Electronic Supplementary Material (ESI) for Polymer Chemistry

Comparing solution and melt-state: association of hydrogen bonds in supramolecular polymers

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Supplement

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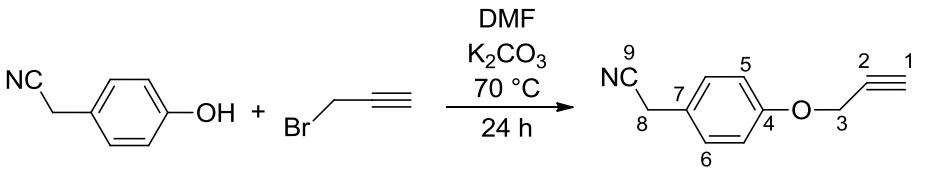
Electronic Supplementary Material (ESI) for Polymer Chemistry

1. Synthesis of 6-(4-(prop-2-yn-1-yloxy)benzyl)-1,3,5-triazine-2,4-diamine (9)

1.1. Synthesis of 2-(4-(prop-2-yn-1-yloxy)phenyl)acetonitrile (10)

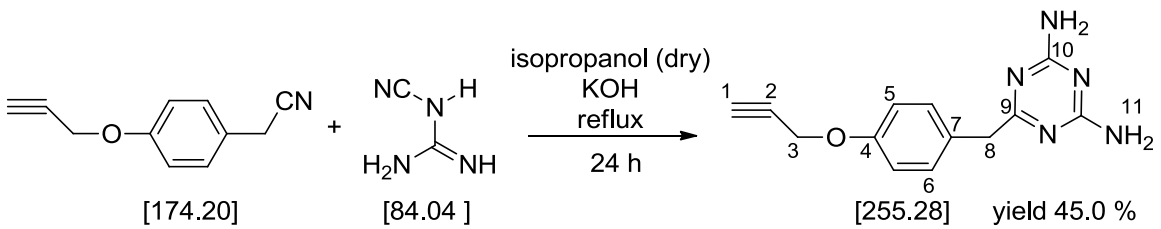


In an one-neck round-bottom flask (250 ml), equipped with magnetic stir bar, 4-hydroxyphenylacetonitrile (35.3 mmol, 4.70 g), potassium carbonate (70.6 mmol, 9.76 g), propargyl bromide (80 wt%-solution in toluene, 70.6 mmol, 10.5 g) and DMF (120 ml) were added. The mixture was stirred for 24 h at 70 °C and poured into 1200 ml cold water. The precipitate was removed by filtration and the filtrate was washed two times with chloroform. The precipitate was dissolved in chloroform and combined with the organic layers. The combined organic layers were washed one time with brine, two times with distilled water, dried over sodium sulfate and filtered. Pure **10** was observed via column chromatography (SiO_2, dichloromethane). Finally, the product was dried in high vacuum to yield 4.65 g of **10** (26.64 mmol; 75.5 %) as a yellow oil which crystallized within several minutes.

dichloromethane = 1
R_f(4-hydroxyphenylacetonitrile) = 0.16
R_f((**10**) = 0.65

^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.26 (d, 2H, H_6, $^3J_{H,H}$ = 8.5 Hz), 6.98 (d, 2H, H_5, $^3J_{H,H}$ = 8.6 Hz), 4.70 (d, 2H, H_3, $^4J_{H,H}$ = 2.3 Hz), 3.69 (s, 2H, H_8), 2.53 (t, 1H, H_1, $^4J_{H,H}$ = 2.4 Hz).
^{13}C-NMR (100 MHz, $CDCl_3$): δ 157.3 (C_4), 129.1 (C_6), 122.8 (C_7), 118.0 (C_9), 115.6 (C_5), 78.2 (C_2), 75.8 (C_1), 55.9 (C_3), 22.8 (C_8).

1.2. Synthesis of 6-(4-(prop-2-yn-1-yloxy)benzyl)-1,3,5-triazine-2,4-diamine (9)



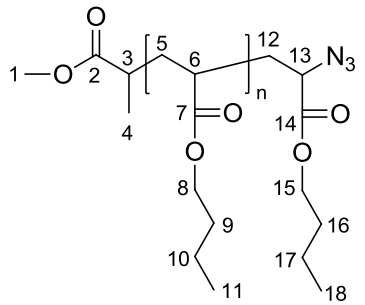
The Synthesis was done under a dry atmosphere of nitrogen. All glassware was heated under vacuum and flushed with argon several times before chemicals where weighed in. In a two-neck round-bottom flask (100 ml), equipped with reflux condenser (with gas inlet tap) and glass stopper, 2-(4-(prop-2-yn-1-yloxy)phenyl)acetonitrile (**10**) (5.74 mmol; 1.00 g), dicyandiamide (11.48 mmol; 964.8 mg), KOH (1.15 mmol; 64.0 mg) and 40 ml dry isopropanol were added. The mixture was heated under reflux condition for 24 h, whereby the formation of a white precipitate was observed. The mixture was cooled to 0 °C and filtered through a glas frit. The solid was stirred with distilled water (50 ml) and filtered again. The neat solid was washed with a small amount of cold methanol (5 ml) and cold diethyl ether (5 ml). Finally, the product was dried in high vacuum to yield 667.0 mg (2.61 mmol, 45.0 %) of **9** as a pale beige solid.

$CHCl_3$:MeOH = 8:1
R_f(**10**) = 0.9
R_f(**9**) = 0.29

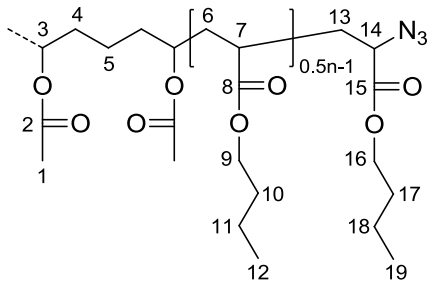
^{1}H-NMR (400 MHz, DMSO-d_6): δ 7.19 (d, 2H, H_6, $^3J_{H,H}$ = 8.6 Hz), 6.90 (d, 2H, H_5, $^3J_{H,H}$ = 8.6 Hz), 6.59 (bs, 4H, H_{11}), 4.74 (d, 2H, H_3, $^4J_{H,H}$ = 2.3 Hz), 3.56 (s, 2H, H_8), 3.52 (t, 1H, H_1, $^4J_{H,H}$ = 2.3 Hz).
^{13}C-NMR (100 MHz, DMSO-d_6): δ 176.4 (C_9), 167.0 (C_{10}), 155.6 (C_4), 130.8 (C_6), 129.8 (C_7), 114.5 (C_5), 79.3 (C_2), 78.0 (C_1), 55.2 (C_3), 43.6 (C_8).

2. NMR

2.1. NMR data of azido-functionalized PnBAs (1a and 2a-b)

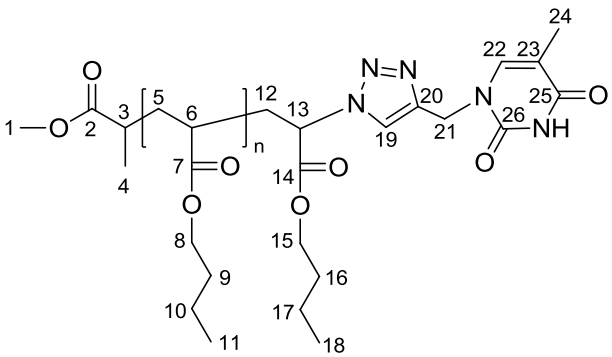


^{1}H-NMR (500 MHz, $CDCl_3$): δ 4.14 (t, 2H, $^{3}J_{H,H}$ = 6.6 Hz, H_{15}), 4.00 (m, n·2H, H_8), 3.82 (m, 1H, H_{13}), 3.61 (s, 3H, H_1), 2.54 (m, 1H, H_3), 2.25 (m, n·1H, H_6), 1.88-1.32 (m, n·6H, $H_{5,9,10,12,16,17}$), 1.08 (m, 3H, H_4), 0.89 (t, n·3H, $H_{11+18,}$ $^{3}J_{H,H}$ = 7.4 Hz).
^{13}C-NMR (125 MHz, $CDCl_3$): δ 176.1 (C_2), 174.9-174.0 (C_7), 169.8 (C_{14}), 65.7 (C_{15}), 64.7-64.2 (C_8), 60.2 (C_{13}), 51.4 (C_1), 41.3 (C_6), 37.2 (C_3), 36.6-33.8 (C_{9+16}), 31.7 (C_{12}), 30.5 (C_5), 19.0-17.6 (C_{10+17}), 16.7 (C_4), 13.6 (C_{11+18}).

