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Polymerization of silicon – carbon heterocycles †

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Abstract. Ring-opening polymerization methods for all known reactive silicon – carbon heterocycles are considered. The data concerning the catalytic polymerization of silicon-containing cyclic monomers published in the last 15 years are generalized. The results of investigations of polymerization mechanisms are presented, the properties of polymers are described and examples of their practical use are given. The bibliography includes 206 references.

I. Introduction

Silicon – carbon heterocycles (SCH) are cyclic compounds having (one or more) silicon heteroatoms in the ring. The silicon atoms are responsible for considerable difference of the properties of these compounds from purely carbon rings. For example, representatives of some types of SCH are reactive monomers that form heterochain organosilicon polymers (HOSP) upon ring-opening polymerization.

The views about SCH as a separate specific class of organosilicon compounds were formed in the 1960 – 1980s. A great contribution to the development of these views was made by fundamental studies of V M Vdovin and his group carried out at the N D Zelinsky Institute of Organic Chemistry of the RAS and A V Topchiev Institute of Petrochemical Synthesis of the RAS. These studies demonstrated that sila- and disilacyclobutanes are reactive monomers; upon thermal or catalytic action, they are able to produce high-molecular-mass HOSP, which possess unique physicochemical properties (see, for example, reviews [1, 2]).

Currently the interest in the chemistry of SCH, first of all, in their polymerization is rather high, judging by the number of relevant publications.

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There are several principal approaches to the synthesis of HOSP, which can be classified into two big groups. The first group includes stepwise polymerization and polycondensation processes, which are accomplished using various modifications of intermolecular hydrosilylation, various modifications of condensations involving Si – X bonds and lithium or magnesium organic compounds, metathesis and co-metathesis of dialkenylsilanes and oxidative condensation of silicon derivatives with two terminal alkynyl substituents. The second group is formed by chain polymerization reactions of various silicon – carbon heterocycles with ring opening at the Si – C bond, metathesis of silacyclopent-3-enes with ring opening at the double bond and polymerization of 1,2-disilacyclobutanes (1,2-DSCB) with ring opening at the Si – Si and Si – C bonds. This group of reactions is the subject of this review. In most cases, stepwise methods lead to polymers with relatively low molecular mass (MM). Meanwhile, chain polymerization of strained SCH (induced by some type of treatment) leads to high-molecular-mass polymers.

Unlike earlier surveying papers, this review is an attempt to consider all sorts of silicon – carbon cyclic systems capable of ring-opening polymerization. The ability of SCH of various types to undergo this polymerization is caused by two key reasons: considerable strain of the cyclic monomer molecule and the presence of the endocyclic $Si^{\delta+} - C^{\delta-}$ bond dipole. Depending on the structure of the monomer and polymerization mechanism, each of these factors plays a more or less important role.

According to the first relevant publications (see references cited in reviews [1, 2]), the rings of monosilacyclobutanes (MSCB) and 1,3-disilacyclobutanes (1,3-DSCB) are highly strained. The strain is caused by deformation of endocyclic angles (in MSCB, the endocyclic CSiC angles are reduced to 80°, and those in DSCB are reduced to 89°) and by the difference between the lengths of endo- and exocyclic Si – C bonds. Representatives of these types of compounds are stable under ambient conditions but, owing to high ring

† The review is devoted to the memory of Professor V M Vdovin (08.12.1931 – 24.04.1992).

strain energies [the polymerization enthalpies ($-\Delta H$) of MSCB and 1,3-DSCB derivatives permethylated at silicon are 83.9 and 71.5 kJ mol^{-1}, respectively [3]], they can polymerize under the action of various initiators and even thermally. The strain in benzosilacyclobutenes (BSCB) is even higher than in MSCB or DSCB and, hence, monomers of this type are much more reactive than the latter: thermal polymerization of 1,1-dimethyl-2,3-benzo-1-silacyclobutene already occurs at 60 °C.

Apart from four-membered SCH (MSCB, BSCB and 1,3- and 1,2-DSCB), this review presents polymerization data for three- and five-membered SCH and eight-membered SCH with endocyclic Si–Si and C≡C bonds.

Silametalloceno(areno)phanes represent a new type of strained cyclic silicon–carbon monomers that polymerize with ring opening at the Si–C bond. They can be polymerized using as diversified methods of catalytic or thermal treatment as are used to polymerize MSCB and DSCB. The polymers obtained from these monomers possess a broad range of important physicochemical properties and are covered by the bibliography of this review to a larger extent than other types of polymers.

Thus, the present review deals with methods of chain polymerization of SCH and some properties and applications of the resulting HOSP. The backbone of these polymers is composed of carbon and silicon atoms, the ratio and mutual arrangement of which depend on the structure of the monomers used. The syntheses and polymerization of the latter have been developed rather thoroughly; numerous works are devoted to practical applications of the polymers.

This review reflects the achievements in this field reported in the last 10–15 years.

II. Polymerization of saturated silicon–carbon heterocycles

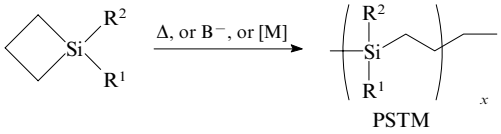
The structural features of MSCB molecules (the ratio of endo- to exocyclic CSiC angles, long endocyclic Si–C bond) facilitate the nucleophilic attack on the silicon atom; this enables the synthesis of this type of monomers with diverse substituents, in particular, with rather large groups giving rise to steric effects. Hence, it is possible to deliberately construct framing of polymer backbones and thus affect the properties of polymers. Copolymerization of MSCB with this type of monomers and with other monomers extends even more the possibilities of targeted control of the properties of the resulting polymers. A similar situation is also observed in the case of 1,3-disilacyclobutanes. The regularities of MSCB and 1,3-DSCB polymerization (except for DSCB with electron-withdrawing substituents at one silicon atom) differ rather little and similar behaviours of these monomers during polymerization initiated in different ways point to the same mechanism of the reactions. These issues have been discussed in considerable detail in the literature.[2]

MSCB and DSCB type monomers are so reactive that they can be polymerized even in the presence of relatively bulky substituents, despite the low fraction of the silacyclobutane moiety in the total bulk of the molecule. In the 1960–1990s, broad possibilities of synthesis of various types of substituted MSCB and DSCB were demonstrated, the methods of preparation of polysiltrimethylenes (PSTM) and polysilmethylenes (PSM), respectively, from them were demonstrated and the polymerization mechanisms were studied to a large extent. Rather comprehensive information on this point and some examples of practical use of PSTM and PSM can be found in a number of publications.[1, 2, 4]

1. Polymerization of monosilacyclobutanes and 1,3-disilacyclobutanes

Polymerization of MSCB can be induced either thermally or by catalysts (initiators) and occurs according to Scheme 1.

Scheme 1



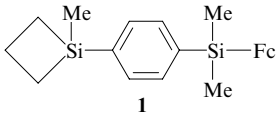
PSTM

B^- = HO^-, $AlkO^-$, *etc.*; [M] is transition metal complex

In the studies of the last 10–15 years, all previously known polymerization methods have been used, new methods or upgraded known methods have been proposed, and new MSCB were prepared and polymerized to give polymers having various, in particular, practically valuable, physicochemical properties.

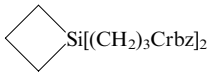
a. Thermally initiated polymerization

In order to design materials for data recording, the following monomers were synthesized:[5] 1-{4-[dimethyl(ferrocenyl)silyl]phenyl}-1-methyl-1-silacyclobutane (**1**) and 1,1-bis[3-(carbazol-9-yl)propyl]-1-silacyclobutane (**2**); thermally initiated polymerization (TIP) of these monomers was performed in toluene to give the corresponding PSTM (process temperatures were 210 and 225 °C and the yields were 71% and 64.3%, respectively).



1

Fc is ferrocenyl

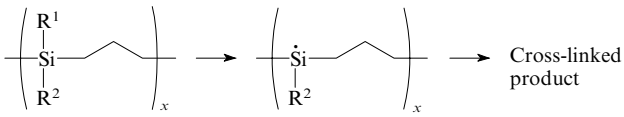


2

Crbz is carbazol-9-yl

The sensitivity of PSTM thin films prepared by TIP of 1,1-dialkyl(aryl)-1-silacyclobutanes to electron beam and UV radiation was studied.[6] It was found that the key reaction induced by radiation and resulting in the cross-linking is elimination of side groups (Scheme 2).

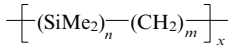
Scheme 2



R^1 = Me: R^2 = 1-Naph, Ph, $(CH_2)_3$Crbz, $(CH_2)_4$Crbz, C_6H_4OPh-4;
R^1 = R^2 = Cy, CH_2SiMe_2Ph, Ph, 1-Naph
(Cy is cyclohexyl, Naphth is naphthyl)

The radiation sensitivity of the films was found to depend on the type of substituents framing the polymer backbone and on the molecular mass of the polymer; when a 50 keV electron beam is used, the radiation sensitivity is in the range from 1.0 to 200 μC cm^{-2}.

Polikarpov *et al.*[7] studied the phase transformations of poly(dimethylsiltrimethylene) and some other Si-permethylated polymers of the general formula



$n = 1$: $m = 0, 1$; $n = 2$: $m = 1, 2$

The phase transition temperatures of these polymers were considerably different. Meanwhile, it was found[8] that temperatures of structural transitions of symmetrically substituted PSTM (R = Cy, Bn, 4-MeC_6H_4, 4-$Me_2NC_6H_4$) differ insignificantly. From comparison of the results of these two works, the predominant role of the backbone in the processes is evident.

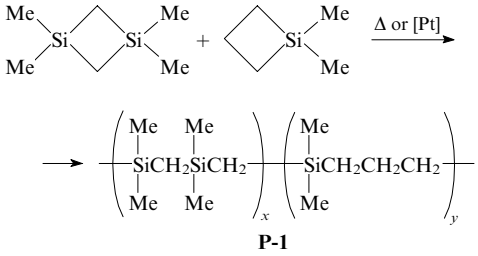
By means of TIP of some MSCB, PSTM samples were prepared to be tested as potential membrane materials able to separate hydrocarbon gases.[9] Table 1 summarizes the results of this study carried out with composite hollow-fibre membranes. Poly(dimethylsiltrimethylene) (the first row in Table 1), being an elastomer ($T_g = -75$ °C), showed high permeability and selectivity with respect to hydrocarbon gases [$\alpha(C_4/C_1) = 27.2$]. The introduction of more bulky groups, including trimethylsilylmethyl groups, induces an increase in the glass transition temperature and decrease in the permeability. The poly(dimethylsilmethylene) elastomer is also included in the Table. It demonstrated the highest permeability and the highest selectivity with respect to hydrocarbons. However, it turned out that even the sample with the highest molecular mass ($> 1.5 \times 10^6$) does not form stable films, whereas crystalline poly(dimethylsiltrimethylene) showed good film-forming behaviour with fairly high selectivity.

In parallel with the studies of gas-separating properties of this series of HOSP, an inverse gas chromatography study of the sorption of n-alkanes C_3-C_7 by dimethyl-substituted PSM and PSTM was carried out.[10] As a result, the experimental and calculated excess enthalpies of mixing (ΔH_m), indicating slight exothermicity of mixing of these two polymers with hydrocarbon sorbates ($\Delta H_m < 0$), were found. Since the gas permeability of rubbers is determined by the solubility of gases in them, Alentiev *et al.*[11] performed a temperature-modulated differential scanning calorimetry (DSC) of melting and crystallization processes in poly(dimethylsiltrimethylene) films pretreated with hexane vapour. The penetrant-induced melting of crystals in a newly formed film at ~35 °C followed by slow recrystallization, resulting in more stable crystals with melting point of ~44 °C, was found to be the principal process responsible for the considerable sorption overshoots.

In a study by Starannikova *et al.*[12] devoted to elucidation of the causes for lower permeability of partly crystalline PSTM as compared with amorphous PSM (prepared by TIP; in both cases, $R^1 = R^2 = Me$), the effect of PSTM crystallinity on the permeabilities for oxygen, nitrogen and methane was studied and the permeability was found to depend on the sample prehistory. At the melting point, the gas permeability coefficients sharply increase and the activation energies for permeability decrease.

Attempts were made[13] to eliminate the key drawback of poly(dimethylsilmethylene), namely, poor mechanical characteristics that preclude the formation of stable films. The most successful solution was copolymerization (thermally initiated or catalytic) of 1,1,3,3-tetramethyl-1,3-disilacyclobutane with 1,1-dimethyl-1-silacyclobutane, resulting in random distribution of units in copolymers **P-1**; this provides good film-forming properties, the high gas separation level being maintained (Scheme 3, Table 2).

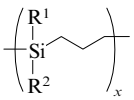
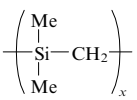
Scheme 3



P-1

The 1,3-DSCB monomers are more easily available than MSCB; therefore, the interest in polymerization of the former has shifted during the last two decades to the applied

Table 1. Physicochemical characteristics of polysiltrimethylenes and membrane properties of this type of polymers supported on hollow fibres of membranes (20 °C, pressure drop on the membrane is 1 atm).[9]

		M_w (M_w/M_n)	T_g/°C (T_m/°C)	Fibre	P/litre m^{-1} h^{-1} atm^{-1}		α	
R^1	R^2				O_2/N_2	C_4H_{10}/CH_4	O_2/N_2	C_4H_{10}/CH_4
Me	Me	1.4×10^6 (1.16)	−75 (+43)	PA	14.1/5.8	457.0/16.8	2.4	27.2
Me	CH_2SiMe_3	1.65×10^6 (1.14)	−51	PA	5.0/2.0	194.0/6.9	2.5	28.1
Me	$(CH_2)_3SiMe_3$	1.42×10^6 (1.2)	−46	PA	8.3/3.6	118.0/4.5	2.3	26.2
Me	C_6H_4Me-3	7.6×10^5 (1.44)	−25	PA	4.1/1.8	76.4/4.4	2.2	17.5
1-Naph	Cy	2.7×10^5 (2.53)	47.5	PA	4.4/1.4	7.4/6.1	3.2	1.2
		3.57×10^5 (3.43)	−92	PS	79.6/39.8	3650/94.0	2.0	38.8
		1.6×10^6 (1.13)	−92	PA	55.1/20.5	2219.0/61.4	2.7	36.1

Note. The following designations are used: T_g is the glass transition temperature, T_m is the melting point, PA is polyamide hollow fibre, PS is polysulfone hollow fibre, P is the permeability, α is the separation factor.

Table 2. Some physicochemical properties and permeability factors at 25 °C for random copolymers **P-1**.[13]

$x:y$	M_w	M_w/M_n	T_g	P/Barrer			
				CH_4	C_4H_{10}		
					$p \to 0$	$\Delta p \to 0$	$\Delta p = 0.4$
80 : 20	7.4×10^5	1.43	−83	—	—	—	—
75 : 25[a]	2.1×10^5	1.87	−79.5	113	1163	—	2340
50 : 50[b]	8.85×10^4	2.1	−76.5	90	—	753	1748

Note. 1 Barrer = 10^{-10} cm^3 (STP) cm cm^{-2} s^{-1} (cm Hg)$^{-1}$, Δp is the pressure drop before and after the membrane.
[a] The permeability was measured by mass spectrometry at a 10^{-3} Torr pressure after the membrane. [b] The permeability was measured by volumetry at a 1 atm pressure after the membrane.

field. Problems were mainly solved using catalytic polymerization method. Traditional thermal initiation of 1,1-dimethyl-1-silacyclobutane was used in the homopolymerization of poly(dimethylsilmethylene) in order to study the permeability of the resulting polymer for hydrocarbons and in the copolymerization with tetramethyl-substituted 1,3-DSCB.[9,13] The thermally induced polymerization was also used[14,15] for homo- and copolymerization of 1,3-DSCB **3a**–**c**. The process was carried out at 300 °C for monomer **3b** and at 170 °C for monomer **3c** (2 h, yield 88%).



