Supporting Information

Blocked isocyanates: An efficient tool for the post-polymerization modification of polymers

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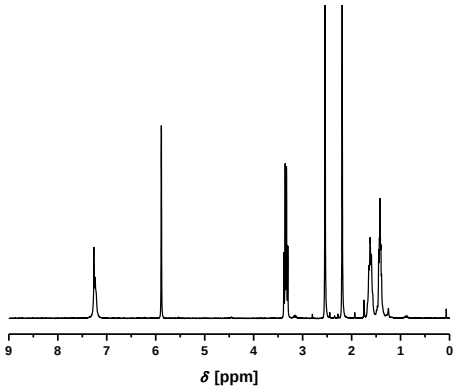
Figures:

a)



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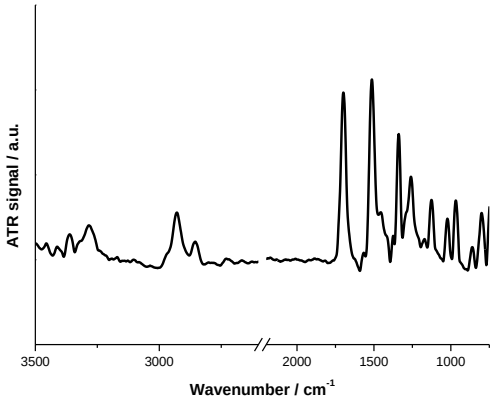
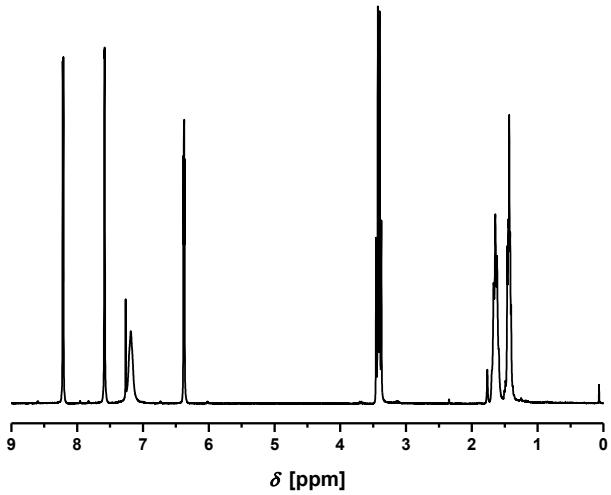


Figure S1: Characterization of **1**: a) ^{1}H NMR spectrum ($CDCl_3$) and b) ATR-FT-IR-spectrum.

a)



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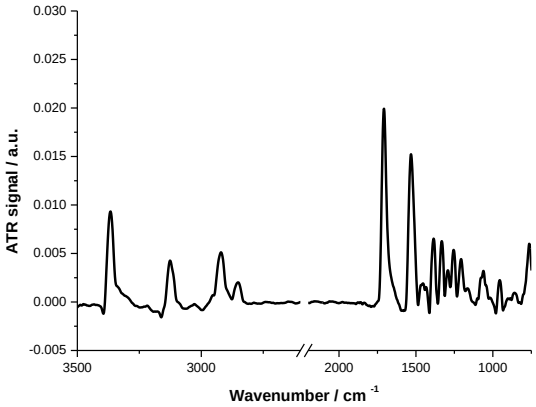


Figure S2: Characterization of **2**: a) ^{1}H NMR spectrum ($CDCl_3$) and b) ATR-FT-IR-spectrum.

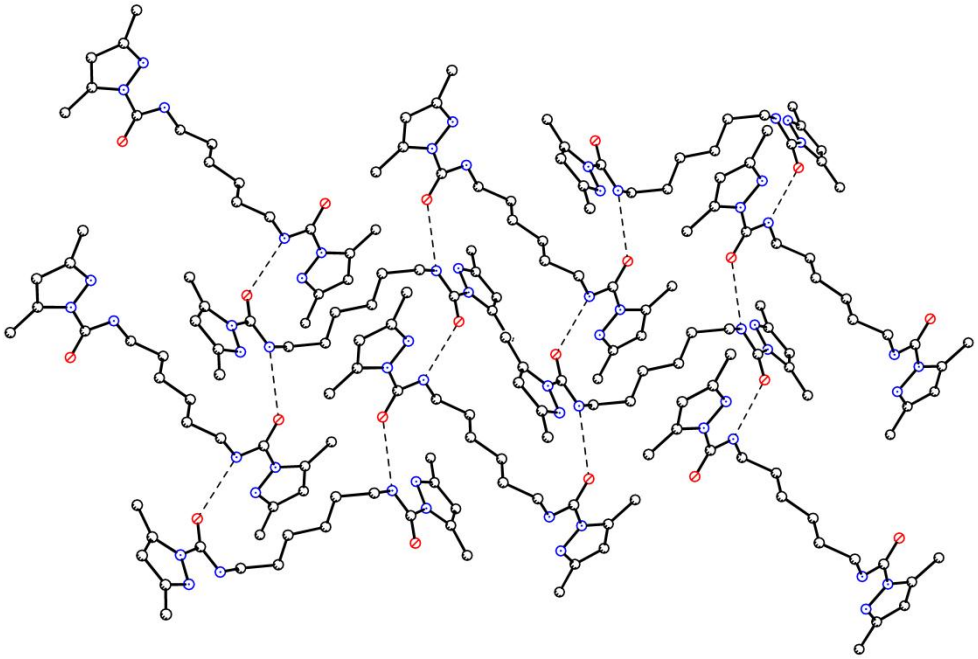


Figure S3: Crystal structure of **1** (hydrogen bonds as dotted lines).