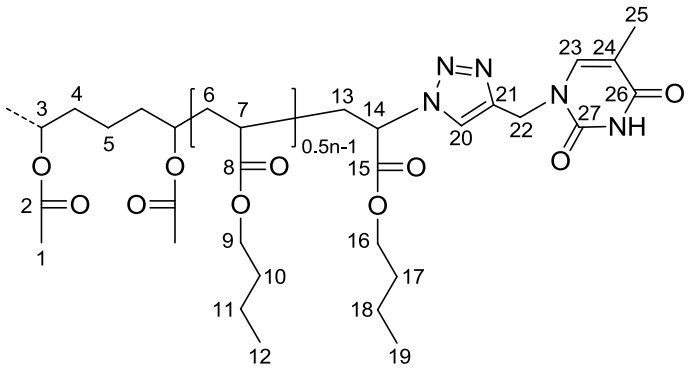


^{1}H-NMR (400 MHz, $CDCl_3$): δ 4.17 (t, 4H, $^{3}J_{H,H}$ = 4.17 Hz, H_{16}), 4.04 (m, n·2H, $H_{3,9}$), 3.85 (m, 2H, H_{14}), 3.63 (s, 6H, H_1), 2.27 (m, n·1H, H_7), 1.90-1.19 (m, n·6H, $H_{4\text{-}6,10,11,13,17,18}$), 0.90 (t, n·3H, $^{3}J_{H,H}$ = 7.3 Hz, $H_{12,19}$).
^{13}C-NMR (100 MHz, $CDCl_3$): δ 175.4 (C_2), 174.4 (C_8), 169.9 (C_{15}), 77.2 (C_3), 65.8 (C_{16}), 64.4 (C_9), 51.4 (C_1), 41.4 (C_7), 36.3-34.0 ($C_{4,10,14,17}$), 31.8 (C_{13}), 30.6 (C_6), 22.6 (C_5), 19.1 ($C_{11,18}$), 13.7 ($C_{12,19}$).

2.2. NMR data of THY-functionalized PnBAs (3a and 4a-b)

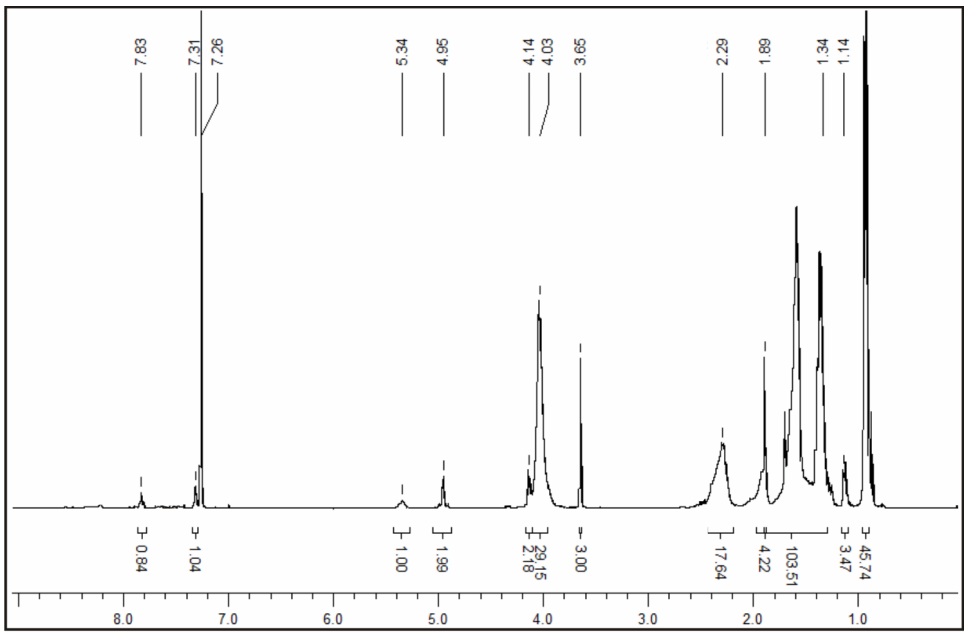


^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.83 (s, 1H, H_{19}), 7.25 (s, 1H, H_{22}), 5.28 (m, 1H, H_{13}), 4.89 (m, 2H, H_{21}), 4.07 (t, 2H, H_{15}, $^{3}J_{H,H}$ = 6.6 Hz), 3.98 (m, n·2H, H_8), 3.59 (s, 3H, H_1), 2.43 (t, 1H, H_3, $^{3}J_{H,H}$ = 7.1 Hz), 2.22 (m, n·1H, H_6), 1.85-1.29 (m, n·6H, $H_{5,9,10,12,16,17,24}$), 1.83 (s, H_{24}), 1.06 (m, 3H, H_4), 0.87 (t, n·3H, $H_{11,18}$, $^{3}J_{H,H}$ = 7.3 Hz).
^{13}C-NMR (100 MHz, $CDCl_3$): δ 176.2 (C_2), 175.0-172.7 (C_7), 167.9 (C_{14}), 163.6 (C_{25}), 150.4 (C_{26}), 149.9 (C_{20}), 140.0 (C_{22}), 123.5 (C_{19}), 111.0 (C_{23}), 66.3 (C_{15}), 65.0-64.3 (C_8), 61.0 (C_{13}), 51.5 (C_1), 42.6 (C_{21}), 41.4 (C_6), 37.3 (C_3), 36.3-34.4 ($C_{9,16}$), 31.7 (C_{12}), 30.6-30.2 (C_5), 19.0-17.6 ($C_{10,17}$), 16.7 (C_4), 13.7-13.5 ($C_{11,18}$), 12.2 (C_{24}).

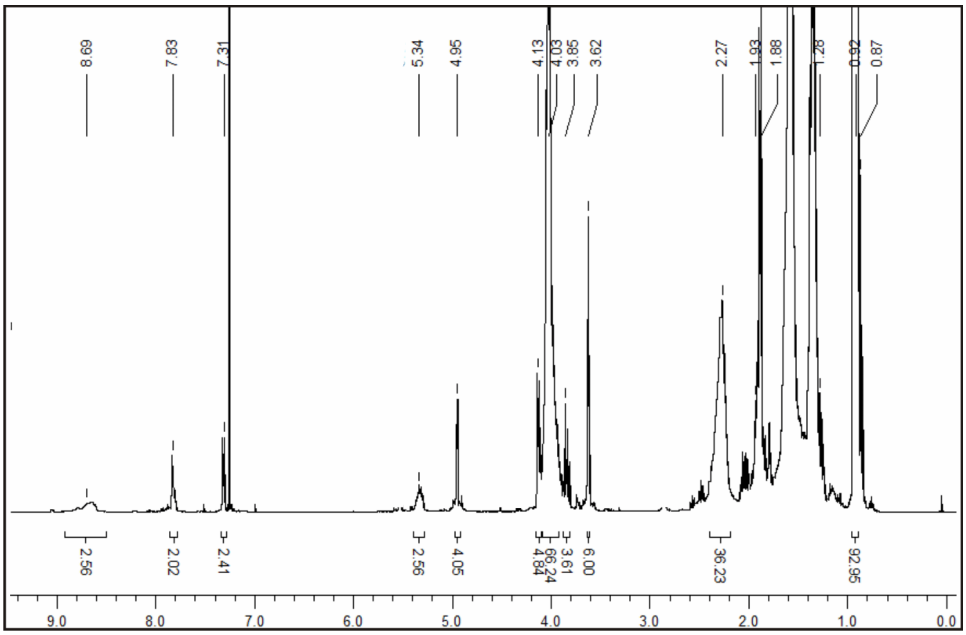


^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.83 (s, 2H, H_{20}), 7.31 (s, 2H, H_{23}), 5.34 (m, 2H, H_{14}), 4.95 (s, 4H, H_{22}), 4.13 (t, 4H, H_{16}, $^{3}J_{H,H}$ = 6.7 Hz), 4.03 (m, n·2H, $H_{3,9}$), 3.62 (s, 6H, H_1), 2.27 (m, n·1H, H_7), 1.93-1.28 (m, n·6H, $H_{4\text{-}6,10,11,13,17,18}$), 1.88 (s, H_{25}), 0.92 (t, n·3H, $H_{12,19}$, $^{3}J_{H,H}$ = 7.3 Hz).