3a–**c**

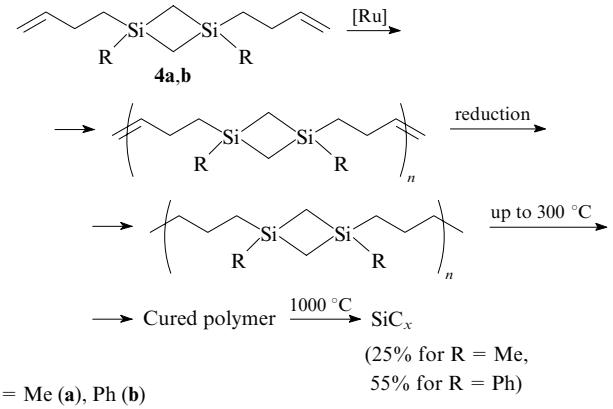
$R^1 = R^2$ = Me (**a**), Ph (**b**); R^1 = Me, R^2 = Ph (**c**)

The static and dynamic mechanical properties of poly(methylphenylsilmethylene) were studied in detail and a way of control over their molecular mass upon thermal initiation by adding specified amounts of trimethylchlorosilane into the reaction mixture was developed.[14,15] Whereas the TIP of monomer **3c** at 230 °C without addition of Me_3SiCl gave a polymer with $M_w = 2.64 \times 10^6$ ($M_w/M_n = 4.1$) in a 75% yield, the Me_3SiCl : **3c** ratios of 0.08, 0.37 and 3.9 resulted in 79%, 81% and 55% yields and the polymer M_w values were 6.48×10^5 ($M_w/M_n = 4.1$), 2.69×10^5 ($M_w/M_n = 2.1$) and 9.0×10^4 ($M_w/M_n = 2.0$), respectively. In the same study, thermal copolymerization of monomers **3b** and **3c** was performed (**3c** : **3b** ≈ 2.2 : 1, 300 °C, 5 h, yield 99%), and the resulting copolymer was insoluble in common solvents.

Thermally induced ring opening of 1,3-DSCB was used for effective cross-linking of cyclolinear polymers prepared from disilacyclobutanes **4a**,**b** by intermolecular condensation metathesis followed by reduction of double bonds (Scheme 4).[16]

A study of the thermal behaviour of saturated cyclolinear polymers with disilacyclobutane moieties in the backbone demonstrated that above the glass transition temperature (R = Me, T_g = −65 °C; R = Ph, T_g = −5 °C), the DSC curves show exothermic effects caused by heat evolution arising from the ring-opening (for

Scheme 4



R = Me (**a**), Ph (**b**)

R = Me, in the 210–300 °C range with a maximum at 250 °C; for R = Ph, in the 220– 290 °C range). The polymers cured upon ring opening proved to be rather thermally stable under nitrogen and did not lose mass up to 470–480 °C. The subsequent heating to 1000 °C gave solid residues of silicon carbides SiC_x.

Poly(dimethylsilmethylene) proved itself as an efficient component of compositions with poly(trimethylsilylpropyne); these compositions were used to manufacture membranes for pervaporation separation of liquids.[17,18]

The comparatively rare use of the TIP of mono- and 1,3-disilacyclobutanes in the publications of the last 15 years is mainly explained by two reasons. First, to reach very high molecular masses for known polymers by TIP, very high purity of monomers is required; second, polar functional groups in new monomers can either fully prevent the TIP by blocking the active sites (for example, fluoroaryl or fluoroalkyl groups[2]) or require considerable temperature rise, which, at the best, will much reduce the polymer molecular mass, and, in the worst case, will produce cross-linked products. In this respect, catalytic polymerization is more convenient; if some type of catalyst is inapplicable due to the character of substituents in the monomers, some other types of catalyst may prove efficient.

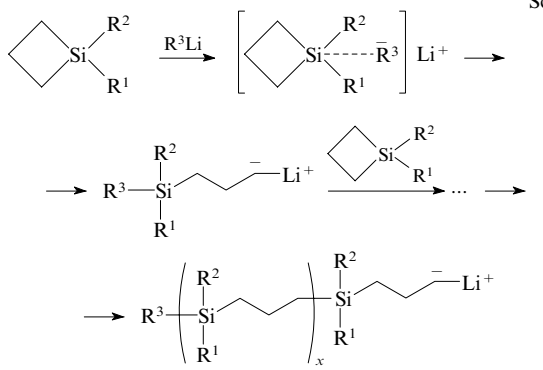
There are several options for catalytic polymerization of MSCB and 1,3-DSCB. These are anionic polymerization induced by organolithium compounds or alkalis in various solvents over a broad temperature range, catalysis by compounds of platinum and related metals, polymerization induced by π-allylic metal complexes and heterogeneous catalysis by various metal salts.

b. Anionic polymerization

It is customary to consider that ring-opening anionic polymerization induced by organolithium compounds involves the formation of a transition state with a five-coordinate Si atom; in relation to MSCB, this process is described by Scheme 5.

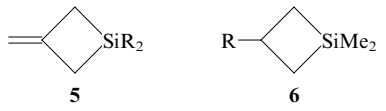
Starting with the late 1980s, low-temperature anionic polymerization at −78 °C under the action of Bu^nLi in THF, in some cases with some hexamethylphosphoramide (HMPA) added, has been used for all types of SCH capable of ring-opening polymerization. This polymerization technique has started to be widely used because low temperature decreases the rate of interactions of C–Li bonds and thus may suppress the side reactions of RLi with various functional groups (*e.g.*, Si–H, Si–CH=CH$_2$, Si–All, Si–O–Si and even Si–O–C). For monomers with alkyl

Scheme 5



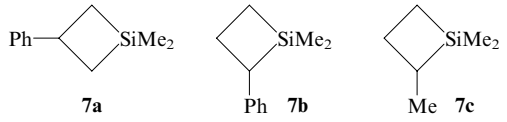
substituents (Me, Et) at silicon, the anionic polymerization follows the living chain mechanism; however, for example, phenyl-substituted monosilacyclobutane does not show in full measure the living polymerization features.[19] This method is also applicable to polymerization of 1,3-DSCB monomers and other types of monomers.

The range of monosilacyclobutane monomers that form regular polymers upon anionic polymerization was extended during the considered period of time by Japanese researchers.[20–23]



5 **6**

R = Me, Pr^n, Ph R = 1-Naph, CH_2(1-Naph), $CH_2C_6H_4$Ph-4

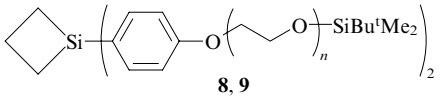


7a **7b** **7c**

The symmetrically substituted MSCB with an exocyclic methylene group at the β-carbon atom (compounds **5**) form polymers both at low temperature in THF and at ambient temperature in a non-polar medium.[20]

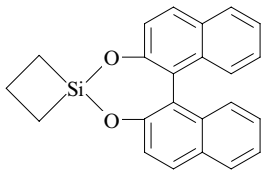
The Bu^{n}Li-initiated anionic polymerization for monomers with bulky substituents in the β-position (for example, compound **6**) occurs efficiently without any complications.[21] A study of the behaviour under conditions of low-temperature anionic polymerization of two isomeric C-phenyl-substituted monomers **7a**,**b** showed[22] that β-phenyl-substituted isomer **7a** demonstrated all regular features inherent in living polymerization, including the further growth of the molecular mass upon introduction of a fresh portion of the monomer ($M_w/M_n = 1.09$). Meanwhile, monomer **7b** with α-phenyl substituent did not show living chain polymerization behaviour. The same study confirmed the above-noted conclusion[19] about complication of the anionic polymerization of 1-methyl-1-phenyl-1-silacyclobutane by attack of the nucleophile on the Si–Ph bond and, hence, polymerization is not living. Unlike α-phenyl-substituted MSCB **7b**, monomer **7c** with α-methyl substituent polymerizes showing all features of a living process.[23] In relation to compound **7c**, the researchers demonstrated the selectivity of anionic polymerization initiated by phenyllithium as compared with platinum catalysis:[23] the anionic process involves exclusively the Si–CH_2 bond (1,4-insertion), while catalysis by platinum compounds leads to equivalent opening of both bonds, Si–CH_2 and Si–CHMe (1,4- and 1,2-insertion, respectively); this was proved by experiments with a deuterated chain-terminating agent.

The use of the *tert*-butyldimethylsilyl protecting group (instead of the usual trimethylsilyl group) in monomers **8** and **9** ensured stability of the protection upon contact with Bu^{n}Li in THF and allowed researchers to prepare stable soluble high-molecular-mass polysiltrimethylenes with oxyethylene groups.[24] Upon removal of the silyl protecting group, the isolated amphiphilic polysiltrimethylenes containing two terminal hydroxyl groups in the side chain of each unit proved to be soluble in methanol and ethanol.



8, **9**

n = 1 (**8**), 3 (**9**)

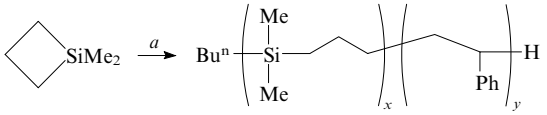


10

Jain *et al.*,[25] who synthesized racemic monomer **10** with a planar heterocycle configuration, had to refer to the anionic polymerization as the platinum-based catalysts they used [Karstedt catalyst and cycloocta-1,5-diene (cod) platinum complex] proved to be inefficient. It should be emphasized that effective polymerization was performed in this case at room temperature and without HMPA or tetramethylethylenediamine (TMEDA).

Copolymerization of two different MSCB or an MSCB with a monomer of a different type capable of anionic polymerization in polar or non-polar medium catalyzed by alkyllithium results in most cases in random copolymers. The successive polymerization (addition of the second comonomer after the first monomer has polymerized) is suitable for preparing various block copolymers. The silacyclobutane components were symmetrically and unsymmetrically substituted derivatives, while styrene, butadiene, isoprene, 2,4-dimethylstyrene and so on were used as comonomers of other types.[26] Scheme 6 illustrates block copolymerization of 1,1-dimethyl-1-silacyclobutane with styrene under conditions favourable for living chain formation (THF : hexane = 1 : 1 by volume, −48 °C).[19]

Scheme 6



(*a*) 1) Bu^{n}Li, THF–C_6H_{14}, −48 °C; 2) CH_2=CHPh; 3) MeOH

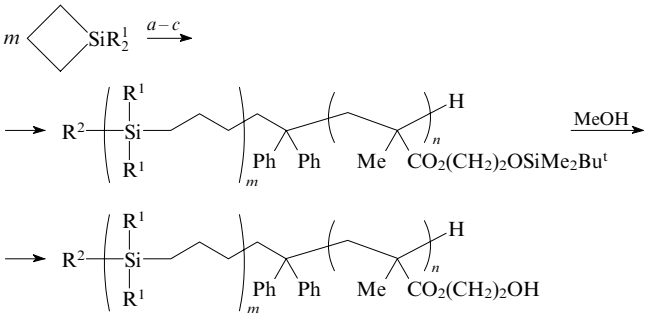
1,1-Diethyl-1-silacyclobutane was used with success as the first comonomer forming living chains. It was used to obtain block copolymers with styrene and its derivatives with alkyl and silyl methacrylates.[19,27]

Attention is drawn by the possibility to prepare block copolymer of compound **5** (R = Me) with styrene both at low temperature (Bu^{n}Li, THF–hexane, −78 °C) and under ambient conditions (Bu^{s}Li, benzene, 25 °C).[27] The low-

temperature method results in a quantitative yield of the block copolymer ($M_n = 4.1 \times 10^3$, $M_w/M_n = 1.49$). At 25 °C, block copolymer ($M_n = 4.0 \times 10^3$, $M_w/M_n = 1.21$) is also formed in a nearly quantitative yield but with a minor admixture of styrene homopolymer.

When block copolymerization involving MSCB monomers is carried out for a period of time sufficient for the initiator (for example, Bu^nLi) to be completely consumed, the active sites are also deactivated to give stable allylic carbanions, which gives rise to homopolymers of the first comonomer in the reaction mixture. This can be avoided by adding rapidly reacting 1,1-diphenylethylene immediately after the reaction of the silacyclobutane monomer with RLi; this additive does not polymerize itself but only forms a more stable carbanion, which efficiently polymerizes more reactive monomers.[28] The copolymer thus formed consists of the polysiltrimethylene and polyvinyl blocks separated by one unit formed from 1,1-diphenylethylene (Scheme 7). The use of the presented succession of stages and subsequent removal of the silyl protection for R^1 = Et and R^2 = Ph led to amphiphilic block copolymer [27,29] able to form monolayes at the air–water interface. The properties of these layers were studied by X-ray reflectometry.[30] Later,[31,32] the synthesis of amphiphilic diblock copolymers from 2-(*tert*-butyldimethylsiloxy)ethyl methacrylate was performed by a similar approach for silacyclobutanes with R^1 = Me, Et, Bu^n using Bu^nLi as the initiator (see Scheme 7).

Scheme 7

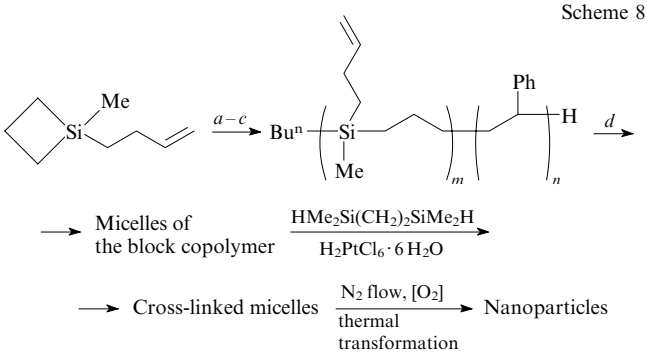


R^1 = Me, Et, Bu^n; R^2 = Bu^n, Ph; (*a*) R^2Li, THF–C_6H_{14}, −48 °C; (*b*) $CH_2{=}CPh_2$; *c* — *n* $CH_2{=}CMeCO_2(CH_2)_2OSiMe_2Bu^t$

Study of the anionic polymerization of 1,1-dimethyl-1-silacyclobutane induced by Bu^sLi in various solvents (hexane, THF, Et_2O, hexane–THF, hexane–TMEDA, cyclohexane–TMEDA, toluene–TMEDA, benzene–TMEDA) and crystallizaton of the polymer are the subjects of a publication by Kawahara *et al.*[33] The polymer with the highest molecular mass was found to form in the hexane–TMEDA system, and the molecular mass can be increased by adding a new portion of the monomer or by adding a comonomer (*tert*-butoxystyrene), which affords block copolymer. The resulting polymer, as was indicated, has a regular heat-to-tail configuration and a high degree of crystallinity.

