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Preliminary communication

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

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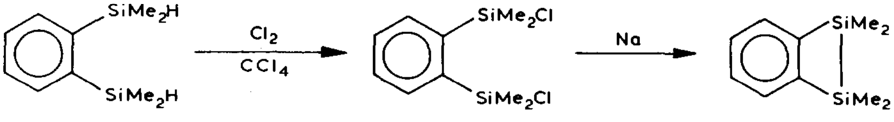
Summary

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]. Futhermore, it is well known that the ring opening polymerization of $[Me_2SiO]_4$ 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. $C_{10}H_{16}Si_2$ calcd.: 192.0789).



(1) (2) (3)

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 contaiminated

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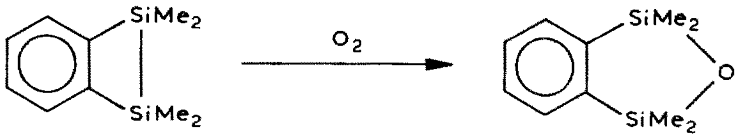
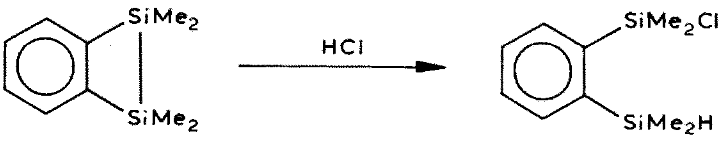
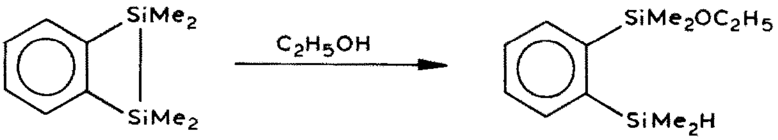
with small amounts of siloxane (**4**), and complete separation of **3** from **4** by fractional distillation was unsuccessful, due to the occurrence of polymerization in the column. In the neat state, spontaneous polymerization of DSBB began to take place within a few hours at room temperature. Also,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



(3) (4)





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

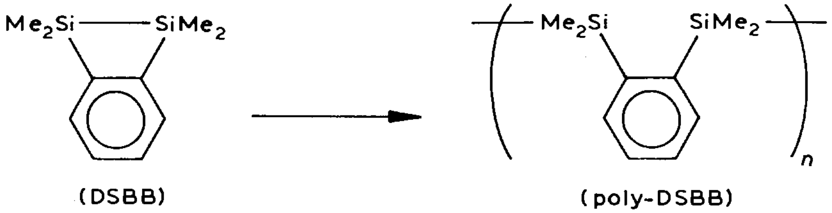
TABLE 1

POLYMERIZATION OF DSBB [a]

DSBB (mol l^{-1})	Catalyst	(mol l^{-1})	Reaction conditions T (°C)	Reaction conditions t (h)	Conversion (%)	$\overline{M}_n$ [b] ($\times 10^{-5}$)
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 N_2. [b] Determined by GPC. [c] $\overline{M}_n$ 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).

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