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Efficient laser-induced generation and polymerization of the highly unsaturated compound diethynylsilene in the gas phase

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Abstract

The CO_2 laser photosensitized (SF_6) decomposition of 1,1-diethynyl-1-silacyclobutane in the gas-phase involves a clean elimination of ethene to give a transient highly unsaturated diethynylsilene, which undergoes very efficient polymerization to yield saturated macromolecules with a cross-linked structure. The results reveal the very large enhancement of the ease of triple –C≡C– bond polymerization for molecules containing proximal C≡C and $Si{=}CH_2$ bonds.

1. Introduction

The laser-induced chemical vapour deposition of organosilicon polymers [1] is one aspect of current research on laser-driven production of novel silicon-containing materials. Two types of these high-molecular weight compounds have been prepared in this way so far, namely (a) organosiloxanes [2,3] obtained by infrared laser multiphoton decomposition of silane in the presence of some common monomers, and (b) polycarbosilanes [4–8], formed by infrared laser photosensitized decomposition of silacyclobutanes and methoxysilanes. Use of the latter technique, involving CO_2-laser heating of a sensitizer [9,10], was shown [11–13] to generate many new pathways in the gas-phase chemistry owing to the elimination of heterogeneous steps that normally occur on hot reactor walls. The laser photosensitized decomposition (LPD) of silacyclobutanes $RMe\overline{SiCH_2CH_2CH_2}$ (R = H, Vi) [4,5] and of 4-silaspiro |3.4| octane [7] is an efficient and selective route to polymers arising from intermediary silenes, whereas conventional thermolysis (CT) of the parent compounds yields mostly silene cyclodimers [14,15] (Scheme 1).

A very interesting feature of LPD of 1-methyl-1-vinyl-1-silacyclobutane (MVSCB) is the polymerization of an intermediary 2-methyl-2-silabuta-1,3-diene (MSD) to give a polymer with no C=C bonds [11–13]. Such polymerization is very unusual, and contrasts with that of 1,2- or 1,4-polymerization of the carbon analogue (isoprene), which yields macromolecules in which half of the double bonds are retained. The fact that both C=C and Si=C bonds in MSD are lost is surprising in view of the great difficulty of polymerizing vinylsilanes [20]. We assume that MSD does not disappear by separate polymerizations at Si=C and C=C bonds, but rather through a sequence of the 1,4- and 1,2-polymerizations (Scheme 2), in which the first step gives a reactive polymer with the Si=C bonds, which drives the reaction to completion.

We now report that LPD of 1,1-diethynyl-1-silacyclobutane (DESCB) yields ethene and a fully saturated polymer, which implies that intermediary diethynylsilene (DES) undergoes very efficient polymerization involving all the unsaturated bonds. This shows that a neighbouring $Si{=}CH_2$ bond greatly increases the ease of polymerization of C≡C bonds, as it does that of C=C bonds, opening the way into a new field of very efficient polymerization reactions in the gas-phase.

2. Results and discussion

1,1-Diethynyl-1-silacyclobutane was prepared in 22% yield by treatment of 1,1-dichloro-1-silacyclobutane (0.1 mole) with sodium acetylide (0.2 mol) in diethyl ether,

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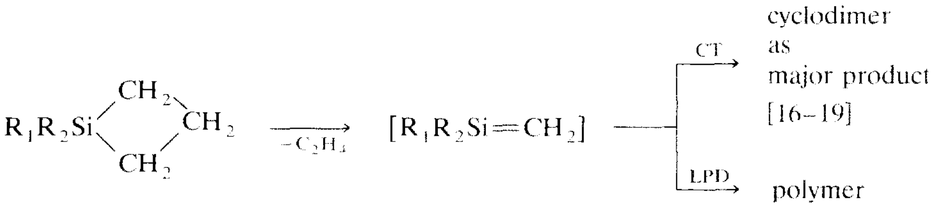


R_1, R_2 = Me, H; Me, Vi; $(CH_2)_5$.