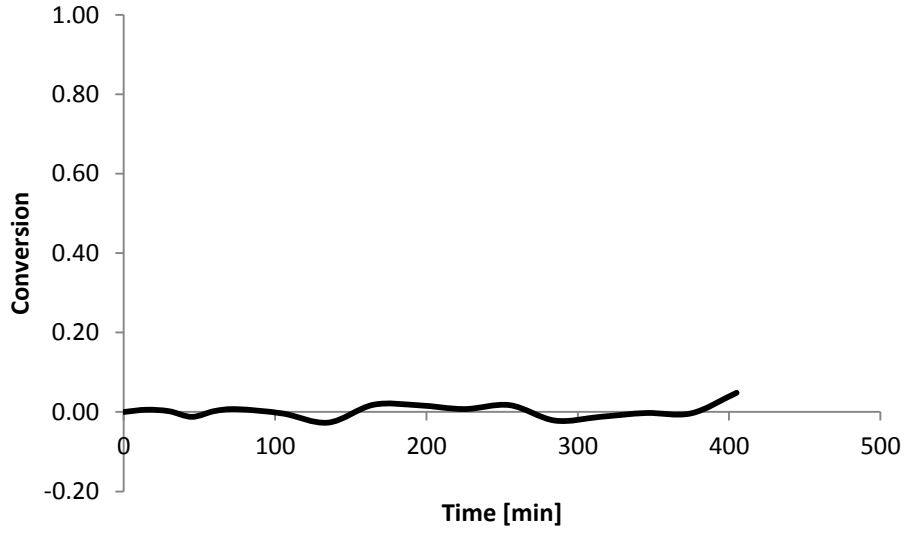
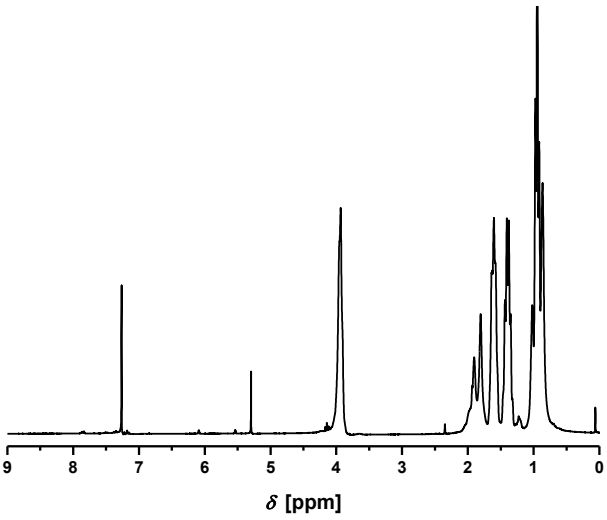


Figure S4: Conversion-time diagram for the reaction of the blocked isocyanate (**1**) with methanol.

a)



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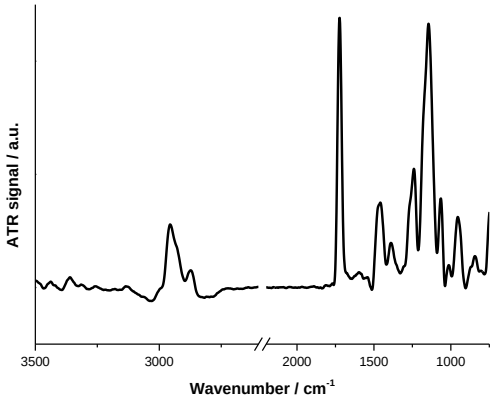

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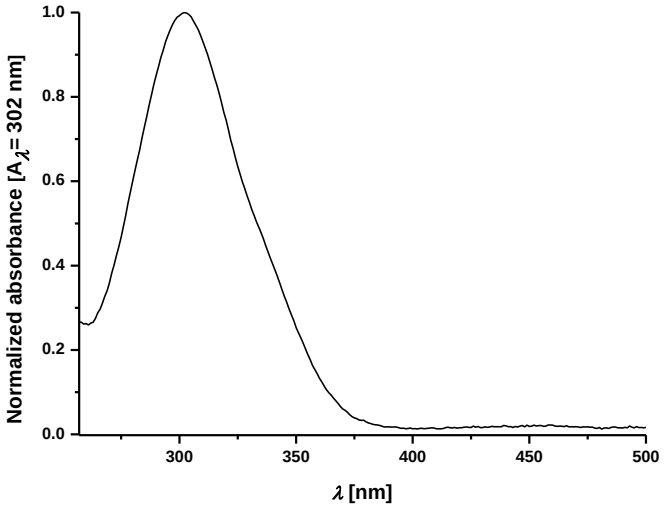


Figure S5: Characterization of **P1a**: a) ^{1}H NMR spectrum (CD_2Cl_2), b) ATR-FT-IR-spectrum and c) UV-Vis-spectrum (in $CHCl_3$).