Matsumoto and Matsuoko[34] synthesized 1-butenyl-1-methyl-1-silacyclobutane, which was subjected to low-temperature anionic polymerization (initiated by Bu^nLi) in THF to give the homopolymer; also block copolymers with styrene were obtained at different ratios of the comonomer units in the blocks (MSCB : styrene = 31 : 16, 54 : 30, 75 : 28). After formation of block copolymer micelles in the selective solvent (dimethylformamide), internal cross-linking at terminal double bonds of the butenyl substituent was carried out by hydrosilylation with 1,2-bis(dimethylsilyl)-ethane in the presence of $H_2PtCl_6 \cdot 6H_2O$. The subsequent heat treatment of the cross-linked micelles yielded nanoparticles (Scheme 8).

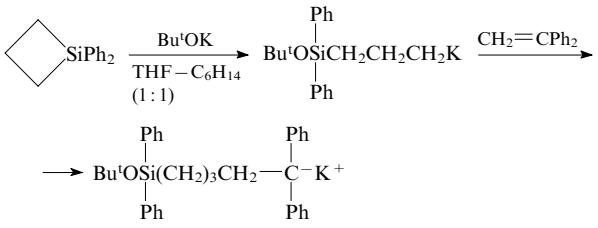
Scheme 8



(*a*) Bu^nLi, THF, −55 °C; (*b*) $CH_2{=}CHPh$, THF, −55 °C; (*c*) MeOH, H_2O; (*d*) selective solvent

The idea of using 1,1-diphenylethylene for preparing block copolymers of MSCB with other types of monomers under the action of Bu^nLi was further developed in the studies dealing with anionic polymerization of various monomers by means of alkali metal alkoxides. This may be accompanied by a considerable contribution of the transformation of the $\equiv Si(CH_2)_3^-$ carbanion formed upon MSCB opening into allylic carbanions stabilized by the neighbouring silicon atom (after potassium hydride elimination and metallation into the allylic position). To prevent this transformation, the reaction of AlkOK with MSCB was carried out in the presence of 1,1-diphenylethylene. By using a four-fold excess of the latter, it is possible to reach a 97% yield of the organopotassium initiator. 1,1-Diphenylethylene actively undergoes nucleophilic addition to the γ-potassium–propyl bond, which has formed upon MSCB ring opening. This leads to a carbanion, more stable than $\equiv Si-(CH_2)_3^-$, which is quite able to initiate polymerization of vinyl monomers (Scheme 9).[35]

Scheme 9



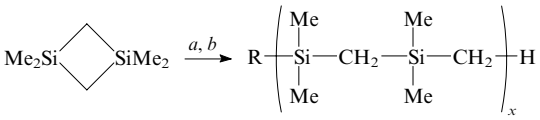
Thus, MSCB reacts rather slowly with potassium alkoxide, replenishing all the while the content of $Bu^tOSiPh_2(CH_2)_3^-K^+$ ion pairs, which rapidly react with $CH_2{=}CPh_2$. Thus, MSCB acts as a pump that supplies primary carbanions into the reaction mixture. This silacyclobutane pump system (carbanion pump) was used to prepare various di- and triblock copolymers.[36,37] A comparative evaluation of two carbanion pump systems based on 1,1-dimethylsilacyclobutane, one involving 1,1-diphenylethylene and the other with α-methylstyrene, was reported.[36]

Despite the fact that 1,3-DSCB adds nucleophiles (hydroxides, alkoxides, potassium and sodium silanolates)

much less efficiently, polymerization of these monomers occurs at moderate temperatures, although slowly (see the bibliography of the reviews [2, 3]). Polar solvents enhance alkoxide catalysis. The process is activated by adding cryptands,[38, 39] although in this case, too, it is rather slow. Therefore, the molecular masses of the polysilmethylenes (as also polysiltrimethylenes) thus formed are substantially lower than with other polymerization techniques.

The low-temperature anionic polymerization of 1,1,3,3-tetramethyl-1,3-disilacyclobutane on treatment with lithium alkyls in the presence of HMPA proved to be quite effective.[40]

Scheme 10



R = Bu^n, Ph, Me_3SiCH_2; (*a*) RLi, THF–HMPA, −78 or −93 °C; (*b*) H_2O

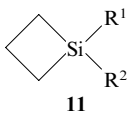
This polymerization was initiated by various RLi at monomer : RLi = 20. The polymer with R = Bu^n had the lowest molecular mass; for R = Ph and Me_3SiCH_2Li, the MM was somewhat higher, although M_n did not exceed 8000. The monomer does not polymerize without HMPA; moreover, the addition of TMEDA also does not produce any effect. A similar situation was observed when $(Me_3Si)_2CHLi$ was used; this is not surprising, as the CH–Li bond is stabilized by two silicon atoms in the α-positions.

c. Polymerization catalyzed by platinum compounds

Platinum group metal compounds are the most versatile catalysts for polymerization of silacyclobutanes, as they are active with respect to all monomers of this type. Often, catalysis for platinum compounds is the only possible way to polymerize some MSCB or 1,3-DSCB monomers.[2, 3] Quite a few papers devoted to application of this method for polymerization of various MSCB and 1,3-DSCB have been published during the considered period.

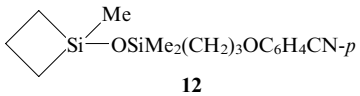
Using the Speier catalyst, polysiltrimethylenes were successfully prepared from monomers with fluorine-containing substituents [1-(3-trifluoromethylphenyl)- and 1-pentafluorophenyl-1-methyl-1-silacyclobutanes].[5]

The platinum complex with divinyltetramethyldisiloxane $Pt_2[VinMe_2SiOSiMe_2Vin]_3$ (TDDP, Vin is vinyl) known as the Karstedt catalyst proved to be very active. Using this catalyst, soluble polymers were obtained from trimethylsiloxy and triphenylsiloxy derivatives of 1-silacyclobutane **11**,[41] 1-silacyclobutanes **12**–**14** with mesogenic groups (MG) connected to the endocyclic Si atoms by various bridges [42] and from 1-methyl-1-phenylethynyl-1-silacyclobutane (**15**).[43]

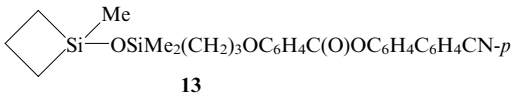


11

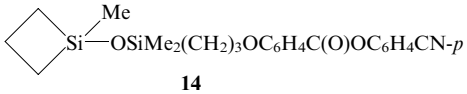
R^1 = Me, R^2 = $OSiPh_3$;
R^1 = Ph: R^2 = $OSiMe_3$, $OSiPh_3$



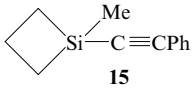
12



13



14



15

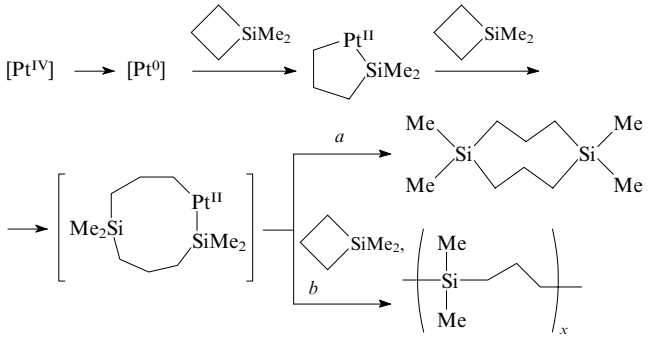
For the last monomer, control of the molecular mass of the resulting polysiltrimethylenes by metered introduction of Et_3SiH was found to be possible.

At 60 °C during 6 h, polymerization of 1-methyl-1-phenylethynyl-1-silacyclobutane in toluene in the presence of the Karstedt complex gives polymers with M_n in the range of 3.9×10^4–6.8×10^4, M_w/M_n = 1.8–2.0 in 50%–60% yields. The metered addition of triethylsilane to the reaction mixture under the same conditions allows one to control the MM of polymers. As the monomer : Et_3SiH molar ratio increases from ~2 : 1 to ~90 : 1, the M_n of the polymers increases from 500 to 58 000. When the monomer : Et_3SiH ratio changes from 2 : 1 to 10 : 1, the yield of polymers with a terminal triethylsilyl group (~40%) is lower than without hydrosilane. Nevertheless, the problem of controlling the MM of polysiltrimethylenes produced by polymerization of MSCB catalyzed by platinum compounds can be considered as solved. As shown below, this method proved to be also efficient for the preparation of polymers with desired MM by polymerization of 2,3-benzo-1-silacyclobut-2-enes.

Rhodium complexes were reported [42] to be inert in the polymerization of MSCB having a nitrile group under conditions that ensure polymerization on Pt-containing catalysts.

In relation to the polymerization of 1,1-dimethyl-1-silacyclobutane in the presence of platinum complexes, the process details were studied and a mechanism for the process was proposed (Scheme 11).[44]

Scheme 11



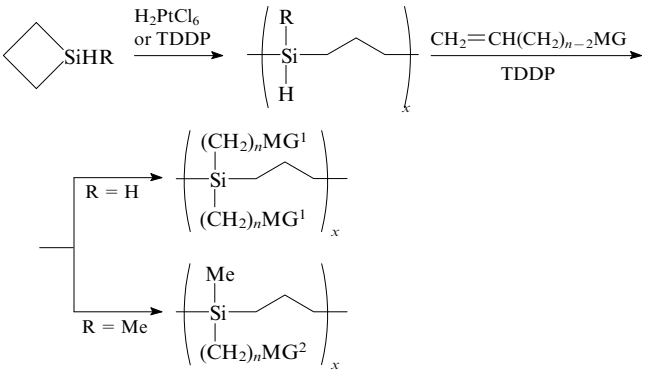
(*a*) Pt complex with P-ligands, (*b*) Pt complex without P-ligands

According to this mechanism, the catalyst based on reduced platinum reacts with the monomer molecule to give a five-membered intermediate, which in turn reacts with the next monomer molecule (by adding to the Si–C bond and elimination or by a four-centre reaction between the Si–C and Pt–Si bonds). This leads to nine-membered Pt-containing intermediate ring. The latter may undergo reductive elimination to give a stable dimer, as occurs under the action of the platinum phosphine complex. Without phosphine ligands [for example, for $Pt(cod)_2$], the approach

of the monomer to the platinum centre is probably substantially easier; this allows the monomer to efficiently react with the platinacyclic intermediate to give the polymer.

Polysiltrimethylenes with Si–H bonds were prepared[45] by polymerization of mono- and dihydro MSCB in the presence of the Speier and Karstedt catalysts. The introduction of the resulting polymers into hydrosilylation at the terminal double bonds of compounds containing alkenyl substituents connected to mesogenic groups afforded liquid-crystalline comb-like polysiltrimethylenes (Scheme 12).

Scheme 12



R = H, Me;

MG^1 = O–C$_6$H$_4$–CH=CH–C$_6$H$_4$–CN, n = 11;

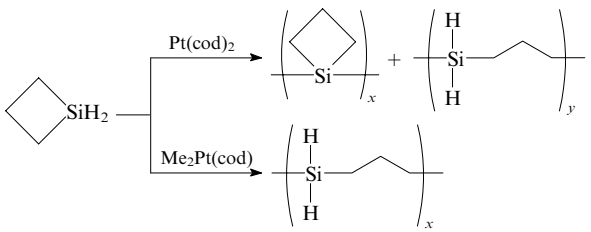
MG^2 = O–C$_6$H$_4$–C(O)O–C$_6$H$_4$–OMe: n = 5, 8;

MG^2 = O–C$_6$H$_4$–C(O)OChol, n = 8 (Chol is cholesteryl)

In the same study, a similar route was used to prepare a polymer from 1,3-dimethyl-1,3-disilacyclobutane and the corresponding mesogen-containing polysilmethylenes from this polymer. Since H_2PtCl_6 and the Karstedt complex are active catalysts for ring-opening polymerization of four-membered SCH and hydrosilylation, Ganicz *et al.*[45] proposed synthesizing comb-like liquid-crystalline PSTM and PSM by combining polymerization of mono- and dihydro MSCB and 1,3-DSCB derivatives with hydrosilylation; this enables the one-pot introduction of substituents comprising both a spacer and a mesogenic group.

A study of dehydrocondensation polymerization of cyclic and open-chain dihydrosilanes[46] showed that MSCB polymerizes in the presence of $Pt(cod)_2$ to give a mixture of two types of polymers, those with intact and opened heterocycle, whereas $Me_2Pt(cod)$ catalyzes only ring opening to give PSTM (Scheme 13).

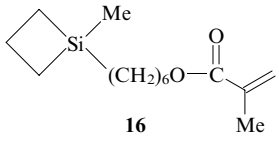
Scheme 13



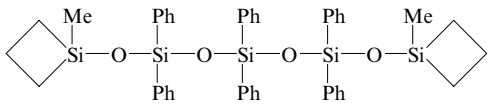
By now, the ring opening polymerization process of SCH performed by platinum compounds has been advanced, new catalyst systems have been developed and polymerization procedures have been elaborated. This concerns polymerization of monomers of the MSCB series and, to a larger extent, of the 1,3-DSCB series.

A new approach has been used to polymerize 1,3-DSCB,[47] namely, photoactivation of platinum compounds that are otherwise inactive, for example, $Pt(acac)_2$ (acac is acetylacetonate) has been carried out. The catalyst, together with the monomer, was UV irradiated for 15 min, and after that, the reaction occurred in the dark at room temperature.

Oligo(methylsilmethylenes) were successfully cured to ceramic precursors by photocatalysis [exposure of platinum bis(β-diketonates) to visible light in the presence of tetravinylsilane].[48] If $Pt(acac)_2$ is introduced in methacrylate **16** with a methylsilacyclobutane moiety and the radical polymerization at the multiple bond is carried out, it turns out that the subsequent photoactivation of $Pt(acac)_2$ present in the solid polymer film makes it a very efficient catalyst for opening of MSCB rings framed by a polymethacrylate chain, and this provides the possibility of effective curing of the film material to obtain high-quality reversed images.[49]



16



17

The synthesis of thermoset oligodiphenylsiloxanes **17** functionalized by silacyclobutane groups was reported.[50] It was found that the curing temperature can be reduced to 110 °C by adding the Karstedt catalyst or to 110–150 °C by adding copper acetylacetonate. The polydiphenylsiloxane exhibited a set of properties that made it applicable as a special coating for copper surfaces.

Poly(methylchlorosilmethylene) prepared by polymerization of 1,3-dichloro-1,3-dimethyl-1,3-disilacyclobutane over the Speier catalyst at 80–90 °C or over $(C_6H_8)_2Pt_2Cl_4$ at room temperature was converted to a series of PSM with various functional groups at silicon (*e.g.*, OCH_2CF_3, OEt, Ac).[51] These groups were used for further transformations or cross-linking.

Crystalline PSM symmetrically substituted by two long-chain n-alkyl groups $(n\text{-}Alk_2SiCH_2)_x$ were found[52,53] to exhibit, during melting, an unusual first-order transition preceding the transition to an isotropic melt, *i.e.*, mesomorphic properties were noted. This is in line with the data on polysiloxanes having analogous alkyl substituents $(n\text{-}Alk_2SiO)_x$.[54] An analogous behaviour was noted for polysilanes $(n\text{-}Alk_2Si)_x$ (Ref. 55) and polyphosphazenes.[56] The symmetrical di-n-alkyl-substiuted crystalline PSM obtained in the presence of the Speier catalyst a year later[57] had low glass transition temperatures:

Alk	Bu^n	n-C_5H_{11}	n-C_6H_{13}
T_g/°C	−30	−55	−56

(for Alk = n-C_5H_{11}, T_g = −41 °C was reported [58]). However, melting of these polymers was accompanied by feebly pronounced phase transitions prior to the formation of the isotropic melt.