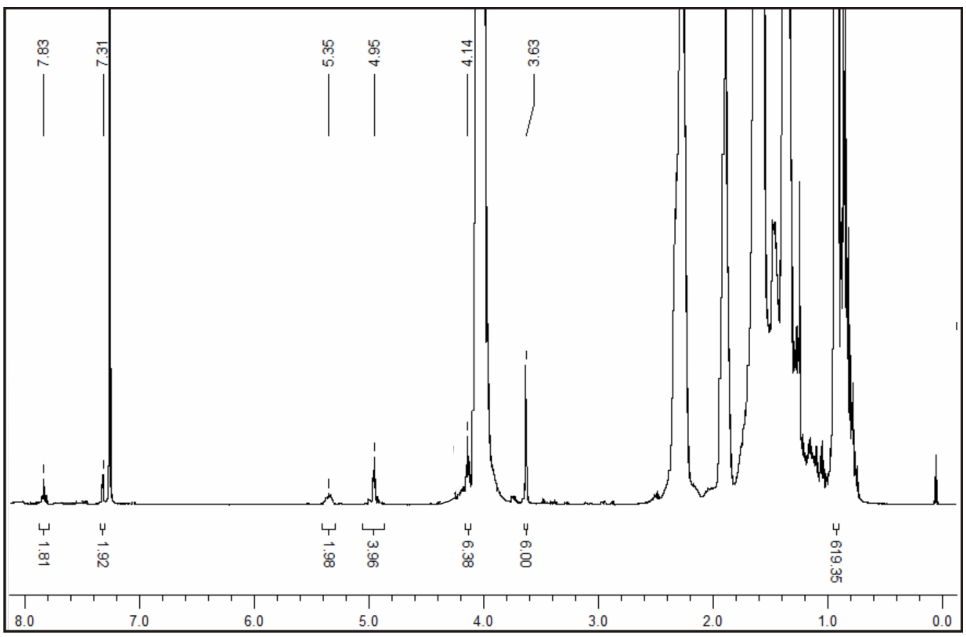
^{13}C-NMR (100 MHz, $CDCl_3$): δ 175.5 (C_2), 174.5 (C_8), 167.9 (C_{15}), 163.8 (C_{26}), 150.6 (C_{27}), 142.0 (C_{21}), 140.0 (C_{23}), 123.4 (C_{20}), 111.0 (C_{24}), 77.2 (C_3), 66.3 (C_{16}), 64.9-64.4 (C_9), 61.1 (C_{14}), 51.4 (C_1), 42.6 (C_{22}), 41.4 (C_7), 36.4-34.1 ($C_{4,10,17}$), 33.2 (C_{13}), 30.6-30.2 (C_6), 23.4 (C_5), 19.1-18.8 ($C_{11,18}$), 13.7-13.5 ($C_{12,19}$), 12.2 (C_{25}).



Supplement 1. ^{1}H-NMR spectrum of THY-functionalized PnBA **3a**.

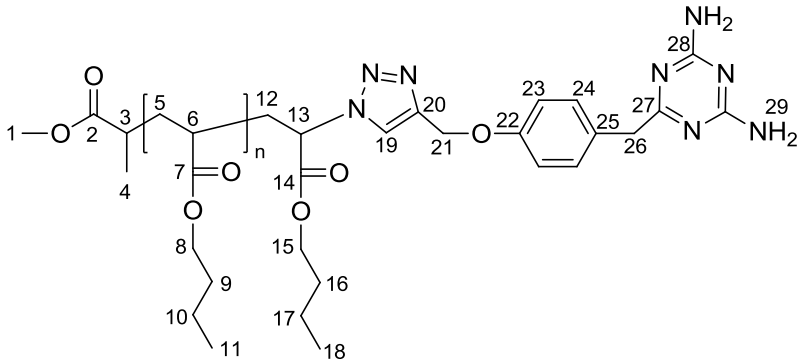


Supplement 2. ^{1}H-NMR spectrum of THY-functionalized PnBA **4a**.



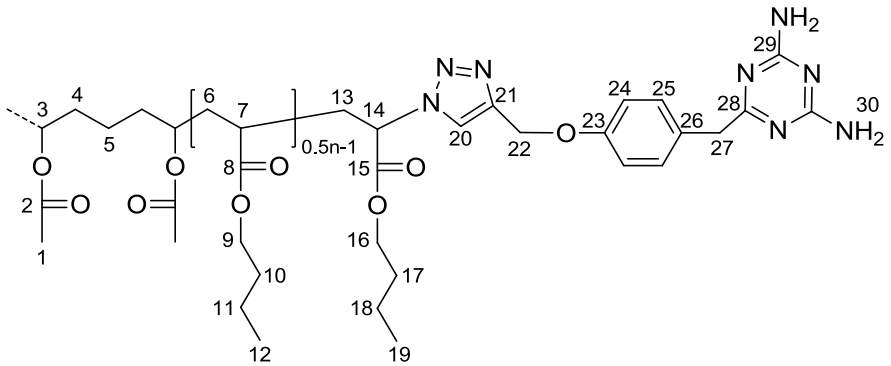
Supplement 3. ^{1}H-NMR spectrum of THY-functionalized PnBA **4b**.

2.3. NMR data of DAT-functionalized PnBAs (5a and 6a-b)



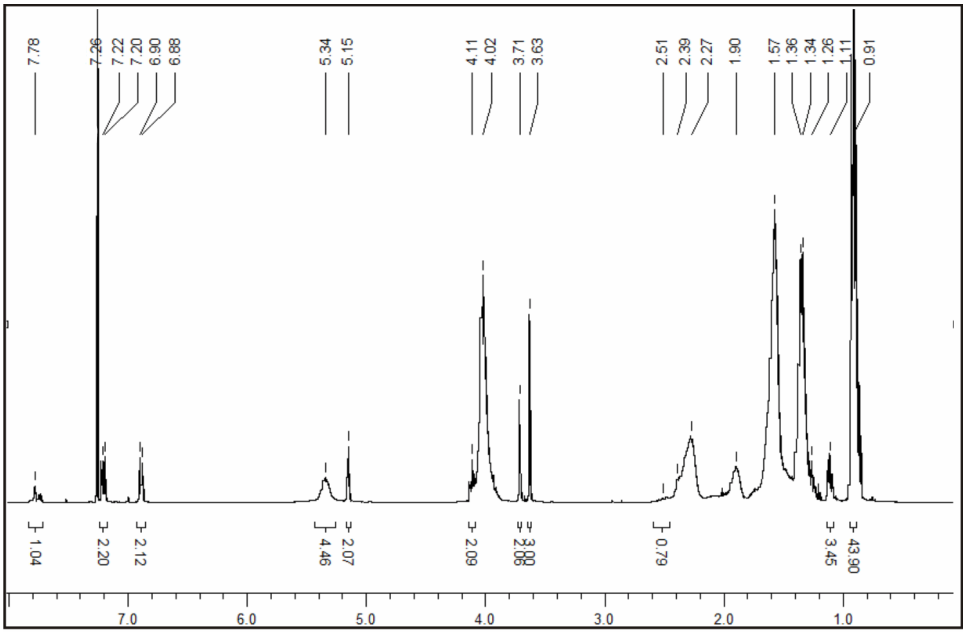
^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.78 (s, H_{19}), 7.21 (d, 2H, H_{24}, $^{3}J_{H,H}$ = 8.0 Hz), 6.89 (d, 2H, H_{23}, $^{3}J_{H,H}$ = 8.3 Hz), 5.34 (bs, 4H, H_{29}), 5.15 (s, 2H, H_{21}), 4.11 (m, 2H, H_{15}), 4.02 (bs, n·2H, $H_{8,13}$), 3.71 (s, 2H, H_{26}), 3.63 (s, 3H, H_1), 2.51 (m, 1H, H_3), 2.27 (bs, n·1H, H_6), 1.90-1.26 (m, n·6H, $H_{5,9,10,12,16,17}$), 1.11 (m, 3H, H_4), 0.91 (t, n·3H, $H_{11,18}$, $^{3}J_{H,H}$ = 7.4 Hz).

^{13}C-NMR (100 MHz, $CDCl_3$): δ 177.9 (C_{27}), 176.2 (C_2), 174.5 (C_7), 168.1 (C_{14}), 167.2 (C_{28}), 157.1 (C_{22}), 144.5 (C_{20}), 130.2 (C_{24}), 129.9 (C_{25}), 122.5 (C_{19}), 114.7(C_{23}), 77.2 (C_{21}), 66.2 (C_{15}), 65.0-64.3 (C_8), 62.1 (C_{13}), 51.6 (C_1), 44.1 (C_{26}), 41.4 (C_6), 37.3 (C_3), 34.5 ($C_{9,16}$), 31.2 (C_{12}), 30.6-30.2 (C_5), 19.0-18.6 ($C_{10,17}$), 16.7 (C_4), 13.7-13.5 ($C_{11,18}$).

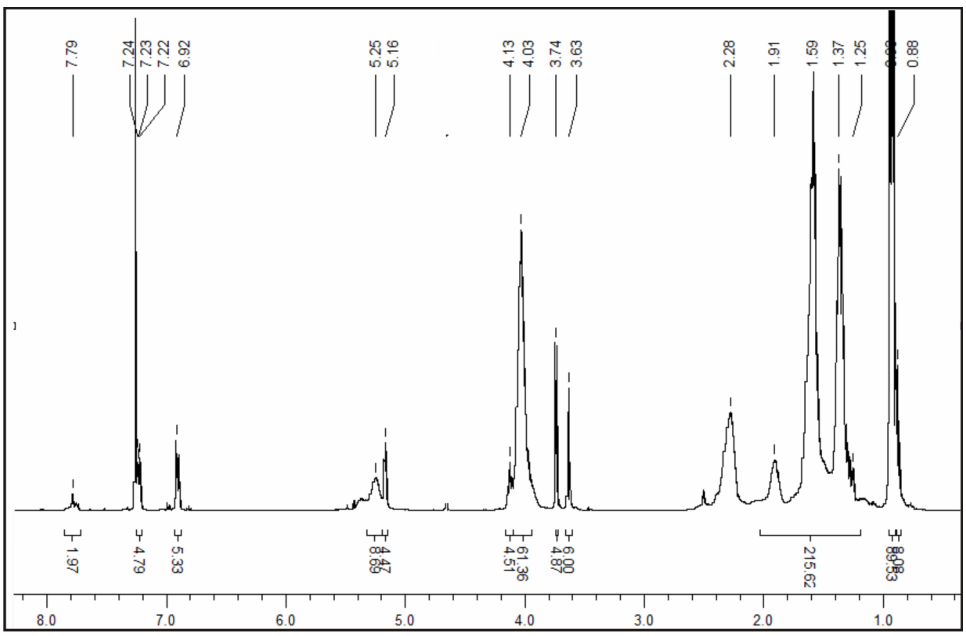


^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.79 (m, 2H, H_{20}), 7.23 (d, 4H, H_{25}, $^{3}J_{H,H}$ = 7.2 Hz), 6.92 (d, 4H, H_{24}, $^{3}J_{H,H}$ = 6.9 Hz), 5.25 (bs, 8H, H_{30}), 5.16 (s, 4H, H_{22}), 4.13 (m, 4H, H_{16}), 4.03 (bs, n·2H, $H_{3,9,14}$), 3.74 (s, 4H, H_{27}), 3.63 (s, 6H, H_1), 2.28 (bs, n·1H, H_7), 1.91-1.25 (m, n·6H, $H_{4\text{-}6,10,11,13,17,18}$), 0.93 (t, n·3H, H_{12}, $^{3}J_{H,H}$ = 7.3 Hz), 0.88 (t, 8H, H_{19}).

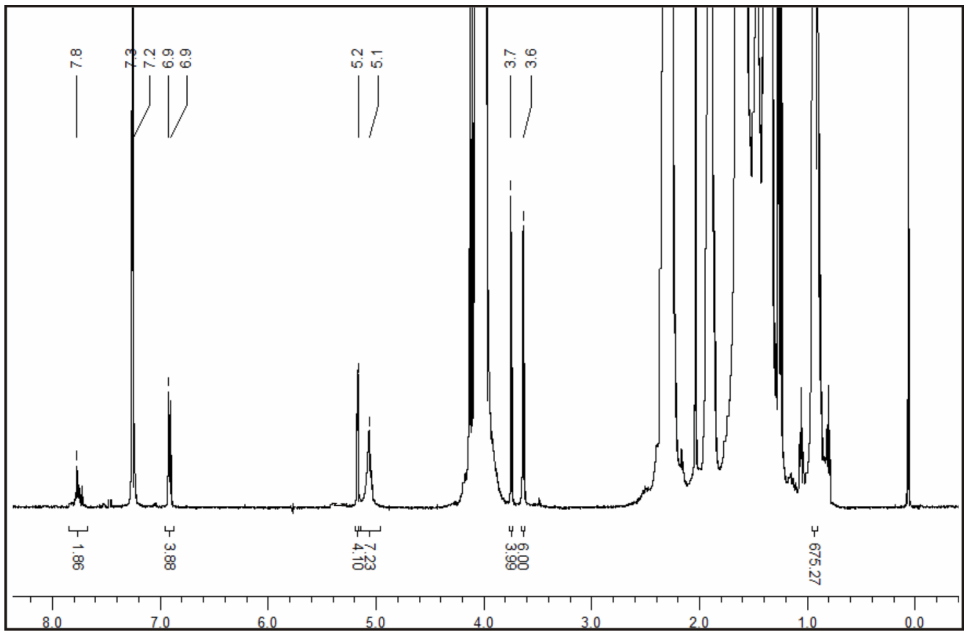
^{13}C-NMR (100 MHz, $CDCl_3$): δ 178.0 (C_{28}), 175.5 (C_2), 174.6 (C_8), 168.3 (C_{15}), 167.2 (C_{29}), 157.2 (C_{23}), 144.4 (C_{21}), 130.2 (C_{25}), 129.9 (C_{26}), 122.4 (C_{20}), 114.9 (C_{24}), 77.2 ($C_{3,21}$), 66.2 (C_{16}), 64.4 (C_9), 62.2 (C_{14}), 51.4 (C_1), 44.2 (C_{27}), 41.4 (C_7), 36.3-35.4 ($C_{4,10,17}$), 31.2 (C_{13}), 30.6-30.3 (C_6), 22.6 (C_5), 19.1-18.9 ($C_{11,18}$), 13.7 (C_{12}), 13.5 (C_{19}).



Supplement 4. [1]H-NMR spectrum of DAT-functionalized PnBA **5a**.

