Electronic Supplementary Material (ESI) for Polymer Chemistry
This journal is © The Royal Society of Chemistry 2012

Journal Name

Dynamic Article Links ►

Cite this: DOI: 10.1039/c0xx00000x

www.rsc.org/xxxxxx

ARTICLE TYPE

Dynamic Supramolecular Poly(isobutylene)s for Self-Healing Materials

Supplement

Florian Herbst[a], **Sebastian Seiffert**[b,c] **and Wolfgang H. Binder***[a]

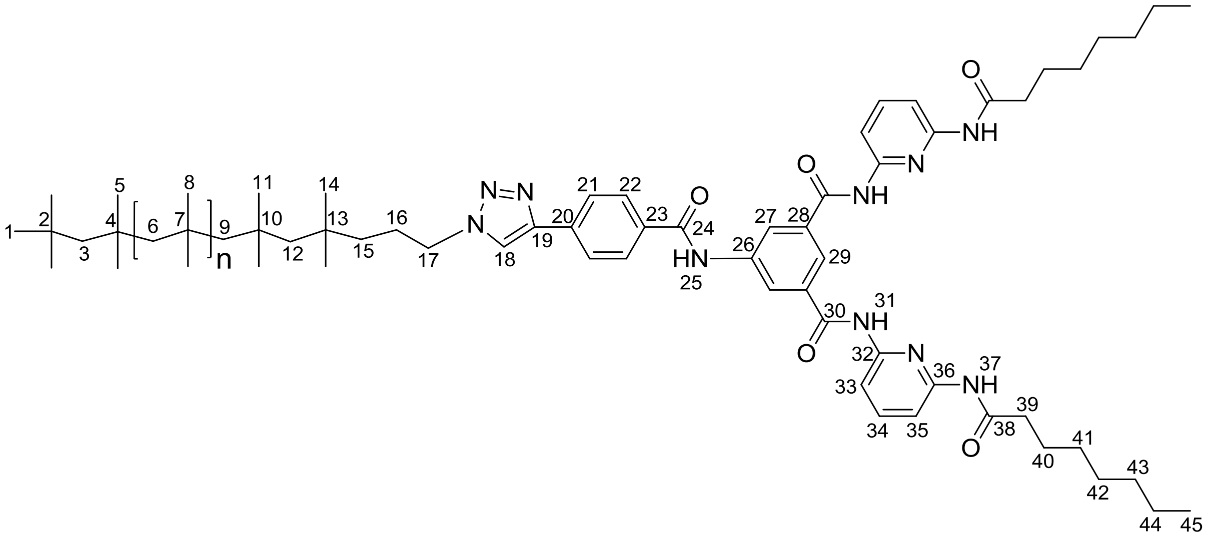
Received (in XXX, XXX) Xth XXXXXXXXX 20XX, Accepted Xth XXXXXXXXX 20XX
DOI: 10.1039/b000000x

[a] *Martin-Luther-University Halle-Wittenberg; Von-Danckelmann-Platz 4; D-06120 Halle (Saale), Germany; E-mail: wolfgang.binder@chemie.uni-halle.de*
[b] *Helmholtz-Zentrum Berlin, F-I2 Soft Matter and Functional Materials, Hahn-Meitner-Platz 1, D-14109 Berlin, Germany; Email: sebastian.seiffert@helmholtz-berlin.de*
[c] *FU Berlin, Institute of Chemistry and Biochemistry, Takustr. 3, D-14195 Berlin, Germany; Email: seiffert@chemie.fu-berlin.de*

Content

1. NMR measurements

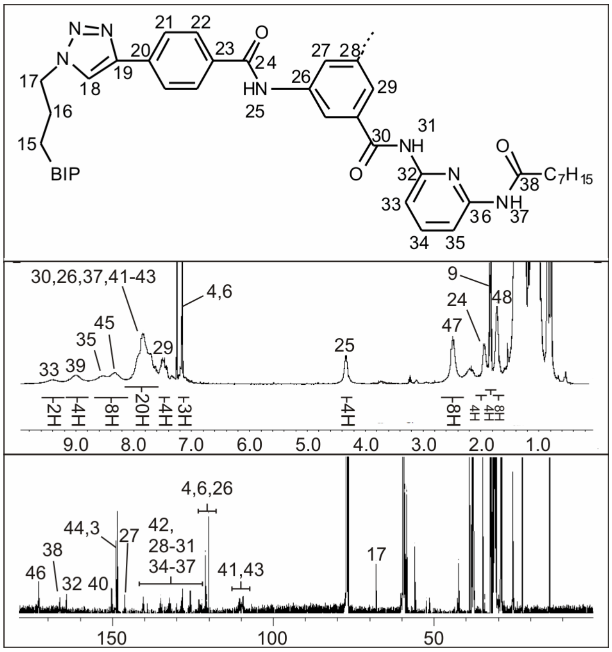
1.1. NMR of monofunctional PIB bearing the hamilton wedge (5a)



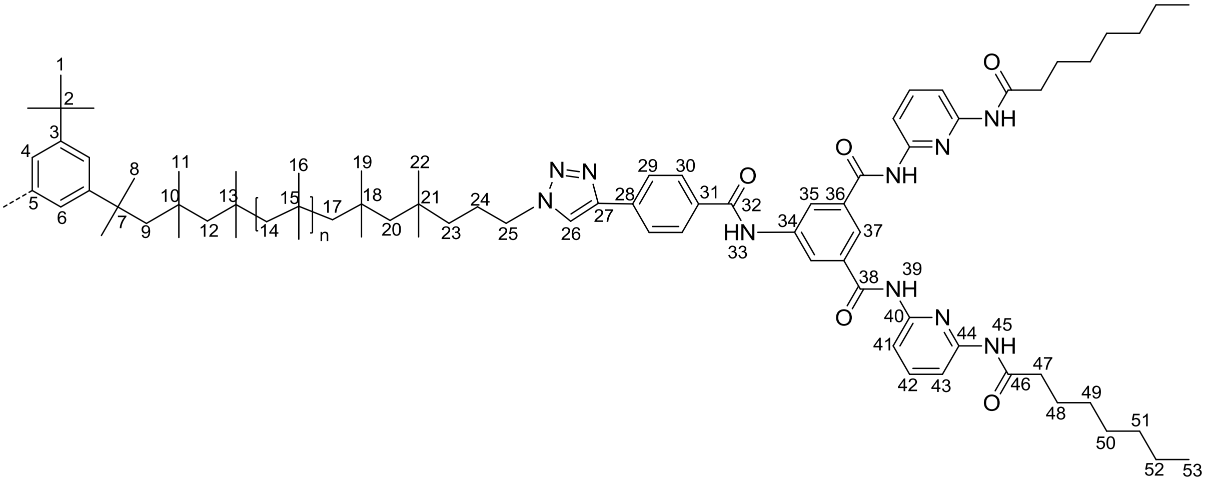
^{1}H-NMR (500 MHz, CDCl$_3$): δ 9.11 (bs, 1H, H$_{25}$), 8.84 (bs, 2H, H$_{31}$), 8.48 (s, 2H, H$_{27}$), 8.39 (s, 2H, H$_{37}$), 8.04 (s, 2H, H$_{22}$), 7.92-7.84 (m, 8H, H$_{18,29,33-35}$), 7.60 (s, 2H, H$_{21}$), 4.37 (t, 2H, H$_{17}$), 2.54 (s, 4H, H$_{39}$), 1.96 (m, 2H, H$_{16}$), 1.76 (m, 4H, H$_{40}$), 1.42 (bs, n·2H, H$_6$), ~1.26 (m, 16H, H$_{41-44}$), 1.11 (bs, n·6H, H$_8$), 0.99 (s, 15H, H$_{1+5}$), 0.86 (t, 6H, $^{3}J_{H,H}$ = 6.5 Hz, H$_{45}$).

^{13}C-NMR (125 MHz, CDCl$_3$): δ 172.9 (C$_{38}$), 166.4 (C$_{30}$), 163.8 (C$_{24}$), 150.2 (C$_{32}$), 148.9 (C$_{36}$), 145.9 (C$_{19}$), 140.6 (C$_{34}$), 139.1 (C$_{26}$), 135.2 (C$_{28}$), 135.0 (C$_{23}$), 130.0 (C$_{21}$), 128.5 (C$_{22}$), 128.1 (C$_{20}$), 126.0 (C$_{27}$), 122.1 (C$_{29}$), 120.7 (C$_{18}$), 110.5 (C$_{33}$), 109.4 (C$_{35}$), 59.5 (C$_6$), 58.8 (C$_3$), 58.2 (C$_9$), 55.9 (C$_{12}$), 51.4 (C$_{17}$), 42.3 (C$_{15}$), 38.2 (C$_7$), 37.8 (C$_4$), 37.8 (C$_{10}$), 37.6 (C$_{39}$), 34.9 (C$_{13}$), 32.6 (C$_2$), 32.4 (C$_1$), 31.7 (C$_{43}$), 31.2 (C$_8$), 30.8 (C$_5$), 30.8 (C$_{11}$), 29.3 (C$_{14}$), 29.2 (C$_{41}$), 29.1 (C$_{42}$), 25.6 (C$_{16}$), 25.5 (C$_{40}$), 22.6 (C$_{44}$), 14.1 (C$_{45}$).

