Pergamon

Tetrahedron Letters, Vol. 38, No. 44, pp. 7809-7812, 1997
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0040-4039/97 $17.00 + 0.00

PII: S0040-4039(97)10043-0

UV Laser-induced Gas-phase Polymerization of Trimethyl(propynyloxy)silane

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Abstract: ArF laser photolysis of gaseous trimethyl(2-propynyloxy)silane is dominated by polymerization at the triple bond and results in the chemical vapour deposition of polytrimethylsiloxy-substituted, partly unsaturated polyhydrocarbon. The reaction represents a unique way for synthesis of polytrialkylsiloxy-substituted macromolecules.
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Lasers are finding increasing use in inducing polymerization, but their role is mostly confined to the liquid phase[1]. Laser-induced polymerization in the gas phase is initiated through excitation of gaseous molecules producing chemically reactive species which intermolecularly react to yield agglomerates. The method is documented in the literature by only few examples such as UV laser photopolymerization of methyl acrylate[2], acrolein[3] and carbon disulphide[4], and IR laser-induced thermal polymerization of azetidine[5], pyridine[6] thiophene[7] and some organosilicon or organogermanium compounds[8,9].

UV photolytically induced gas-phase polymerization of organic compounds possessing C≡C bonds has been known for long and regarded as a nuisance rather than a useful feature (see e.g. refs.[10,11]). With intense radiation from lasers, this reaction can, however, serve for chemical vapour deposition of polymeric coatings. Although the oligomers and polymers of acetylenic compounds R-C≡CH (R = alkyl, alkoxy, CN and other substituents) can be obtained by using catalysts in the liquid phase or plasma in the gas phase (e.g. refs.[12,13]), their properties are affected by small amounts of catalyst inadvertently embedded in the polymer or by specific steps occurring in the ionized gas.

This paper is dedicated to Professor Milan Horák on the occasion of his forthcoming 70th birthday.

We now report on UV laser-initiated gas-phase polymerization of trimethyl(2-propynyloxy)silane (TMPSi) and show that this reaction affords a white smog consisting of solid agglomerates having trimethylsiloxy substituted polyhydrocarbon framework and some degree of C=C unsaturation. The laser photolysis experiments were carried out in a reactor which consisted of two orthogonally positioned Pyrex tubes, one fitted with two quartz windows and the other furnished with two NaCl windows. TMPSi (18 Torr, absorptivity at 193 nm 1.06×10^{-2} $Torr^{-1}.cm^{-1}$) was irradiated at a repetition frequency of 10 Hz by pulses from an ArF (ELI 94, 193 nm) laser at an incident energy of 12 mJ effective on the area 0.6 cm^2. The progress of photolysis was monitored by FTIR spectroscopy (a Nicolet Impact FTIR spectrometer) using absorption band of TMPSi at 1112 cm^{-1}, and by gas chromatography on a Shimadzu GC 14A chromatograph (programmed temperature 20 - 180 °C, 1.5 m long column packed with Porapak P) connected with Shimadzu CR 5A Chromatopac data processor. Identification of gaseous side products was accomplished by means of FTIR spectroscopy and GC/MS technique (a Shimadzu QP-1000 mass spectrometer, 70 eV, Porapak P, programmed temperature). Properties of the deposits were measured by FTIR spectroscopy and scanning electron microscopy (a Tesla BS 350 ultra high vacuum instrument).

The ArF laser irradiation of TMPSi results in TMPSi depletion (Fig. 1), formation of negligible amounts of volatile ethyne, hexamethyldisiloxane and a $Si_2C_5H_{14}O$ compound {mass fragmentation pattern [m/z (relative intensity): 146 (100), 103 (71), 75 (44), 73 (26), 59 (14)]} assignable to a tetramethyldisilaoxacyclobutane, and of copious amounts of a white smog which is observed throughout all the reactor volume and which slowly descends upon its lowest parts. A white solid film, which is opaque to the 193 nm radiation, is also deposited on the entrance quartz window and it is detrimental to photolytic progress. Thus, the 80 % depletion of TMPSi was achieved at irradiation times of ca. 10 min only with successive positioning the laser beam onto clean parts of the entrance reactor window. Each of the volatile products -ethyne, hexamethyldisiloxane and a $Si_2C_5H_{14}O$ compound - are produced in very low yields (< 6 %). Hence, more than 90 % of the photolysed TMPSi is consumed for the formation of the solid deposit which must originate from TMPSi polymerization.

