Journal of Organometallic Chemistry, 391 (1990) 275–282
Elsevier Sequoia S.A., Lausanne

JOM 20872

Production of poly(silaisoprene) by laser-induced decomposition of 1-methyl-1-vinyl-1-silacyclobutane

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(Received February 12th, 1990)

Abstract

Continuous CO_2 laser-induced decomposition of 1-methyl-1-vinyl-1-silacyclobutane (MVS) in the presence of energy conveying sulfur hexafluoride provides a highly selective method for production of poly(2-methyl-2-silabuta-1,3-diene) (polysilaisoprene). Trapping with hexafluoroacetone and tetrafluoroethene confirms the intermediacy of 2-methyl-2-silabuta-1,3-diene (silaisoprene), polymerization of which depends on the ratio MVS/SF_6. The IR spectrum of the polymer deposited from the gas-phase on to the reactor surface reveals that silaisoprene polymerizes by participation of both double bonds.

Introduction

Interest in studies of polymerization in the gas-phase has recently increased owing to the use of cloud chamber [1–3], exciplex [4,5] or infrared [6,7] laser radiation, particle beam [8], and plasma [9,10] techniques which are well suited to use in this field.

We previously described the CO_2 laser-induced reactions in SiH_4/olefin mixtures which result in the formation in gas-phase of organosilicon polymers, which are deposited on the cold reactor surface [11–13].

Another type of polymerization in the gas-phase has been initiated by CO_2 laser-photosensitized (SF_6) decomposition of silacyclobutanes [6,7]. Conventional thermal decomposition (CTD) of these compounds is known [14,15] to yield reactive silaethenes, which, in the absence of traps, undergo a variety of reactions such as isomerization into silylene, insertion into the Si–H bond, cyclodimerization, and polymerization. It was therefore surprising to find that the silaethenes generated by

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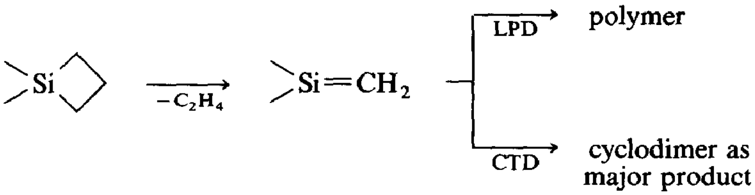


Scheme 1

laser-photosensitized (SF_6) decomposition (LPD) of 1-methyl-1-silacyclobutane [6] and 4-silaspiro(3.4)octane [7] in a surface-less reactor undergo exclusively polymerization (Scheme 1).

It has been shown previously [16–18] that CTD of 1-methyl-1-vinyl-1-silacyclobutane (MVS) gives rise to the unstable 2-methyl-2-silabuta-1,3-diene (silaisoprene), whose existence was confirmed through its reactions with 1,1-dimethyl-1-silaethene, phenol and methanol. On the assumption that the LPD of silacyclobutanes would undergo exclusive polymerization we thought it of interest to examine whether LPD of MVS could be used to prepare the previously unknown poly(2-methyl-2-sila-1,3-diene) (polysilaisoprene).

Experimental

Continuous-wave (CW) CO_2 laser-photosensitized (SF_6) decomposition of 1-methyl-1-vinyl-1-silacyclobutane was carried out by irradiation of mixtures of MVS (16 torr) with SF_6 (4–10 torr), and of MVS (20 torr) with SF_6 (15 torr) and a trapping agent (hexafluoroacetone, 1,3-butadiene, tetrafluoroethene and hexafluoropropene, 65 torr) in a glass tube (10 cm × 3.6 cm I.D.) reactor filled with two NaCl windows, a sleeve with rubber septum, and a valve through which the reactor was connected to a standard vacuum-line [19]. The CO_2 laser [20] was operated at the P(20) line of the $00^01 \rightarrow 10^00$ transition (944.19 cm^{-1}) and its beam was focused with a NaCl lens (50 cm focal length). The mixtures were irradiated using a laser output of 15 W for chosen times and the IR spectrum then recorded. Subsequently, helium was expanded into the reactor and samples of the gaseous mixtures were withdrawn through the septum by syringe and injected into the mass spectrometer. The analyses were performed with a gas chromatograph-mass spectrometer (GCMS, Shimadzu, Model QP 1000 column packed with silicon elastomer OV-17 or Porapak P, programmed temperature) and an IR spectrometer Specord 75 W. A Giede model GCHF 183 gas chromatograph (flame ionization, column packed with alumina deactivated with silicone oil) coupled with a computing integrator model Cl 100 was used for determination of the relative amounts of gaseous products.