A large review is devoted to the chemistry and prospects for the use of polycarbosilanes as ceramic precursors.[59] After it had been published, several experimental works related to this subject appeared.

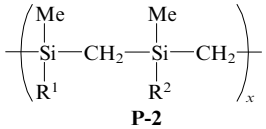
Polymerization of appropriate 1,3-DSCB catalyzed by H_2PtCl_6 gave silicon-functionalized polysilmethylenes such as $[Si(OCH_2CF_3)_2CH_2]_x$, $[Si(OCH_2CF_3)MeCH_2]_x$, $[Si(OEt)MeCH_2]_x$ and $[Si(OEt)_2CH_2]_x$.[60,61] On treatment with a H_2O–HCl mixture in ethanol, the last-mentioned compound forms siloxane bridges, which induces formation of a gel. Its pyrolysis yields silicon oxycarbides (SiO_xC_y) — amorphous ceramic materials, which can be considered as hybrids of SiO_2 and SiC. In a similar way, poly(diethoxysilmethylene) was converted to silicon oxycarbides using the Karstedt catalyst.[62] High thermal stability of the oxysilicon carbide glasses obtained in this way was demonstrated.[63] Using platinum catalysts, a number of new polycarbosilanes were synthesized from polysilmethylene $(SiH_2CH_2)_x$.[64]

The use of poly(methylsilmethylene) for the preparation of poly(methylorganylsilmethylenes) $[RSiMeCH_2]_x$ [R = Alk, Et_2N, Crbz, $MeO(CH_2CH_2O)_2$] by means of hydrosilylation on the Karstedt catalyst was considered.[65,66] Linear and hyperbranched polysilmethylenes are proposed [67] as the synthetic platform for the design of new functional polymer materials.

The hard-to-access 3,3-dimethyl-1,1-diphenyl-1,3-disilacyclobutane was synthesized (the yield of the pure compound was 32%).[68] Bulk polymerization (100 °C) and polymerization in toluene (4–50 °C) of this product in the presence of the Speier catalyst dissolved in dimethoxyethane furnished poly(dimethyldiphenylsilmethylene). Its properties were studied in detail and compared with the properties of other polysilmethylenes; in particular, the following series of glass transition temperatures of various silmethylene polymers was reported:

Polymer	T_g/°C	Polymer	T_g/°C
$(SiMe_2CH_2)_x$	−87	$(SiMe_2CH_2SiPh_2CH_2)_x$	50
$(SiMe_2CH_2SiMePhCH_2)_x$	−35	$(SiPh_2)_x$	140
$(SiMePh)_x$	−28		

The synthesized 1,3-dimethyl-1,3-diphenyl- and 1-*p*-anisyl-1,3-dimethyl-3-dimethylamino-1,3-disilacyclobutanes were converted, in the presence of the same catalyst, to the corresponding polysilmethylenes, which served as the basis for a wide range of functional polysilmethylenes **P-2**.[69]



P-2

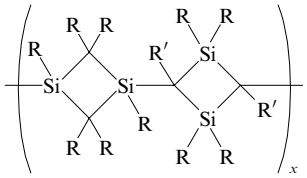
$R^1 = R^2$ = All, Vin, C≡CH, NMe_2, OMe, OTf; R^1 = Ph, R^2 = OTf

Cycloocta-1,5-diene(dichloro)dirhodium and bis(triphenylphosphino)dichloroplatinum proved to efficiently catalyze polymerization of 1,3-dimethyl-1,3-diphenyl-1,3-disilacyclobutane [15] giving the corresponding polysilmethylene.

Catalyst	Solvent	T/°C	Time/h	Yield (%)	M_w
[Rh]	PhMe	45	45	69	3.47×10^5
[Pt]	THF	80	24	77	$\sim 8.2 \times 10^4$

Shen and Interrante [70] synthesized 1-methyl-1,3,3-triethoxy- and 1,1,3-trichloro-3-(trichlorosilyl)methyl-1,3-disilacyclobutanes and accomplished H_2PtCl_6-catalyzed polymerization of these monomers and tetrachloro- and tetraethoxydisilacyclobutanes and copolymerization of the first two of the listed monomers. The structural characteristics of the resulting PSM were studied. 1,3-Dicyano-1,3-dimethyl- and 1,1,3,3-tetracyano-1,3-disilacyclobutanes synthesized by Lienhard *et al.*[71] failed to polymerize upon many-hour contact with $(C_6H_{10})_2Pt_2Cl_4$ at 120 °C.[71] The corresponding polycyanomethyl- and polydicyanosilmethylenes were prepared by polymer-analogous replacement of chlorine atom by CN group on treatment of polychloromethyl- and polydichlorosilmethylene with a 50% excess of trimethylsilyl cyanide.

Of particular interest are photoluminesent poly(disilacyclobutanes) prepared by reactions of RLi (mainly Bu^tLi) with dichlorodivinylcarbosilanes; these are cyclolinear structures in which the endocyclic silicon atoms of one ring are linked to the endocyclic carbon atoms of another ring.



R = Alk; R′ = H, Alk

The ways of synthesis of these polymers were described in patents.[72–74] Their cross-linking upon ring opening may give different (depending on the type of side groups) precursors of silicon carbide or silicon oxycarbide materials.

One more type of insertion of 1,3-DSCB rings in the backbone composed of alternating disilacyclobutane rings and *trans*-stilbene units was implemented [75] by metathesis polycondensation of 1,3-dimethyl-1,3-bis(*p*-styryl)-1,3-disilacyclobutane catalyzed by the second-generation Grubbs ruthenium catalyst. After thermal or photochemical cross-linking, films of this cyclolinear polymer exhibit photoluminescence not inferior in intensity to the initial non-cross-linked films.

Polysilmethylenes prepared from 1,3-DSCB with Si–H bonds are extensively covered by patents. These PSM were employed to synthesize silicon carbide precursors for the design of semiconductor multilayer microchips.[76,77] The use of polymers made of these silacyclobutane derivatives for the preparation of thermally stable dielectric multilayer ceramic coatings was patented.[78]

Cross-linked polycarbosilanes thermally stable up to 450 °C were formed based on polysilmethylenes obtained from DSCB. Study of their properties demonstrated good prospects of these polymers as interlayer dielectrics needed for the development of new technologies.[79] Polysilmethylenes with various substituents, in particular, with Si–H

bonds are effective, after curing, as silicon carbide precursors for the formation of ceramic composite silicon carbide nanomaterials.[80,81]

d. Other polymerization methods

The methods of MSCB and DSCB polymerization by heterogeneous catalysts (Ag, Cu, Bi halides, *etc.*) or homogeneous π-allyl nickel complexes studied in the 1960s–1970s (see references cited in reviews[1–3]) have not been very popular for the last 15 years. During this period, only Ogawa[14] used CuCl for homopolymerization of 1,3-dimethyl-1,3-diphenyl-1,3-disilacyclobutane (xylene, 140 °C, 17 h, yield 80%, $M_w = 3.5 \times 10^4$), for its copolymerization with 1,1,3,3-tetramethyl-1,3-disilacyclobutane (the first to second monomer ratio 2.15 : 1, xylene, 140 °C, 5 h, yield 88%, $M_w = 1.24 \times 10^5$) and for block copolymerization of these monomers (3.73 mmol of the first monomer, 1.2 ml of xylene, 140 °C, 6 h; then addition of 1.71 mmol of the second monomer and 5 ml of xylene, 140 °C, 15 h, yield 95%, $M_w = 4.6 \times 10^4$). Copper compounds combined with radical initiators were used for the *in situ* preparation of binary blends of homopolymers with block or graft copolymers by heating 1,1,3,3-tetramethyl-1,3-disilacyclobutane and preliminarily prepared poly(methylphenylsilmethylene) in xylene.[82,83]

Other methods have also been used to polymerize silacyclobutanes. Laser-driven decomposition of silaspiroheptane and silaspirooctane,[84] owing to the presence of a silacyclobutane component in the spiro system, leads to elimination of ethylene to give silaethylene, which efficiently polymerizes yielding a material potentially suitable for the production of silicon carbides. Laser UV photolysis of 1,3-DSCB in oxygen was used to deposit nanosized polyoxycarbosilane films on surfaces from the gas phase.[85] It was found[86] that exposure of 1,3-DSCB to laser IR radiation results in thickening of the arising silaethylene ($SiH_2{=}CH_2$) and gives polycarbosilane, while the same treatment of 1,3-DSCB in the presence of CS_2 gives a copolymer, polythiacarbosilane.

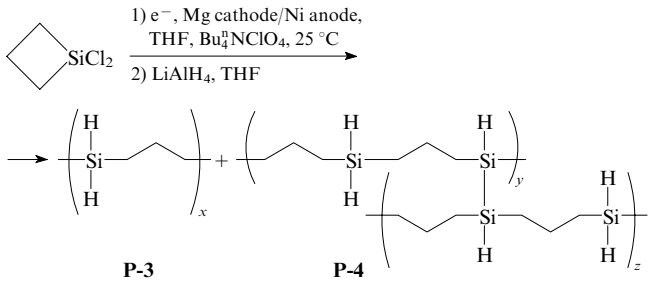
An attempt was made[87] to obtain PSM by telomerization of tetramethyl-1,3-disilacyclobutane with hydrosilanes in the presence of photoactivated $Pt(acac)_2$; however, the reaction afforded only dimers.

Poly(diphenylsilmethylene) thin films cannot be prepared by traditional methods, as this polymer is insoluble in common solvents and melts at high temperature (~350 °C). Therefore, a method for preparing thin films from this polymer by using particles of ultrapure metal (Pt, Pt/Pd, Au, Cu and Ag) catalysts sputtered on the monomer film is being developed.[88] The properties of the prepared $(SiPh_2CH_2)_x$ thin films were studied;[89] it was shown that sustainable lifetimes on exposure to visible light and laser UV radiation are the same as the lifetimes of stable films synthesized by TIP. The considered method was upgraded[90,91] by conducting polymerization of 1,1,3,3-tetraphenyl-1,3-disilacyclobutane directly on the substrate where a polymer layer was to be deposited. In a dedicated high-vacuum apparatus, the monomer film was bombarded by nanoparticles obtained by laser ablation of metals (Pt, Cu or Ag). The particles penetrated the monomer; after that, the monomer was heated to 280 °C for 10 min. Owing to the catalytic action of metallic nanoparticles, short-term heating resulted in the formation of the polymer film. The highest efficiency was found for platinum, while copper and silver were less active.

Plasma-induced polymerization of silacyclobutane for the production of hydrofluorosilicon oxycarbide (HFSiOC)[92] and hydrosilicon oxycarbide (HSiOC)[93] films with low dielectric constants used in the manufacture of semiconductors was patented.

Finally, polycarbosilane ceramic precursors were prepared by electropolymerization of 1,1-dichloro-1-silacyclobutane[94] carried out under nitrogen in an electrochemical cell in THF in the presence of $Bu^n_4NClO_4$ (0.02 mol litre^{-1}) as the supporting electrolyte for 33.5 h at a direct current of 40 mA and a current density of ~1.0 mA cm^{-2} (Scheme 14).

Scheme 14



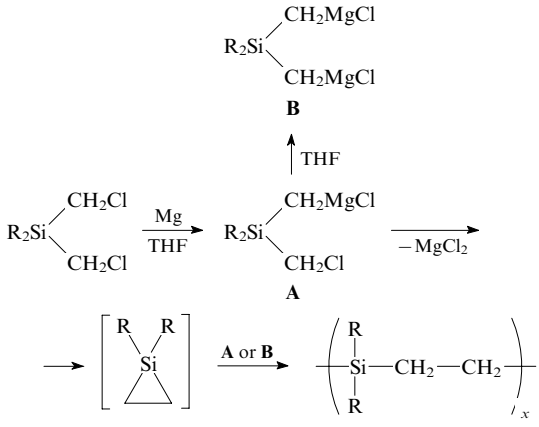
After completion of the polymerization, the mixture was treated with $LiAlH_4$ to replace the Si–Cl bonds in the polymer by Si–H bonds. The soluble fraction (yield 48.8%) was a sticky light-yellow polymer (**P-3**) with $M_n \approx 5760$. The insoluble fraction (yield 42%) was a white solid (**P-4**).

2. Polymerization of silacyclopropanes

In 1972, Seyferth and Lambert‡ demonstrated the possibility of preparing stable silacyclopropanes by their kinetic stabilization achieved by introducing bulky shielding substituents to both ring carbon atoms. However, focused investigation of the polymerization of silacyclopropanes was started less than 15 years ago.

The reaction of bis(chloromethyl)diorganylsilanes with magnesium resulted[95] in the generation of intermediate 1,1-diorganyl-1-silacyclopropane, which is converted, upon the nucleophilic attack by mono- or dimagnesium (chloromagnesiummethylsilyl) organic compound to a carbanion that propagates the polymerization (Scheme 15).

Scheme 15



R = Me, All, Bn, Ph

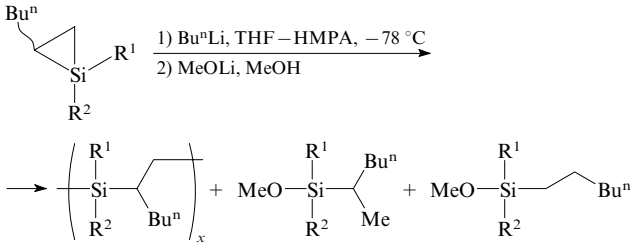
For polysildimethylenes with R = Me, All, the yields were 46% and 34%, $M_w = 3.4 \times 10^3$ and 6.2×10^2,

‡ See R L Lambert Jr, D Seyferth *J. Am. Chem. Soc.* **94** 9246 (1972).

$M_n = 2.4 \times 10^3$ and 4.2×10^2, respectively. In relation to polysildimethylene with R = Ph, the polymer yield was demonstrated to depend on the reaction time. As the reaction time increased from 0.5 to 1 h, the yield of poly(diphenylsildimethylene) increased from 69% to 83%. Further increase in the reaction time to 2–8 h did not cause increase in the yield any longer.

The synthesis and low-temperature anionic polymerization of individual 2-n-butyl-1-*sec*-butyl-1-*tert*-butyl- and 2-n-butyl-1-*tert*-butyl-1-isobutyl-1-silacyclopropanes was reported.[96] At −78 °C in THF with HMPA admixture and at the ratio Bu^nLi : monomer = 1 : 10, these silacyclopropanes form the corresponding polysildimethylenes with conversions of 85% and 84% and M_n of 890 and 940, respectively. A decrease in the Bu^nLi : monomer ratio to 1 : 20 increases M_n to 1.2×10^3 but the conversion thus decreases to 60%. The authors found that performing polymerization in the presence of lithium methoxide with some methanol added produces both the polymer and monomer products of opening of three-membered SCH with the methoxy group at silicon (Scheme 16). By analyzing the mixture of these methoxy derivatives, it was clarified which of the two endocyclic Si–C bonds of the silacyclopropane ring is cleaved under the action of nucleophiles. Cleavage of the bond between the silicon atom and the carbon atom in position 3 was found to be preferred (see Scheme 16). This result is natural, as the primary carbanion formed upon 1,3-cleavage is more stable than the secondary carbanion formed upon 1,2-cleavage.

