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CO_2 laser photosensitised decomposition of 1,3-diphenyldisiloxane in the liquid phase: formation of poly(phenylsiloxanes) via extrusion/insertion of phenylsilanone

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Abstract

CO_2 laser-induced graphite-photosensitised decomposition of liquid 1,3-diphenyldisiloxane $H_2PhSiOSiPhH_2$ (DPDS) affords a blend of poly(phenylsiloxanes) which are explained as formed via extrusion of PhHSi=O and its subsequent insertion into DPDS.

Keywords: 1,3-Diphenyldisiloxane; Laser-induced decomposition; Poly(phenylsiloxanes); Phenylsilanone

Intensively studied perorganylsiloxanes possess high thermal stability [1–3]. It is well known that (i) polydimethylsiloxanes thermally degrade in conventional pyrolytic reactors via cleavage of the thermodynamically stable Si–O bond [4–6] and that (ii) IR laser induced thermolysis of gaseous hexamethyldisiloxane and liquid polydimethylsiloxane is controlled by cleavage of the relatively weak Si–C bond [7,8]. These findings can only be explained by an enhancement of the Si–O cleavage via heterogeneous steps on the hot reactor surface in the conventional decomposition and by absence of these steps in the laser-induced decompositions wherein hot zone is deliberately positioned far from cold reactor walls.

Thermal behaviour of siloxanes was examined decades ago (e.g. [9–12]), but that of siloxanes with exclusively Si–H bonds was for a long time a virtually unknown reaction. Our recent observations of both Si–C and Si–O bond cleavages in the IR laser-induced homogeneous gas-phase decomposition of 1,1,3,3-tetramethyldisiloxane $(CH_3)_2HSiOSi(CH_3)_2H$ [13] and of the Si–O bond cleavage in the IR laser induced homogeneous gas-phase decomposition of disiloxane $H_3SiOSiH_3$ [14] indicate a feasible cleavage of the Si–O bond in disiloxanes possessing Si–H bonds and suggest that the ease of this cleavage is enhanced by H-substitution at the silicon.

sym-Diorganodisiloxanes $(RH_2Si)_2O$, whose improved synthesis has been recently described [15,16], are suitable models on which thermal decomposition of polyhydridosiloxanes can be further explored. Here we report on laser-induced graphite-photosensitised decomposition of liquid 1,3-diphenyldisiloxane (DPDS) and reveal that this reaction is controlled by extrusion of phenylsilanone PhHSi=O and its multiple insertion into DPDS.

Experiments were carried out in an evacuated Pyrex vessel furnished with three KBr windows and PTFE valve, and enabling observation of volatile products by

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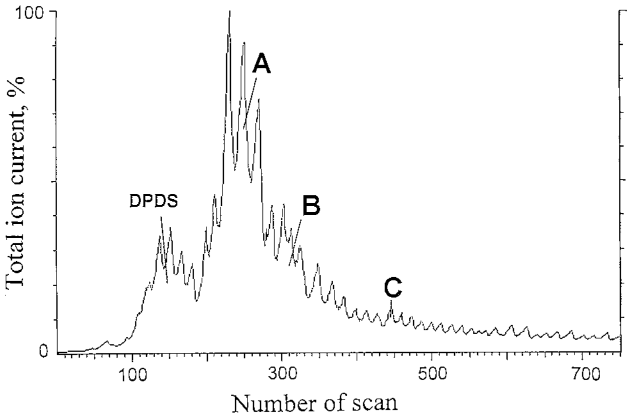


Fig. 1. TIC vs. number of scans plot obtained with MS ion trap/heated inlet system (35–300°C).