The effective mean temperature [21] of the MVS decomposition was estimated from the rate of the CW CO_2 laser-photosensitized decomposition of ethyl acetate (EA) at the same reactant/SF_6 ratios and under the same irradiation conditions. The decomposition of EA was monitored by use of the IR bands at 1385, 1080 and 1040 cm^{-1}. The effective temperature was calculated from the Arrhenius parameters for EA decomposition taken from ref. 22. The rate of decomposition of MVS was determined by monitoring of the IR band at 1120 cm^{-1}.

Scanning electron microscopy of the deposit was performed with a Tesla BS 350 microscope equipped with an energy dispersive analyser of X-ray radiation Edax 9100/65. The samples were fixed with Leit-c-plast and examined as produced or after sputtering of a layer (20 nm) of Au onto them.

Sulfur hexafluoride, hexafluoroacetone, 1,3-butadiene (all Fluka), helium (Messer Greisheim), ethyl acetate (Lachema) and hexafluoropropene (Aldrich) were commercial samples. 1-Methyl-1-vinyl-1-silacyclobutane was prepared as described in ref. 23.

Results and discussion

Continuous-wave, CO_2 laser-induced decomposition of MVS was carried out in the presence of energy-conveying SF_6 and found to result in formation of the single gaseous product, ethylene, and a solid material which was deposited on the cold glass surface of the reactor. This reaction takes a quite different course from that of the CTD of MVS, which was reported [16–18] to yield 1,3-dimethyl-1,3-divinyl-1,3-disilacyclobutane and ethene, and at higher temperatures also smaller amounts of allene and propyne. The latter compounds can be observed during the LPD of MVS at lower MVS/SF_6 ratios (higher effective temperatures), as can be seen from Table 1. The LPD can be conducted as a non-explosive or explosive gas-phase reaction. The latter is observed at higher pressures of SF_6, and can be carried to completion with irradiation times within 1 sec.

The LPD of MVS shows first order kinetics. The dependence of the rate coefficient (Fig. 1) on the mean effective temperature estimated by use of the decomposition of ethyl acetate as a marker enabled as to determine the Arrhenius parameters as log A (s^{-1}) = 16.0 and E (kJ mol^{-1}) = 249.5. These values are very close to those obtained earlier for the CTD of MVS (log A (s^{-1}) = 15.64, E (kJ mol^{-1}) = 261.5, ref. 18) and prove that the rate of CTD and LPD are determined in the same reaction step, which was previously assumed [18] to be the cleavage of the carbon–carbon bond.

It is known [14] that silaethenes show a high reactivity towards carbonyl groups or protic species, as well as towards olefins and dienes. 2-Methyl-2-silabuta-1,3-diene (MSD) was detected through its reaction with phenol and methanol [17], and also through the addition to 1,1-dimethyl-1-silaethene [18]. We attempted to prove

Table 1

The LPD of MVS

SF_6/MVS	Total pressure, torr	Effective temperature, K	Gaseous products	Note
0.11–0.50	20	705–750	C_2H_4	non-explosive reaction
0.56	26	750	C_2H_4	explosion/visible luminescence
1.0–0.7	20	770	C_2H_4 [a], $CH_2{=}C{=}CH_2$, $CH_3{=}CH{=}CH_2$ C_4H_8	explosion/visible luminescence