1.2. NMR of bifunctional PIB bearing the hamilton wedge (6a)



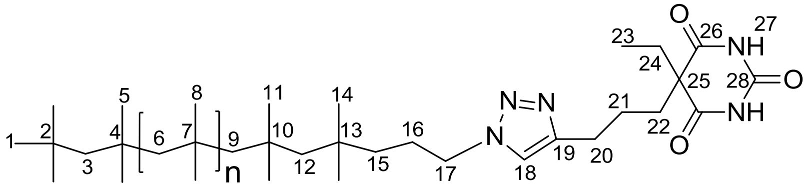
Suppl. 1ß. ^{1}H-NMR and ^{13}C-NMR spectra of Hamilton-functionalized PIB **6a**.



^{1}H-NMR (500 MHz, $CDCl_3$): δ 9.41 (bs, 2H, H_{33}), 9.00 (bs, 4H, H_{39}), 8.53 (bs, 4H, H_{35}), 8.33 (bs, 4H, H_{45}), 7.85 (m, 20H, $H_{30,26,37,41\text{-}43}$), 7.50 (bs, 4H, H_{29}), 7.17 (s, 3H, $H_{4,6}$), 4.33 (bs, 4H, H_{25}), 2.49 (bs, 8H, H_{47}), 1.95 (bs, 4H, H_{24}), 1.83 (s, 4H, H_9), 1.72 (bs, 8H, H_{48}), 1.42 (bs, n·2H, H_{14}), 1.32 (m, 32H, $H_{49\text{-}52}$), 1.11 (bs, n·6H, H_{16}), 0.85 (t, 12H, $^3J_{H,H}$ = 6.3 Hz, H_{53}).

^{13}C-NMR (525 MHz, $CDCl_3$): δ 173.0 (C_{46}), 166.4 (C_{38}), 164.2 (C_{32}), 150.2 (C_{40}), 149.0 ($C_{44,3}$), 148.5 (C_5), 146.2 (C_{27}), 140.4 (C_{42}), 139.1 (C_{34}), 135.0 (C_{36}), 134.7 (C_{31}), 130.0 (C_{29}), 128.5 (C_{30}), 128.3 (C_{28}), 125.8 (C_{35}), 122.3 (C_{37}), 121.2 (C_6), 120.0 (C_{26}), 120.1 (C_4), 110.5 (C_{41}), 109.4 (C_{43}), 59.5 (C_{14}), 58.6 (C_{17}), 56.0 (C_{20}), 51.4 (C_{25}), 42.3 (C_{23}), 39.0 (C_7), 38.2 (C_{15}), 37.9 (C_{18}), 37.8 (C_{10}), 37.5 (C_{47}), 34.9 (C_{21}), 34.8 (C_2), 32.3 (C_8), 31.7 (C_{51}), 31.7 (C_1), 31.3 (C_{16}), 30.9 (C_{11}), 30.8 (C_{19}), 29.3 (C_{22}), 29.2 (C_{49}), 29.1 (C_{50}), 25.6 (C_{24}), 25.5 (C_{48}), 22.6 (C_{52}), 14.1 (C_{45}).

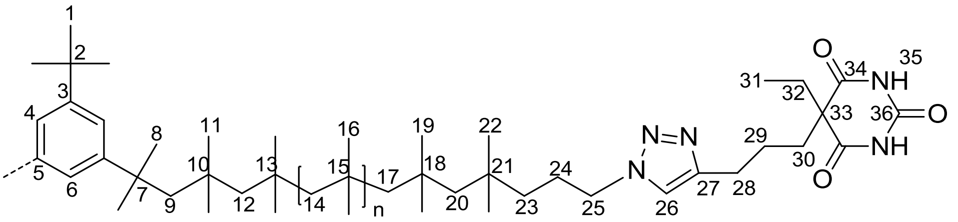
1.3. NMR of monofunctional PIB bearing the barbituric acid (3a)



^{1}H-NMR (500 MHz, $CDCl_3$): δ 8.38 (bs, 2H, H_{27}), 7.26 (s, 1H, H_{18}) 4.36 (t, 2H, H_{17}, $^3J_{H,H}$ = 7.3 Hz), 2.71 (t, 2H, H_{20}, $^3J_{H,H}$ = 7.3 Hz), 2.05 (m, 6H, $H_{21+22+24}$), 1.42 (bs, n·2H, H_6), 1.11 (bs, n·6H, H_8), 0.99 (s, 15H, H_{1+5}), 0.92 (t, 3H, H_{23}, $^3J_{H,H}$ = 7.4 Hz).

^{13}C-NMR (125 MHz, $CDCl_3$): δ 172.0 (C_{26}), 153.4 (C_{28}), 148.1 (C_{19}), 128.4 (C_{18}), 59.5 (C_6), 58.8 (C_3), 58.2 (C_9), 57.1 (C_{25}), 55.8 (C_{12}), 42.3 (C_{15}) 38.1 (C_7), 37.8 (C_4), 37.7 (C_{10}), 34.9 (C_{13}), 32.7 (C_{22}), 32.5 (C_2), 32.4 (C_1),), 31.9 (C_{21}), 31.2 (C_8), 30.8 (C_5), 30.7 (C_{11}), 29.2 (C_{14}), 26.2 (C_{16}), 9.4 (C_{23}).

1.4. NMR of bifunctinal PIB bearing the barbituric acid (4a)



^{1}H-NMR (500 MHz, $CDCl_3$): δ 8.29 (bs, 4H, H_{35}), 7.26 (s, 2H, H_{26}), 7.17 (s, 3H, $H_{4,6}$), 4.30 (t, 4H, H_{25}, $^3J_{H,H}$ = 7.4 Hz), 2.74 (t, 4H, H_{28}, $^3J_{H,H}$ = 7.4 Hz), 2.05 (m, 12H, $H_{29,30,32}$), 1.85 (s, 4H, H_9), 1.42 (bs, n·2H, H_{14}), 1.11 (bs, n·6H, H_{16}), 1.02 (s, 12H, H_{22}), 0.89 (t, 6H, H_{31}, $^3J_{H,H}$ = 7.5 Hz).

^{13}C-NMR (125 MHz, $CDCl_3$): δ 171.9 (C_{34}), 153.8 (C_{36}), 149.0 (C_3), 148.5 (C_5), 148.1 (C_{27}), 128.8 (C_{26}), 121.2 (C_6), 120.1 (C_4), 59.5 (C_{14}), 59.2 (C_{12}), 59.1 (C_{17}), 58.6 (C_9), 57.1 (C_{33}), 55.8 (C_{20}), 42.4 (C_{23}), 39.0 (C_7), 38.2 (C_{15}), 38.0 (C_{13}), 37.9 (C_{18}), 37.8 (C_{10}), 34.8 (C_{21}), 34.8 (C_2), 32.7 (C_{30}), 32.3 (C_8), 31.9 (C_{29}), 31.6 (C_1), 31.2 (C_{16}), 30.8 (C_{11}), 30.7 (C_{19}), 29.2 (C_{22}), 25.5 (C_{24}), 22.7 (C_{32}), 9.4 (C_{31}).

1.5. NMR-titration experiments

NMR titration experiments were performed on a *Varian Unity Inova 500* (500 MHz) spectrometer in $CDCl_3$ (Armar AG, 99.8 Atom%D) at 25 °C. 64 Scans were performed for each sample. Chemical shifts were recorded in ppm (δ; parts per million) and referred to the solvent residue peak of $CDCl_3$ at 7.26 ppm. For determination of $K_{aasn.}$ of the Hamilton-barbituric acid interaction the following equation was used:[1-3]

$$\delta = \delta_H + \frac{\delta_C - \delta_H}{2 * [H]} * \left[[H] + [G] + \frac{1}{K_{assn.}} - \sqrt{\left([H] + [G] + \frac{1}{K_{assn.}} \right)^2 - 4 + [H] + [G]} \right]$$

The experimentally determined parameters are: [H] and [G] (in mol/l), the total host and guest concentrations, δ the observed shift, and δ_H, the shift of the host in absence of guest. Parameters determined through fitting are $K_{assn.}$, the host-guest association constant, and δ_C, the chemical shift of the host-guest complex.

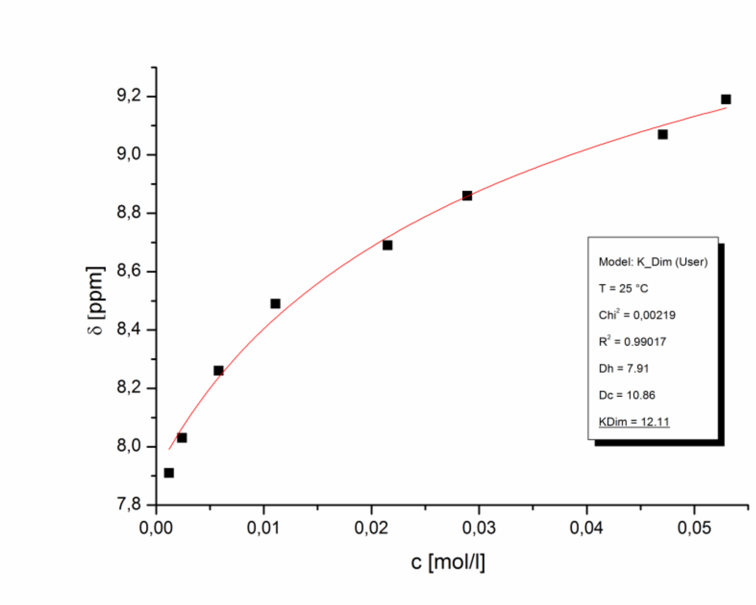
For determination of the dimerization constant of the barbituric acid- barbituric acid and Hamilton wedge-Hamilton wedge interaction, respectively, the following simplified equation was used (assumption: [H] = [G]):

$$\delta = \delta_H + \frac{(\delta_C - \delta_H)}{[H]} * \left[[H] + \frac{1}{4 * K_{dim}} - \sqrt{\left([H] + \frac{1}{4 * K_{dim}} \right)^2 - [H]^2} \right]$$

In this case δ_H is the shift at the lowest concentration.