FTIR spectrum of the deposit on NaCl after exposing it to high vacuum for several hours consists of bands at ν/cm^{-1}: 800w, 837w (ν_{Si-C} and δ_{CH_3Si}), 1060vs (ν_{Si-O}), 1178w, 1257w, 1381w (both δ_{CH_3Si}), 1620m ($\nu_{C=C}$), 1730w , 2838vw, 2916w and 2956w(all ν_{H-C-}), and it is in accord with a partly unsaturated polyhydrocarbon with Si-O bonds. No absorption due to $\nu_{H-C=}$ stretch behind 3000 cm^{-1} but a significant absorption due to ν_{H-C-} reveals that H atoms are very mostly bonded to saturated fractions of the polymer framework.

The deposit is insoluble in organic solvents (tetrahydrofuran, dichloromethane, acetone, toluene), which is compatible with a higly crosslinked structure. SEM pattern of the deposited white smog (Fig. 2) reveals agglomerates which are bonded together. This indicates that the deposited particles retain some degree of polymerization reactivity. The partly unsaturated structure is confirmed by UV spectrum of the deposit which shows absorption peaking at 190 nm, having a shoulder at ~260 nm and tailing to 500 nm.

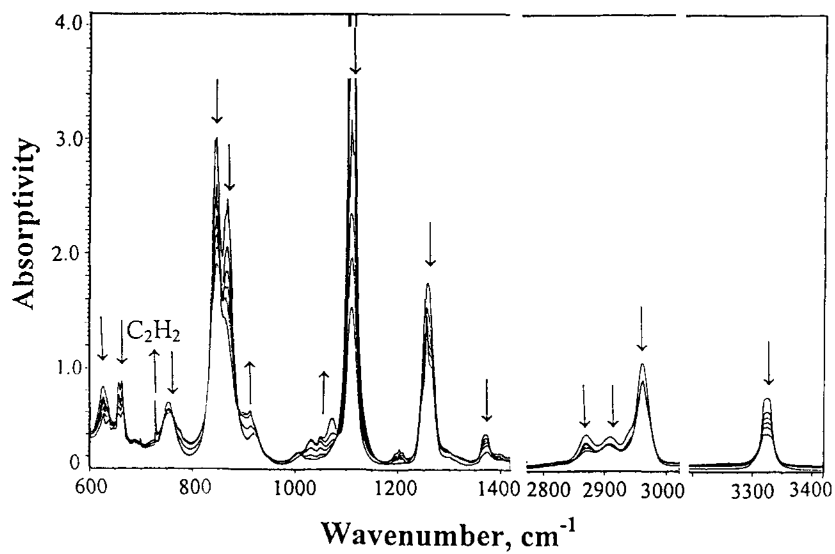

Fig. 1.
FTIR spectra of TMPSi (initially 18 Torr) depleted upon irradiation of ArF laser. (Irradiation time, 0, 1, 3, 6, 10, 15 min).

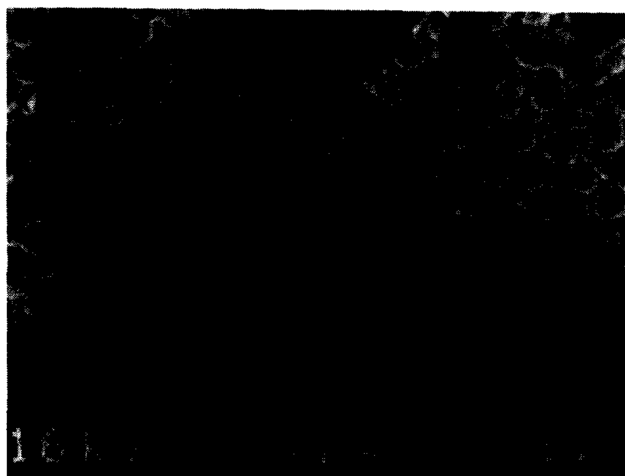

Fig. 2.
SEM of the deposit.

The results thus show that the ArF laser photolysis of TMPSi is dominated by the efficient polymerization on the triple bond, which results in the formation of agglomerates with —{[$(CH_3)_3SiOCH_2$]C=CH}— and mostly –{[$(CH_3)_3SiOCH_2$]C-CH}$_y$ units. The known reactivity of $(CH_3)_3$Si-O moiety towards hydrolysis[14] makes these macromolecules promising precursors to macromolecules possessing OH bonds which can find use as permeation barrier coatings[10], pH responsive films[15] and sensing materials[16].

Acknowledgement: The work was supported by the Grant Agency of Czech Republic (grant no. 203/96/1217) and by the Japan Society for the Promotion of Science. The authors thank to Dr. J. Šubrt for the SEM analysis.

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(*Received in UK* 23 *July* 1997; *revised* 1 *September* 1997; *accepted* 5 *September* 1997)