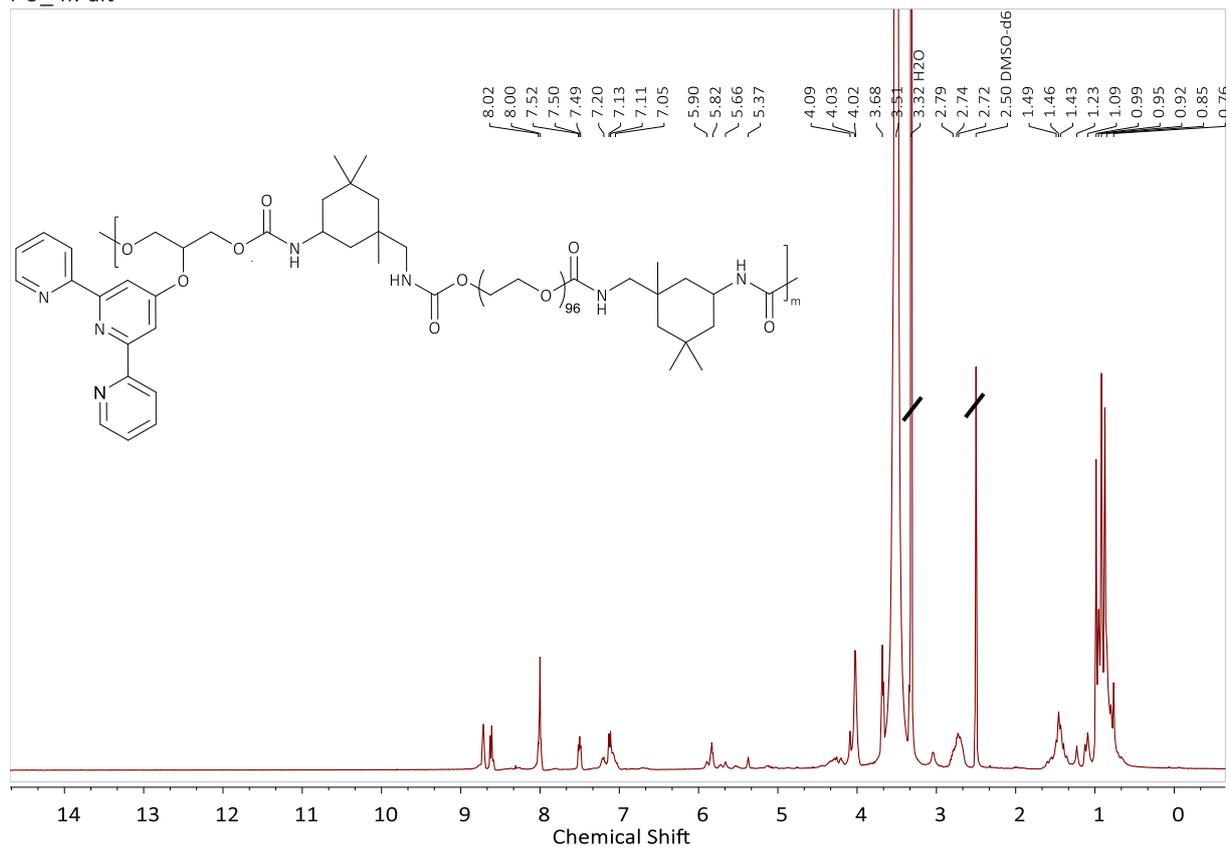
Figure S15: ^{1}H-NMR of PU-alt (400 MHz, DMSO-d$_6$).

