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# Laser-induced decomposition of 1,1-dichloro-1-silacyclobutane for gas-phase deposition of reactive solid polycarbosilane

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## Abstract

Continuous-wave $CO_2$ laser photosensitized ($SF_6$) decomposition of 1,1-dichloro-1-silacyclobutane (DCSCB) leads to volatile ethene, methyltrichlorosilane, 1,1,3,3-tetrachloro-1,3-disilacyclobutane (TCDSCB) and a solid material. The reaction is assumed to be initiated by competitive (2 + 2) cycloreversion and dehydrochlorination. The amounts of depleted DCSCB and those of the ethene and $CH_3SiCl_3$ that are formed, as well as detection of methyltrichlorosilane-$d_1$ and methyltrichlorosilane-$d_2$ in the decomposition of DCSCB carried out in an excess of DCl provide indirect evidence for the intermediacy of dichlorosilene $Cl_2Si{=}CH_2$ and chlorosilyne $ClSi{\equiv}CH$. The solid deposit is judged to be mostly poly(dichlorocarbosilane); it reacts with gaseous methanol, trifluoroethanol, trifluoroacetic acid and water.

*Key words:* Silane; Laser-induced deposition; Polycarbosilane; Chlorosilyne

## 1. Introduction

Laser-powered homogeneous pyrolysis (LP) of silacyclobutanes $CH_3R\overline{SiCH_2CH_2CH_2}$ ($R = H$, $CH_2{=}CH$) has been reported [1,2] as an efficient route for the gas-phase deposition of organosilicon polymers formed by polymerization of intermediary silenes $CH_3RSi{=}CH_2$. The difference between the fates of these transient species under conditions of LP and those in conventional pyrolysis (CP) [3,4] (Scheme 1) prompted us to extend our LP studies [5] to structurally different silacyclobutanes and to find out whether the highly efficient polymerization route applies to other silacyclobutanes.

This paper deals with LP of 1,1-dichloro-1-silacyclobutane (DCSCB). Conventional pyrolysis of this compound has been intensively studied in the past [6–9], and is judged to be controlled by two independent processes, one yielding hydrogen chloride and the other giving dichlorosilene (DCS), which undergoes both addition of HCl and cyclodimerization (Scheme 2).

Studies of the LP of DCSCB are of interest in view of its potential for forming new reactive polycarbosilanes $-(Cl_2SiCH_2)_n-$. Only poly[(methylchlorosilylene)methylene] [10] and polysilapropylene [11] have been prepared previously, and it is assumed that this new family of reactive organosilicon polymers can be regarded as precursors of various novel functional or crosslinked polymeric structures.

## 2. Experimental section

Continuous-wave $CO_2$ laser photosensitized decomposition of DCSCB was carried out by irradiation of mixtures of DCSCB (1.1–3.6 kPa)-$SF_6$ (sensitizer, 1.2–2.4 kPa) in a glass tube (10 cm × 3.6 cm I.D.) reactor with two KBr windows. The $CO_2$ laser was operated at the P(20) line of the $00^01$–$10^00$ transition (944.19 $cm^{-1}$) and its beam was focused with a Ge lens (10 cm focal length). The reactor was pretreated with trimethylchlorosilane vapour and subsequently evacuated to remove any traces of water bonded to the reactor surface. The mixtures were irradiated for measured intervals (using a laser output 10 W and incident

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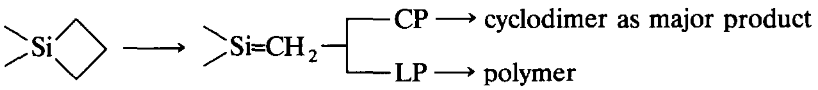


Scheme 1.

radiation energy 30 W $cm^{-2}$), and the IR spectrum was periodically recorded.

