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

Supplement

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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$_{HH}$ = 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$_{12}$), 148.9 (C$_{36}$), 145.9 (C$_{19}$), 140.6 (C$_{34}$), 139.1 (C$_{26}$), 135.2 (C$_{29}$), 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$_{19}$), 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. 1B. $^1\text{H}$-NMR and $^{13}\text{C}$-NMR spectra of Hamilton-functionalized PIB 6a.

$^1\text{H}$-NMR (500 MHz, CDCl$_3$): $\delta$ 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$_{30,26,37,41-43}$), 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$_{49-52}$), 1.11 (bs, n·6H, H$_{16}$), 0.85 (t, 12H, $^3\text{J}_{\text{H,H}} = 6.3$ Hz, H$_{53}$).

$^{13}\text{C}$-NMR (525 MHz, CDCl$_3$): $\delta$ 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$_{11}$), 130.0 (C$_{29}$), 128.5 (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$_{22}$), 42.3 (C$_{23}$), 39.0 (C$_7$), 38.2 (C$_{13}$), 37.9 (C$_{18}$), 37.8 (C$_{10}$), 37.5 (C$_{27}$), 34.9 (C$_{21}$), 34.8 (C$_2$), 32.3 (C$_4$), 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$_{30}$), 25.6 (C$_{24}$), 25.5 (C$_{48}$), 22.6 (C$_{32}$), 14.1 (C$_{45}$).
In this case for determination of the dimerization constant of the barbituric acid (4a), 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 $^\circ$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 $K_{\text{assn.}}$ of the Hamilton-barbituric acid interaction the following equation was used$^{1,3}$:

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

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

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

In this case δH is the shift at the lowest concentration.
NMR-titration protocol for determination of the association constant $K_{\text{asgn}}$:

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

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</tr>
<tr>
<td>6a</td>
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</tr>
</tbody>
</table>

$^a$ Temperature at midpoint of transition.

3. Rheology measurements

![Suppl. 6. Frequency sweep measurement of 4b at 20 °C.](image)
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 linear 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 subtraction and smoothing of the recorded spectra were performed using a Savitzky-Golay algorithm. The instrument was calibrated with poly(ethylene glycol) (PEG) standards (Mₙ = 2000 g/mol and Mₚ = 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). Although 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·Cu]⁺ (C₁₈₂H₃₅₇N₁₁O₃Cu; n = 41). The theoretical m/z value for a species [M·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-LiCu]⁺ (C₁₈₂H₃₅₆N₅O₃LiCu; n = 41). The theoretical m/z value for a species [M-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-Na₂Cu]⁺ (C₁₇₀H₃₁₃N₁₀O₃Na₂Cu; n = 38). The theoretical m/z value for a species [M-Na₂Cu]⁺ (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 –NHCO– 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-CuLiNa]⁺ (C₁₉₈H₃₉₅N₁₅O₃CuLiNa; n = 37). The theoretical m/z value for a species [M-CuLiNa]⁺ (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-CuLiNa]⁺ (C₁₉₈H₃₉₅N₁₅O₃CuLiNa; n = 37). The theoretical m/z value for a species [M-CuLiNa]⁺ (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 CHCl₃ and column chromatography (SiO₂) was performed in CHCl₃ (Rf(10) = 0) and after several fraction the solvent was changed to CHCl₃/MeOH (v:v = 10:1) (Rf(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 %.

1H-NMR (400 MHz, CDCl₃): δ  8.22 (d, 1H, H₁₂, 3J_H,H = 7.2 Hz),  7.70-7.65 (m, 3H, H₁₁),  7.45 (s, 1H, H₁₀),  7.11-6.79 (m, 6H, H₉),  4.74 (s, 2H, H₈),  4.24 (t, 2H, H₇, 3J_H,H = 6.1 Hz),  3.68-3.15 (m, 8H, H₆),  1.95 (t, 2H, H₅),  1.80 (q, 2H, H₄),  1.42 (bs, n·2H, H₃),  1.11 (bs, n·6H, H₂),  0.99 (s, 15H, H₁).

6. Literature