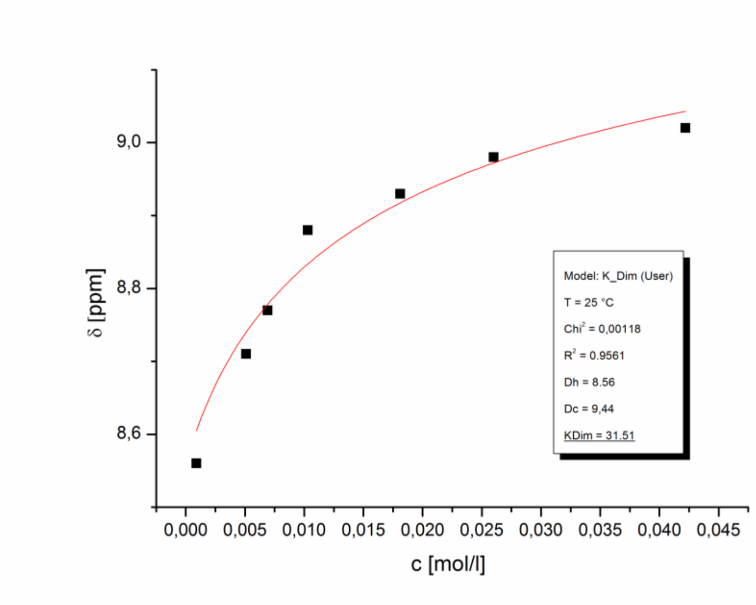
NMR-titration protocol for determination of the association constant K_{assn}:
A stock solution of barbituric acid-functionalized PIB **3a** (host) and $CDCl_3$ was prepared (0.00097 mol/l). Different amounts of Hamilton-functionalized PIB **5a** (guest) were weighted into small glass vials, varying from 0.78 mg (0.0002 mmol) to 2.92 mg (0.021 mmol). Exactly 0.7 ml of the stock solution was added to each vial. After PIB **5a** was dissolved, the resulting solution was transferred to the NMR-tube.

1.5.1 Dimerization constant of barbituric acid-functionalized PIB 3a

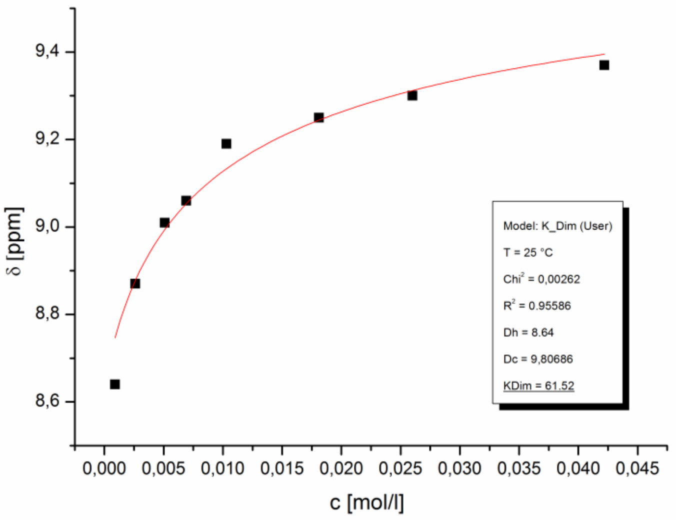


Suppl. 2. NMR-titration experiment for determination of the dimerization constant for the barbituric acid group using PIB **3a**.

1.5.2 Dimerization constant of Hamilton-functionalized PIB 5a

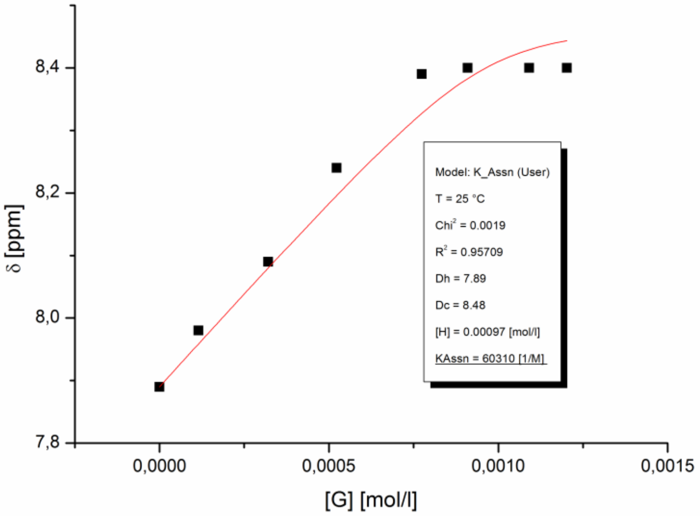


Suppl. 3. NMR-titration experiment for determination of the first dimerization constant for the Hamilton wedge group using PIB **5a**.