Scheme 16



$R^1 = Bu^t$, $R^2 = Bu^s$; $R^1 = Bu^i$, $R^2 = Bu^t$

Other polymerization methods were also tested for the silacyclopropanes listed above.[96] The radical polymerization in the presence of benzoyl peroxide resulted in the polymer with $M_n = 910$ and $M_w/M_n = 1.95$. However, the Speier catalyst proved inefficient at 60 °C, the reaction yielding only monomeric ring-opening products having hex-1- or 1-methylpent-1-yl substituent at silicon, which were generated upon β-hydride elimination from the platinum complex with the monomer. An interesting feature of the obtained polysildimethylenes is high hydrophobicity, which is not only much higher than that of poly(dimethylsiltrimethylene) or polypropylene but even approaches the hydrophobicity of polytetrafluoroethylene.

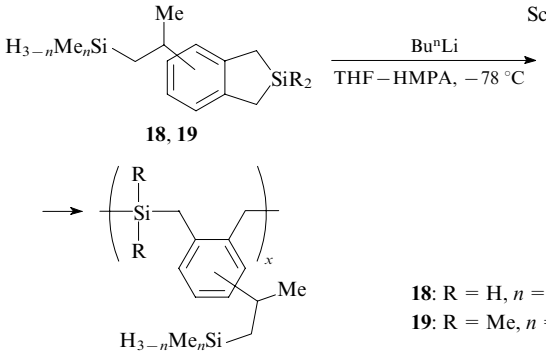
III. Polymerization of unsaturated silicon–carbon heterocycles

Silacarbocycles with sp^2-hybridized endocyclic carbon atoms are much more reactive than silacycloalkanes, in particular, towards ring-opening polymerization. The reason is not only the possibility that some reactions involve multiple bonds (as in the case of silacycloalkenes) but also higher strain and some specific properties of silicon-alkenes. For example, an allylic position of the sp^2-hybridized system in the ring relative to the heteroatom weakens the endocyclic $Si-C_{allyl}$ (or $Si-C_{benzyl}$) bond. This enables polymerization opening of five-membered silacarbocycles to give high-molecular-mass compounds.

1. Polymerization of 3,4-benzo-1-silacyclopent-3-enes (silaindans) and 2,3-benzo-1-silacyclobut-2-enes

In the late 1980s–early 1990s, low-temperature anionic (on lithium compounds) polymerization accompanied by ring opening at the $Si-C_{benzyl}$ bonds was shown to proceed for various 3,4-benzo-1-silacyclopent-3-enes, in particular, those with Si–H bonds. The publications of this period have been considered in detail in a review.[2] The subsequent investigation of the polymerization of 3,4-benzo-1-silacyclopent-3-enes with Si–H bonds was aimed at the preparation of monomers and polymers with a larger number of Si–H bonds in the molecule. Park *et al.*[97,98] synthesized monomers of this type (**18** and **19**) and performed their low-temperature polymerization with Bu^nLi in the THF–HMPA system (Scheme 17).

Scheme 17



Monomer	Polymer yield (%)	M_w	M_n
18	48	9.2×10^2	5.3×10^2
19	60	3.4×10^3	2.4×10^3

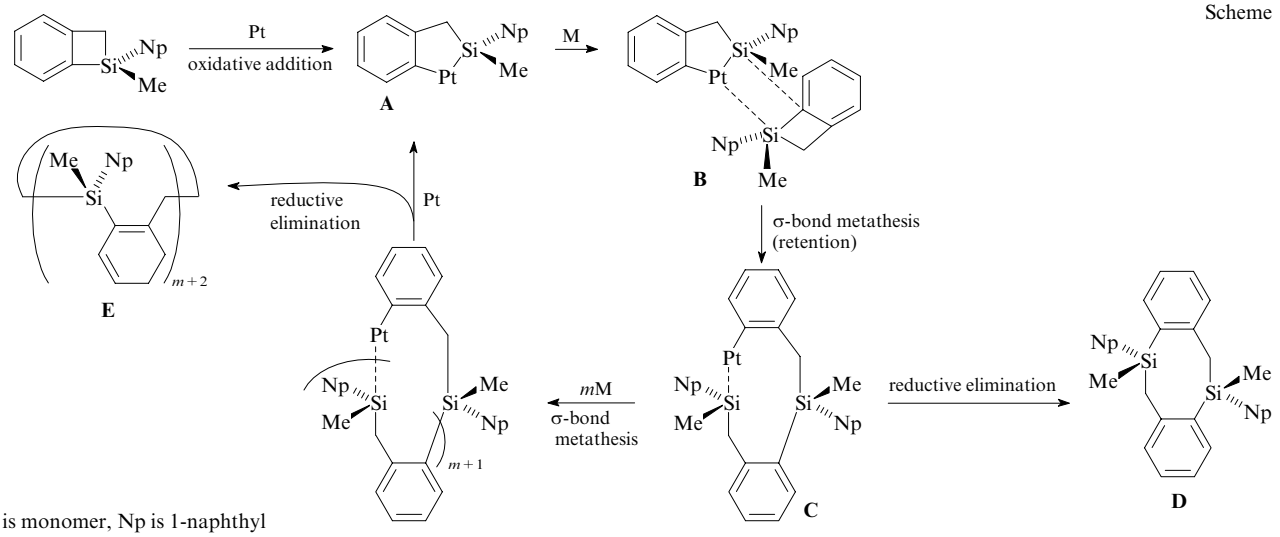
The synthesis of polycarbosilanes from these monomers was targeted to increase the content of silicon and decrease the content of carbon in the product, which is desirable for the formation of precursors of silicon carbide and ceramic materials. Homopolymers of such silaindans and their random and block copolymers with analogous monomers and 1-silacyclopent-3-enes were described in patents devoted to the development of photocured precursors of industrial ceramics and ceramic fibres[99] and design of the equipment for curing and ceramization processes for polymers of this type.[100]

While turning to 2,3-benzo-1-silacyclobut-2-enes, it should be noted that monomers of this type are not quite readily available. Nevertheless, their polymerization induced by anionic initiators (RLi) and catalyzed by platinum was studied in the considered period of time.

a. Anionic polymerization of benzosilacyclobutenes

The key regularities of living anionic polymerization catalyzed by lithium compounds can be observed at low-temperature polymerization of 1-methyl-1-(1-naphthyl)-2,3-benzo-

Scheme 18



M is monomer, Np is 1-naphthyl

1-silacyclobut-2-ene.[101] It was shown that the molecular mass of the polymer (for a $\geqslant 90\%$ yield) grows with increase in the monomer : initiator ratio not only in the case of initiation by n-butyllithium (C-anion) but also in the case of $Ph_2MeSiLi$ initiation (Si-anion). At -78 °C in THF, the highest MM values ($M_w > 5.0 \times 10^4$) and yields of $\geqslant 90\%$ are achieved in 5 min. The addition of a portion of fresh monomer after the first portion has polymerized induces further polymerization to give a polymer with higher MM and more narrow molecular-mass distribution (MMD).

In relation to racemic 1-naphthyl-containing monomer, the regioselectivity of ring opening in the reactions with excess Bu^nLi and with $Ph_2MeSiLi$ was studied. Regiospecificity ($>99\%$) and the possibility of effective control over the polymer MM were found. By examining the ^1H NMR spectra of poly(1-methyl-1-naphthyl-2,3-benzosilacyclobutenes), it was possible to determine the quantitative ratio of different triads in the polymers obtained upon chain propagation on carbanionic and silanionic sites. It was found that in both cases, atactic polymers with a ratio of isotactic, heterotactic and syndiotactic segments of $\sim 25 : 50 : 25$ are formed. It turned out that the polymers obtained from optically active (+)-monomer with Bu^nLi and $Ph_2MeSiLi$ initiation are also optically active and have the same sign of optical rotation but much lower stereoregularity compared with the polymers prepared from the racemic monomer.

b. Polymerization catalyzed by platinum compounds

A comprehensive study [102] of the catalytic polymerization of 1-methyl-1-(1-naphthyl)-2,3-benzo-1-silacyclobut-2-ene solved some problems set in earlier works. This concerns the mechanism of platinum catalysis and the possibility to control the MM of the resulting polymers. In this respect, 1-methyl-1-(1-naphthyl)-2,3-benzo-1-silacyclobut-2-ene used as the investigation object was a good choice.

First, it was found that MM may by controlled by varying the amount of the telogen added (Et_3SiH) rather than by varying the monomer : catalyst ratio. Second, it was shown in this study that the use of optically pure (+)-monomer affords also optically pure polymer with the opposite sign of rotation ($[\alpha]_D^{28} = -33.5$). Third, the dimer formed as a minor product upon polymerization of pure (without controlling additives) monomer is cyclic.

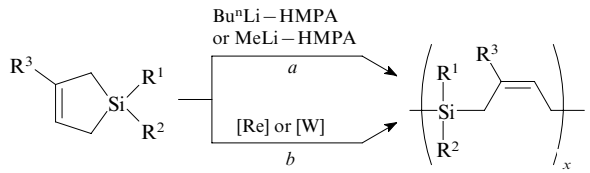
On the basis of the foregoing, the authors proposed the mechanism of polymerization of 1-methyl-1-(1-naphthyl)-2,3-benzo-1-silacyclobut-2-ene catalyzed by platinum compounds, which implies the formation of cyclic macromolecules (Scheme 18). According to this mechanism, the first step is the oxidative addition of the catalyst accompanied by the cleavage of the four-membered ring of the monomer at the $Si-C_{aryl}$ bond to give 3,4-benzo-1-sila-2-platinacyclopent-3-ene (**A**). Then this five-membered ring containing platinum and silicon atoms reacts with the monomer molecule to give four-centre coordination complex **B**, which undergoes σ-bond metathesis to be converted to nine-membered ring system **C** consisting of two monomer molecules with opened four-membered rings and a platinum atom. The subsequent repeating coordination and σ-bond metathesis steps upon reactions with monomer molecules result in polymer chain growth. Chain termination (both upon the formation of dimer **D** and proper chain termination) is realized within this mechanism as reductive elimination of platinum to give cyclic dimer **D** and ring macromolecule **E**.

For concluding the brief consideration of the study cited,[102] note that using the Karstedt catalyst gave a polymer with high MM values ($M_n = 1.21 \times 10^6$, $M_w/M_n = 1.77$).

2. Polymerization of 1-silacyclopent-3-enes

Unlike silaindans possessing only one function for polymerization-induced ring opening (the $Si-C_{benzyl}$ bond), 1-silacyclopent-3-enes can not only undergo anionic ring-opening polymerization at the Si–C allylic bond but can also form polymers upon ring opening at the endocyclic double bond *via* olefin metathesis reaction catalyzed by transition metal compounds (Scheme 19).

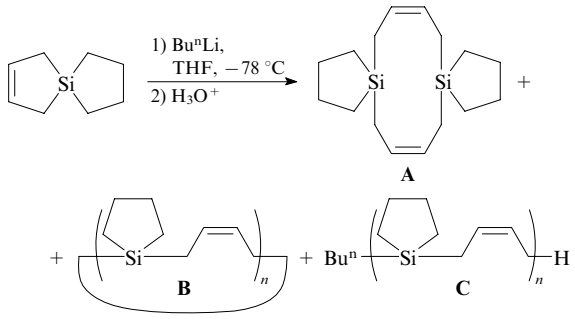
Scheme 19



(*a*) R^3 = H: $R^1 = R^2$ = Me, Vin, Ph; R^1 = Me, R^2 = H; R^1 = Ph: R^2 = H, Me, Vin; $R^1 = R^2 = R^3$ = Me;
(*b*) R^3 = H: $R^1 = R^2$ = Me, Ph

All of 1-silacyclopent-3-enes with various substituents synthesized in the late 1980s–early 1990s were successfully used as monomers for homopolymerization and as comonomers for random and block copolymerization with similar monomers and with 3,4-benzosilacyclopent-3-enes.[99, 100, 103, 104] The goal of these works was to develop silicon carbide ceramic materials for various purposes. The advances made along this line were reflected in a number of publications.[2, 81, 105] In particular, it was found that upon low-temperature anion treatment (Bu^nLi, THF–HMPA, −78 °C), spiro compounds comprising at least one silacyclopentene ring with an unsubstituted double bond form different products depending on the pattern of substitution in the other five-membered ring of the spiro system, either soluble high-molecular-mass polymers with a mixed cyclolinear backbone, a mixture of the cyclolinear polymer with the dimer, or only the dimer. 5-Sila-spiro[4.4]non-2-ene[106] comprising silacyclopentene and silacyclopentane moieties, prepared by the reaction of tetramethylenedimagnesium bromide with 1,1-dichloro-1-silacyclopent-3-ene, tended to form cyclic dimer (**A**) and low-molecular-mass oligomer (**B**+**C**) under the same conditions but without addition of HMPA (Scheme 20). Moreover, it was found that this oligomer consists of a number of mainly cyclic macromolecules **B**. The number of linear molecules of oligomer **C** with the same degree of polymerization is lower by more than an order of magnitude. This prompts an idea that closure of two alkyl substituents in a silacyclopent-3-ene molecule to a five-membered ring, *i.e.*, the formation of the spiro system of 5-silaspiro[4.4]non-2-ene, makes these monomers inclined to terminate the chain in the Bu^nLi-catalyzed polymerization *via* elimination of Bu^n Li to give cyclic macromolecules. This is promoted by low temperature, which substantially decreases the rates of other possible chain termination reactions. This might be attributable to hypervalence bonding of silicon in the five-coordinate transition complex.

Scheme 20



Whereas anionic low-temperature polymerization of 1,1-dimethyl-1-silacyclopent-3-ene provides rather high MM of the polymer and the metathesis polymerization of the same monomer results in molecular masses not exceeding 5.5×10^3, in the case of 1,1-diphenyl-1-silacyclopent-3-ene, conversely, it is metathesis that furnishes a polymer with higher molecular mass. The fact that silacyclopentene cannot be converted to a high-molecular-mass polymer using various homogeneous and heterogeneous metathesis catalysts was attributed to the existence of a monomer–polymer equilibrium. The thermodynamics of metathesis polymerization of 1,1-dimethyl-1-silacyclopent-3-ene and the thermodynamic properties of the resulting polymer were studied.[107] The polymerization enthalpy and entropy were found to be negative at temperatures below 340 K, the upper limiting temperature of this process being 291 K.

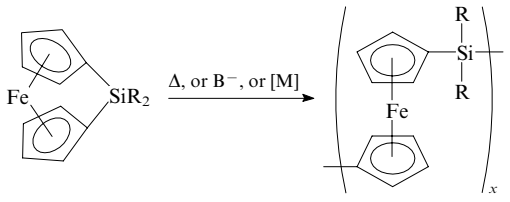
The possibility of ring-opening anionic polymerization of 1,1-dimethyl-1-silacyclobut-2-ene, resulting in polymers with low MM, was demonstrated.[108] Polymers with silacyclobutene moieties prepared from functional derivatives of silacyclobutene monomers are known; these monomers are synthesized by [2+2]-cycloaddition of silaethylene generated *in situ* with acetylene derivatives. The silacyclobutene moieties are responsible for luminescence properties of these polymers.[72, 109, 110] A number of polymers of this type, as well as monomers, were patented as photoluminescence materials.[72, 109]

3. Polymerization of silametalloceno(areno)phanes

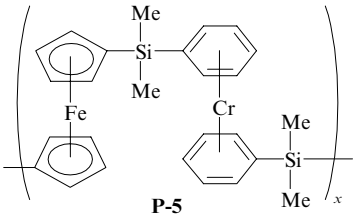
Of considerable interest for studies of ring-opening polymerization and for the preparation of promising polymeric materials with attractive physicochemical properties are [1]silametalloareno- and [1]silametallocenophane systems — heteroannular derivatives of arene and cene structures with bridges containing one silicon (germanium or tin) atoms between the rings. All known structures of this type — [1]sila(germa,stanna)metalloareno(ceno)phanes (ferroceno-, chromareno-, vanadareno- and the like) have distorted bond angles at the bridging silicon (germanium, tin) atoms and non-parallel planes of aromatic ligands, which causes strain of the whole cyclophane system. For example, in dimethyl- and dihydro[1]silaferrocenophanes, the angles between the planes of the cyclopentadienyl rings are 20.8° and 19.1°, respectively;[111] in diphenyl-, dimethyl[1]silachromarenophanes, bis(phenyl[1]silavanadarenophane) and trimethylene[1]silavanadarenophane, the angles between the planes of the arene ligands are 14.4° and 16.6° (Ref. 112), 20.8° (Ref. 113) and 19.9° (Ref. 114), respectively.