The decomposition of DCSCB was monitored at 533 $cm^{-1}$. Ethene and methyltrichlorosilane were determined at 1890 and 3100 $cm^{-1}$, and at 1274 $cm^{-1}$, respectively. Volatile products formed upon the irradiation were removed by thorough evacuation of the reactor. The IR spectrum of the solid material deposited on KBr windows was then recorded, and gaseous methanol, 1,1,1-trifluoromethanol, air, or trifluoroacetic acid were admitted to the reactor and allowed to react with the deposited material. The introduction of these volatile compounds and their evacuation were repeated several times and the changes in the composition of the solid material were analysed by recording the IR spectrum after each reactant introduction/evacuation cycle.

Scavenging experiments for identifying intermediate species were carried out by the irradiation of DCSCB (2 kPa)–$SF_6$–DCl (both 11 kPa) mixtures in a stainless steel cell with two germanium windows with AR coating. Analysis of volatile products was carried out by GC/MS with a Shimadzu QP-1000 mass spectrometer (70 eV, Porapak P, programmed temperature).

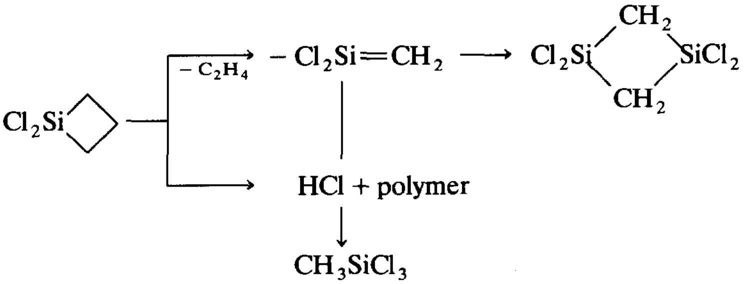
Properties of the deposit were also measured by SEM analyses. For this purpose a deposit on an alumina sheet was produced in experiments in which pieces of the sheet were housed in the reactor before irradiation. Scanning electron microscopy studies of the deposits were performed on a Tesla BS 350 ultrahigh vacuum instrument equipped with an Edax 91000/65 energy dispersive analyser of X-ray radiation.

Sulfur hexafluoride (Fluka) was commercial sample and DCSCB was made as reported previously [12]. Pure methyltrichlorosilane was available in our laboratory. Deuterium chloride (95%) was obtained by reaction between $SiCl_4$ and $D_2O$ on a vacuum-line pretreated with methyltrichlorosilane.

## 3. Results and discussion

Laser heating of $SF_6$–DCSCB mixtures at total pressure 3.8–6.0 kPa results in the formation of volatile ethene, methyltrichlorosilane and traces of methane, a non-volatile material being concurrently deposited on the cold surface of reactor (Fig. 1). The volatile compounds were identified through their absorptions at 960, 1440, 1890, and 3100 $cm^{-1}$ ($C_2H_4$), 450, 580, 760, 800 and 1275 $cm^{-1}$ ($CH_3SiCl_3$), and 1300 $cm^{-1}$ ($CH_4$). The absorption bands at 670 and 740 $cm^{-1}$ are indicative of the presence of 1,1,3,3-tetrachloro-1,3-disilacyclobutane (TCDSCB, cyclodimer), determination of which is hampered by its low volatility (the TCDSCB gives absorption bands at 460, 530, 670, 740, 795 and 965 $cm^{-1}$ [9,13], and indeed the absorption bands at 460 and 740 $cm^{-1}$, which do not overlap with those of other volatile products, become more pronounced when the reactor is heated.) The deposited material that cannot be removed by prolonged evacuation of the reactor shows absorptions at 530 $cm^{-1}$ {$\nu_s(SiCl_2)$}, 590 $cm^{-1}$ {$\nu_{as}(SiCl_2)$}, 660 $cm^{-1}$ {$\nu(SiC)$}, 710, 730, 770, 840, 950, 1060 and 2960 $cm^{-1}$ {$\nu(CH)$} (Fig. 1, bottom). A broad band at 1060 $cm^{-1}$ can be ascribed to both $\nu(SiCH_2Si)$ and $\nu(SiOSi)$ vibrations. Much stronger absorption in this region, apparently arising from the siloxane linkage was observed previously [6] for the mixture of products formed by CP of DCSCB.