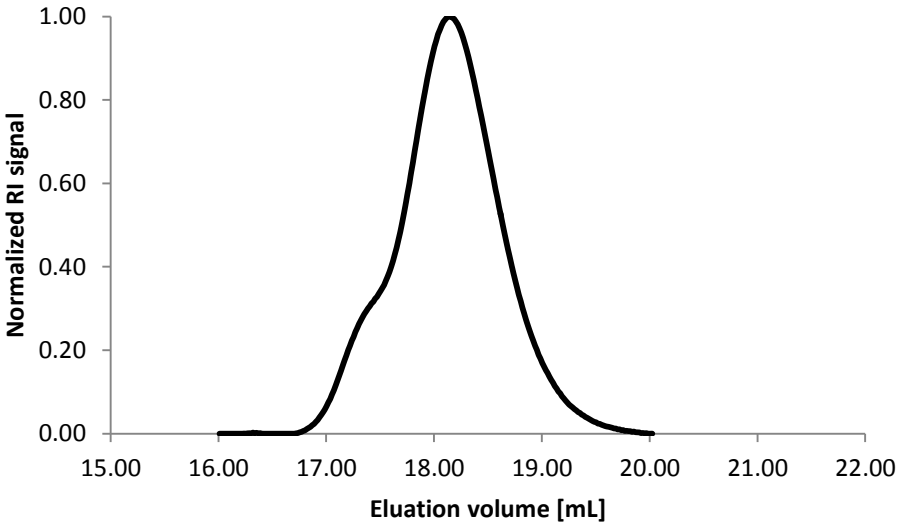
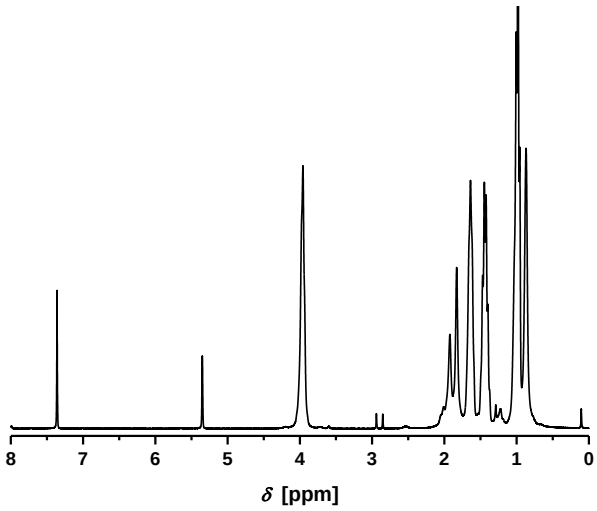


Figure S6: SEC curve of polymers **P2a** (eluent DMAc + 0.21% LiCl).

a)



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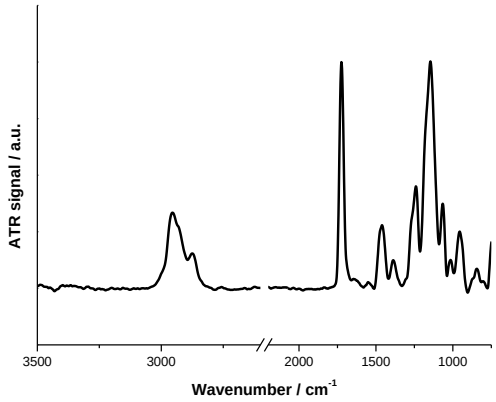


Figure S7: Characterization of **P2a**: a) ^{1}H NMR spectrum (CD_2Cl_2) and b) ATR-FT-IR-spectrum.

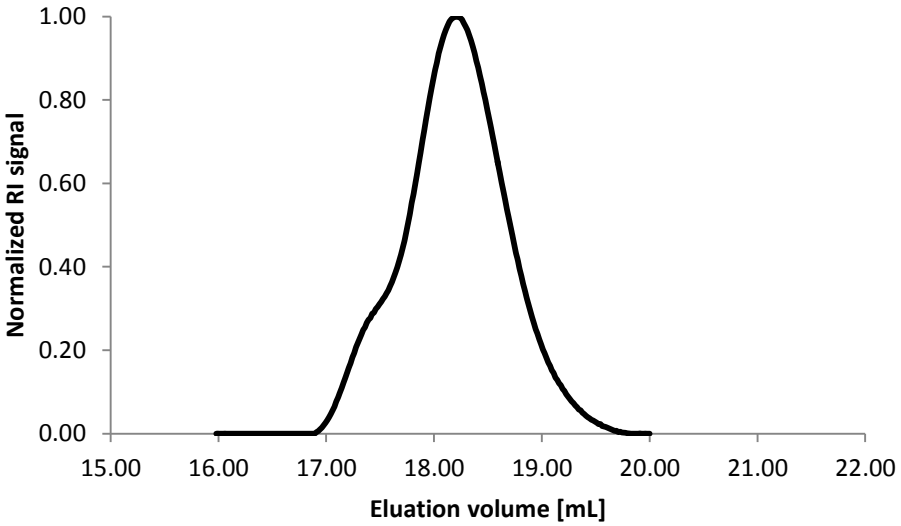
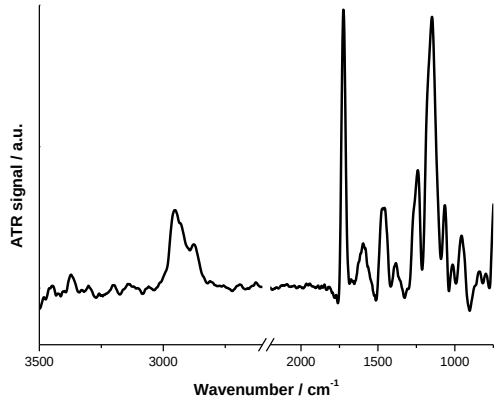


Figure S8: SEC curve of polymers **P3a** (eluent DMAc + 0.21% LiCl).

a)