The [1]silaferrocenophane system is so strained that it is susceptible for all versions of ring-opening polymerization characteristic of silacyclobutanes, including thermal initiation. Although the poly(ferrocenylenesilanes) have been known since the 1960s (oligomeric products obtained by polycondensation methods), it was not until 1992 that thermal polymerization of [1]silaferrocenophanes was reported.[115] The resulting polymers had M_w from 5.0×10^5 to 2.0×10^6. Subsequently, anionic polymerization[116, 117] and polymerization catalyzed by transition metal compounds[118, 119] were reported for [1]silaferrocenophanes (Scheme 21).

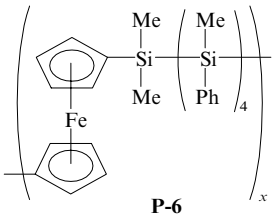
Scheme 21



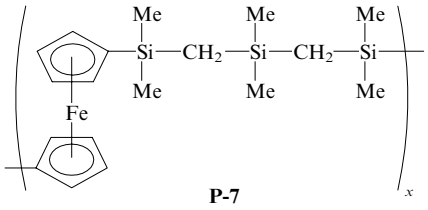
By thermal initiation, it is possible to obtain both homopolymers from dihydro- and dimethyl[1]silaferrocenophanes (the glass transition temperatures are 16 and 33 °C, respectively) and random copolymers.[111] The polymerization of dimethyl[1]silaferrocenophane and its germanium analogue induced by various Pt and Pd complexes at room



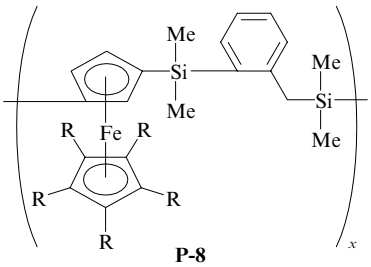
P-5



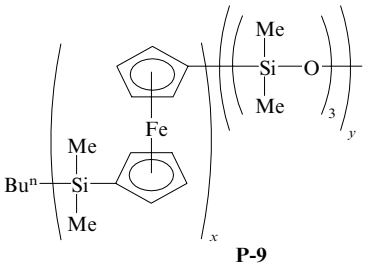
P-6



P-7



P-8



P-9

temperature and their random copolymerization were reported.[119]

Unlike dimethyl[1]silaferrocenophane, which readily forms high-molecular-mass polymers upon thermal (130 °C) and anionic initiation, dimethyl[1]silachromarenophane does not form even a dimer under these conditions. However, the TIP method proved suitable for copolymerization of dimethyl[1]silaferrocenophane with dimethyl[1]silachromarenophane or with cyclic monomer of a different type, cyclotetrasilane.[112, 120] This gave random copolymers **P-5** and **P-6**. The difference between the behaviours of dimethyl[1]silachromarenophane and dimethyl[1]silaferrocenophane was attributed[112] to lower energy of the Cr–arene bond ($\sim$170 kJ mol^{-1}) compared to the Fe–Cp bond ($\sim$220 kJ mol^{-1}) (Cp is cyclopentadienyl). Pudelski and Manners[121] argued for a heterolytic nature of the TIP of [1]silaferrocenophanes.

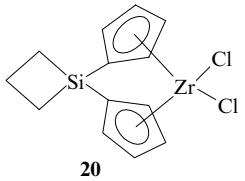
By using platinum catalysts, it is possible to copolymerize sila[1]ferrocenophanes with mono- and disilacyclobutanes to give random copolymers,[122] for example, copolymer **P-7**.

The copolymerization of 1,1-dimethyl-2,3-benzo-1-silacyclobut-2-ene with symmetric dimethyl[1]ferrocenophane[121] and with unsymmetric dimethyl[1]silaferrocenophane with one cyclopentadienyl ring being unsubstituted and the other ring being methyl-substituted at the rest four carbon atoms[123] (copolymer **P-8**) was carried out using $PtCl_2$ or $Pt(cod)_2$ (toluene, 25 °C). Symmetric ferrocenophane afforded random copolymers (yield 60%) with $M_w = 2.5 \times 10^4$ and 1.6×10^4, $M_n = 1.7 \times 10^4$ and 9.0×10^3 at comonomer ratios of 1 : 1 and 1 : 2, respectively. Copolymerization of an equimolar mixture of unsymmetric ferrocenophane and benzosilacyclobutene in the presence of $\sim$1% of Pt catalyst at 25 °C affords random block copolymer **P-8** with $M_n = 2.4 \times 10^4$ and unimodal MMD ($M_w/M_n = 2.3$). The copolymer has two glass transition temperatures (66 and 147 °C). Homopolymers of these monomers have $T_g = 48$ and 158 °C, respectively. Obviously, in this copolymer, the blocks are arranged randomly but their length is sufficient for the existence of independent glass transition temperatures. However, the length of these segments still does not apparently suffice for macromolecules to pack into crystalline entities and, therefore, the copolymer is amorphous. Finally, block copolymers **P-9** of dimethyl[1]ferrocenophanes and hexamethylcyclotrisiloxane were prepared by building-up of the latter onto the terminal carbanion of living chains formed by treatment of silaferrocenophanes with Bu^nLi.[124]

Despite the fact that in stanna[1]ferrocenophane with *tert*-butyl[125] and bulky mesityl[126] and 2,4,6-triisopropylphenyl[127] substituents at the bridging tin atoms, the angles between the planes of the cyclopentadienyl rings are only 14.0 and 14.7°, respectively, and the Sn–Cp bond lengths (2.209, 2.180 Å) and the Fe–Sn distances (2.994 Å) are rather long, the strain of these rings is sufficient for their thermal polymerization. Apparently, sharp acceleration of the polymerization and decrease in the polymerization temperature of stanna[1]ferrocenophanes upon the addition of polar nucleophilic compounds (for example, pyridine, amines), discovered by Jäkle *et al.*,[126] who named this phenomenon 'nucleophilic assistance', is related to the specific behaviour of tin and the Sn–C bond. The amine coordination to the Sn atom results in the formation of a five-coordinate complex in which the nucleophilicity of the C_{Cp} atom linked to the Sn atom is increased, although no carbanion is formed. This enables the attack of the Sn atom of another monomer molecule on this carbon atom followed by the formation of the Sn–C bond and chain propagation. Later the same polymerization mechanism was proposed in another work.[128]

Chloromethyl-, β-chloroethyl- and γ-chloropropylmethyl[1]ferrocenophanes synthesized by Power-Billard *et al.*[129] polymerize both under the action of $PtCl_2$ and upon thermal initiation; however, only γ-chloropropyl substituents in the polymer proved to be able to quaternize 4-dimethylaminopyridine in (DMF) solution to give water-soluble polymeric pyridinium salt (yield 57%).

A peculiar behaviour under the action of the Karstedt catalyst was displayed by spiro system **20**:[130] the dichlorozirconocene moiety of the spiro system was retained, polymerization being accompanied by silacyclobutane ring opening to give polycarbosilane $[(CH_2)_3Si(\eta^5\text{-}C_5H_4)_2.\ .ZrCl_2]_x$.



20

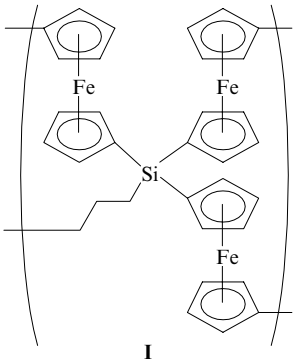
Thermal polymerization and polymerization initiated by transition metal compounds of [1]silaferrocenophanes with Si–Cl bonds were described [131] as routes to poly(ferrocenylenesilanes) of a specified structure. Treatment of these monomers with Bu^nLi gives first monomeric butyl derivatives, and the excess of butyllithium initiates the polymer chain growth by the anionic scheme to give the corresponding poly(ferrocenylenesilane) with butyl substituents.

The behaviour of the polymerization of [1]ferrocenophanes with bridging silicon atoms was investigated and a heterogeneous mechanism of their Pt-catalyzed ring-opening polymerization was proposed.[132] According to this mechanism, $Pt(cod)_2$ is inserted at the Si–Cp bond of [1]silaferrocenophane with the loss of one cod ligand (oxidative addition) to give [2]platinasilaferrocenophane. The reductive elimination of the initial monomer molecule and cod ligand from this product results in colloidal platinum, which serves as the catalyst, which oxidatively adds to the monomer and propagates the chain.

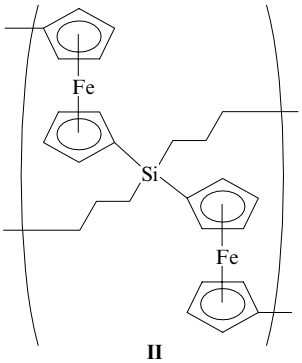
The potential of anionic polymerization of dimethyl[1]-silaferrocenophane induced by butyl-, phenyl- or ferrocenyllithium and multiblock copolymerization of this monomer with styrene and hexamethylcyclotrisiloxane was studied.[133] On heating at 180 °C, dimethyl[1]silachromarenophane decomposes, whereas at lower temperature the reaction does not proceed; however, this monomer copolymerizes with dimethyl[1]silaferrocenophane at 140 °C.[112, 121] Copolymer is also formed upon anionic polymerization of these comonomers.

Dimethylsila[1]ferrocenophane and spirocyclic [1]ferrocenophane with the silacyclobutane ring as the second component of the spiro system were embedded into ordered hexagonal channels of mesoporous silica gel. The fact that thermal polymerization of these monomers occurred inside the silica gel pores was established by DSC.[134] The subsequent pyrolysis (900 °C, under N_2) inside the pores furnished superparamagnetic ceramic nanocomposites.

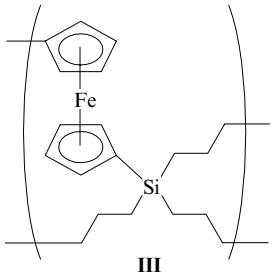
From the practical standpoint, the studies of polyferrocenylenesilanes mainly refer to the area of ceramic production. Magnetic ceramics were obtained from metal-containing polymeric networks synthesized by polymerization of metal-containing organosilicon monomers — dimethylsila[1]ferrocenophane and spirane composed of sila[1]ferrocenophane and silacyclobutane ring, the spirane being used for cross-linking. The cross-linking produces all three possible types of binding (**I**, **II**, **III**). This yields shaped ceramics with controlled magnetic properties.[135, 136]



I



II



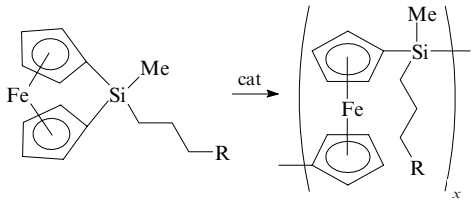
III

A study of poly(dimethylsila[1]ferrocenophane) as a material used for the solution of technical problems that require plasma etching has shown that it is approximately 50 times more stable than polyisoprene under conditions of ionic etching with oxygen and tetrafluorocarbon plasma.[137]

The photooxidation and photoconductivity of thin polyferrocenylenesilane films were studied. Upon irradiation of films cast from a chloroform solution of poly(methylphenylsila[1]ferrocenophane), photooxidation of the ferrocene sites in the backbone of this compound takes place. The degree of oxidation of the polymer (from 0% to 5%) can be controlled by varying the irradiation time and chloroform concentration. The photooxidized product has a higher conductivity than the initial polymer before irradiation. Polymers with methylated cyclopentadienyl rings form much more stable materials.[138]

Polymerization of γ-methyl(phenyl)amino-, γ-4-methoxyphenyl- and γ-carbazol-9-ylpropyl(methyl)sila[1]ferrocenophanes catalyzed by transition metal compounds resulted in the formation of polyferrocenylenesilanes (Scheme 22) and their charge transfer complexes (CTC) with iodine and tetracyanoethylene.[139] The molecular masses of these polymers (M_w) do not exceed 1.1×10^5.

Scheme 22



R = NMePh, 4-$MeOC_6H_4$, Crbz;
cat is a transition metal compound

R	M_w	M_w/M_n	T_g/°C	$T_{5\%}$/°C
NMePh	9.1×10^4	3.0	26	350
4-$MeOC_6H_4$	1.08×10^5	1.9	62	322
Crbz	1.2×10^4	2.2	68	320

Note. $T_{5\%}$ is the 5% mass loss temperature in the thermogravimetric analysis.

The complexation of these polymers with iodine occurs faster than with tetracyanoethylene. The structural characteristics of the CTC of these polymers were studied by IR and Mössbauer spectroscopy and their magnetic characteristics were measured.

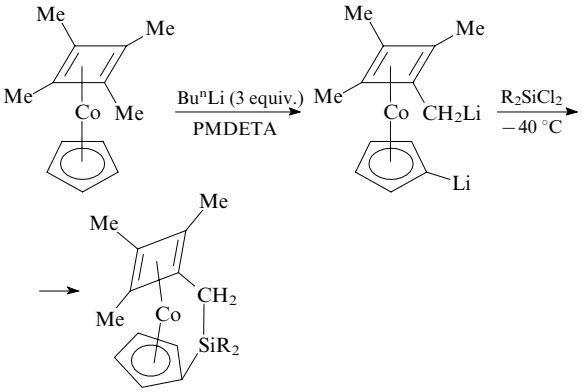
The amphiphilic block copolymers consisting of polyferrocenylenesilane and poly(dimethylaminoethyl) methacrylate blocks were synthesized by treatment of dimethylsila[1]ferrocenophane with $Bu^tMe_2SiO(CH_2)_3Li$, transforma-

tion of the terminal γ-hydroxypropyl group of the polymer into potassium alkoxide (treatment with KH) and polymerization of a methacrylate monomer catalyzed by the resulting compound.[140, 141] These block copolymers are capable of self-organization and in the authors' opinion, they can be used to prepare water-soluble cylindrical nanotubes with the organometallic core.

It was shown [142] that by initiating the polymerization of methyl(ethyl)sila[1]ferrocenophane by a terminal living polystyrene carbanion, it is possible to obtain block copolymers with various ratios of the blocks with M_w of up to 7.09×10^4 and a narrow MMD (M_w/M_n of 1.0 to 1.04).[142]

The search for synthetic routes for novel metalloarenophanes is in progress. The results of the first studies in the chemistry of neutral 18-electron metalloarenophanes were published.[143] In particular, [2]cobaltoarenophanes with a diorganylsilylmethylene bridge between the cyclopentadienyl and cyclobutadienyl ligands were successfully synthesized (Scheme 23).