The conditions used for LP of DCSCB do not differ from those of the previously reported LP of $RCH_3\overline{SiCH_2CH_2CH_2}$ (R = H, $CH_2$=CH) carried out [1,2] at mean effective temperature 700–800 K. Representative runs for irradiations carried out for no longer than 10 min (Table 1) show that the amounts of DC-



Scheme 2.

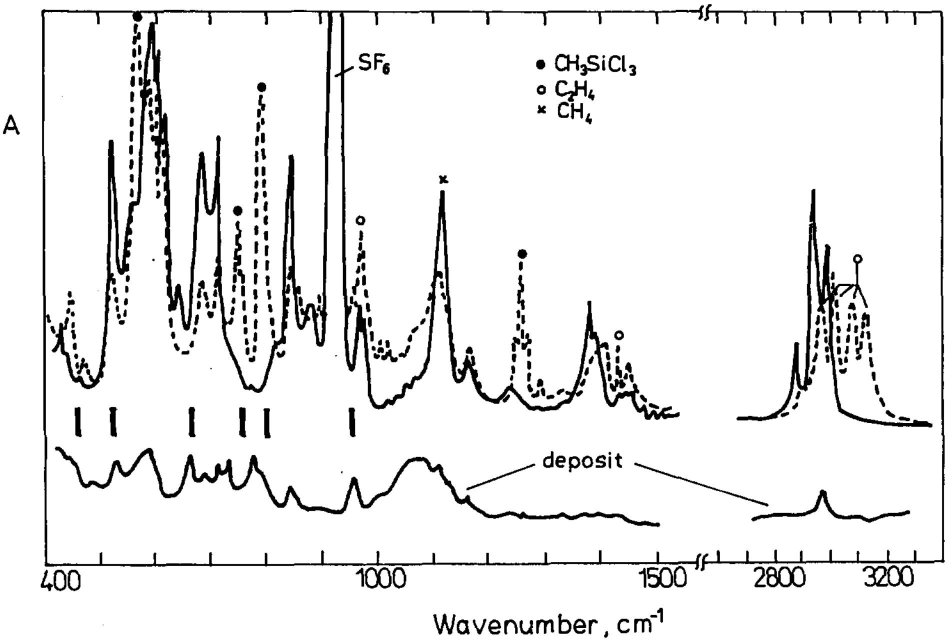


Fig. 1. Typical IR spectrum of DCSCB–$SF_6$ mixture before (solid line) and after (dotted line) irradiation and that of deposit (bottom). Absorption of TCDSCB is designated with thick lines.

SCB decomposed are roughly equal to those of the ethene produced. The ratio of methyltrichlorosilane to decomposed DCSCB is about 0.25 and this ratio does not change when the content of DCSCB in the initial mixture is increased. Propene, found among the products from CP of DCSCB, was not detected. The observations support the mechanism involving cleavage of ethene from, and dehydrochlorination of DCSCB as initial competing steps (Scheme 3).