Suppl. 4. NMR-titration experiment for determination of the second dimerization constant for the Hamilton wedge group using PIB **5a**.

1.5.3. Association constant of Hamilton wedge-functionalized PIB 5a and barbituric acid-functionalized PIB 3a



Suppl. 5. NMR-titration experiment for determination of the association constant for the Hamilton wedge and barbituric acid group using PIB **3a** and **5a**.

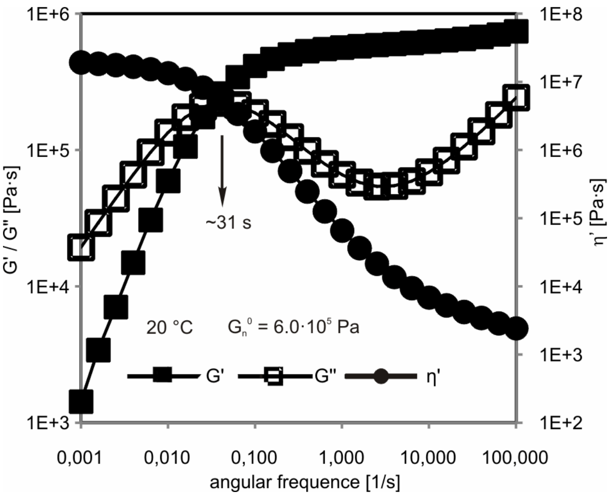
2. DSC measurements

Table-Suppl. 1. DSC data of all PIBs.

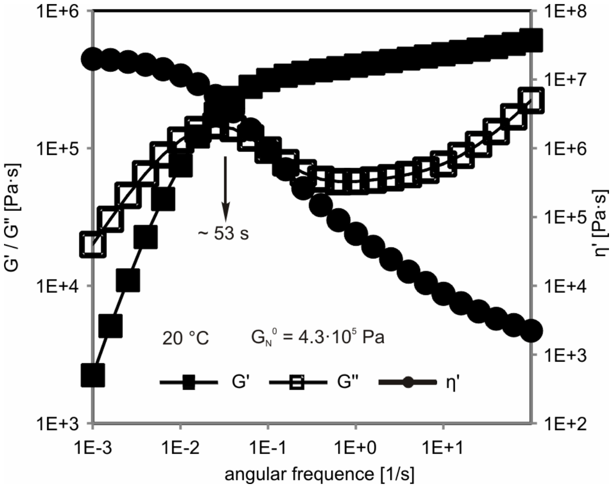
Polymer	T_g [°C]^a
1a ^{e}	-72.8
1b ^{e}	-67.1
1c ^{e}	-68.8
2a ^{e}	-70.1
2b ^{e}	-69.1
2c ^{e}	-67.4
2d ^{e}	-68.7
3a	-68.4
3b	-67.5
3c	-66.5
4a	-59.2
4b	-64.5
4c	-64.2
4d	-65.7
5a	-66.8
5b	-66.1
5c	-66.4
6a	-60.1

^{a} Temperature at midpoint of transition.