[a] Dominant product (> 99%)

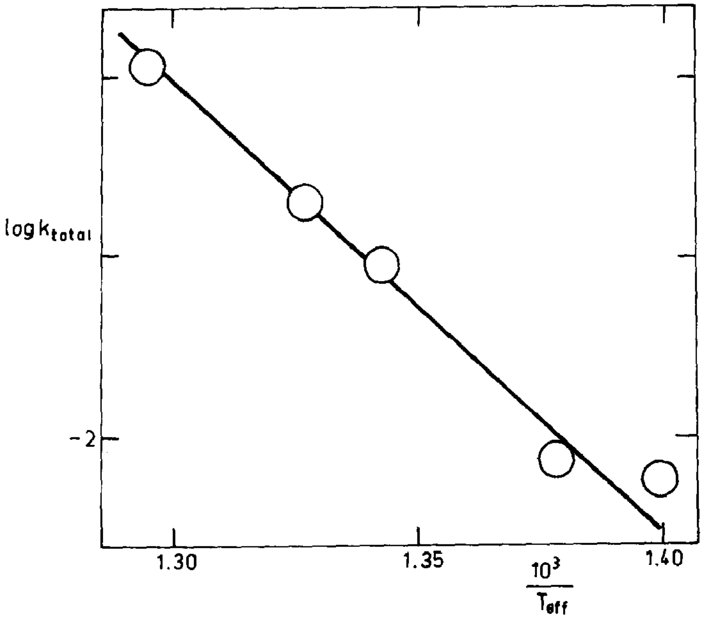


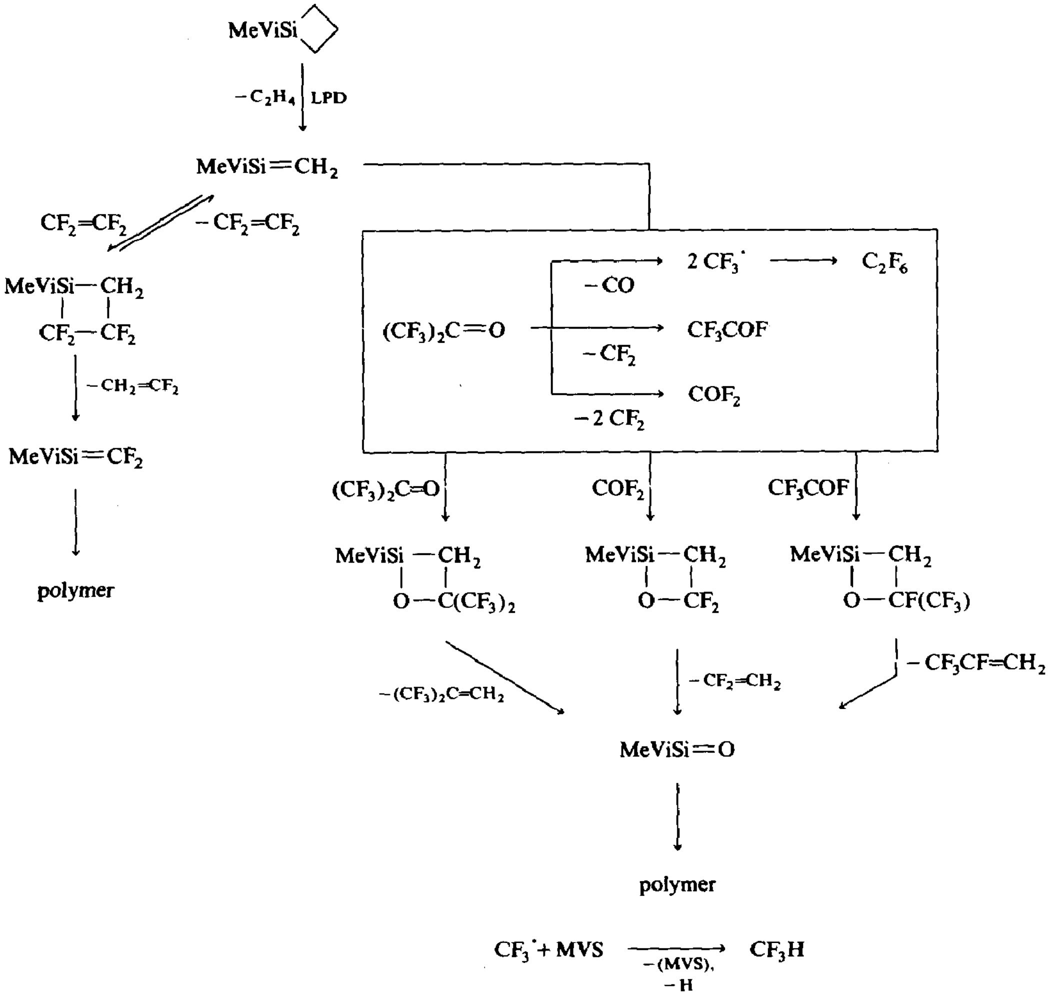
Fig. 1. The dependence of the rate coefficient of MVS decomposition on the effective temperature.