The latter reaction, as well as possible [14] dehydrochlorination of DCS, inevitably result in the formation of the elusive species **I** and **II** (or **III**). The detection of these intermediates presents difficulty because of the multitude of reactions they can undergo; as well as isomerization from silyne to silavinylidene [4], the transient species containing a Si=C or Si≡C bond can undergo addition of hydrogen chloride [4], cyclodimerization (DCS), and polymerization (both DCS and II). Support for the transient presence of these species comes, however, from the fact that the yield of ethene exceeds the difference between the amount of the DCSCB decomposed and that of the methyltrichlorosilane formed. Moreover, the decomposition of DCSCB carried out in an excess of deuterium chloride revealed the presence of three different isotopomers of methyltrichlorosilane, *viz.* $CH_3SiCl_3$, $CH_2DSiCl_3$ and $CHD_2SiCl_3$. The evidence for them was provided by comparison of molecular ion peak distributions in the mass spectrum of a standard sample of $CH_3SiCl_3$ {*m/z* (relative intensity) 152(4), 150(11), 149(1), 148(11)} and in that of a methyltrichlorosilane formed in the presence of DCl {154(< 1), 153(2), 152(2), 151(7), 150(4), 149(8), 148(3)} as well as by a statistical treatment of the ratios of the intensities of the particular samples (Table 2). Silynes are considered to be even less stable than silenes [4], and we emphasize that this is, to the best of our knowledge, the first (though indirect) experimental evidence of their existence (we note that the transient formation of fluorosilyne and the dehydrofluorination of $H_2Si{=}CF_2$ into HSi≡CF and then to SiC

TABLE 1. Products of laser-powered homogeneous pyrolysis of DCSCB (all quantities kPa)

| DCSCB | DCSCB : $SF_6$ | DCSCB reacted | Gaseous products | | $CH_3SiCl_3$ : DCSCB decomposed |
|---|---|---|---|---|---|
| | | | $C_2H_4$ | $CH_3SiCl_3$ | |
| 1.8 | 0.9 | 1.3 | 1.4 | 0.30 | 0.23 |
| 3.5 | 1.5 | 2.3 | 2.6 | 0.50 | 0.22 |
| 3.6 | 1.8 | 2.5 | 2.4 | 0.45 | 0.18 |
| 3.3 | 2.1 | 2.4 | 2.1 | 0.60 | 0.25 |

TABLE 2. Intensity ratios for molecular ions of methyltrichlorosilane

| Intensity ratio [a] | Sample from LP of DCSCB in excess of DCl | Standard sample |
|---|---|---|
| $I_{150}:I_{148}$ | 1.40* | 1.00* |
| $I_{151}:I_{149}$ | 1.00** | – |
| $I_{152}:I_{148}$ | 0.71*** | 0.35* |
| $I_{153}:I_{149}$ | 0.36* | – |

[a] Relative error 18(*), 5(**), and 11(***) per cent.

was assumed by us to account for details of the reaction between silane and chlorodifluoromethane [14]).

Deposited polymeric material must be composed mostly of -($Cl_2SiCH_2$)- units, and arise mainly via polymerization of DCS. There are two reasons for this assumption: first, 2 + 2 cycloreversion of DCSCB is favoured over dehydrochlorination, and second, silyne can disappear upon the addition of HCl and be changed into DCS (Scheme 3).

The deposited polymeric material rapidly reacts with vapours of methanol, 1,1,1-trifluoroethanol, trifluoroacetic acid or water. Upon addition of each of these reagents, hydrogen chloride is evolved and the IR absorption spectrum pattern of the deposit in the re-evacuated cell is changed (Fig. 2): the characteristic vibrations of $CH_3O$- {$\nu$(SiOC) 1090 $cm^{-1}$, $\rho(CH_3)$ 815 $cm^{-1}$ and $\delta(CH_3)$ 1465 $cm^{-1}$}, $CF_3CH_2O$- {$\nu$(SiOC) 1030 $cm^{-1}$ and $\nu$(C–F) 1150 $cm^{-1}$} or $CF_3C(O)O$- {$\nu$(CF) and $\nu$(C(O)OSi) 1170, 1175, 1130, 1230 $cm^{-1}$} and $\nu$(C=O) 1770 $cm^{-1}$ prove the occurrence of the gas-solid phase esterification of the Si–Cl moieties of the chlorosubstituted organosilicon polymer. This reaction (Scheme 4) can be facilitated by the presence of the catalytically acting [15] hydrogen chloride.