Scheme 1.

and obtained as a liquid boiling at 67–78°C/4 kPa. Characterization data: IR spectra (gas) 3300s, 2985m, 2940m, 2885w, 2040s, 1340m, 1115m, 895w, 860s, 700vs, and 680vs cm^{-1}. ^1H NMR spectra ($CDCl_3$) δ 1.30 triplet (4H), 2.17 multiplet (2H) and 2.64 singlet (2H). The ^{13}C shifts (with respect to $CDCl_3$) −61.14, −58.44, 7.40 and 19.35 ppm.

The experiments were carried out with a cw CO_2 laser operating at the P(20) line of the 00°1 → 10°0 transition (944.19 cm^{-1}) with 10 W output. Mixtures of DESCB (0.3 kPa):SF_6 sensitizer (0.8 kPA):cyclohexane (internal standard, 0.3 kPA):Ar (12 kPa) were irradiated with a focused beam (incident energy 20 W cm^{-2}) in a vertically positioned glass tube (equipped with NaCl windows) which formed a part of a set-up permitting GLC monitoring of the disappearance of DESCB and the appearance of gaseous products. Alternatively, the LPD of DESCB was monitored by IR and GC-MS spectrometry; in this case mixtures DESCB (0.5–0.8 kPa) and SF_6 (0.8–3.3 kPa) were used in a similar reactor fitted with NaCl windows and a sleeve with rubber septum. The mean effective temperature [9] of the DESCB decomposition was estimated in separate runs from the rate of LPD of chloroethane. This value is in the range 700–780 K, depending on the SF_6 pressure, but the maximum temperature inside the hot zone, where thermolysis effectively takes place, is probably considerably higher [10].

The LPD of DESCB takes a very simple course, yielding ethene (together with minor quantities of ethyne) and a yellow solid deposited on the cold reactor surface. The decomposition in mixtures DESCB-SF_6, monitored by IR spectra at 2040 cm^{-1}, can be driven only to 20% conversion, since large amounts of the deposit coat the entrance window of the reactor. The $C_2H_2:C_2H_4$ ratio is, irrespective of the initial SF_6 content, *ca.* 0.20. The decomposition in the presence of argon (lesser initial amounts of DESCB) can be taken to higher conversions and the $C_2H_2:C_2H_4$ ratio increases from ~0.05 to 0.15 as the reaction progresses (Fig. 1). Ethyne cannot be the product of the decomposition of ethene, as verified independently by irradiation of a C_2H_4 (0.7 kPa):SF_6 (2 kPa) mixture. The material balance (Fig. 1) is in line with the assumption that the predominant route in the DESCB decomposition involves elimination of ethene. A similar mode of fragmentation is also evident from the mass spectrum of DESCB. MS (70 eV; *m/z*, relative intensity): 120 (M, 5), 119 (M − 1, 19), 105 (10), 92 (M − 27, 100), 77 (10), 66 (33), 53 (78), 28 (10). Small amounts of ethyne are probably formed by cleavage of the C(sp)–Si bond and a subsequent abstraction of hydrogen from the parent by a $HC_2\cdot$ radical. The presence of diethynylsilene (DES) as an intermediate was detected by trapping it with methanol; irradiation of DESCB (0.5 kPa):SF_6 (4 kPa):CH_3OH (7 kPa) did not afford solid material, volatile diethynyl(methoxy)methylsilane being the dominant product; MS (70 eV, *m/z*, relative intensity) 124 (M, < 1), 109 (M − 15,

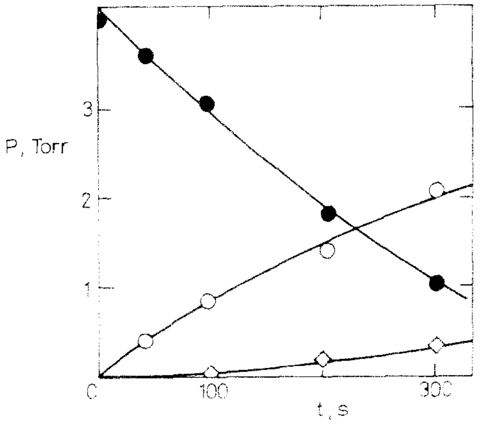
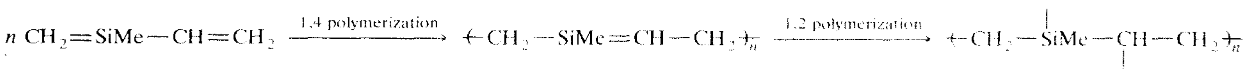