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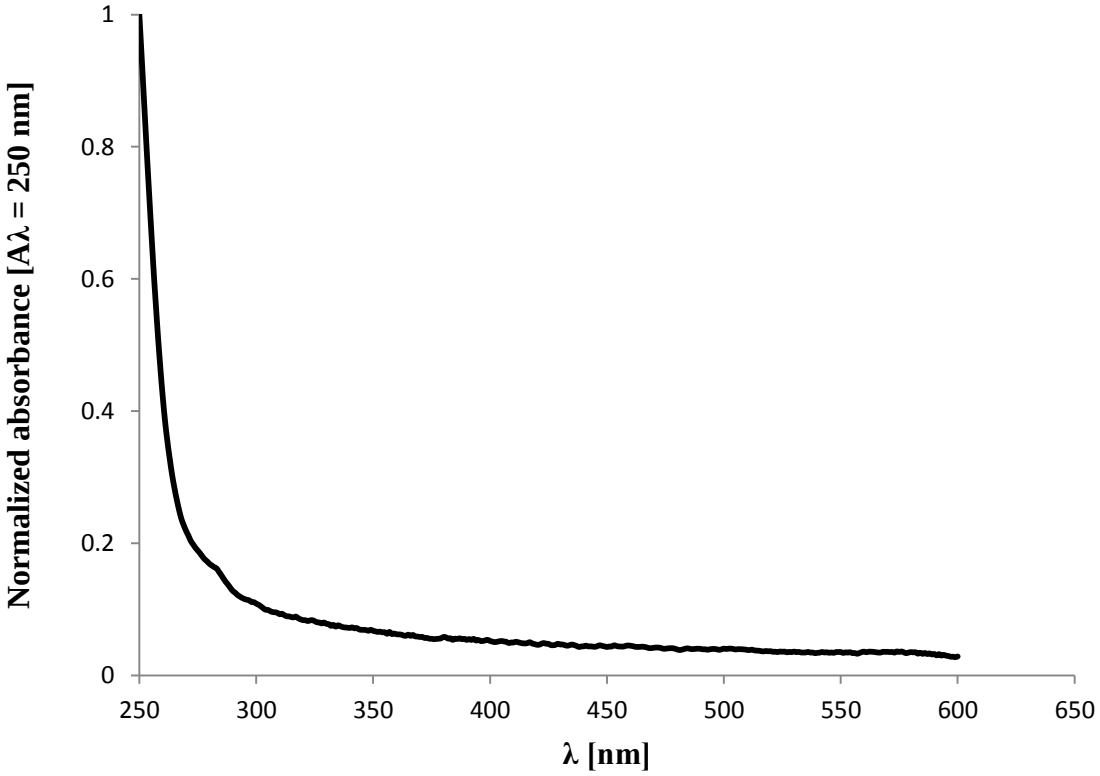
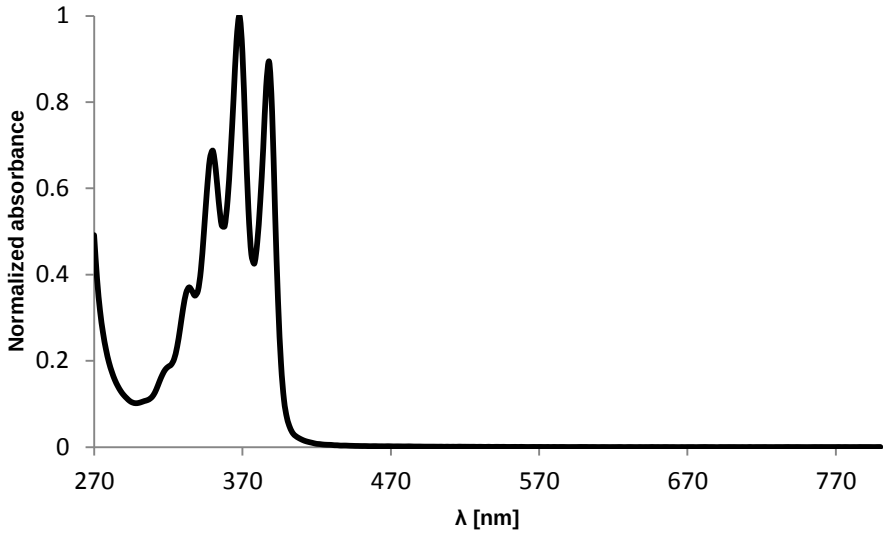


Figure S9: Characterization of **P3a**: a) ATR-FT-IR-spectrum and b) UV-Vis spectrum (in $CHCl_3$).

a)



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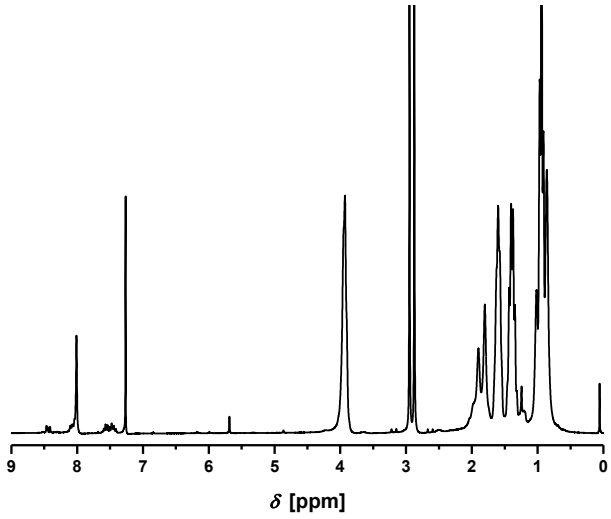
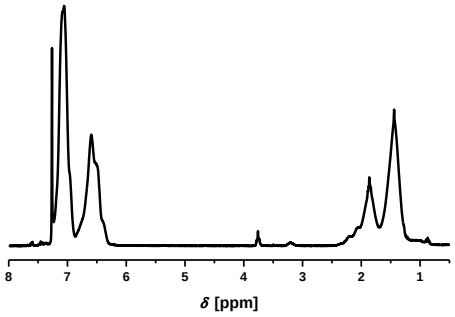


Figure S10: Characterization of **P5**: a) UV-Vis spectrum (in DMAc + 0.21% LiCl) and b) ^{1}H NMR spectrum in $CDCl_3$.

a)