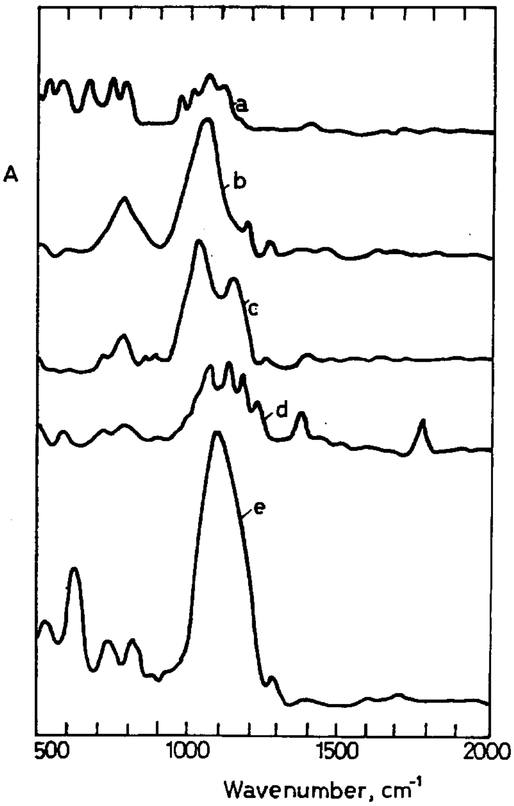
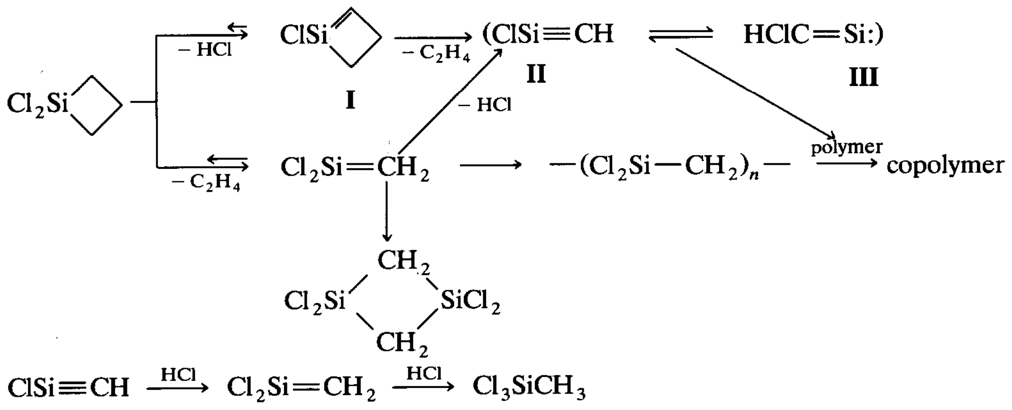


Fig. 2. IR spectrum of the deposit yielded by LP of DCSCB (a) and of that obtained by subsequent treatment with gaseous methanol (b), 1,1,1-trifluoroethanol (c), trifluoroacetic acid (d) and water (e).

The exposure of the chlorinated polymer to water vapour results in the production of a siloxane, which implies that the Si–OH bonds which must have been primarily formed upon the gas-solid phase hydrolysis, and whose presence revealed by a weak and broad absorption band at 3400 $cm^{-1}$ are not so far separated as to prevent their condensation. The IR spectrum of the polymer with SiOSi groups shows typical absorption at 500 $cm^{-1}$ $\nu_s$(SiOSi); 600–800 $cm^{-1}$ $\nu$(SiC); 1040–1130 $cm^{-1}$ $\nu_{as}$(SiOSi); and 3400 $cm^{-1}$ ($\nu$OH ··· O) (Fig. 2e). Similar experiments were performed with alkoxy-substituted organosilicon polymers (Fig. 3). A methoxy-substituted organosilicon polymer



Scheme 3.