Fig. 1. The product distribution in LPD of DESCB. (● DESCB, ○ ethene, ◇ ethyne).



$$n\,CH_2{=}SiMe{-}CH{=}CH_2 \xrightarrow{\text{1,4 polymerization}} {+}CH_2{-}SiMe{=}CH{-}CH_2{+}_n \xrightarrow{\text{1,2 polymerization}} {+}CH_2{-}\overset{|}{Si}Me{-}\underset{|}{C}H{-}CH_2{+}_n$$

Scheme 2.

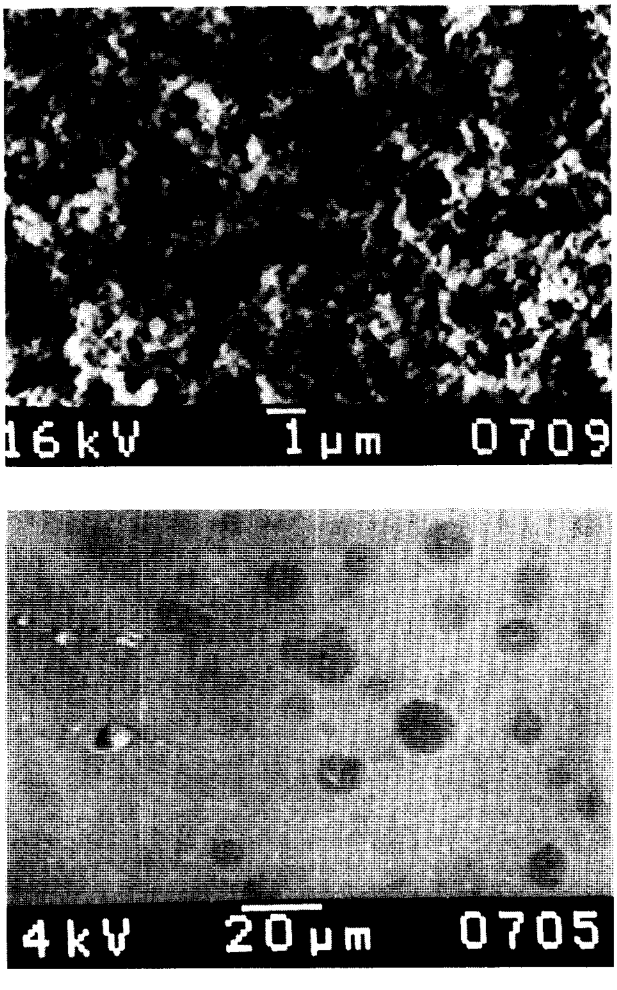


Fig. 2. SEM image of the deposit.

100), 79 (26) and 53 (20). This transient species, the most unsaturated silene generated so far, must therefore be a precursor of the observed deposited material.

The deposit is insoluble in organic solvents, suggesting that it has a cross-linked structure. Scanning electron microscopy (Fig. 2) reveals network morphology or, with a thicker film, a compact surface. The IR spectrum (Fig. 3) consists of broad bands at 650, 800, 1050 and 2500 cm^{-1} assignable [21,22] to stretching vibrations of Si–C, C–C, Si–C–Si and C–H bonds, respectively. The band centred at 1050 cm^{-1} obviously has some contribution from ν(Si–O) or ν(C–O) vibrations, since very strong absorption bands at this wavenumber and at 1600–1700 and 3450 cm^{-1} appear when the deposit is exposed to the atmosphere; these bands relate to δ(OH) and $\nu(OH \cdots H)$ vibrations. This result reveals the reactivity of the deposit towards oxygen and moisture in the air which is evidently the result of the presence of a very small number of unsaturated carbon and/or silicon centres embedded in the polymer framework [23]. The deposit shows no absorption at 3300 or 2040 cm^{-1} (observed with DESCB), nor that of $-\overset{|}{C}{=}CH-$ bonds, indicating that both ethynyl groups in DES react to give an almost completely saturated system. This is in line with the very efficient polymerization of DES, which can occur either via separate 1,2-polymerizations at $Si{=}CH_2$ and $C{\equiv}CH$ bonds (path A), or via a 1,4-polymerization (path B), both leading to saturated macromolecules (Scheme 3):

