A Novel Imide Synthesis via Silyl-Blocked Diamines

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Two groups\textsuperscript{1,2} have reported the synthesis of organosilylated polyamic acid resins from N,N'-bis-(trimethylsilyl)diamines and their subsequent conversion to polyimides (Scheme A).

\begin{align*}
\text{(CH}_3\text{)Si-NH-A-NH-Si(CH}_3\text{)}_3 & \xrightarrow{\text{dianhydride/THF, r.t.}} \text{Polyimide} \\
\left[\text{(CH}_3\text{)Si(OOC)}_2\text{COOSi(CH}_3\text{)}_3\right]_n & \xrightarrow{\text{heat}} \text{Polyimide} + \text{(CH}_3\text{)SiOH}
\end{align*}

Scheme A
Table: Experimental Conditions and Results of the Synthesis of Compounds 2.

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Reaction Conditions</th>
<th>Yield (%)</th>
<th>m.p.</th>
<th>Elemental Analysis</th>
<th>Imide</th>
<th>L.R. (cm⁻¹)</th>
<th>Silyl-R², R¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>2a</td>
<td>DMF, 23 hr, 124°C</td>
<td>89%</td>
<td>235.5-238°</td>
<td>calc. C 71.69 H 4.41</td>
<td>1781&lt;sup&gt;a&lt;/sup&gt;</td>
<td>1236&lt;sup&gt;a&lt;/sup&gt;</td>
<td>Silyl-R², R¹</td>
</tr>
<tr>
<td>2b</td>
<td>Diglyme, 27 hr, 156-161°C</td>
<td>61%</td>
<td>255-257.5°</td>
<td>calc. C 74.45 H 4.28</td>
<td>1780&lt;sup&gt;a&lt;/sup&gt;</td>
<td>1240, 780&lt;sup&gt;a&lt;/sup&gt;</td>
<td>Silyl-R², R¹</td>
</tr>
<tr>
<td>2c</td>
<td>DMF, 24 hr, 130-141°C</td>
<td>88%</td>
<td>314.5-317°</td>
<td>calc. C 76.66 H 4.18</td>
<td>1784&lt;sup&gt;a&lt;/sup&gt;</td>
<td>692&lt;sup&gt;a&lt;/sup&gt;</td>
<td>Silyl-R², R¹</td>
</tr>
</tbody>
</table>

<sup>a</sup>Crude yield. <sup>b</sup>Uncorrected. <sup>c</sup>KBr pellet. <sup>d</sup>Broad. <sup>e</sup>Weak.
mediate and thus allow the production of a polyimide of higher molecular weight than can be achieved by conventional means.

Bis-[N,N-bis-(trimethylsilyl)-4-aminophenyl]-methylphenylsilane (1b):
To a stirred anhydrous ethereal solution of N,N-bis-[trimethyl-
silyl]-4-bromoaniline (66 g, 0.209 mol) was added 2.25 N butyl-
lithium (93 ml, 0.209 mol) at 0° under nitrogen. After a reaction
period of 1 hr at room temperature, dichloromethylphenylsilane
(20.0 g, 0.1045 mol) was added dropwise. The resultant solution
was stirred overnight; after a 2 hr reflux, the lithium chloride was
removed by filtration and the ether removed in vacuo. Distillation
afforded 1b; yield: 36.7 g (59%); b.p. 202–204.5°/0.03 torr;

C_{31}H_{27}N_5Si_5 calc. C 62.77 H 8.84
(593.2) found 62.56 8.89

I.R. (neat): ν_{max} = 1246, 830, 695 cm⁻¹; this spectrum showed no
NH absorption.

³¹P-N.M.R. (CDCl₃): δ = 7.27 (center of m, 13H_{aromatic}), 0.84 (s, 3H,
single methyl group on silicon), 0.14 ppm (s, 36H, trimethylsilyl
protons).

N,N'-Bis-[4-aminophenolphthalimido]-methylphenylsilane (2b):
Bis-[N,N-bis-(trimethylsilyl)-4-aminophenyl]-methylphenylsilane
(1b: 4.120 g, 0.0069 mol) and recrystallized phthalic anhydride
(2.060 g, 0.0139 mol) in anhydrous diglyme (55 ml) under nitrogen
were refluxed as shown in the Table, collecting 1.021 g (45%) of
hexamethyldisiloxane. The purity of this material was judged to
be ~ 95% by G.L.C. n_{eff}² = 1.3776 (Lit. reports n_{eff}² = 1.3741) as
the reaction progressed. With cooling and the addition of a small
amount of water, the dimide crystallized out of solution to give
a crude, dry product, m.p. 239–242°. Recrystallization from
pyridine/water gave pure 2b: yield: 2.39 g (61%); m.p. 255–257.5°.

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