PU_4k-ran
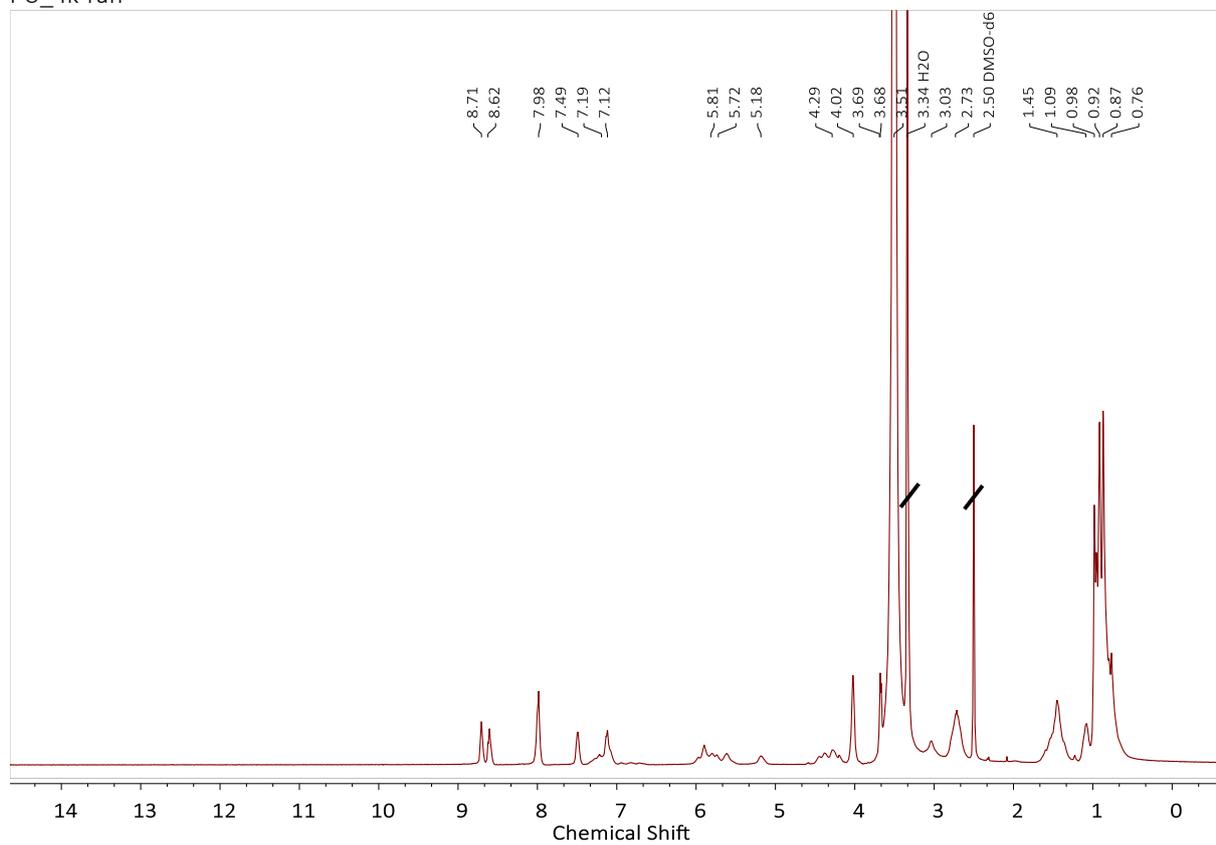
Figure S16: ^{1}H-NMR of PU_4k-ran (400 MHz, DMSO-d$_6$).

PU_6k-alt
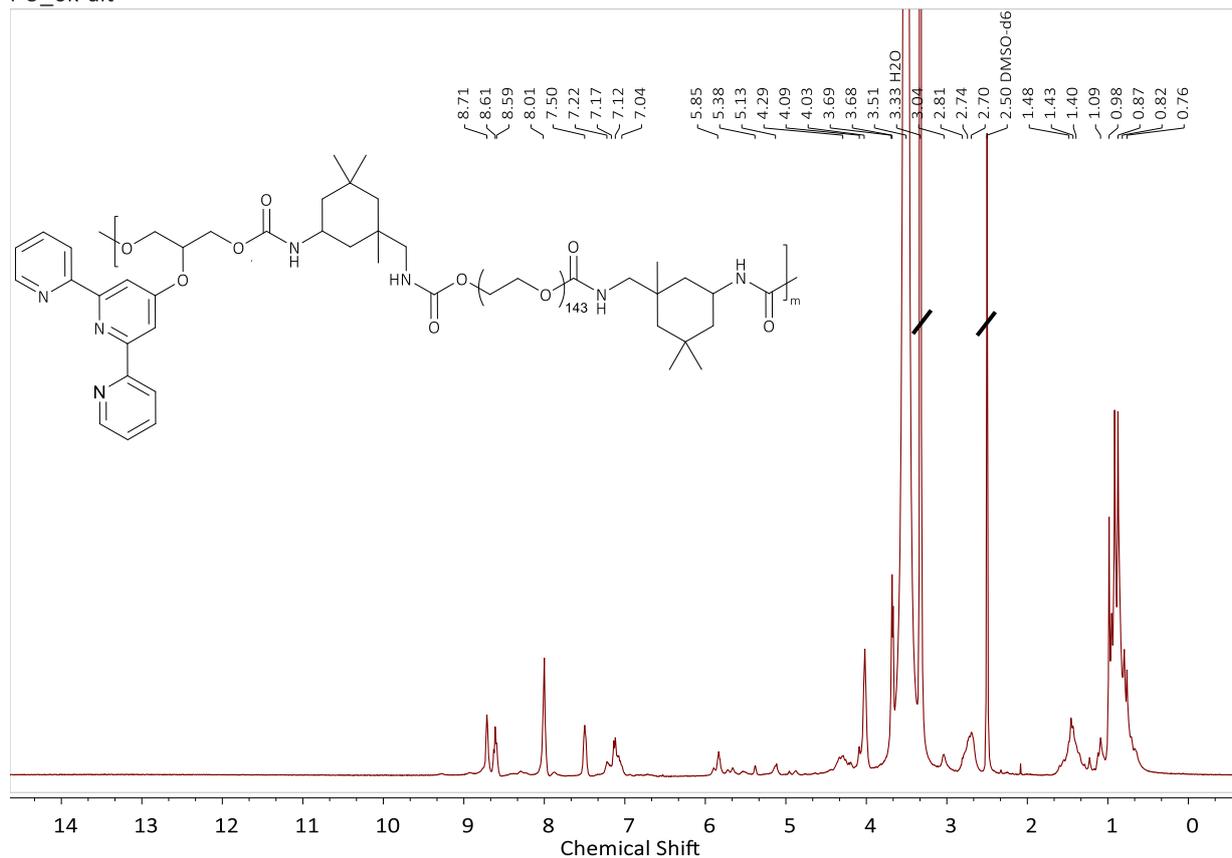
Figure S17: ^{1}H-NMR of PU_6k-alt (400 MHz, DMSO-d$_6$).