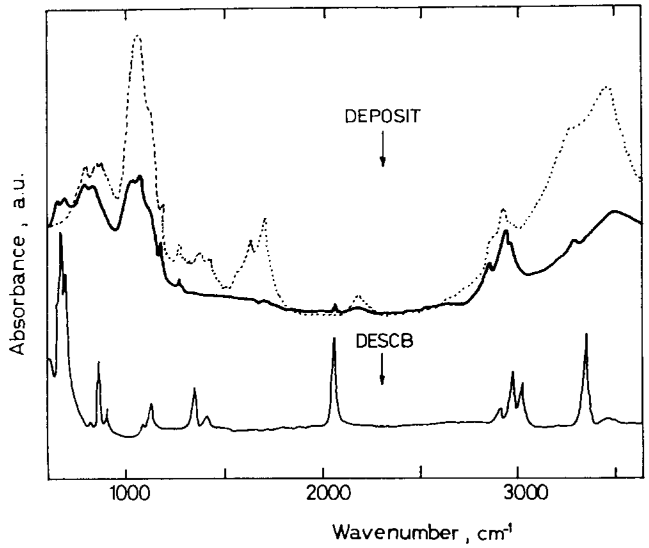
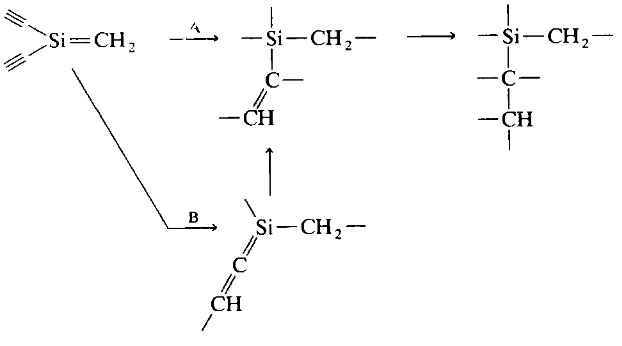


Fig. 3. IR spectrum of the deposit (upper part) after evacuation of the reactor (solid line) and after 48 h exposure to the atmosphere (dotted line), and that of DESCB (lower part).

This polymerization is very interesting when viewed in the light of the very inefficient thermal polymerization of vinylsilanes [22] and ethynylsilanes [24], which both give only very low yields of low-molecular substances. Comparison of thermal behaviour of DES with that of its carbon analogue, vinylacetylene, is also appropriate. The latter is known [25–27] to decay below



Scheme 3.

1000 K predominantly to give dimers, oligomers and polymers along with a small amount of decomposition. In contrast to LPD of DESCB (short irradiation time, low pressure), thermal polymerization of vinylacetylene requires high pressures and long heating periods, and gives only low yields of polymers. Furthermore, high-molecular substances obtained from vinylacetylene incorporate significant numbers of unsaturated bonds [28,29].

The great difference in the case of thermal polymerization of $HC{\equiv}C{-}Si{=}CH_2$ and $HC{\equiv}C{-}C{=}CH_2$ means that new types of polymers can be produced from highly unsaturated hydrocarbons containing $Si{=}CH_2$ bonds. Even a small amount of a catalyst embedded in the polymer framework leads to undesired properties of the polymers, and the thermal mode of polymerization described in this paper eliminates this disadvantage and offers a new entry into the field of polycarbosilanes [30,31].