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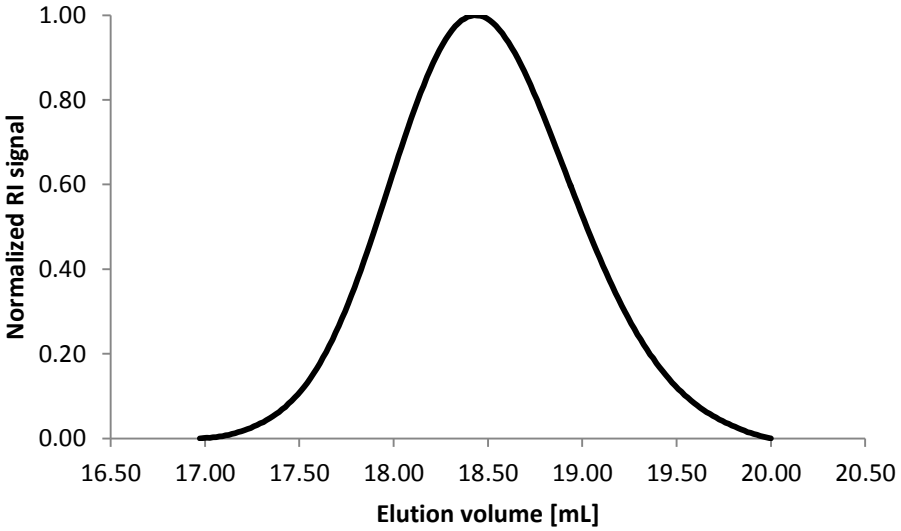

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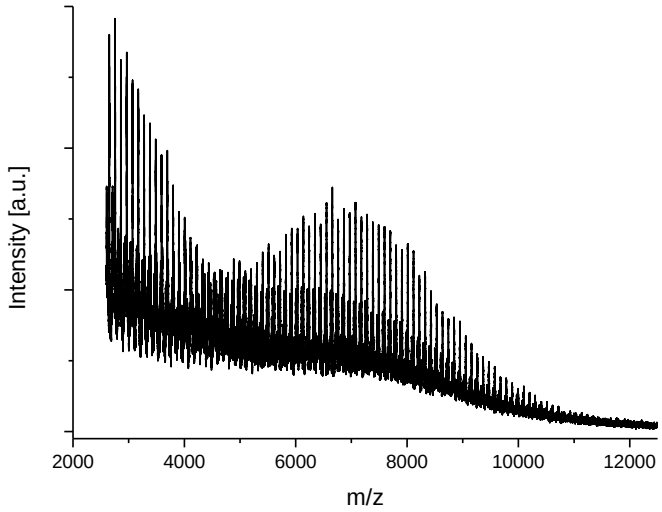

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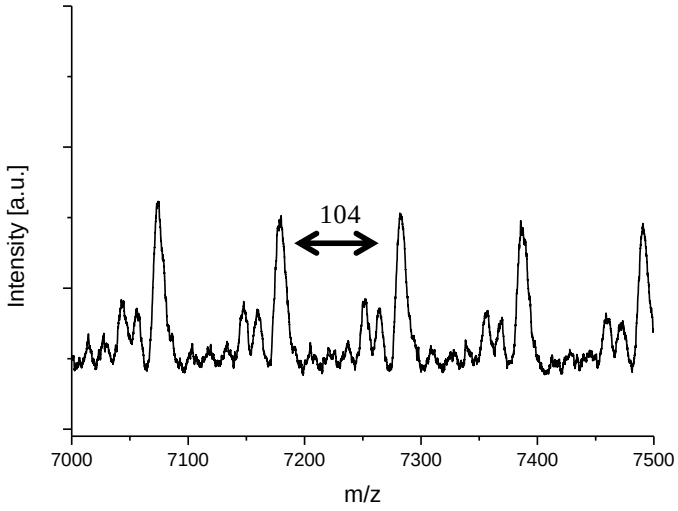
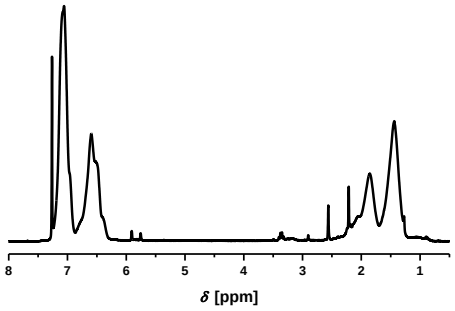


Figure S11: Characterization of **P6b**: a) ^{1}H NMR spectrum in $CDCl_3$, b) SEC curve eluent DMAc + 0.21% LiCl, c) MALDI-ToF-MS spectrum and d) zoom of the MS spectrum.

a)



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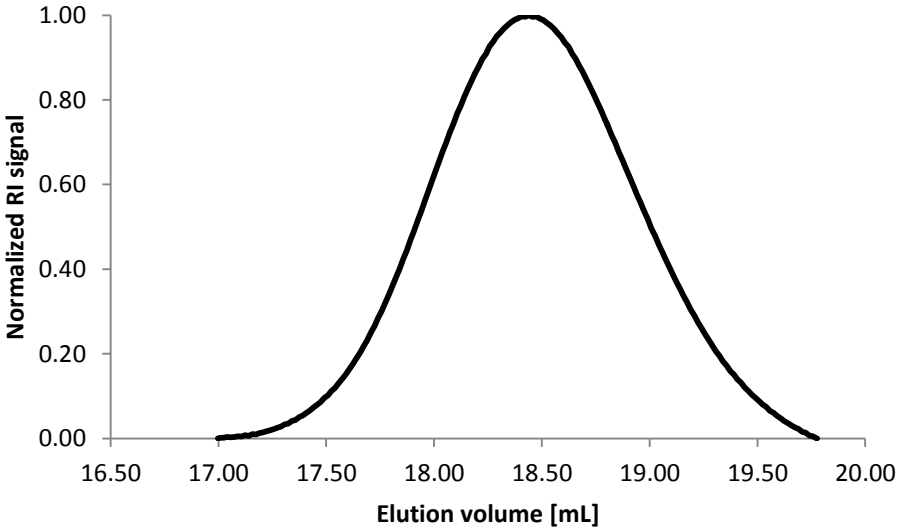
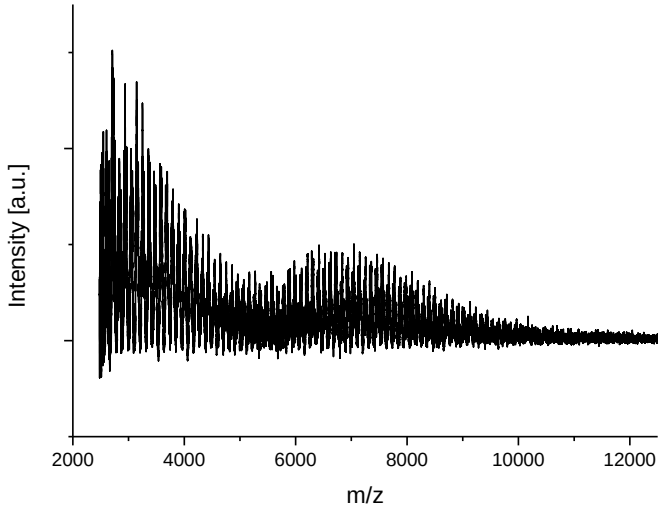


c)



d)