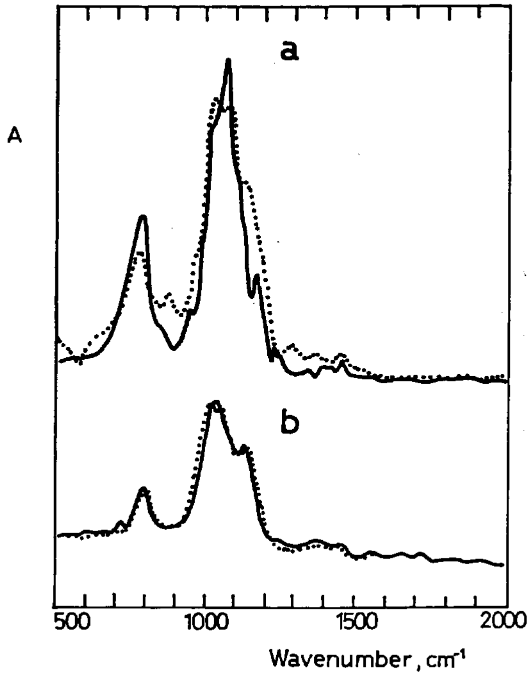


Fig. 3. IR spectrum of methoxy-substituted organosilicon polymer before (———) and after (······) treatment with trifluoroethanol (a), and that of trifluoroethoxy-substituted organosilicon polymer before (———) and after (······) treatment with methanol (b).

upon treatment by several $CF_3CH_2OH$ exposure/evacuation cycles undergoes the gas-solid phase alcoholysis (Scheme 5) to yield 1,1,1-trifluoroethoxy-substituted organosilicon polymer. The reverse reaction appears to be rather slow, since similar treatment with methanol of trifluoroethoxy substituted organosilicon polymer, formed by the reaction of the chlorinated polymer with trifluoroethanol, does not cause significant changes in the IR spectrum of the solid, although formation of some gaseous $CF_3CH_2OH$ (bands at 1140 and 1180 $cm^{-1}$) was detected.

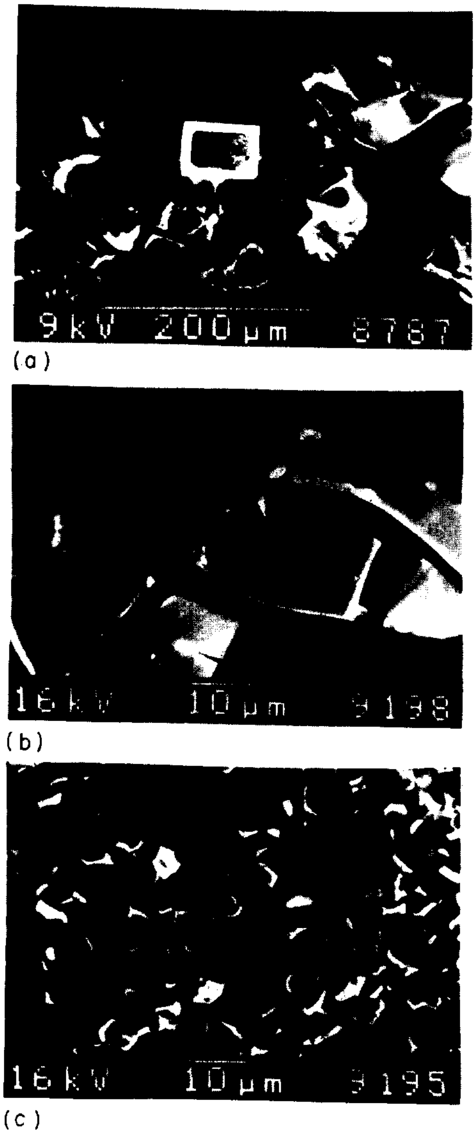
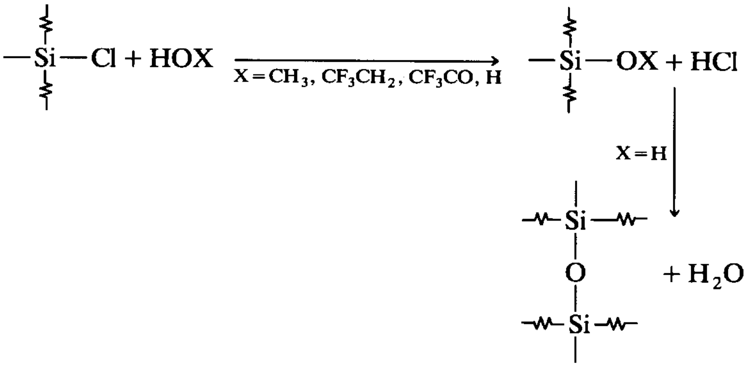
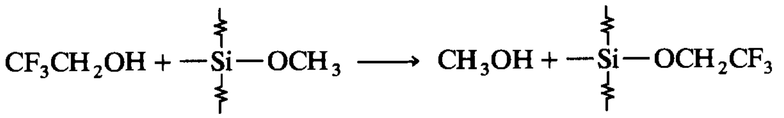