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References

1 J. Pola, in A.R. Bassindale and P.P. Gaspar (eds.), *Frontiers of Organosilicon Chemistry*, Royal Society of Chemistry, Cambridge, 1991, p. 159.
2 R. Alexandrescu, J. Morjan, C. Grigoriu, I.N. Michailescu, Z. Bastl, J. Tláskal, R. Mayer and J. Pola, *Appl. Phys. A*, *46* (1988) 768.
3 Z. Papoušková, Z. Bastl, J. Tláskal and J. Pola, *J. Macromol. Sci.-Chem. A*, *27* (1990) 1015.
4 J. Pola, V. Chvalovský, E.A. Volnina and L.E. Guselnikov, *J. Organomet. Chem.*, *341* (1988) C13.
5 J. Pola, E.A. Volnina and L.E. Guselnikov, *J. Organomet. Chem.*, *391* (1990) 275.
6 J. Pola, D. Čukanová, M. Minárik, A. Lyčka and J. Tláskal, *J. Organomet. Chem.*, *426* (1992) 23.
7 J. Pola, M. Sedláčková, E.A. Volnina and L.E. Guselnikov, *J. Anal. Appl. Pyrol.*, *14* (1989) 345.
8 J. Pola, R. Alexandrescu, J. Morjan and D. Sorescu, *J. Anal. Appl. Pyrol.*, *18* (1990) 71.
9 W.M. Shaub and S.H. Bauer, *Int. J. Chem. Kinet.*, *7* (1985) 509.
10 D.K. Russel, *Chem. Soc. Rev.*, *19* (1990) 407.
11 J. Pola, *Spectrochim. Acta A*, *46* (1990) 607.
12 E.A. Volnina, P. Kubát and J. Pola, *J. Org. Chem.*, *54* (1987) 268.
13 J. Pola, A. Lyčka, L.E. Guselnikov and V.V. Volkova, *J. Chem. Soc., Chem. Commun.*, (1992) 20.
14 L.E. Guselnikov and N.S. Nametkin, *Chem. Rev.*, *79* (1979) 529.
15 G. Raabe and J. Michl, *Chem. Rev.*, *85* (1985) 419.
16 R.T. Conlin and D.L. Wood, *J. Am. Chem. Soc.*, *103* (1981) 1843.
17 L.E. Guselnikov, in J.Y. Corey, E.R. Corey and P.P. Gaspar (eds.), *Silicon Chemistry*, E. Horwood, Chichester, 1988, p. 533.
18 N. Auner and J. Grobe, *J. Organomet. Chem.*, *197* (1980) 13.
19 I.M.T. Davidson, A.M. Fenton, P. Jackson and F.T. Lawrence, *J. Chem. Soc., Chem. Commun.*, (1982) 806.
20 A.M. Polyakova, V.V. Korshak, A.A. Sekharova, A.D. Petrov, V.F. Mironov and G.I. Nikishin, *Izv. Akad. Nauk SSSR*, (1956) 979.
21 *Infrared Structural Correlation Tables and Data Cards*, Heyden, Spectrum House, London, 1969.
22 N.S. Nametkin, V.D. Oppengeim, V.I. Zavyalov, S.I. Puschevaya and V.M. Vdovin, *Izv. Akad. Nauk SSSR, Ser. Khim.*, (1965) 1547.
23 I.M.T. Davidson, C.E. Dean and F.T. Lawrence, *J. Chem. Soc., Chem. Commun.*, (1981) 52.
24 O.A. Novikova, B.P. Kuznecova and K.A. Kornev, *Ukr. Khim. Zh.*, *33* (1967) 931.
25 C.F. Cullis and I.A. Read, *Trans. Faraday Soc.*, *66* (1970) 920.
26 R. Ludgard and J. Heicklen, *Int. J. Chem. Kinet.*, *16* (1984) 125.
27 T. Ikegami, *Rev. Phys. Chem. Jpn.*, *33* (1963) 15.
28 A.A. Matnishyan, S.G. Grigoryan and E.T. Pogosyan, *Arm. Khim. Zh.*, *34* (1981) 342.
29 O. Kretschmer, H. Hopf and H. Naarmann, *Synth. Met.*, *41–43* (1991) 1567.
30 G. Fritz and E. Matern, *Carbosilanes, Syntheses and Reactions*, Springer-Verlag, Berlin, 1986.
31 D. Seyferth, in M. Zeldin, K.J. Wynne and H.R. Allcock (eds.), *Inorganic and Organometallic Polymers*, ACS Symposium Series 360, Washington, D.C., 1988.