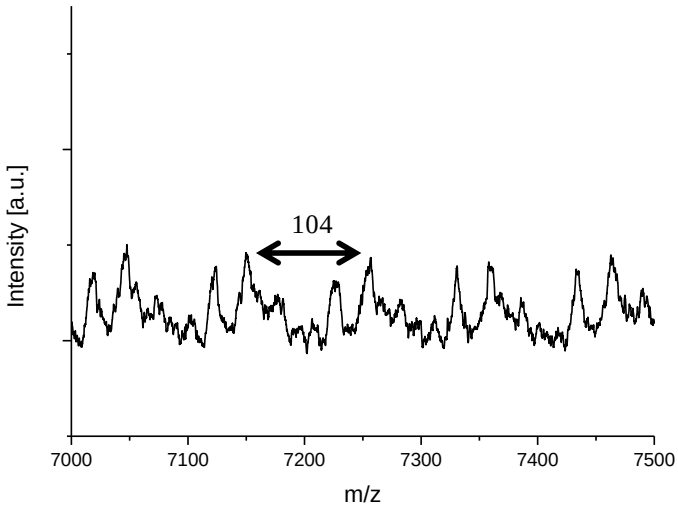
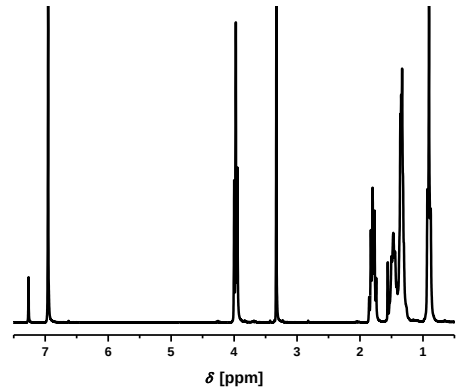
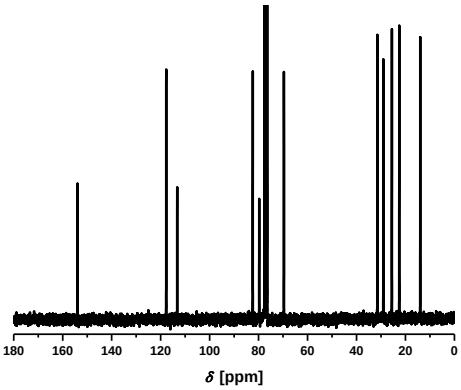


Figure S12: Characterization of **P7b**: a) ^{1}H NMR spectrum in $CDCl_3$, b) SEC curve eluent DMAc + 0.21% LiCl, c) MALDI-ToF-MS spectrum and d) zoom of the MS spectrum.

a)





b)

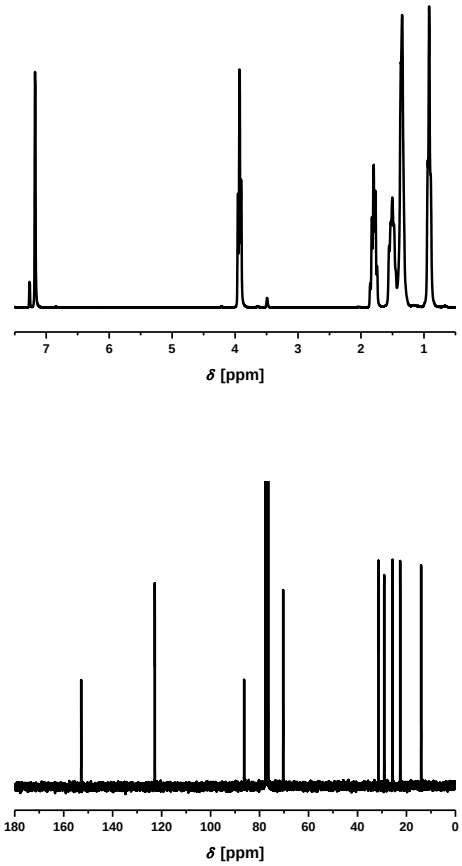
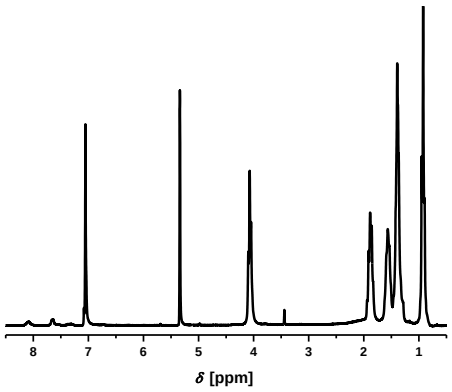


Figure S13: ^{1}H and ^{13}C NMR spectra of a) 2,5-dihexyloxy-1,4-diethynyl-benzene and b) 2,5-dihexyloxy-1,4-diiodo-benzene.

a)