Fig. 4. SEM micrographs of the deposit obtained upon contact with air moisture (a), trifluoroethanol (b), and methanol (c).



Scheme 4.



$$CF_3CH_2OH + -Si-OCH_3 \longrightarrow CH_3OH + -Si-OCH_2CF_3$$

Scheme 5.

Scanning electron micrographs of the deposits obtained by the exposure of the chlorinated polymer with water, trifluoroethanol, or methanol (Fig. 4) reveal a continuous structure of a thin film, with some cracks. We conclude that these cracks and a partial peeling of the films (observable in Fig. 4a–c), are produced upon reaction of the Si–Cl bonds of the initial deposit with the volatile ROX compounds, and that they are brought about by a penetration of the ROX compounds between the film and the substrate. EDX-SEM analysis of the deposit after exposure to air for several days (Fig. 5) reveals that it contains Si, O and also Cl, which indicates that some proportion of the Si–Cl bonds remains unhydrolyzed even upon long contact of the film with the atmosphere.

The esterification of chlorosilane or their alcoholysis in solution is well documented, and so are preparations of various chemically inert organosilicon polymers in the liquid phase [16]. Up to now poly[(methylchlorosilylene)methylene] [10] and polysilapropylene [11] were the only ones among new reactive organosilicon polymers that could be used as precursors for various novel polymeric structures. The present report of LP of DCSCB and the chemical vapour deposition of the polycarbosilane materials could be of interest for preparation of agglomerates or thin films possessing reactive functional groups that can be modified by subsequent reactions.

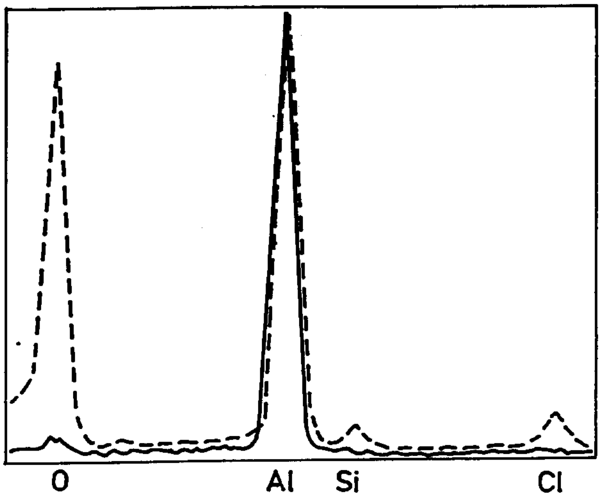


Fig. 5. EDX-SEM trace of the deposit obtained upon contact with air moisture. The solid line relates to the uncoated (aluminium substrate) area, whereas the dashed one relates to coated spot (bordered area in Fig. 4a).

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