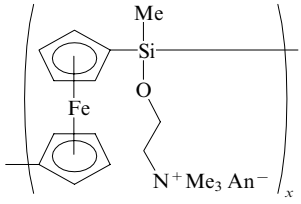
Scheme 23



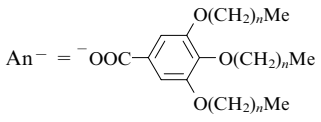
PMDETA is pentamethyldiethylenetriamine;
R = Me, Pr^i

Block copolymers consisting of polysilaferrocenylene and polyphosphazene blocks were synthesized by building up a diphenylphosphine group on the terminal poly(dimethylsila[1]ferrocenophane) carbanion; by oxidative chlorination, this group was converted to the PPh_2Cl_2 group and subsequently, by means of polymerization condensation and reduction, to the polyphosphazene block.[144] These structures form a new class of organometallic block copolymers.

New thermotropic liquid-crystalline and redox-active polyferrocenylenesilane complexes **P-10** capable of ionic self-organization were prepared by $PtCl_2$-catalyzed polymerization of methyl(chloro)sila[1]ferrocenophane and



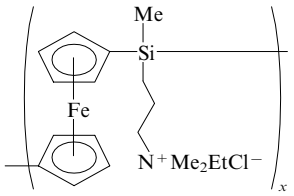
P-10



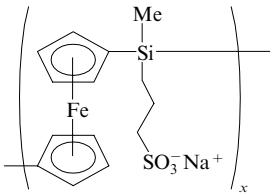
replacement of chlorine atoms by a dimethylaminoethoxy group followed by quaternization and replacement of the halide anion by the 3,4,5-trisubstituted benzoate anion.[145]

A study of the controlled morphology of the methyl(ethyl)sila[1]ferrocenophane – styrene block copolymers in a confined three-dimensional space of colloidal silica gel crystals demonstrated that these block copolymers are shaped like cylinders around the core mass.[146] In the same year,[147] amorphous block copolymers were prepared using living copolymerization of styrene and methyl(ethyl)sila[1]ferrocenophane (M_n from 5.0×10^4 to 2.5×10^5, M_w/M_n = 1.05–1.17) and their bulk self-organization was studied.

The optical properties of polyferrocenylenesilane-based polyionic multilayer thin films were studied [148] by spectroscopic ellipsometry. The study concerned polycationic and polyanionic polyferrocenylenesilanes **P-11** and **P-12**.



P-11



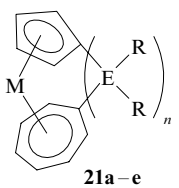
P-12

Samples of polycationic and polyanionic polyferrocenylenesilanes had the following molecular mass characteristics:

Polymer	M_w	M_n
P-11	2.91×10^5	1.79×10^5
P-12	2.65×10^4	1.34×10^4

The integrated refractive index of the polyionic films prepared by a layer-by-layer method varies from 1.53 (in the near IR region) to 1.8 (in the UV region).

During the two decades that have passed since the first publication dealing with the ring-opening polymerization of [1]silaferrocenophanes, quite a few studies appeared describing the syntheses of various metalloceno- and metalloarenocyclophane structures able to form polymers upon thermal and anionic initiation or under the action of Pt and other transition metal compounds. A variety of new compounds of this type were synthesized and polymerization of these compounds was attempted;[149] in particular, telechelic polyferrocenylenesilanes were prepared.[150] A [1.1]silaferrocenophane containing five-coordinate silicon was obtained.[151] Sharma *et al.*[152] studied the ring opening for new compounds, $(\eta^5\text{-}C_5H_4)Fe(CO)_2CH_2SiR_2$, which the authors called 1-sila-3-metallacyclobutanes; this gave rise to a new class of organometallic polymers;[152] the synthesis and properties of poly(ferrocenylenebutylmethylsilanes)



21a–e

Compound **21**	M	E	*n*	R
a	V	Si	1	Me
b	V	Si	1	Ph
c	V	Si	2	Me
d	Cr	Si	1	Me
e	Cr	Ge	1	Me

with non-symmetric substitution at silicon were reported.[153] [1]- and [2]silatrovacenophanes **21a–c**,[154] and dimethyl[1]-silatrochrocenophane (**21d**)[155] and dimethyl[1]germatrochrocenophane (**21e**)[156] were prepared. Monomer **21d** was polymerized on the Karstedt catalyst.[155] The first [1]silamanganesarenophane containing cyclopentadienyl and benzene rings was also synthesized.[157]

The possibility of photolytic anionic polymerization of [1]silaferrocenophane monomers in the presence of an anionic initiator such as cyclopentadienylsodium was documented.[158–160] The mechanism proposed for this process differs basically from the mechanism of photolytic polymerization involving Bu^nLi and involves cleavage of the Fe–Cp bond rather than the $Si-C_{Cp}$ bond. Moreover, in terms of this mechanism, Si-substituted cyclopentadienyl anions, which are less basic than Fe-coordinated Cp anions, function as the active sites of the growing polymer chain.

[1]Stannaferrocenophanes **22** with bulky substituents (Bu^t, mesityl) very slowly form polymers at ambient temperature in non-polar solvents. However, the addition of nucleophiles (pyridine, amines) results in sharp spontaneous acceleration of the polymerization of these monomers, which affords high-molecular-mass polymers (nucleophilic assistance).[161] The proposed mechanism of nucleophilic assistance includes four steps (Scheme 24). The first step is amine coordination to the tin atom of the monomer to give molecules with five-coordinate tin atom, and, hence, the nucleophilicity of the Cp ring carbon bonded to tin increases. The equilibrium concentration of these intermediates is very low, because the equilibrium is strongly shifted to the left. The Cp ring carbon with enhanced nucleophilicity attacks the tin atom of another monomer molecule. This is accompanied by heterolytic cleavage of the Sn–C bond in amine-coordinated stannaferrocenophane without generation of free anion but giving the ate complex $NuSn^+R_2(\eta^5\text{-}C_5H_4)Fe(\eta^5\text{-}C_5H_4)Sn^-R_2(\eta^5\text{-}C_5H_4)Fe(\eta^5\text{-}C_5H_4)$ as an intermediate. Then the next monomer molecules add (the chain grows) until the monomer is exhausted.

In the same work,[161] it was demonstrated that polymerization of dimesityl[1]stannaferrocenophane in the presence of small amounts of HOTf or Bu^n_3SnOTf follows a cationic mechanism. First, the monomer rapidly reacts with the triflate with opening of the stannaferrocenophane ring at the Sn–C bond, resulting in diorganylferrocenyltriflatestannane $(\eta^5\text{-}C_5H_4R^1)Fe(\eta^5\text{-}C_5H_4Sn^+R^2_2)OTf$. The latter reacts with the next molecule of the [1]stannaferrocenophane monomer thus providing ring opening and polymer chain growth. Presumably, polymerization of di-*tert*-butyl[1]stannaferrocenophane initiated by HCl also follows a cationic mechanism.

The technological applications of cross-linked polysilaferrocenophanes in the dialkyl, alkyl(alkoxyl), dialkoxyl, alkyl(aryl), alkyl(alkenyl), *etc*. framing with spirane [1]silabisferrocenophane as the cross-linking agent were described in patents.[162, 163]

Some issues of the practical use of silaferrocenophane-based polymers are reflected in the literature.[164–168]

IV. Polymerization of silicon–carbon heterocycles with endocyclic Si–Si bonds

Since the nature and properties of Si–Si bonds differ considerably from those of Si–C bonds and the amount of literature concerning ring opening polymerization of SCH with endocyclic Si–Si bonds is much smaller, the possibility of polymerization of all sorts of heterocycles, namely, containing rings of different size, both saturated and unsaturated, with one or more endocyclic Si–Si bonds will be considered in one and the same section.

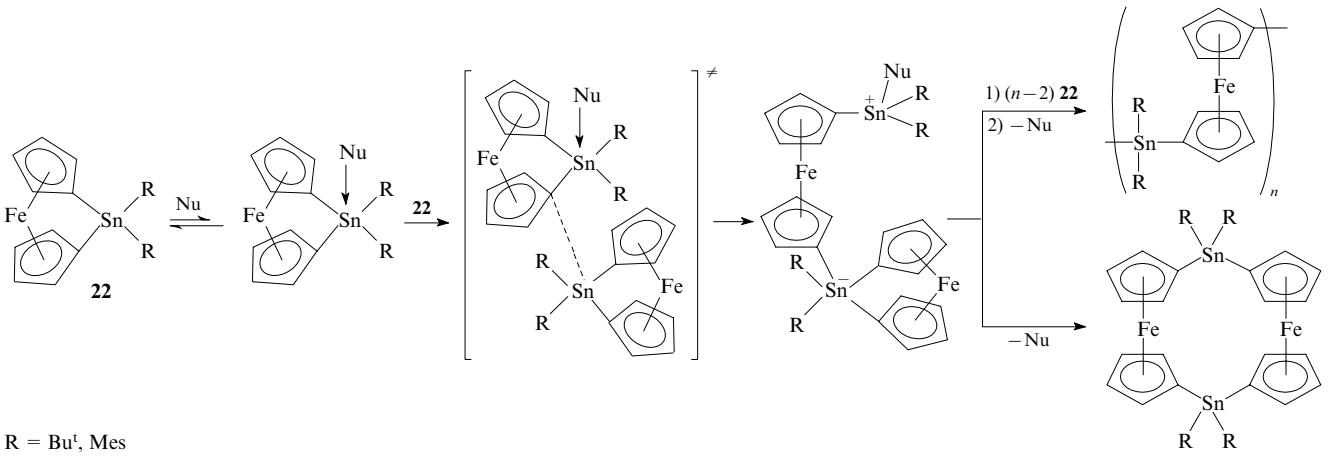
1. Polymerization of saturated silicon–carbon heterocycles with endocyclic Si–Si bonds

a. 1,2-Disilacyclobutanes

1,2-Disilacyclobutanes (1,2-DSCB) are the least abundant class as compared with other four-membered silicon–carbon heterocycles, including 1,3-disilacyclobutanes isomeric to them, which were considered in Section II. The reason is not only the difficulty of preparation of 1,2-DSCB but also the low stability of their lower homologues, which brings about additional problems involved in their synthesis and isolation. Therefore, researchers' efforts were mainly directed at the synthesis and study of 1,2-DSCB with bulky substituents at all atoms of the ring, which are stable under ambient conditions.[169–171]

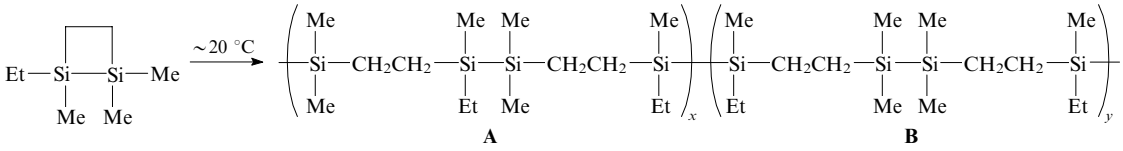
A method of gas-phase dehalogenation of 1,2-bis(dimethylchlorosilyl)ethane with alkali metal vapour was developed;[172–174] this allowed the authors to synthesize 1,1,2,2-tetramethyl-1,2-disilacyclobutane, the first 1,2-disilacyclobutane unsubstituted in the carbon part of the ring. This compound, unlike its 1,3-isomer (1,1,3,3-tetramethyl-

Scheme 24



R = Bu^t, Mes

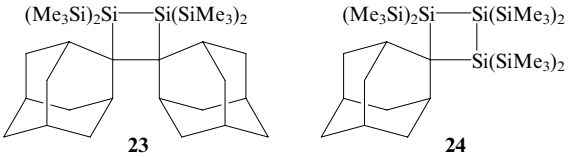
Scheme 25



1,3-disilacyclobutane), is so reactive that complete ring opening at the Si–Si bond (spontaneous polymerization) occurs at room temperature over a period of several minutes to give a regular polymer the backbone of which consists of alternating bis(dimethylsilane) ($Me_2SiSiMe_2$) and dimethylene (CH_2CH_2) units. The structure of this poly[ethylene(tetramethyldisilene)] was studied by IR and Raman spectroscopy.[175] Further studies of the polymerization and copolymerization with styrene[176] demonstrated that spontaneous polymerization occurs *via* homolytic cleavage of the Si–Si bond and, hence, it has a radical nature. The next homologue, 2-ethyl-1,1,2-trimethyl-1,2-disilacyclobutane, proved to be less reactive than tetramethyl-1,2-disilacyclobutane. Its spontaneous polymerization at room temperature is completed within 5–6 days.[177] This yields amorphous polymer ($T_g = -75$ °C), unlike the polymerization of the symmetric tetramethyl-substituted monomer, which gives a crystalline product. Evidently, the asymmetry of the monomer molecule is responsible for the formation of two types of attachment of monomer units, heat-to-tail and head-to-head ones, during polymerization (**A** and **B**, respectively, in Scheme 25).

The spontaneous copolymerization of 1,1,2,2-tetramethyl- and 2-ethyl-1,1,2-trimethyl-1,2-disilacyclobutanes affords partially crystalline random copolymers. The lower reactivity of 1,1,2-trimethyl-2-ethyl-1,2-disilacyclobutane in the spontaneous radical Si–Si bond cleavage compared with tetramethyl-substituted 1,2-DSCB might be due to the slight increase in the size of the substituent at this bond (Et instead of Me).

The presence of more bulky substituents compared with methyl at the silicon atom in 1,2-DSCB hampers but not prevents the homolytic cleavage of the Si–Si bond. For example, monomer **23** with sterically hindered groups is capable of ring-opening polymerization.



Sterically overcrowded 1,1,2,2-tetrakis(trimethylsilyl)-dispiro[3,3′,4,4′-biadamantane-1,2-disilacyclobutane] (**23**) undergoes two types of decomposition upon thermal treatment (150 °C), one to give disilene and 1,2-biadamantylidene and one into halves to give two sila-adamantylidene molecules.[171] Sila-adamantylidene undergoes [2+2]-cycloaddition to disilene to give trisilacyclobutane **24**. This is accompanied by formation of a polymer (yield 23%, $M_w = 1.18 \times 10^4$, $M_w/M_n = 1.4$), which is formally the copolymer of **23** and **24** with **23**:**24** = 2:1. Unlike compound **23**, thermolysis of germanium analogue occurs only as decomposition into $(Me_3Si)_2Ge{=}Ge(SiMe_3)_2$ and biadamantylidene, the latter being subsequently polymerized.[178]

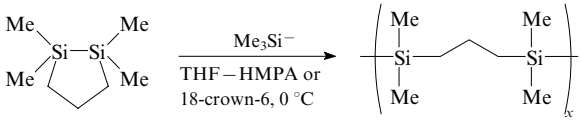
The analogue of monomer **23** with 2,4-bis(*tert*-butylphenyl) substituents at ring carbon atoms in place of the adamantylidene groups proved to be stable under ambient conditions.[170]

b. 1,2-Disilacyclopentanes

Five-membered heterocycles with endocyclic Si–Si bonds, 1,2-disilacyclopentanes (1,2-DSCP), are less strained structures; nevertheless, lower Si–Si bond energy compared with the C–C bond energy and the possible cleavage of this bond upon various sorts of treatment make them polymerizable.