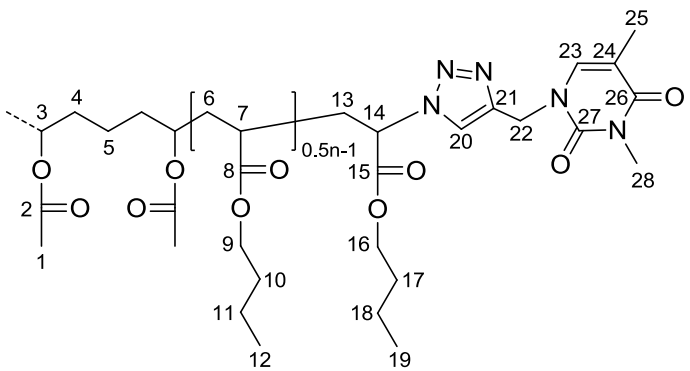


Supplement 5. [1]H-NMR spectrum of DAT-functionalized PnBA **6a**.



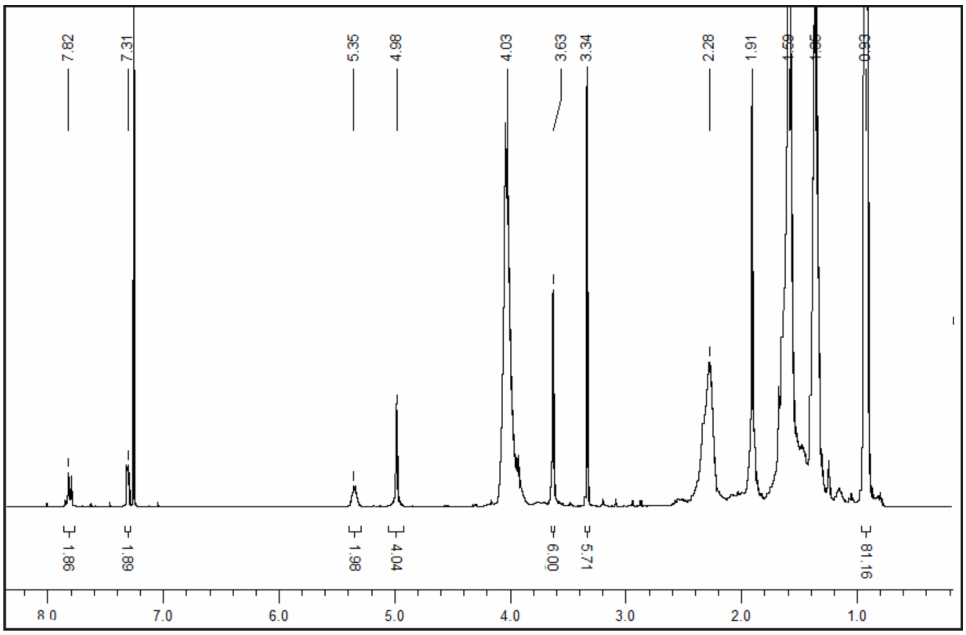
Supplement 6. ^{1}H-NMR spectrum of DAT-functionalized PnBA **6b**.

2.4. NMR data of „capped“ THY-Me-functionalized PnBA (7a)



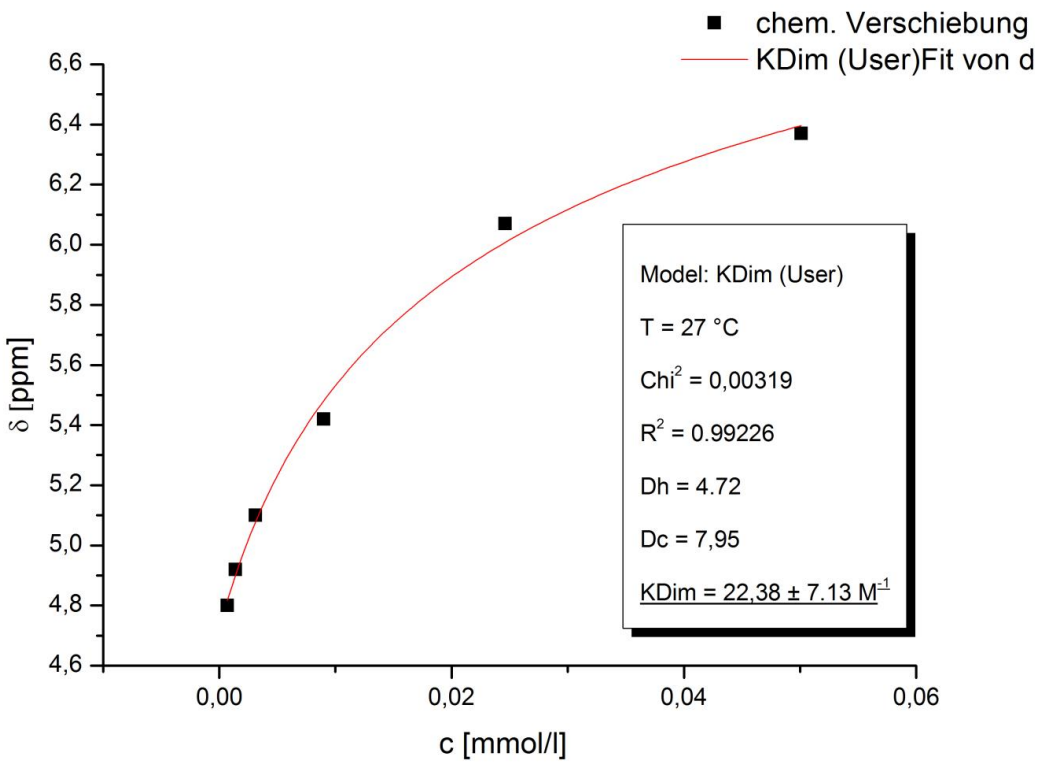
^{1}H-NMR (500 MHz, $CDCl_3$): δ 7.82 (s, 2H, H_{20}), 7.31 (s, 2H, H_{23}), 5.35 (m, 2H, H_{14}), 4.98 (s, 4H, H_{22}), 4.03 (m, n·2H, $H_{3,9,16}$), 3.63 (s, 6H, H_1), 3.34 (s, 5.8H, H_{28}), 2.28 (m, n·1H, H_7), 1.91-1.35 (m, n·6H, $H_{4\text{-}6,10,11,13,17,18}$), 1.91 (s, H_{25}), 0.93 (t, n·3H, $H_{12,19}$, $^{3}J_{H,H}$ = 7.3 Hz).

^{13}C-NMR (125 MHz, $CDCl_3$): δ 175.5 (C_2), 174.5 (C_8), 168.5 (C_{15}), 163.9 (C_{26}), 151.5 (C_{27}), 142.4 (C_{21}), 137.9 (C_{23}), 123.1 (C_{20}), 110.1 (C_{24}), 77.2 (C_3), 65.0 (C_{16}), 64.4 (C_9), 60.9 (C_{14}), 51.4 (C_1), 43.6 (C_{22}), 41.4 (C_7), 36.4-34.3 ($C_{4,10,17}$), 33.1 (C_{13}), 30.6-30.5 (C_6), 28.0 (C_{28}), 24.9 (C_5), 19.1 ($C_{11,18}$), 13.7 ($C_{12,19}$), 13.0 (C_{25}).