the presence of intermediary MSD during the LPD of MVS by carrying out the reaction in the presence of an excess of tetrafluoroethene, hexafluoropropene, or 1,3-butadiene and hexafluoroacetone. We did not detect any products of reaction between MSD and the trapping agents after irradiation of MVS-SF_6 mixtures in an excess of 1,3-butadiene and hexafluoropropene, but LPD of MVS in an excess of tetrafluoroethene yielded ethene and 1,1-difluoroethene, and that in excess of hexafluoroacetone afforded a mixture of ethene, 1,1-difluoroethene, 1,1,1-trifluoro-2-trifluoromethylpropene, trifluoromethane, 1,1,1-trifluoropropene, trifluoroacetyl fluoride, 1,1,1-trifluoro-2-fluoropropene, hexafluoroethane, tetrafluoroethene, and carbon monoxide. These compounds were identified by means of their infrared and mass spectra. The formation of the fluorinated olefins (the mass spectra (*m/z* relative intensity) for which are: (i) $CH_2{=}CF_2$, 64 (*M*, 19), 45 (100), 26 (61) and 25 (19); (ii) $(CF_3)_2C{=}CH_2$, 164 (*M*, 11), 145 (56), 95 (84), 81 (24), 76 (20), 75 (48); 65 (100), 31 (48), (iii) $CF_3CF{=}CH_2$, 114 (*M*, 15), 113 (53), 95 (24), 69 (100), 64 (44), 45 (40), 44 (24), 31 (53), 26 (14)) show that MSD is involved as an intermediate in the reactions (Scheme 2).

Such reactions are consistent with the observation that laser-photosensitized decomposition of hexafluoroacetone yields [24] C_2F_6, CO, COF_2, CF_3COF and C_2F_4. Formation of 1,1,1-trifluoropropene (mass spectrum; 96 (*M*, 22), 95 (25), 77 (50), 76 (7), 75 (13), 69 (12), 51 (31), 46 (18), 31 (23), 27 (100), 26 (37)) can be explained in terms of the following sequence:

$$CF_3{-}\dot{C}{=}O + MVS \rightarrow CF_3{-}CHO \xrightarrow[-\,MeViSi{=}O]{Me(Vi)Si{=}CH_2} CF_3{-}CH{=}CH_2$$

We note that both CF_3COF and COF_2 are produced upon irradiation of hexafluoroacetone/SF_6 mixture, but only the former is observed upon irradiation of



Scheme 2

mixture of hexafluoroacetone, SF_6 and MVS (Fig. 2). The absence of COF_2 can be attributed to its reaction with MSD to yield $CF_2{=}CH_2$.