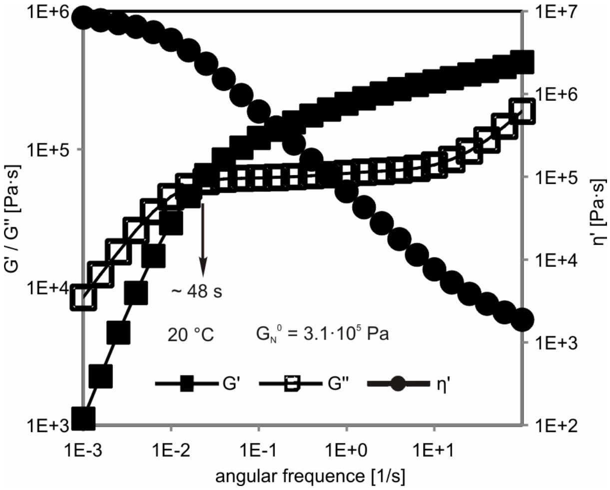
3. Rheology measurements



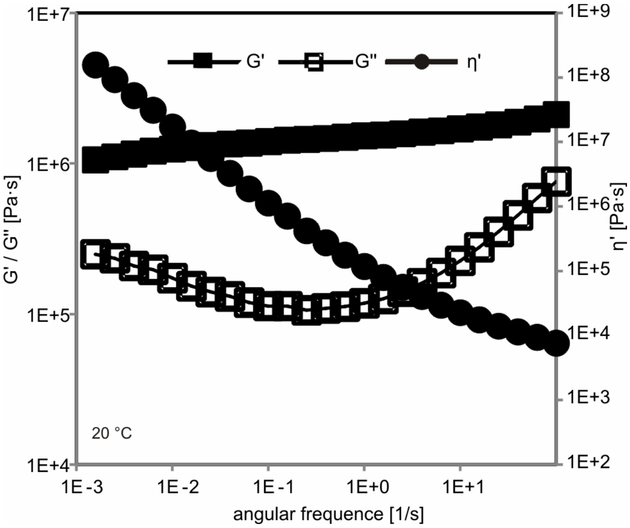
Suppl. 6. Frequency sweep measurement of **4b** at 20 °C.



Suppl. 7. Frequency sweep measurement of **4c** at 20 °C.



Suppl. 8. Frequency sweep measurement of **4d** at 20 °C.



Suppl. 5. Frequency sweep measurement of **4kbi-M** at 20 °C.

4. MALDI-TOF-MS measurements

MALDI-TOF-MS experiments were performed on a *Bruker Autoflex III* system operatin in reflectron and liniar modes. Data evaluation was carried out on *flexAnalysis* software (vers. 3.0). Ions were formed by laser desorption (smart beam laser at 355 nm, 532 nm, 808 nm and 1064 nm ± 5 nm; 3 ns pulse width; up to 2500 Hz repetition rate), accelerated by voltage of 20 kV and detected as positive ions. Baseline substraction and smoothing of the recorded spectra were performed using a *Savitzky-Golay* algorithm. The instrument was calibrated with poly(ethylene glycol) (PEG) standards (M_n = 2000 g/mol and M_p = 4000 g/mol) applying a quadratic calibration method with an error of 1-2 ppm. PEG standards (analyte) were dissolved in THF at a concentration of 20 mg/ml. *trans*-2-[3-(4-*tert*-Butylphenyl)-2-methyl-2-propenylidene]malononitrile (DCTB) (matrix) and lithium trifluoroacetate (LiTFA) (salt) were dissolved in THF at a concentration of 20 mg/ml. For PEG standards the ratio of matrix:analyte:salt was 100:10:1 and 1 µl of the solution was spotted on the MALDI-target plate. Samples of PIBs were prepared by dissolving the polymer in THF at a concentration of 20 mg/ml. Matrix and salt were dissolved in THF at a concentration of 20 mg/ml.

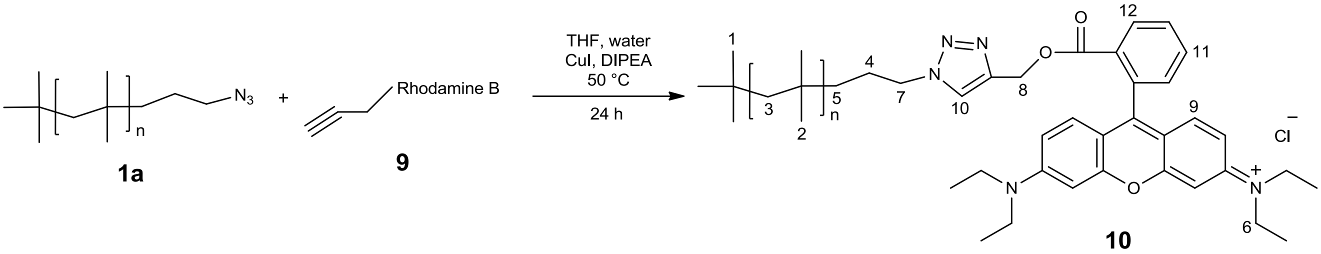
4.1. MALDI-TOF-MS of barbituric acid functionalized PIB 3a (monofunctional)

For **3a** the best spectrum was obtained by ionization with Li-ions (matrix: DCTB:LiTFA:Analyte = 100:1:10). The spectrum shows three important series, where each series of ions were separated by ~56 Da, the mass of the repeating unit (calculated 56.1 Da). Altough LiTFA was used as salt all series show ions including Cu(I) which was still present from the "click"-reaction where excess of CuBr was applied. During workup of **3a** the Cu(I)-ion were oxidized to Cu(II)-ions. These Cu(II)-ions can easily be reduced to Cu(I)-ions again by the matrix during the ionization process, so that molecule ions containing Cu(I) were observed. The most intensive signal of the main series at 2727.316 Da can be assigned to a species $[M\cdot Cu]^+$ ($C_{182}H_{357}N_5O_3Cu_1$; n = 41). The theoretical m/z value for a species $[M\cdot Cu]^+$ (n = 41) is 2726.729 Da, a value that agrees well with the signal at 2727.316 Da (deviation 215 ppm). For both minor series one (or two) of the acidic protons of the barbituric acid group were exchanged by an ion. The most intensive signal of the first minor series at 2733.306 Da can be assigned to a species $[M\cdot LiCu]^+$ ($C_{182}H_{356}N_5O_3Li_1Cu_1$; n = 41). The theoretical m/z value for a species $[M\cdot LiCu]^+$ (n = 41) is 2732.737 Da, a value that agrees well with the signal at 2733.306 Da (deviation 208 ppm). The most intensive signal of the second minor series at 2601.976 Da can be assigned to a species $[M\cdot Na_2Cu]^+$ ($C_{170}H_{331}N_5O_3Na_2Cu_1$; n = 38). The theoretical m/z value for a species $[M\cdot Na_2Cu_1]^+$ (n = 38) is 2602.505 Da, a value that agrees well with the signal at 2601.976 Da (deviation 203 ppm). The calculated isotopic patterns of all series match well with the observed patterns.

