A Novel Imide Synthesis via Silyl-Blocked Diamines

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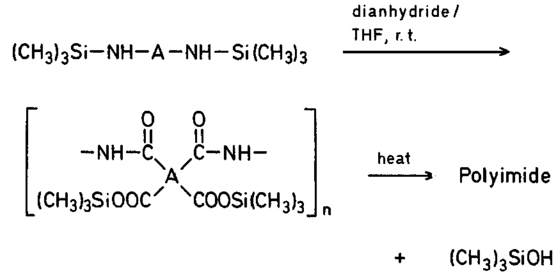
Two groups[1,2] have reported the synthesis of organosilylated polyamic acid resins from N,N'-bis-[trimethylsilyl]-diamines and their subsequent conversion to polyimides (Scheme **A**).



Scheme **A**

Tabelle. Fortsetzung von S. 223

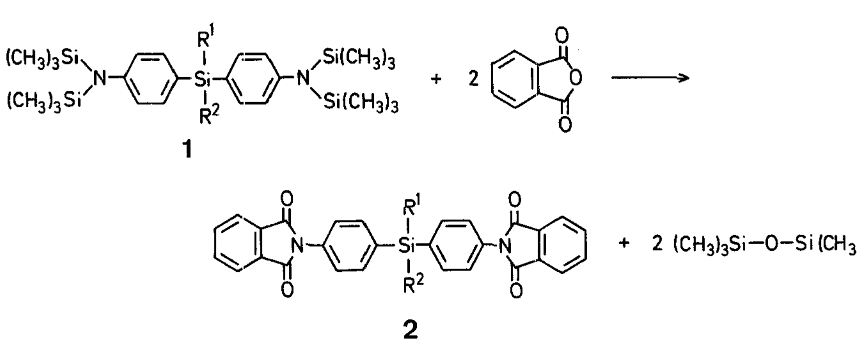
Analyse						Amide 5[b] $[\alpha]_{578}^{22}$ (C=1, Wasser)
$C_{19}H_{25}O_{10}NS$ (459.5)	ber.	C 49.67	H 5.49	N 3.05	S 6.98	+73.7
	gef.	49.62	5.38	3.07	6.83	
$C_{19}H_{24}O_{10}NSBr$ (538.4)	ber.	C 42.39	H 4.49	N 2.60	S 5.96	+67.5
	gef.	42.09	4.49	2.69	5.94	
$C_{18}H_{24}O_{10}N_2S$ (460.4)	ber.	C 46.95	H 5.25	N 6.08	S 6.96	+80.4
	gef.	46.60	5.22	6.11	7.05	
$C_{17}H_{23}O_{10}N_3S$ (461.4)	ber.	C 44.25	H 5.02	N 9.11	S 6.95	+86.2[c]
	gef.	44.08	4.99	8.99	6.75	
$C_{17}H_{27}O_{11}NS$ (453.5)	ber.	C 45.02	H 6.00	N 3.09	S 7.07	+91.7
	gef.	44.68	5.94	3.10	7.12	

[c] Umkristallisation aus 90%igen Äthanol; F: 168–169°.

$C_{11}H_{17}O_7N_3S$ (335.3)	ber.	C 39.40	H 5.11	N 12.53	S 9.56
	gef.	39.08	5.66	12.97	9.19

[d] Die optischen Drehwerte der sirupösen Verbindungen dürften mit einem geringen Fehler behaftet sein.

Efforts in these laboratories have resulted in the production of some trimethylsilyl-blocked diamines, which have been employed in a novel manner for the synthesis of polyimide model compounds. We have prepared three new silicon-containing diimides by reacting 1 mol of bis-[N,N'-bis-(trimethylsilyl)-4-aminophenyl]-disubstituted silanes[2] (**1**) with 2 mol of phthalic anhydride, thus establishing the reactivity of fully silylated diamines in imide formation (Scheme **B**).



a $R^1 = R^2 = CH_3$
b $R^1 = CH_3$, $R^2 = C_6H_5$
c $R^1 = R^2 = C_6H_5$

Scheme **B**

Polymerization of the fully silylated diamines **1** to polyimides is currently under investigation. Our feeling is that the incorporation of additional trimethylsilyl groups during polymerization will engender increased solubility to the inter-

Table. Experimental Conditions and Results of the Synthesis of Compounds **2**.

	Solvent	Reaction Conditions	Yield (%)	m. p.	Elemental Analysis			Imide	I.R.[c] (cm⁻¹) Silyl-R[1], R[2]
2a	DMF	23 hr, 124°	89[a]	235.5–238°[b]	calc.	C 71.69	H 4.41	1781[d]	1236[e]
					found	71.84	4.67	1707[d]	801[d]
2b	Diglyme	27 hr, 156–161°	61	255–257.5°[b]	calc.	C 74.45	H 4.28	1780[d]	1240, 780[d]
					found	74.57	4.22	1710[d]	700[d]
2c	DMF	24 hr, 130–141°	88[a]	314.5–317°[b]	calc.	C 76.66	H 4.18	1784[d]	692[d]
					found	76.60	4.25	1712[d]	

[a] Crude yield. [b] Uncorrected. [c] KBr pellet. [d] Broad. [e] 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-[trimethylsilyl]-4-bromoaniline (66 g, 0.209 mol) was added 2.25 *N* butyllithium (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; $n^{24} = 1.5369$. A sample was recrystallized with difficulty from pentanes, m.p. 93–95°.

$C_{31}H_{52}N_2Si_5$	calc.	C 62.77	H 8.84
(593.2)	found	62.56	8.89

I.R. (neat): $\nu_{max} = 1246, 830, 695\ cm^{-1}$; this spectrum showed no NH absorption.

^{1}H-N.M.R. (CCl_4): $\delta = 7.27$ (center of m, $13H_{arom}$), 0.84 (s, 3H, single methyl group on silicon), 0.14 ppm (s, 36H, trimethylsilyl protons).

N,N′-Bis-[4-aminophenylphthalimido]-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. $n_D^{22} = 1.3776$ (Lit. reports $n_D^{25} = 1.3741$) as the reaction progressed. With cooling and the addition of a small amount of water, the diimide 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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[2] G. Greber, D. Lohmann, *Angew. Chem.* **81**, 918 (1969); *Angew. Chem. Internat. Edit.* **8**, 899 (1969).