

Preliminary communication

THE FIRST SUCCESSFUL RING OPENING POLYMERIZATION AT THE Si–Si BOND: A NOVEL *o*-(DISILANYLENE)PHENYLENE POLYMER

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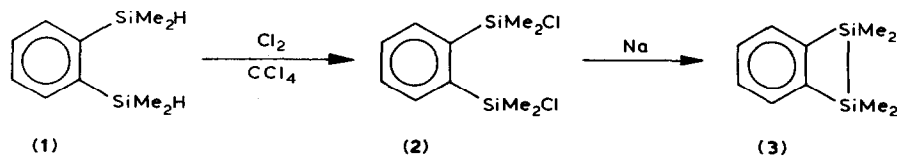
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Summary

A new type of polymer, poly[*o*-(disilanylene)phenylene] was prepared via ring opening polymerization, at the Si–Si bond, of 1,1,2,2-tetramethyl-1,2-disilabenzocyclobutene.

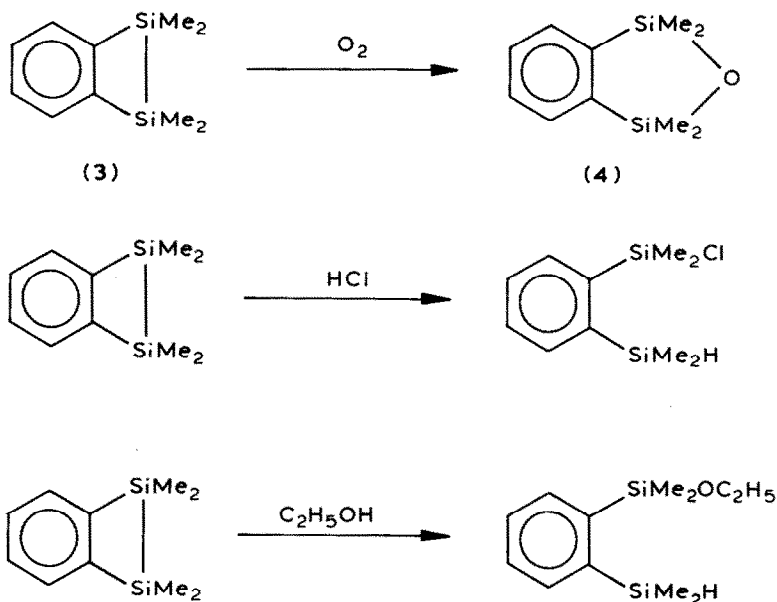
Considerable attention has recently been focused on the synthesis of polysilane polymers starting from organo-dichlorosilanes and organo-bis(chlorosilyl) compounds by condensation with sodium in toluene [1–4]. Furthermore, it is well known that the ring opening polymerization of $[\text{Me}_2\text{SiO}]_4$ and organosilicon heterocycles such as mono- and di-silacyclobutanes and silabenzocyclobutene affords silicones and polysilaalkylenes, respectively [5]. It therefore is intriguing to study a cyclic compound having a disilanylene unit in the ring system that is synthesized conveniently, stable enough to handle, and capable of ring opening polymerization. 1,1,2,2-Tetramethyl-1,2-disilabenzocyclobutene (DSBB) would be the compound of choice for this purpose.

The monomer, DSBB (3), has been prepared using 1,2-bis(dimethylsilyl)benzene (1) [6] as the starting material. Chlorination of 1 by chlorine (in CCl_4 , 0°C) to 1,2-bis(dimethylchlorosilyl)benzene (2) (92% yield), followed by treatment of 2 with molten Na in refluxing toluene gave 3 in 60–85% yield (exact mass, Found; 192.0786. $\text{C}_{10}\text{H}_{16}\text{Si}_2$ calcd.: 192.0789).



DSBB was easily isolated, almost pure from the mixture by distillation in vacuo at a temperature as low as 40°C . However, the distillate was inevitably contaminated

with small amounts of siloxane (4), and complete separation of 3 from 4 by fractional distillation was unsuccessful, due to the occurrence of polymerization in the column. In the neat state, spontaneous polymerization of DSBB began to take place within a few hours at room temperature. Also, because of its ring strain, the Si-Si bond in DSBB is extremely reactive to both nucleo- and electrophiles as well as oxygen.



These reactions proceeded quantitatively at or below room temperature, exothermically.

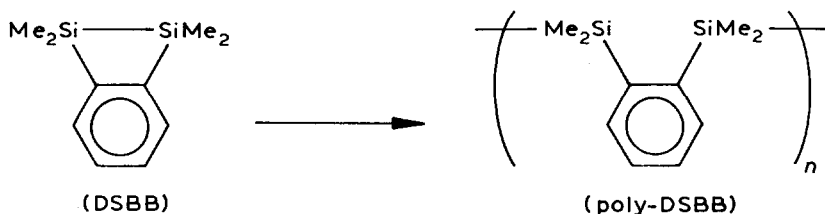
Besides the uncatalyzed polymerization, DSBB in toluene at low temperatures, was polymerized satisfactorily by a Lewis acid as catalyst, (Table 1) and gave a

TABLE 1
POLYMERIZATION OF DSBB ^a

DSBB (mol l ⁻¹)	Catalyst	(mol l ⁻¹)	Reaction conditions		Conversion (%)	\bar{M}_n^b ($\times 10^{-5}$)
			<i>T</i> (°C)	<i>t</i> (h)		
1.7×10^{-2}	BPO	(1.7×10^{-4})	60	5	2	—
1.7×10^{-2}	BPO	(8.5×10^{-4})	60	5	5	—
1.7×10^{-2}	—	—	60	5	3	—
1.5×10^{-1}	AlCl ₃	(2.5×10^{-3})	-15	120	55	1.10
1.5×10^{-1}	AlCl ₃	(2.5×10^{-3})	0	48	89	1.33
1.1×10^{-1}	AlCl ₃	(3.6×10^{-3})	30	14	100	0.56
1.5×10^{-1}	—	—	40	24	47	0.51
1.5×10^{-1}	—	—	60	48	57	3.49 ^c

^a Polymerization was carried out in a sealed tube, which was charged with a toluene solution of DSBB under N₂. ^b Determined by GPC. ^c \bar{M}_n 374,000 by membrane osmometry.

novel, high molecular weight, cotton wool-like material after precipitation from ethanol.



This transformation is a new type Si-Si redistribution [7] leading to the polymer.

Poly-DSBB is soluble in many solvents such as benzene, toluene, THF, cyclohexane, carbon tetrachloride and chloroform, and readily cast into a film, but it is insoluble in alcohols, n-hexane, and dimethylformamide. The polymer shows an intense absorption band at 257 nm (in cyclohexane).

References

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