PU_6k-ran
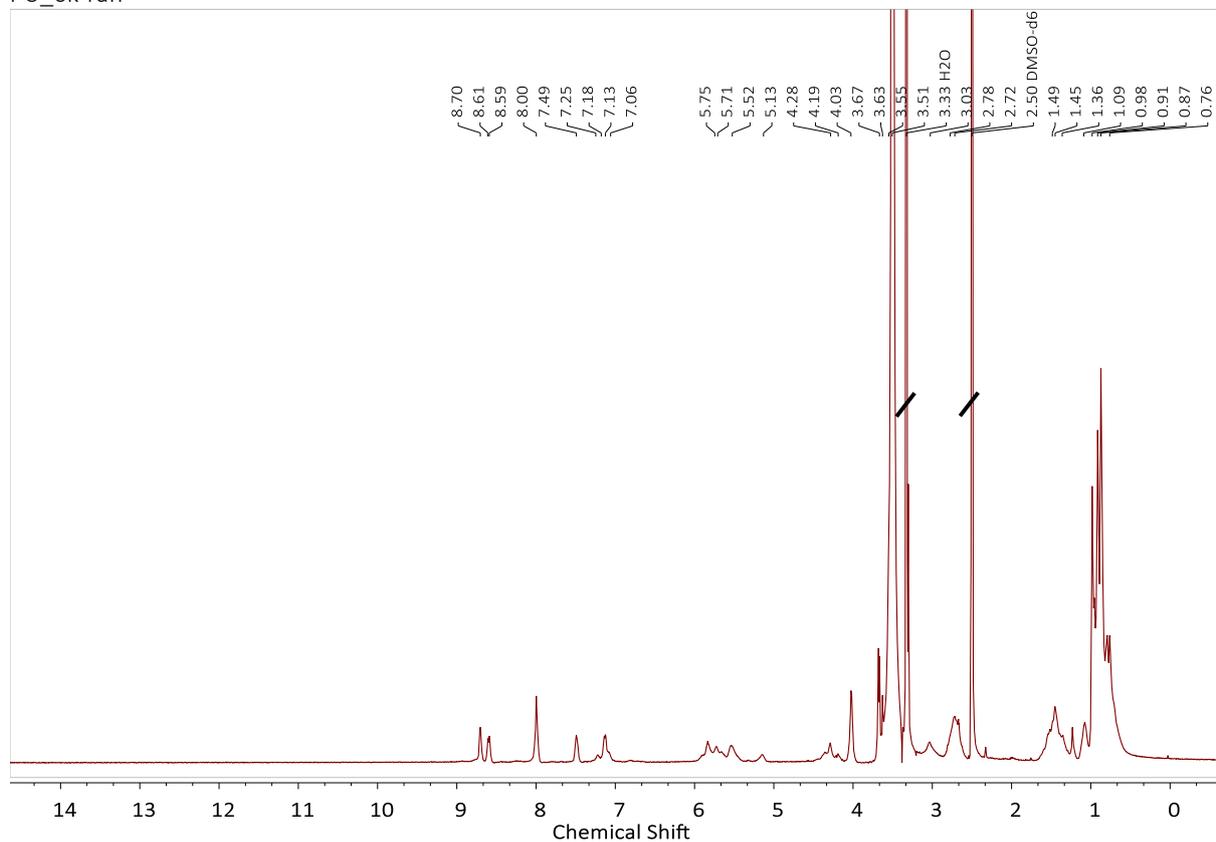
Figure S18: ^{1}H-NMR of PU_6k-ran (400 MHz, DMSO-d$_6$).

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