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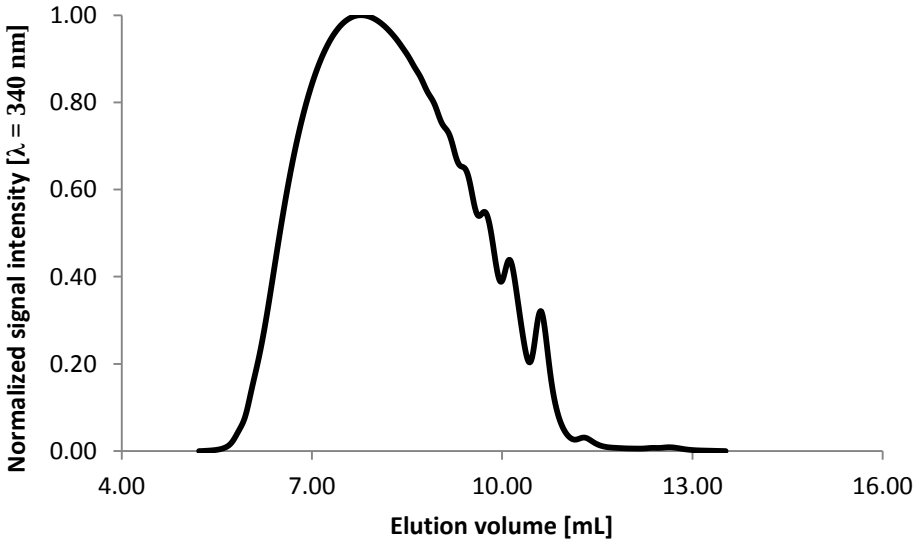
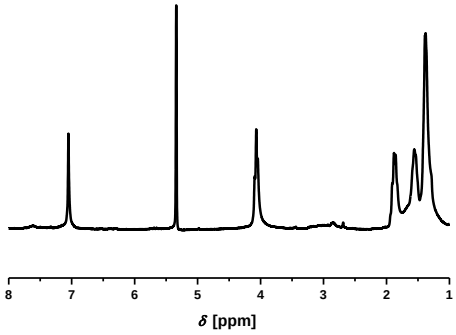


Figure S14: Characterization of **P8**: a) ^{1}H NMR spectrum in CD_2Cl_2 and b) SEC curve (chloroform/*iso*-propanol/triethylamine [94/2/4]; UV-Vis detector, λ = 340 nm).

a)



b)

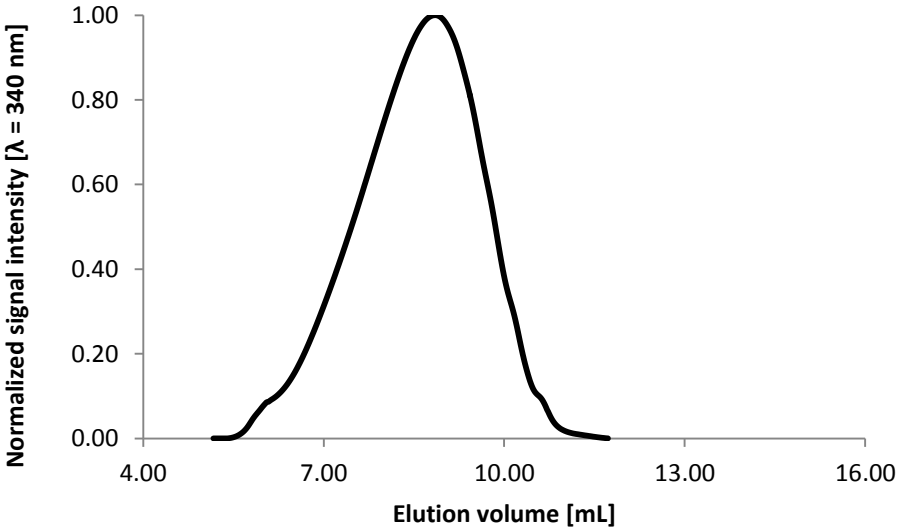
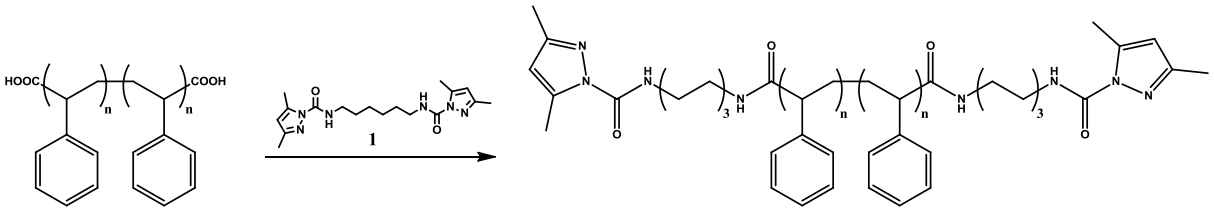


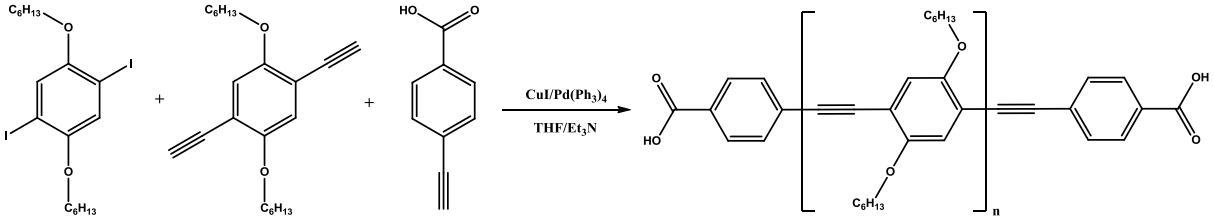
Figure S14: Characterization of **P9**: a) ^{1}H NMR spectrum in CD_2Cl_2 and b) SEC curve (chloroform/*iso*-propanol/triethylamine [94/2/4]; UV-Vis detector, λ = 340 nm).

Schemes:



P6 **P7**

Scheme S1: Schematic representation of the synthesis of **P7**.

