Spread and Set Silicone-Boronic Acid Elastomers
Laura Zepeda-Velazquez, a Benjamin Macphail a and Michael A. Brook a*

Supporting Information

NMR monitoring of protecting group hydrolysis
Experiments were performed on a Bruker Avance 600 MHz nuclear magnetic resonance spectrometer using deuterium oxide (D₂O) as solvent. The proton impurity of the deuterated solvent was used as a reference for ¹H NMR spectra (HOD @ 4.80 ppm). Catecholate hydrolysis was monitored by collecting a ¹H-NMR spectrum of a sample composed of CSiBA-73 (~10 mg) on D₂O (~0.6 mL) in a glass NMR tube after the sample had aged for ~120 min. Pinacol deprotection was monitored by collecting a ¹H NMR spectrum of a sample composed of PSiBA-73 (~10 mg) on D₂O (~0.6 mL) in a glass NMR tube after sample had aged for ~120 min. Dimethyl-L-tartrate deprotection was monitored over the course of 100 h by collecting ¹H NMR spectra of a sample composed of TSiBA-17 (~30 mg) on D₂O (~0.6 mL) in a glass NMR tube. For all samples, the quantity of free protecting group was estimated by comparing the integration for the proton impurity of the solvent to the integration of the free protecting group signal(s).

Table 1. ¹H NMR detection of hydrolyzed SiBA protecting groups

<table>
<thead>
<tr>
<th>Sample</th>
<th>Relative integration a</th>
<th>Time [h]</th>
</tr>
</thead>
<tbody>
<tr>
<td>TSiBA-17</td>
<td>0.0015</td>
<td>0.08</td>
</tr>
<tr>
<td></td>
<td>0.0448</td>
<td>5.5</td>
</tr>
<tr>
<td></td>
<td>0.0761</td>
<td>21.5</td>
</tr>
<tr>
<td></td>
<td>0.0812</td>
<td>99.5</td>
</tr>
<tr>
<td>CSiBA-99</td>
<td>0.0026</td>
<td>2</td>
</tr>
<tr>
<td>PSiBA-99</td>
<td>N/A</td>
<td>2</td>
</tr>
</tbody>
</table>

a Relative integration of dimethyl-L-tartrate CH₃ (6 total) protons, catechol C-H protons (4 total) or pinacol methyl protons (12 total) to HOD integration normalized to an integration of 1; b This represents liberation of ~100% dimethyl tartrate – no further changes were observed. c Represents ~14% catechol release. d No visible signal for pinacol CH₃ were present in spectrum.
Figure S-1. $^1$H NMR of A: TSiBA-73 (in CDCl$_3$) and B., C: SiBA-73 (in solution and solid state) showing ortho proton signals at 7.7-7.8 ppm consistent with free or hydrogen-bonded boronic acids rather than boroxines.

A: TSiBA-73 (solution, CDCl$_3$)
B: SiBA-73 (solution, CDCl₃)

Current Data Parameters

NAME           TSiBA Elastomer
EXPNO                10
PROCNO                1

F2 - Acquisition Parameters

Date_           20160427
INSTRUM           av600
PROBHD   5 mm PABBO BB-
PULPROG            zg30
AUNM              au_zg
TD                77824
SOLVENT         Acetone
NS                   16
DS                    2
SWH           10775.862 Hz
FIDRES         0.138465 Hz
AQ            3.6110799 sec
RG                228.1
DW               46.400 usec
DE                 6.50 usec
TE                298.0 K
D1           1.50000000 sec

======== CHANNEL f1 ========
NUC1                 1H
P1                13.69 usec
PL1               -1.00 dB
SFO1        600.1342009 MHz

F2 - Processing parameters

SI                65536
SF          600.1300168 MHz
WDW                  EM
SSB      0
LB                 0.20 Hz
GB       0
PC                 1.00

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C: SiBA-73 (Solid state)
Figure S-2. Sequence showing i) placement of TSiBA on water (4 s); demonstration of supported water droplets on the formed viscoelastic films; the elastomeric film with constrained water droplets is readily removed.

Drop about to be added (3.5 s)  
Drop of TSiBA hits the water surface (4 s)

Water droplet (blue) added to film 12 s  
14s

Additional water added 15 s  
Red drops are also water (26s)

30 s  droplet starts to breach the viscoelastic film  
34s

35.5 s  picking up the elastomeric film  
Water droplets do not mix 36 s