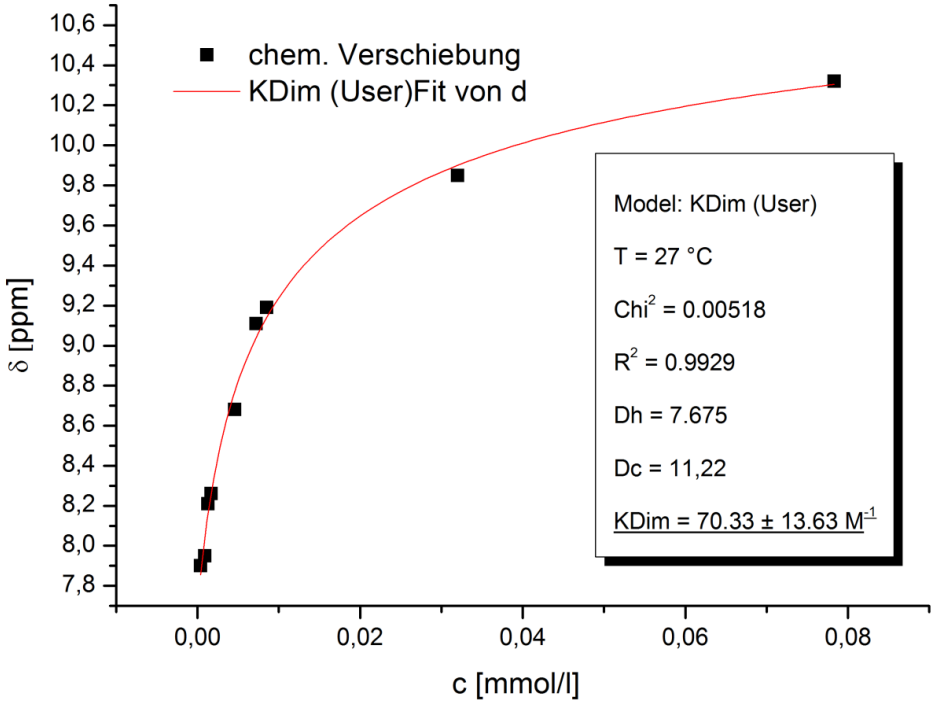


Supplement 7. [1]H-NMR spectrum of "capped" THY-functionalized PnBA **7a**.

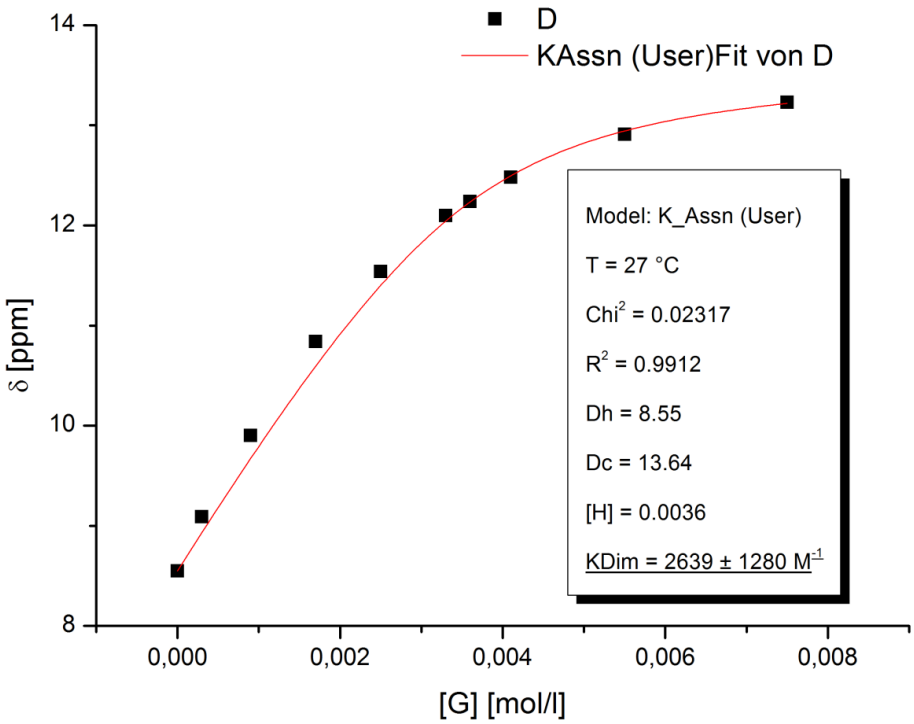
3. NMR-titration experiments



Supplement 8. NMR-titration experiment of DAT-functionlized PnBA **5a**.



Supplement 9. NMR-titration experiment of THY-functionlized PnBA **3a**.



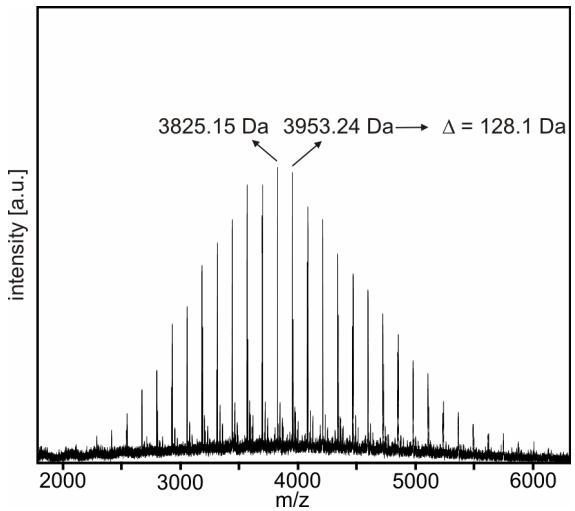
Supplement 10. NMR-titration experiment of THY-functionlized PnBA **3a** [H] with DAT-functionlized PnBA **5a** [G]. [H] = const. = 3.6 mmol/l.

4. MALDI-TOF-MS measurements

4.1. MALDI-TOF-MS measurement of 3a

In agreement with earlier observation made in our group the most intensive signal of the minor series at 2260.503 Da can be assigned to a species $[M{\cdot}Na_2]^+$ ($C_{117}H_{194}N_5O_{34}Na_2$; n = 14), assuming the exchange of the acidic CO–N*H*–CO proton of the thymine group.[1-2] The theoretical m/z value for a species $[M{\cdot}Na_2]^+$ (n = 14) is 2260.3434 Da, a value that agrees well with the signal at 2260.503 Da (deviation 64 ppm).

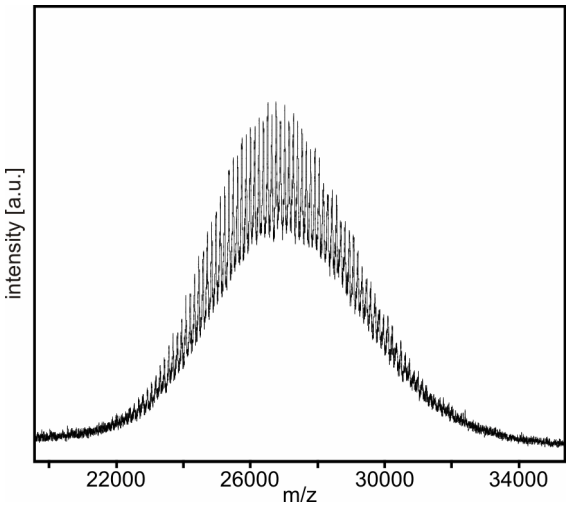
4.2. MALDI-TOF-MS measurement of 4a



Supplement 11. MALDI-TOF-MS spectrum of THY-functionalized PnBA **4a**.