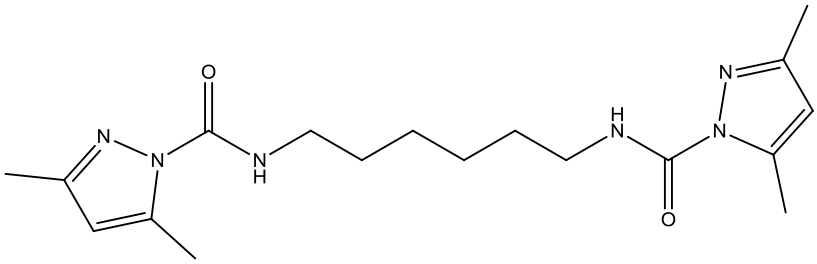


P8

Scheme S2: Schematic representation of the synthesis of **P8**.

Experimental Section:

3,5-Dimethylpyrazole blocked isocyanate (1):[S1]



11.5 g of 3,5-Dimethyl-pyrazole (0.12 mol) and 0.02 g dibutlytin laurate were dissolved in 120 mL dry toluene. Subsequently, 10 g hexamethylene diisocyanate (0.06 mol), which were dissolved in 25 mL dry toluene, were added slowly to the reaction mixture. Afterwards the solution was refluxed for 3 hours. Subsequently, the reaction mixture was cooled down and stored at 0 °C overnight. Thus, a white precipitate formed which was isolated by filtration, washed with cold toluene and dried *in vacuo* at 50 °C.

Yield: 20.2 g of a white solid, 94%

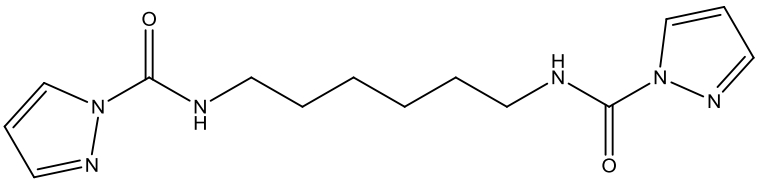
^{1}H NMR (250 MHz, $CDCl_3$, δ): 1.39 – 1.60 (m, 8H, -C*H*$_2$), 2.19 (s, 3H, -C*H*$_3$), 2.54 (s, 3H, -C*H*$_3$), 3.34 (q, *J* = 6.5 Hz, 4H, HN-C*H*$_2$), 5.89 (s, 2H, =C*H*), 7.24 (s, 2H, -N*H*) ppm.

^{13}C NMR (62.5 MHz, $CDCl_3$, δ): 13.5 (*C*H_3), 13.9 (*C*H_3), 26.5 (*C*H_2), 29.6(*C*H_2), 39.9 (*C*H_2), 109.6 (C_{Py}), 143.4(C_{Py}), 149.9(C_{Py}), 151.4 (*C*O) ppm.

Anal. calcd. for $C_{18}H_{28}N_6O_2$: C 59.98, H 7.83, N 23.32; found: C 60.03, H 7.96, N 23.37.

Crystal Data for **1**: $C_{18}H_{28}N_6O_2$, Mr = 360.46 gmol^{-1}, colorless prism, size 0.06 × 0.06 × 0.06 mm^3, monoclinic, space group P 2_1/c, a = 8.1867(4), b = 9.2410(3), c = 12.6932(6) Å, β = 92.520(2)°, V = 959.35(7) Å^3 , T= –140 °C, Z = 2, $\rho_{calcd.}$ = 1.248 gcm^{-3}, μ (Mo-K$_\alpha$) = .85 cm^{-1}, multi-scan, F(000) = 388, 5200 reflections in h(-8/10), k(-11/11), l(-15/14), measured in the range 2.73° ≤ Θ ≤ 26.37°, completeness Θ_{max} = 99.5%, 1957 independent reflections, R_{int} = 0.0624, 1614 reflections with $F_o > 4\sigma(F_o)$, 174 parameters, 0 restraints, $R1_{obs}$ = 0.0485, wR^2_{obs} = 0.1060, $R1_{all}$ = 0.0622, wR^2_{all} = 0.1142, GOOF = 1.085, largest difference peak and hole: 0.292 / –0.226 e Å^{-3}.

Pyrzaol blocked isocyanate (2):[S1]



2.85 g of Pyrazole (0.042 mol) and 0.01 g dibutlytin dilaurate were dissolved in 120 mL dry toluene. Subsequently, 3.5 g hexamethylene diisocyanate (0.021 mol), which were dissolved in 50 mL dry toluene, were added slowly to the reaction mixture. Afterwards the solution was refluxed for 3 hours. Subsequently, the reaction mixture was cooled down and stored at 0 °C overnight. Thus, a white precipitate formed which was isolated by filtration, washed with cold toluene and dried *in vacuo* at 50 °C.

Yield: 5.9 g of a white solid, 92%

^{1}H NMR (250 MHz, $CDCl_3$, δ): 1.40 – 1.62 (m, 8H, -CH_2), 3.42 (q, J = 6.75 Hz, 4H, HN-CH_2), 6.38 (dd, J = 2.5 Hz, J = 1 Hz, 2H, =C*H*), 7.19 (s, 2H, -N*H*), 7.58 (d, J = 1 Hz, 2H, =C*H*), 8.22 (d, J = 2.5 Hz, 2H, =C*H*) ppm.

^{13}C NMR (62.5 MHz, $CDCl_3$, δ): 26.4 (CH$_2$), 29.5(CH$_2$), 40.1 (CH$_2$), 108.2 (C_{Py}), 128.5 (C_{Py}), 141.9(C_{Py}), 159.7 (CO) ppm.

Anal. calcd. for $C_{14}H_{20}N_6O_2$: C 55.25, H 6.62, N 27.61; found: C 55.10, H 6.72, N 27.71.

References:

[S1] A. Mühlebach, *J. Polym. Sci., Part A: Polym. Chem.*, 1994, **32**, 753–765.