The anionic polymerization of 1,1,2,2-tetramethyl-1,2-disilacyclopentane was initiated by the trimethylsilyl anion arising upon cleavage of hexamethyldisilane with methyllithium or potassium (sodium) alkoxides in a THF–HMPA mixture at 0 °C (Scheme 26).[179]

Scheme 26



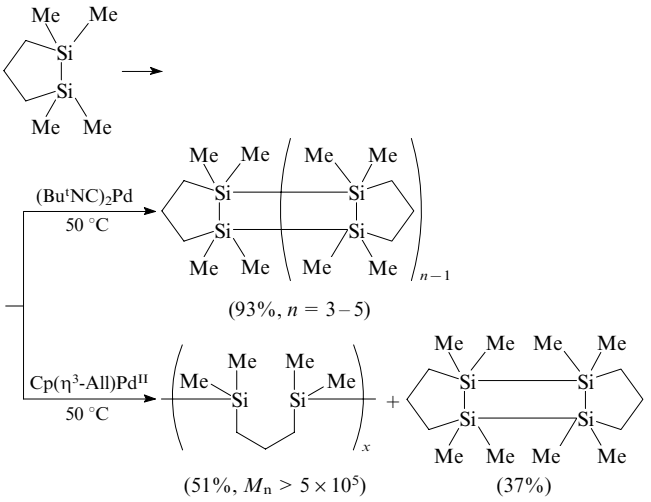
The highest yield (86%) and the highest molecular mass ($M_n = 1.3 \times 10^3$) were attained when using Me_3SiLi. For anionic polymerization of 1,1,2-trimethyl-2-phenyl-1,2-disilacyclopentane, catalysts of two types were used: tetra-n-butylamonium fluoride (in THF) and dimethylphenylsilylpotassium (in THF–HMPA)[180] at temperatures from 0 °C to −50 °C. The yields of polymers vary from 72% to 97%, M_n are from 6×10^3 to 1.9×10^4, and M_w/M_n are from 1.91 to 3.22.

1,1,2,2-Tetramethyl-1,2-disilacyclopentane was found to polymerize under the action of palladium complexes such as $PdCl_2$(dppb), $PdCl_2$(dbpb) [dppb and dbpb are bis(diphenylphosphino)- and bis(dibutylphosphino)butane] in the presence of tetramethyldifluorodisilane. This gives a polymer with a higher MM ($M_w > 3 \times 10^5$) than achieved by anionic polymerization.[181]

The use of di(organyl isocyanide) complexes of zerovalent palladium $(RNC)_2Pd^0$ (R = Bu^i, Pr^i, Bu^tCMe_2, 2,6-$Me_2C_6H_3$, 1-adamantyl) for metathesis of the Si–Si bond of 1,1,2,2-tetramethyl-1,2-disilacyclopentane[182, 183] results in oligomerization to give macrocycles (mainly tri-, tetra- and pentamers) (Scheme 27). Unlike the just mentioned Pd^0 isocyanide complexes, π-allyl complex of Pd(II), Cp(η^3-All)Pd^{II}, initiates polymerization of this monomer to give polymers with high MM (see Scheme 27). The replacement of one methyl group by phenyl group or of two methyl groups at the same silicon atom by ethyl groups in the 1,2-DSCP results in a decrease in the monomer reactivity in the Si–Si bond metathesis: in the former case, a dimer (50%) and trimer (9%) mixture is formed, while in the latter case, only dimer (12%) is formed. Other

cyclic disilanes such as permethylated 1,2-disilacyclohexane, 1,2-dimethyl-1,2-dimethoxy-1,2-disilacyclohexane and even permethylated 1,2-DSCB, and also cyclic trisilane, 1,1,2,2-tetramethyl-4,4-diphenyl-1,2,4-trisilacyclopentane, fail to undergo oligomerization metathesis of the Si–Si bonds.

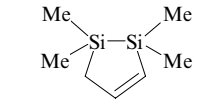
Scheme 27



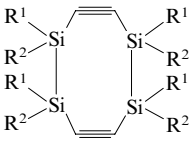
Polymerization of 1,1,2,2-tetramethyl-1,2-disilacyclopentane was initiated by the stable complex of palladium(IV) obtained by oxidative addition of one equivalent of (η^5-cyclopentadienyl)(η^3-allyl)palladium(II) to the Si–Si bond of a spirocyclic trisilane — 1,1,6,6-tetramethyl-1,5,6-trisilaspiro[4.4]nonane.[184] The yield of the polymer at 50 °C was 46%, $M_n = 8.5\times10^4$, $M_w/M_n = 1.88$. The proposed mechanism of catalysis by this complex implies the formation of the intermediate with divalent palladium, which undergoes oxidative addition to the Si–Si bond of the monomer. This affords pallada(IV)cyclic intermediate. The new Si–Si bond is formed upon reductive elimination from this intermediate, which is a chain propagation step. According to this mechanism, the chain is terminated when a polymer chain with the cyclopentadienyl–silicon bond at the end is reductively eliminated from the active site (intermediate).

2. Polymerization of unsaturated silicon–carbon heterocycles with endocyclic Si–Si bonds

Unsaturated four- and five-membered cyclic disilanes are more strained than the saturated analogues and, hence, they are more reactive. However, their reactivity is often manifested as easy reactions with various reagents without compaction to polymers or with the formation of only dimers.[185–189] When the ability of 3,4-benzo-1,2-disilacyclobutene to undergo spontaneous polymerization at room temperature in the presence of a cationic initiator ($AlCl_3$, −15 °C) had been demonstrated,[190] the subsequent studies were carried out mainly with more stable derivatives having bulky substituents at the silicon atom. 3,4-Benzo-1,2-disilacyclobutene derivatives easily react with oxygen, alkynes, alkenes and dienes[191–193] or form cyclic dimers.[194–196] Therefore, only a few studies devoted particularly to polymerization of heterocycles of this type are available. In particular, ring-opening polymerization was implemented for monomers **25**–**28**.

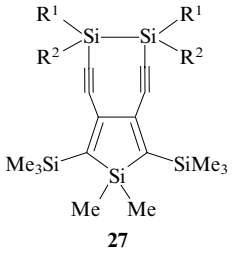


25



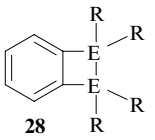
26

R^1 = Me: R^2 = Bu^n, n-C$_6$H$_{13}$, Et, Ph; R^1 = R^2 = Me, Et, Bu^n



27

R^1 = R^2 = Me, Et;
R^1 = Me, R^2 = Bu^n



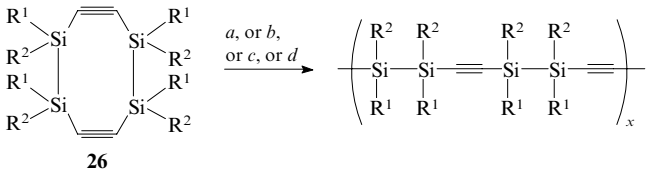
28

E = Si, R = Me;
E = Ge, R = Et

As has already been noted, polymerization of saturated 1,2-DSCP proceeds as polymerization metathesis of Si–Si bonds, while 1,1,2,2-tetramethyl-1,2-disilacyclopent-3-ene (**25**) can form a polymer in 96% yield according to the pattern of double bond metathesis on Schrock type molybdenum imido-alkylidene complexes.[197]

Eight-membered rings of 1,2,5,6-tetrasilacycloocta-3,7-diynes (**26**) are strained due to the presence of two triple bonds, which accounts for their reactivity towards polymerization. These compounds are trifunctional monomers: their polymerization-induced ring opening may occur both *via* Si–C or Si–Si bond cleavage and *via* metathesis of the C≡C bonds. Monomers **26** polymerize upon the action of anionic[198] and radical[199] initiators, upon thermal initiation[199,200] and according to the triple bond metathesis route.[201] However, unlike saturated heterocycles containing Si–Si bonds, in the polymerization of monomers **26**, Si–Si bond cleavage does not occur at any treatment (Scheme 28).

Scheme 28



26

(*a*) [W], 25 °C; (*b*) Bu^{n}Li, THF, 20 °C; (*c*) (Bu^{t}O)$_2$, 150 °C; (*d*) 230°C

For metathesis polymerization, Schrock type carbyne complexes were used: $(CF_3Me_2CO)_3W{\equiv}CMe$, $(Bu^tO)_3W{\equiv}CEt$ and $(CF_3Me_2CO)_6W_2$. The polymer obtained by polymerization of the monomer with R^1 = R^2 = Me in the presence of $(Bu^tO)_3W{\equiv}CEt$ proved to be poorly soluble due to high crystallinity, and hence it was impossible to reach high MM: the polymer precipitated from the reaction mixture as an inert solid phase, while the low-molecular-mass oligomer remained soluble. The monomer with R^1 = R^2 = Et being initiated by $(CF_3Me_2CO)_3W{\equiv}CMe$ is converted to the corresponding poly(disilanylenethynylene) in a quantitative yield (M_n = 4300, M_w/M_n = 1.4); the use of $(CF_3Me_2CO)_6W_2$ as a catalyst for the polymerization of the monomer with R^1 = Me, R^2 = Et provides a polymer with M_n = 31 000 and M_w/M_n = 1.4.

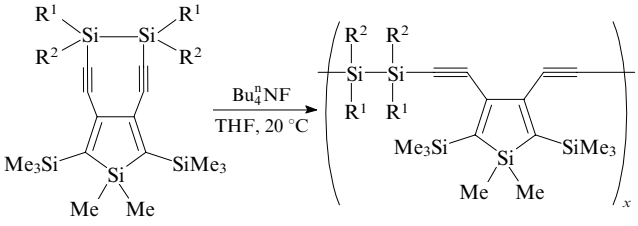
The anionic polymerization of 1,2,5,6-tetrasilacycloocta-3,7-diynes initiated by Bu^nLi starts with the nucleophilic attack on the silicon atom followed by Si–C bond cleavage and smoothly occurs for all monomers **26**. The highest MM ($M_w = 1.21 \times 10^5$, yield 88%) is achieved at R^1 = Me, R^2 = Et. Poly(disilanylenethynylenes) with R^1 = Me: R^2 = Ph, Et and $R^1 = R^2$ = Et have high degrees of crystallinity and melting points of 60 –85, 140–145 and 156–158 °C, respectively. Two other polymers, with R^1 = Me: $R^2 = Bu^n$, n-C_6H_{13} have $M_w = 3.09 \times 10^4$ and 6.54×10^4, respectively, and are viscous oils.

The possibility of radical polymerization of 1,2,5,6-tetrasilacycloocta-3,7-diynes was demonstrated in a study of their thermal polymerization. It was found that benzyl peroxide does not induce polymerization at 100 °C but *tert*-butyl peroxide induces the formation of poly(disilanylenethynylenes) from all monomers **26** at temperartures above 150 °C. The *tert*-butoxyl radical attacks the sp-hybridized carbon atom and ruptures the endocyclic Si–C bond and the radical centre on the silicon atom thus formed propagates the chain. The molecular masses of poly(disilanylenethynylenes) (M_w) vary from 7.0×10^3 to 1.59×10^5, the yields not exceeding 84%.

Thermal polymerization of diynes **26** (230–260 °C, heating of the degassed monomer in a sealed tube) results in polymers with the highest molecular mass ($M_w \leqslant 3.84 \times 10^5$) and occurs *via* homolytic cleavage of endocyclic Si–C bonds.

4,5,10-Trisilabicyclo[6.3.0]undeca-1(11),8-diene-2,6-diynes (**27**) represent one more sort of systems that polymerize with ring opening. Polymerization of this type of monomers involves the eight-membered heterocycle incorporating two C≡C triple bonds and one Si–Si bond between them. This ring is fused to silacyclopentadiene containing two Me_3Si groups at endocyclic carbon atoms. These heterocycles having four sp- and two sp^2-hybridized carbon atoms and two silicon atoms linked to each other are highly strained and readily polymerize by the anionic mechanism at room temperature with ring opening at the Si–C bond under the action of catalytic amounts of tetrabutylammonium fluoride (Scheme 29).[202]

Scheme 29



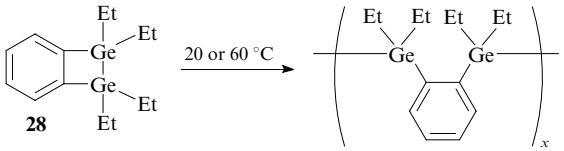
27

R^1	R^2	M_w	M_w/M_n	Yield (%)
Me	Me	9400	1.38	75
Et	Et	$3.03 \cdot 10^4$	1.66	87
Me	Bu^n	$4.63 \cdot 10^4$	–	80

The initiation by MeLi in THF provides somewhat higher molecular masses of polymers at low temperature. For example, polymerization of monomer **27** ($R^1 = R^2$ = Et) induced by MeLi in THF at –90 °C gives a polymer in a yield of 77% ($M_w = 4.79 \times 10^4$, $M_w/M_n = 1.26$).

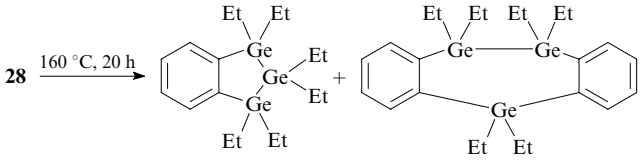
Finally, 1,1,2,2-tetraethyl-3,4-benzo-1,2-digermacyclobut-3-ene (**28**), the perethylated analogue of the above-mentioned permethylated 3,4-benzo-1,2- disilacyclobutene, is also strained and polymerizes spontaneously at room temperature both in the bulk and in solution (in toluene or hexane) (yield 90%, $M_w = 7.4 \times 10^5$, $M_w/M_n = 1.7$) (Scheme 30).[203]

Scheme 30



The threefold decrease in the initial concentration of the monomer decreases the molecular mass ($M_w = 5.6 \times 10^5$, $M_w/M_n = 1.6$). The same effect is observed upon increase in the polymerization temperature to 60 °C ($M_w = 3.0 \times 10^5$ in toluene and $M_w = 1.8 \times 10^4$ in hexane). In this study it was found that polymerization-induced ring opening in monomers **28** occurs *via* homolytic cleavage of the Ge–Ge bond. At higher temperature (thermolysis at 160 °C), the primary bis-germyl biradical, as at temperatures of < 60 °C, attacks the Ge atom of another monomer molecule by one Ge radical centre. The dimeric radical complex arising in this way is predominantly involved into the intramolecular reaction to give 4,5-benzo-1,2,3-trigermacyclopent-4-ene and to extrude the biradical in which one radical centre is located on the Ge atom of the diethylgermyl group, while the other radical centre is located on the *ortho*-carbon atom of the benzene ring. This extruded biradical then reacts with a monomer molecule to give a seven-membered heterocycle fused to two benzene rings (Scheme 31).

Scheme 31



The specific combination of alternating C≡C and Si–Si bonds of the backbone of the polymers obtained from monomers **26** and **27** ensures their electrical conductivity.[204–206]

* * *

In our opinion, the material of this review attests to persistent interest of researchers in the chemistry of silicon–carbon heterocycles, first of all, in their polymerization and study of the properties of the resulting heterochain polymers. During the last 10–15 years, the range of cyclic monomers and polymerization catalysts has been substantially extended. A new class of reactive organosilicon monomers, silametalloceno(areno)phanes, and heterochain polymers based on them have been created and studied in detail. The principal applied advances are related to the production of silicon–carbon fibres, ceramics and gas separation membranes. The achievements in the field of polymerization of heterocycles considered in this review gave an impetus for studies on the application of these polymers in modern technology.

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