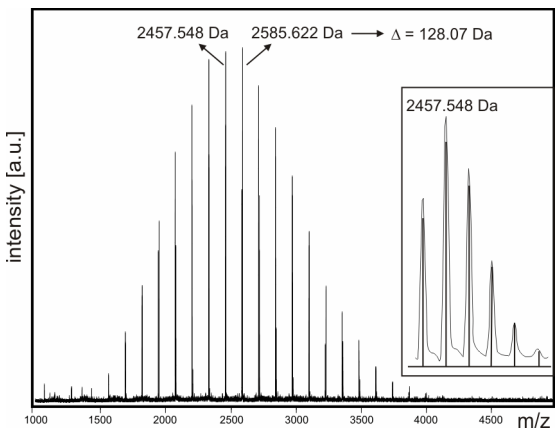
For THY-functionalized PnBA **4a** the best spectrum was obtained by ionization with Na-ions (matrix: IAA:NaTFA:Analyte = 100:10:1). The spectrum shows four important series, where each series of ions were separated by ~128.1 Da, the mass of the repeating unit (calculated 128.1 Da). The most intensive signal of the main series at 3825.146 Da can be assigned to a species $[M{\cdot}Na]^+$ ($C_{200}H_{330}N_{10}O_{58}Na_1$; n = 24). The theoretical m/z value for a species $[M{\cdot}Na]^+$ (n = 24) is 3825.314 Da, a value that agrees well with the signal at 3825.146 Da (deviation 44 ppm). For the first and second minor series the acidic proton(s) of the thymine group was exchanged by an ion. The most intensive signal of the first minor series at 3847.132 Da can be assigned to a species $[M{\cdot}Na_2]^+$ ($C_{200}H_{329}N_{10}O_{58}Na_2$; n = 23). The theoretical m/z value for a species $[M{\cdot}Na_2]^+$ (n = 23) is 3847.296 Da, a value that agrees well with the signal at 3847.132 Da (deviation 43 ppm). The most intensive signal of the second minor series at 3869.278 Da can be assigned to a species $[M{\cdot}Na_3]^+$ ($C_{200}H_{328}N_{10}O_{58}Na_3$; n = 23). The theoretical m/z value for a species $[M{\cdot}Na_3]^+$ (n = 23) is 3869.086 Da, a value that agrees well with the signal at 3869.278 Da (deviation 50 ppm). The most intensive signal of the third minor series at 4057.955 Da can be assigned to a species $[M{\cdot}H]^+$ ($C_{214}H_{355}N_{10}O_{62}Na_3$; n = 25). The theoretical m/z value for a species $[M{\cdot}H]^+$ (n = 25) is 4059.499 Da, a value that agrees well with the signal at 4057.955 Da (deviation 380 ppm). The calculated isotopic patterns of the main and first minor series match well with the observed patterns (only for low molecular weight peaks visible).

4.3. MALDI-TOF-MS measurement of 4b



Supplement 12. MALDI-TOF-MS spectrum of THY-functionalized PnBA **4b**.

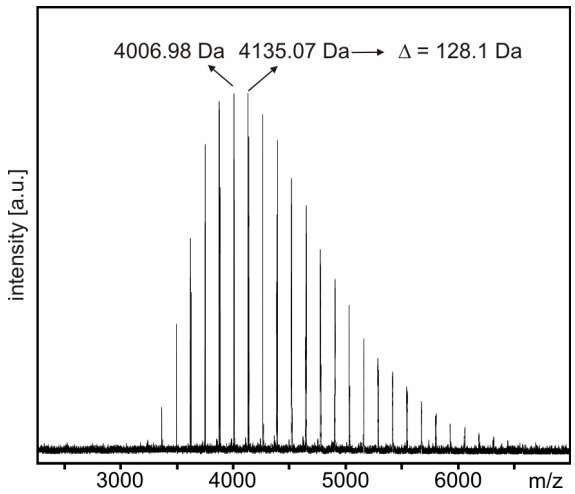
4.4. MALDI-TOF-MS measurement of 5a



Supplement 13. MALDI-TOF-MS spectrum of DAT-functionalized PnBA **5a**.

For the monofunctional PnBA bearing the DAT group (**5a**) the best spectrum was obtained by ionization with Na-ions (matrix: IAA:NaTFA:Analyte = 100:10:1). Only one series is visible where each peak is separated by ~128.1 Da, reflecting the mass of the monomer repeating unit (calculated 128.08 Da). The most intensive signal of the main series at 2585.622 Da can be assigned to a species $[M{\cdot}Na]^+$ ($C_{136}H_{224}N_8O_{37}Na_1$; n = 16), a value that agrees well the theoretical m/z value of 2585.622 Da (deviation 16 ppm).

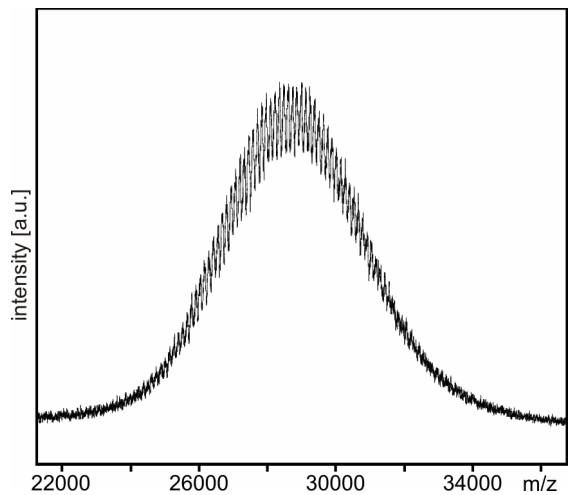
4.5. MALDI-TOF-MS measurement of 6a



Supplement 14. MALDI-TOF-MS spectrum of DAT-functionalized PnBA **6a**.

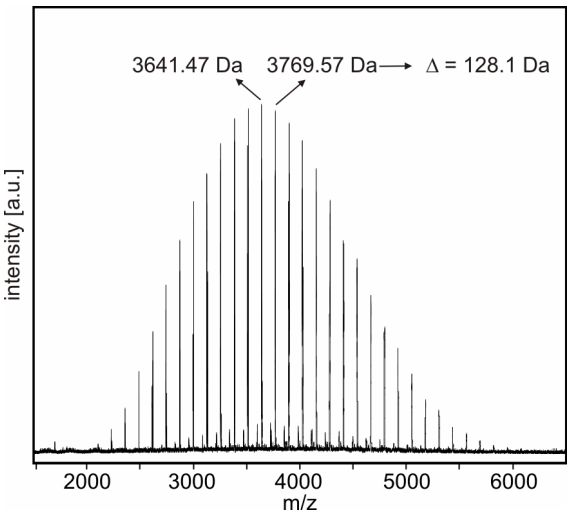
For DAT-functionalized PnBA **6a** the best spectrum was obtained by ionization with Na-ions (matrix: IAA:NaTFA:Analyte = 100:10:1). The spectrum shows one important series, where each series of ions were separated by ~128.1 Da, the mass of the repeating unit (calculated 128.08 Da). The most intensive signal of the main series at 4006.981 Da can be assigned to a species $[M{\cdot}Na]^+$ ($C_{210}H_{340}N_{16}O_{56}Na_1$; n = 23). The theoretical m/z value for a species $[M{\cdot}Na]^+$ (n = 23) is 4007.4211 Da, a value that agrees well with the signal at 4006.981 Da (deviation 110 ppm). The calculated isotopic pattern matches well with the observed pattern.

4.6. MALDI-TOF-MS measurement of 6b



Supplement 15. MALDI-TOF-MS spectrum of DAT-functionalized PnBA **6b**.

4.7. MALDI-TOF-MS measurement of 7a



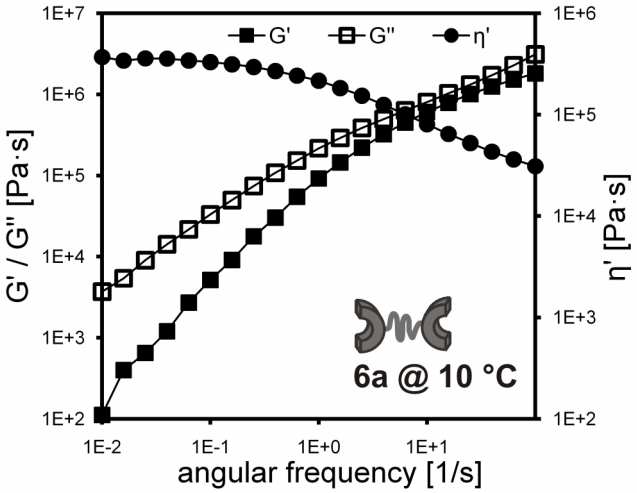
Supplement 16. MALDI-TOF-MS spectrum of "capped" THY-functionalized PnBA **7a**.