The polymer deposited during the irradiation of MVS/SF_6 mixtures with a MVS : SF_6 ratio 0.25 is soluble in benzene and tetrahydrofuran and scanning electron microscopy (SEM) (Fig. 3a) reveals its droplet structure. The deposit obtained during the irradiation of MVS/SF_6 mixtures at a MVS/SF_6 ratio of 1 shows very good adhesion to the glass surface, and is insoluble in the above solvents. The morphology of this polymer is different (Fig. 3b), and it can be seen that it consists of solid particles with a size reaching 1 μm^2. The IR spectra of the two polymers (Fig. 4). are very similar, and differ only in the region between 1000–1100 cm^{-1}. The absence of absorption bands associated with vinyl groups bonded to silicon (650, 925, 1010, 1600, and above 3050 cm^{-1}) as well as those associated with silacyclobutane ring vibrations (956, 1120 cm^{-1}) confirms that neither the 4-membered ring nor the double bond are incorporated in the polymer.

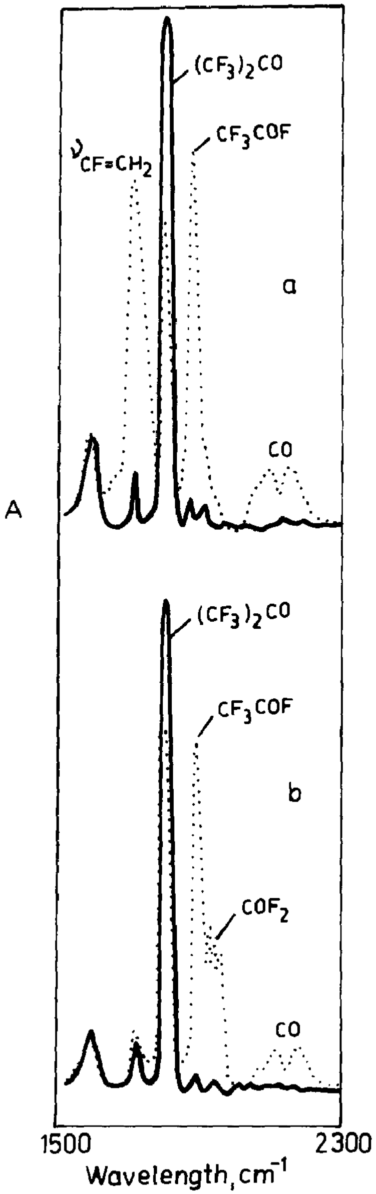


Fig. 2. Infrared spectra before (solid line) and after (dotted line) the irradiation of $(CF_3)_2CO$ (40 torr)/SF_6 (15 torr) (a, 15 W, 80 s) and of $(CF_3)_2CO$ (20 torr)/SF_6 (5 torr) (b, 15 W, 80 s) mixtures.

This observation indicates that the polymerization of MSD is very different from that of its carbon analogue (isoprene), with both double bonds taking part in the polymerization and being lost. The UV spectrum of the soluble polymer recorded in n-hexane shows that there is absorption only below 200 nm, which implies [25] the absence of polysilane species. The laser-induced decomposition of MVS carried out as a very fast explosive reaction could find application in the deposition of polymer layers on the thermally unstable surfaces.

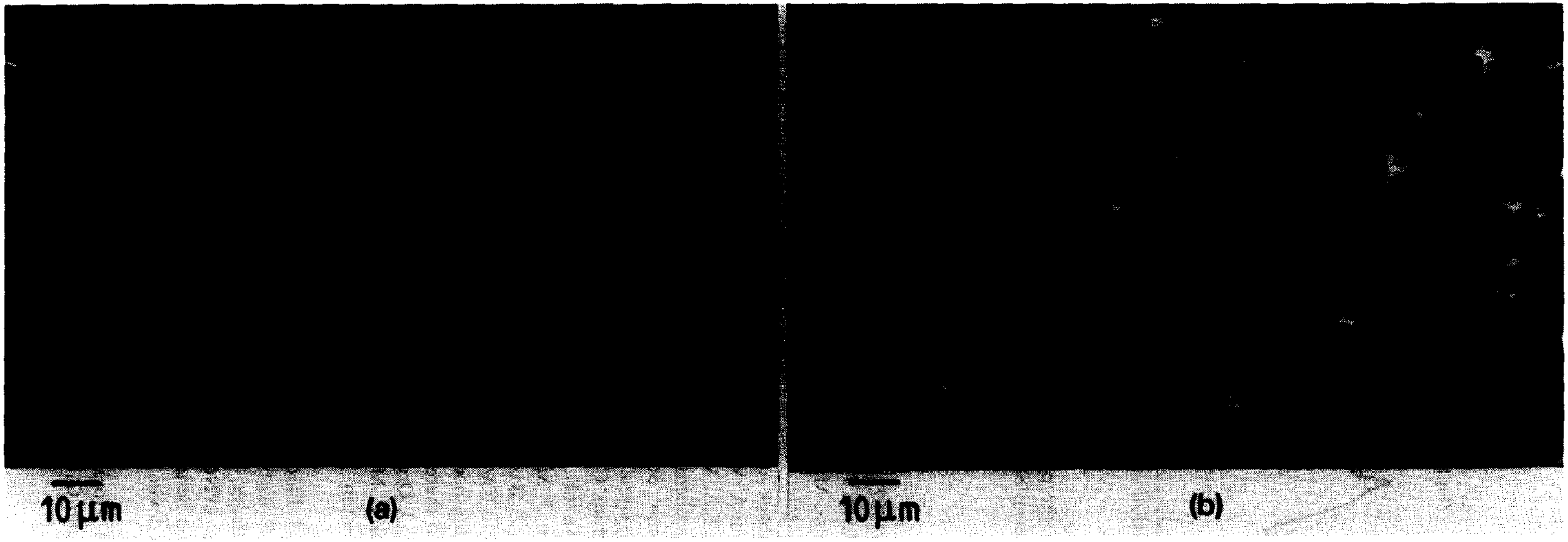


Fig. 3. SEM of (16 kV) of poly(silaisoprene) obtained with low (a, SF_6/MVS = 0.1–0.5) and high (b, SF_6/MVS = 0.5) content of SF_6 in parent MVS/SF_6 mixture.

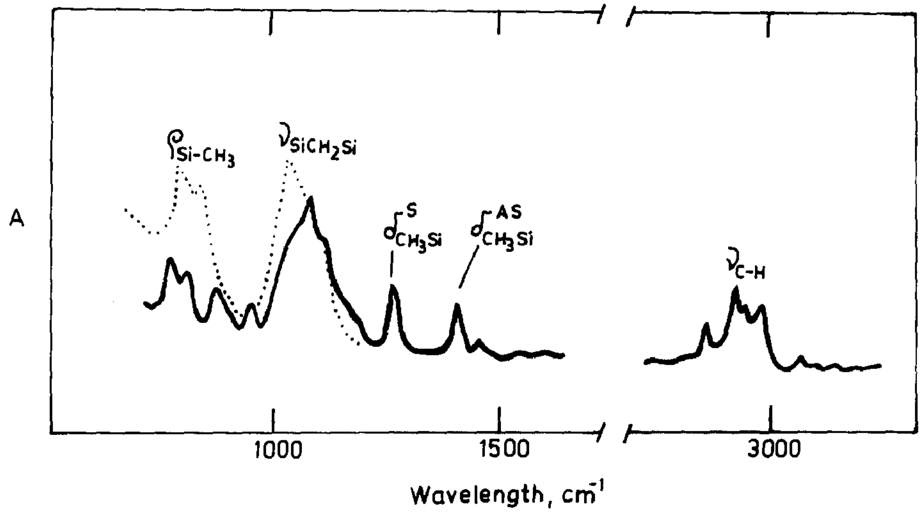


Fig. 4. Infrared spectra of the polymer produced upon the irradiation of MVS (16 torr)/SF_6 (4 torr) (solid line) and MVS (10 torr)/SF_6 (10 torr) mixtures.

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