4.2. MALDI-TOF-MS of Hamilton wedge functionalized PIB 5a (monofunctional)

For **5a** the best spectrum was obtained by ionization with Ag-ions (matrix: DCTB:AgTFA:Analyte = 100:1:10). The spectrum shows two important series, where each series of ions were separated by ~56 Da, the mass of the repeating unit (calculated 56.1 Da). Although AgTFA was used as salt none of the detected molecule ions include Ag(I).Cu(I) was still present from the "click"-reaction where excess of CuBr was applied. During workup of **5a** the Cu(I)-ion were oxidized to Cu(II)-ions. These Cu(II)-ions can easily be reduced to Cu(I)-ions again by the matrix during the ionization process, so that molecule ions containing Cu(I) were observed. For all series four (or five) of the –N*H*CO– protons of the hamilton receptor end group were exchanged by another ion. The most intensive signal of the main series at 3069.063 Da can be assigned to a species $[M\cdot CuLi_4Na_1]^+$ ($C_{198}H_{355}N_{10}O_5Cu_1Na_1Li_4$; n = 37). The theoretical m/z value for a species $[M\cdot CuLi_4Na_1]^+$ (n = 37) is 3069.772 Da, a value that agrees well with the signal at 3069.063 Da (deviation 230 ppm). The most intensive signal of the minor series at 3063.830 Da can be assigned to a species $[M\cdot CuLi_3Na_1]^+$ ($C_{198}H_{356}N_{10}O_5Cu_1Na_1Li_3$; n = 37). The theoretical m/z value for a species $[M\cdot CuLi_3Na_1]^+$ (n = 37) is 3063.764 Da, a value that agrees well with the signal at 3063.830 Da (deviation 21 ppm). The calculated isotopic patterns of all series match well with the observed patterns.

5.1. Synthesis of rhodamine B-functionalized PIB (10)



In an one-necked round-bottom flask azido-functionalized PIB **1a** (0.084 mmol, 217 mg) was dissolved in THF (11.5 ml). Rhodamin-alkyne (**9**) was dissolved in water (3.2 ml) and DIPEA (3.78 mmol, 675 µl) was added. Both solution were combined and sparged with nitrogen for 30 min. CuI (0.0084 mmol, 1.6 mg) was added and the reaction was heated at 50 °C for 48 h. After the solvent was removed, the crude polymer was washed 5-times with MeOH (50 ml) and 3-times with acetone (50 ml). The polymer was dissolved in a small amount of $CHCl_3$ and column chromatography (SiO_2) was performed in $CHCl_3$ (R_f(**10**) = 0) and after several fraction the solvent was changed to $CHCl_3$/MeOH (v:v = 10:1) (R_f(**10**) = 0.4). Finally, the polymer was dissolved in a small of *n*-hexane and precipitated into a 10-fold excess of methanol. Yield: 95 mg; 36.0 %.

^{1}H-NMR (400 MHz, $CDCl_3$): δ 8.22 (d, 1H, H_{12}, $^3J_{H,H}$ = 7.2 Hz), 7.70-7.65 (m, 3H, H_{11}), 7.45 (s, 1H, H_{10}), 7.11-6.79 (m, 6H, H_9), 4.74 (s, 2H, H_8), 4.24 (t, 2H, H_7, $^3J_{H,H}$ = 6.1 Hz), 3.68-3.15 (m, 8H, H_6), 1.95 (t, 2H, H_5), 1.80 (q, 2H, H_4), 1.42 (bs, n·2H, H_3), 1.11 (bs, n·6H, H_2), 0.99 (s, 15H, H_1).

6. Literature

1. R. Deans, G. Cooke and V. M. Rotello, *J. Org. Chem.*, 1997, **62**, 836-839.
2. F. Ilhan, M. Gray and V. M. Rotello, *Macromolecules*, 2001, **34**, 2597-2601.
3. R. S. Macomber, *J. Chem. Educ.*, 1992, **69**, 375.