For "capped" THY-functionalized PnBA **7a**. the best spectrum was obtained by ionization with Na-ions (matrix: IAA:NaTFA:Analyte = 100:10:1). The spectrum shows two important series, where each series of ions were separated by ~128.1 Da, the mass of the repeating unit (calculated 128.1 Da). The most intensive signal of the main series at 3641.474 Da can be assigned to a species $[M{\cdot}Na_3]^+$ ($C_{188}H_{308}N_{10}O_{54}Na_3$; n = 21). The theoretical m/z value for a species $[M{\cdot}Na]^+$ (n = 24) is 3641.142 Da, a value that agrees well with the signal at 3641.474 Da (deviation 91 ppm). Binder *et al*. reported that the acidic –CO–N*H*–CO– proton of the thymine group can be exchanged during the ionization process, leading to molecule ions bearing e.g. several sodium atoms, but only one positive charge.[2] This kind of exchange is not possible for **PFH-063-1** since the –CO–N*H*–CO– position is blocked with methyl groups (–CO–NCH_3–CO–). Kurinovich et al. reported for several uracil derivates, which are very similar to thymine, that beside the N1 and N3 sites (which are both blocked in our case), the C5 and C6 site of uracil are positions with relatively high acidity as well.[3] Therefore we assume an exchange of the acidic protons of the thymine groups in C6 position, leading to a species $[M{\cdot}Na_3]^+$.

The most intensive signal of the first minor series at 3727.514 Da can be assigned to a species $[M{\cdot}K]^+$ ($C_{194}H_{320}N_{10}O_{56}K$; n = 22), whereby only one of the two thymine groups is bearing the methyl group, indicating incomplete functionalization. Since the integration in ^{1}H-NMR fits well with the expected values we assume the content of the monofunctionalized side-product to be negligible small. The theoretical m/z value for a species $[M{\cdot}K]^+$ (n = 22) is 3727.220 Da, a value that agrees well with the signal at 3727.514 Da (deviation 79 ppm). The calculated isotopic patterns of the main and first minor series match well with the observed patterns.

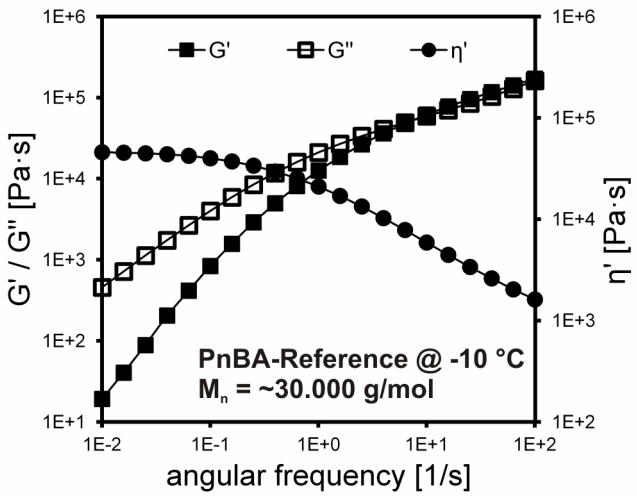
5. Rheology

5.1. Low molecular weight PnBAs ($M_n \approx 4.000$ g/mol)

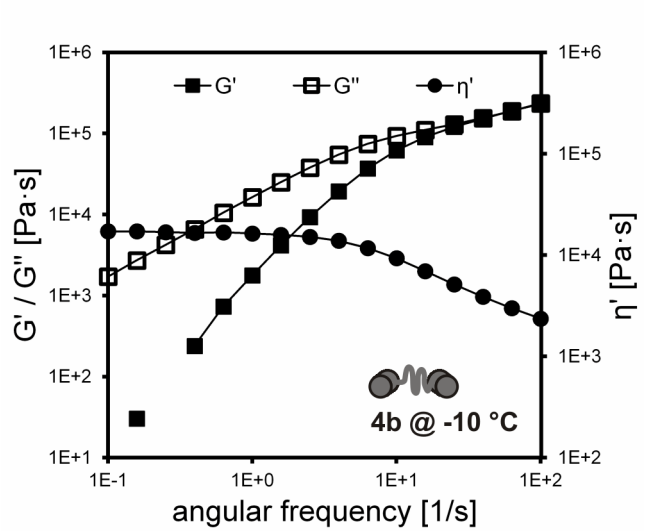


Supplement 17. Frequenzy sweep measurement of DAT-functionalized PnBA **6a** at 10 °C showing the onset of the transition to the glass transition.

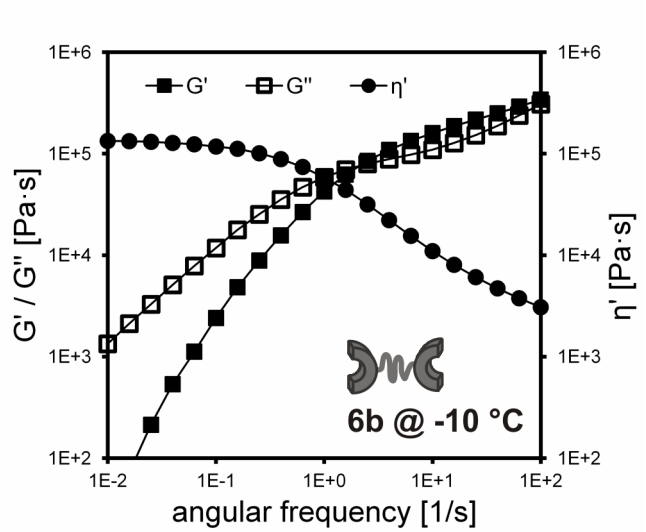
5.2. High molecular weight PnBAs ($M_n \approx 25.000$ g/mol)



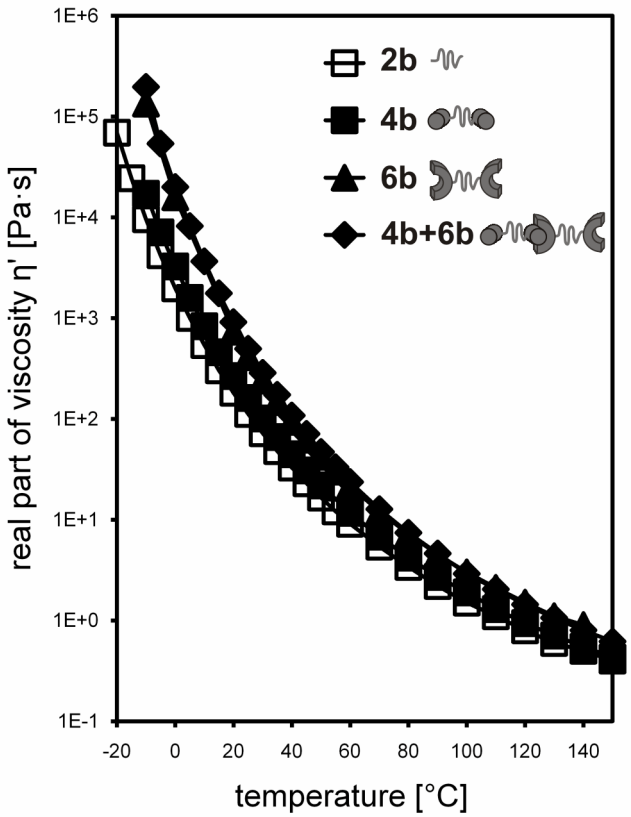
Supplement 18. Frequence sweep measurement of a reference PnBA (analogue to **2b**) with a molecular weight of 30.000 g/mol.



Supplement 19. Frequenzy sweep measurement of THY-functionalized PnBA **4b** at -10 °C.



Supplement 20. Frequenzy sweep measurement of DAT-functionalized PnBA **6b** at -10 °C.



Supplement 21. Logarithmic plot of the zero shear viscosity vs. temperature for bifunctional PnBAs with $M_n \approx 25000$ g/mol.

1. F. Herbst, K. Schröter, I. Gunkel, S. Gröger, T. Thurn-Albrecht, J. Balbach and W. H. Binder, *Macromolecules*, 2010, **43**, 10006-10016.
2. W. H. Binder, M. J. Kunz, C. Kluger, G. Hayn and R. Saf, *Macromolecules*, 2004, **37**, 1749-1759.
3. M. Kurinovich and J. Lee, *J. Am. Soc. Mass. Spectrom.*, 2002, **13**, 985-995.