Supporting Information

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

Stefan Bode, Marcel Enke, Helmar Görls, Stephanie Hoeppener, Ralf Weberskirch, Martin D. Hager,* Ulrich S. Schubert*

**Figures:**

a)

![1H NMR spectrum (CDCl₃) Image](image1)

b)

![ATR-FT-IR-spectrum Image](image2)

Figure S1: Characterization of 1: a) $^1$H NMR spectrum (CDCl₃) and b) ATR-FT-IR-spectrum.
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.
Figure S5: Characterization of P1a: a) $^1$H NMR spectrum (CD$_2$Cl$_2$), 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).
Figure S7: Characterization of P2a: a) $^1$H NMR spectrum (CD$_2$Cl$_2$) and b) ATR-FT-IR-spectrum.
Figure S8: SEC curve of polymers P3a (eluent DMAc + 0.21% LiCl).
Figure S9: Characterization of P3a: a) ATR-FT-IR-spectrum and b) UV-Vis spectrum (in CHCl₃).
Figure S10: Characterization of P5: a) UV-Vis spectrum (in DMAc + 0.21% LiCl) and b) $^1$H NMR spectrum in CDCl$_3$. 
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.
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.
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.
Figure S14: Characterization of P8: a) $^1$H NMR spectrum in CD$_2$Cl$_2$ and b) SEC curve (chloroform/iso-propanol/triethylamine [94/2/4]; UV-Vis detector, $\lambda = 340$ nm).
Figure S14: Characterization of P9: a) $^1$H NMR spectrum in CD$_2$Cl$_2$ and b) SEC curve (chloroform/iso-propanol/triethylamine [94/2/4]; UV-Vis detector, $\lambda = 340$ nm).
Schemes:

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

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

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

11.5 g of 3,5-Dimethylpyrazole (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, -CH$_2$), 2.19 (s, 3H, -CH$_3$), 2.54 (s, 3H, -CH$_3$), 3.34 (q, J = 6.5 Hz, 4H, HN-CH$_2$), 5.89 (s, 2H, =CH), 7.24 (s, 2H, -NH) ppm.

$^{13}$C NMR (62.5 MHz, CDCl$_3$, δ): 13.5 (C$_H$), 13.9 (C$_H$), 26.5 (CH$_2$), 29.6(CH$_2$), 39.9 (CH$_2$), 109.6 (C$_Py$), 143.4(C$_Py$), 149.9(C$_Py$), 151.4 (CO) ppm.

Anal. calcd. for C$_{18}$H$_{28}$N$_6$O$_2$: 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$_6$O$_2$, Mr = 360.46 g mol$^{-1}$, 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, ρ$_{calc}$ = 1.248 gcm$^{-3}$, μ (Mo-K$_{α}$) = .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$_{o}$ > 4σ(F$_{o}$), 174 parameters, 0 restraints, R$_{1 obs}$ = 0.0485, wR$_{2 obs}^2$ = 0.1060, R$_{1 all}$ = 0.0622, wR$_{2 all}^2$ = 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\(_3\), \(\delta\)): 1.40 – 1.62 (m, 8H, -CH\(_2\)_2), 3.42 (q, \(J = 6.75\) Hz, 4H, HN-CH\(_2\)_2), 6.38 (dd, \(J = 2.5\) Hz, \(J = 1\) Hz, 2H, =CH), 7.19 (s, 2H, -NH), 7.28 (d, \(J = 1\) Hz, 2H, =CH), 8.22 (d, \(J = 2.5\) Hz, 2H, =CH) ppm.

\(^{13}\)C NMR (62.5 MHz, CDCl\(_3\), \(\delta\)): 26.4 (CH\(_2\)_2), 29.5(CH\(_2\)_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\(_6\)O\(_2\): C 55.25, H 6.62, N 27.61; found: C 55.10, H 6.72, N 27.71.

References: