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Preliminary communication

IR laser photosensitized decomposition of 1-methyl-1-silacyclobutane. Efficient gas-phase polymer deposition *

Josef Pola*, **Václav Chvalovský**,
Institute of Chemical Process Fundamentals, Czechoslovak Academy of Sciences, 165 02 Prague 6 (Czechoslovakia)

Elvira A. Volnina and Leonid E. Guselnikov
Topchiev Institute of Petrochemical Synthesis, Academy of Sciences, Moscow (U.S.S.R.)

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Abstract

Laser-induced thermolysis of 1-methyl-1-silacyclobutane is a highly selective method for the gas-phase deposition of organosilicon polymer, which is formed by the elimination of ethene and the major participation of methylsilaethene and dimethylsilylene in the polymerization.

There is continuing interest [1,2] in the thermal fragmentation of silacyclobutanes $R_2\overline{SiCH_2CH_2C}H_2$ (R = alkyl, H) owing to its capability to yield reactive silaethenes. In the gas-phase, the latter are only transient species that, in the absence of traps, undergo numerous reactions such as isomerization, cyclodimerization, insertion into the Si–H bond, and polymerization. The study of the relative importance of these reactions with different silacyclobutanes under different conditions has up to now not been paid much attention. It is known that the low-pressure pyrolysis of 1-methyl-1-silacyclobutane (MSCB) favors the insertion of dimethylsilylene into the Si–H bond at lower temperatures [3] and that during pyrolysis of 1,1-dimethyl-1-silacyclobutane, under the same conditions, further polymerization takes place if the distance between the hot and the cold trapping sites is decreased [4,5]. Lasers are considered to be very useful tools for inducing both unimolecular decompositions [6], and polymerizations [7], one advantage being the elimination of heterogeneous stages of these reactions on the hot-wall surface. This effect is obviously responsible also for a cleaner, multiphoton IR induced decomposition of 1,1-dimethyl-1-sila-

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* Dedicated to Professor C. Eaborn in recognition of his important contributions to organosilicon chemistry.

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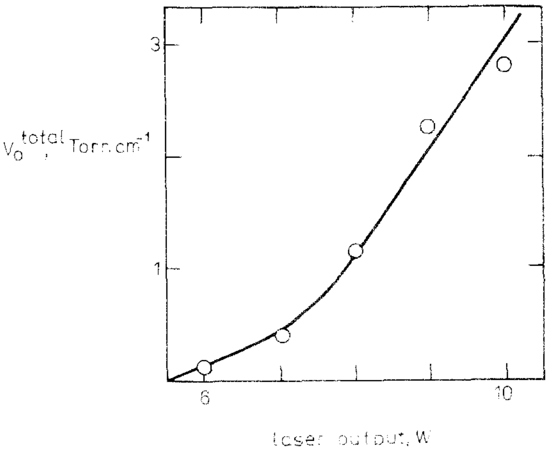
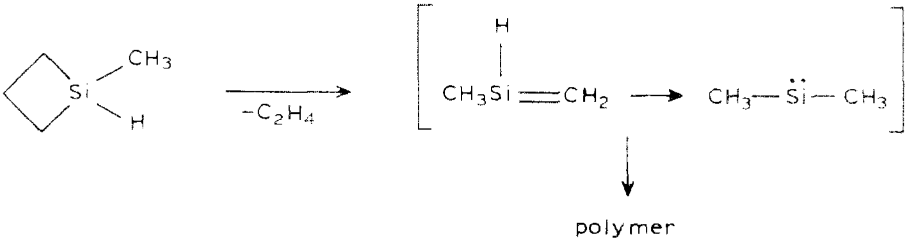


Fig. 1. The dependence of the initial rate of C_2H_4 formation on the output of the laser.

cyclobutane [8] in which the cyclodimerization of 1,1-dimethyl-1-silaethene is more favored over its polymerization than in conventional heat-induced processes.

Herein we report a continuous wave (cw) CO_2 laser photosensitized (SF_6) decomposition of MSCB and show that this reaction leads exclusively to the gas-phase polymerization and to the deposition of the polymer on a cold reactor surface. The experiments were carried out with a cw CO_2 laser, by procedures reported previously [9,10]. Mixtures of MSCB (28 Torr) and energy-conveying SF_6 (7 Torr) were irradiated with a mildly focussed laser beam (the P(20) line of 10.6 μm transition, laser output 6–10 W) in a stainless-steel cylinder (i.d. 3.6 cm, length 1.4 cm) equipped with two NaCl windows, a valve and a sleeve with a rubber septum. Progress of MSCB decomposition was monitored by IR and GC-MS spectrometry. Upon irradiation, only the depletion of MSCB, the formation of gaseous ethene along with propene (3–4% of ethene), and gradual build-up of a transparent polymer on the reactor walls was observed. The quantities of MSCB reacted and ethene generated were almost equal attaining conversions of 90–100%. The rate of MSCB decomposition grows with increasing laser output as shown in Fig. 1. In experiments in which 1,3-butadiene was added to a mixture of MSCB (28 Torr)/SF_6 (35 Torr)/C_4H_6 (110 Torr) irradiation with a 10 W laser beam, yielded ethene along with 1,1-dimethyl-1-silacyclopentenes and 1-methyl-1-silacyclohexene in the ratio 3.8/1. These three compounds indicate [11] the presence of the methylsilaethene-to-dimethylsilylene isomerization [12]. Our results thus show that the laser-driven decomposition of MSCB can best be described as:



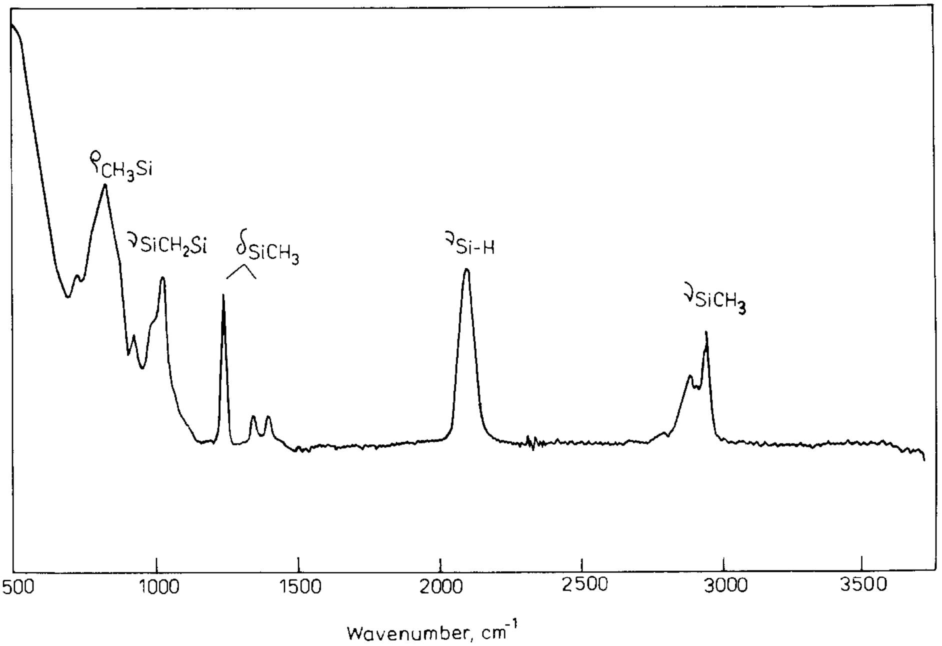


Fig. 2. IR spectrum of the polymer.

A mean effective temperature was estimated by a technique for interacting systems [13] using decomposition of ethyl acetate as a marker [14]. It ranges from 750 K (laser output 6 W) to 800 K (laser output 10 W). The infrared spectrum of the polymer (wavelength, cm^{-1} (transmittance, %)) consists of the following bands: 826 (29), 931 (57), 1030 (46), 1244 (49), 1346 (71), 1401 (71), 2099 (45), 2888 (64), 2944 (56) and can be interpreted as in Fig. 2. The absence of the characteristic bands of the silacyclobutane ring (1185, 1122 and 925 cm^{-1} [15]) confirms that no such rings were incorporated. The polymer is insoluble in benzene and shows very good adhesion to metal surface. No polymer fragmentation is observed when heated to 300 °C in the direct inlet section of the mass spectrometer, or when exposed to the red glow of a platinum target in a vacuum. The polymerization can thus be assumed to occur mainly via radical polymerization of the $CH_3Si(H):CH_2$ and $(CH_3)_2Si$: species, the insertion of $(CH_3)_2Si$: into the Si–H bond apparently being a minor contribution.

References

1 L.E. Guselnikov and N.S. Nametkin, Chem. Rev., 79 (1979) 529.
2 I.M.T. Davidson, S.I. Magsoodi, T.J. Barton and N. Tillman, J. Chem. Soc., Chem. Commun., (1984) 478 and refs. therein.
3 R.T. Conlin and D.L. Wood, J. Am. Chem. Soc., 103 (1981) 1843.
4 N.S. Nametkin, L.E. Guselnikov, E.A. Volnina and V.M. Vdovin, Dokl. Akad. Nauk SSSR, 220 (1975) 386.
5 E.A. Volnina, Ph.D. Thesis, Topchiev Institute of Petrochemical Synthesis, Moscow, 1975.
6 N. Bloembergen and E. Yablonovitch, Physics Today, (1978) 23.
7 K. Kleinermanns and J. Wolfrum, Angew. Chem. Int. Ed. Engl., 26 (1987) 38.

8 H.M. Frey, A. Kashoulis, L.N. Ling, S.P. Lodge, I.M. Pidgeon and R. Walsh, J. Chem. Soc., Chem. Commun., (1981) 915.

9 J. Pola, M. Farkačová, P. Kubát and A. Trka, J. Chem. Soc., Faraday Trans. 1, 80 (1984) 1499.

10 J. Pola and Z. Chvátal, J. Fluor. Chem., 37 (1987) 197.

11 R.T. Conlin and Y.W. Kwak, Organometallics, 3 (1984) 918.

12 J. Drahnak, J. Michl and R. West, J. Am. Chem. Soc., 103 (1981) 1845.

13 W.M. Shaub and S.H. Bauer, Int. J. Chem. Kinet., 7 (1975) 509.

14 W.C. Danen and J.C. Jang in J.I. Steinfeld (Ed.), Laser Induced Chemical Processes, Plenum Press, New York, 1981.

15 N.S. Nametkin, V.D. Oppengeim, V.I. Zavyalov, K.S. Puschevaya and V.M. Vdovin, Izv. Akad. Nauk SSSR, (1965) 1547.