IR spectroscopy. Liquid DPDS (0.1 ml) containing suspended graphite powder (20 mg) was irradiated by a TEA (transversely excited, atmospheric) CO_2 laser operated at the repetition frequency of 1 Hz on the P(16) line of the $00^{0}1 \rightarrow 10^{0}0$ transition (947.74 cm^{-1}) with fluence of 0.5 J cm^{-2}. DPDS absorbs laser radiation directly due to its strong absorption band centred at 948 cm^{-1}. Apart from that, graphite acts as a heterogeneous sensitiser [17], because it is a very efficient absorber of the CO_2 laser radiation and its particles become heated to high temperatures within the liquid DPDS. Very fast heating of the irradiated sample was indicated by a violent ablation of the liquid after each pulse and resulted in the formation of gaseous ethyne (IR absorption at 731 cm^{-1}, only less than 1% of DPDS decomposed) and a mixture of phenylsilane and phenylsiloxanes of which only those sufficiently volatile could be detected by mass spectroscopy. In this regard the technique of heated inlet (Spectronex AG, 35–300°C)) proved more powerful than GC/MS technique and enabled determination of ca. 50 weight per cent of the liquid products; the other half of liquid products remained unobserved due to its insufficient volatility. A fraction of the higher molecular-weight products soluble in tetrahydrofuran (THF) was analysed by gel-permeation chromatography (polystyrene standards, THF eluent) to reveal that they possess a weight average M_w of ca. 7000.

The lower molecular-weight poly(phenylsiloxanes) were identified via their molar masses considering CI-ions and CI-fragments in methane and acetonitrile [18] and their EI mass spectra, as well as by the technique of mass fragmentography. They are $PhH_2SiO(PhHSiO)_nSiPhH_2$ ($n = 1–3$) and $(PhHSiO)_n$ ($n = 3–5$). The linear polyphenylsiloxanes show significantly higher total ion current (TIC) and are therefore produced in much higher yields than the cyclopolysiloxanes. Formation of both kinds of products is illustrated in Figs. 1 and 2, where linear $PhH_2SiO(PhHSiO)_nSiPhH_2$ and cyclic $(PhHSiO)_n$ polysiloxanes are referred to as L_n and C_n, respectively.

The observed products can, in principle, be formed by two different mechanisms. The more probable one is an intramolecular decomposition of DPDS into phenylsilane and transient phenylsilanone which subsequently undergoes insertion into the Si–O bond of DPDS and of products of this insertion to produce $PhH_2SiO(PhHSiO)_nSiPhH_2$ compounds (Scheme 1).

The less probable mechanism is an intermolecular exchange of hydride and siloxy groups on silicon, which is known to operate only in the presence of acidic clays which act as effective catalysts [19]. While the observed linear $PhH_2SiO(PhHSiO)_nSiPhH_2$ polysiloxanes may be produced by both routes, the identified cyclooligomers $(PhHSiO)_n$ give strong support for the occurrence of the intramolecular route, since these compounds can be only formed by cyclomerization [20] of phenylsilanone PhHSi=O.

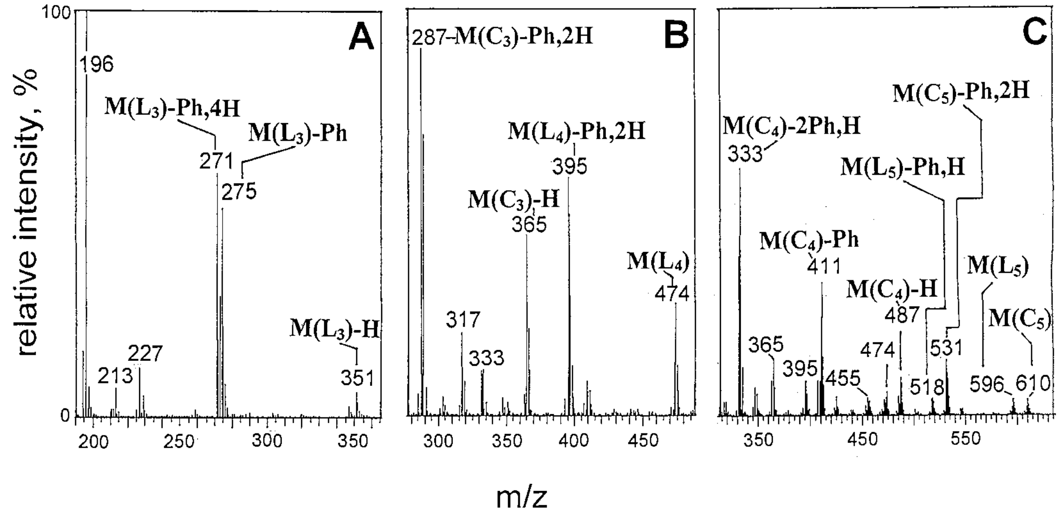
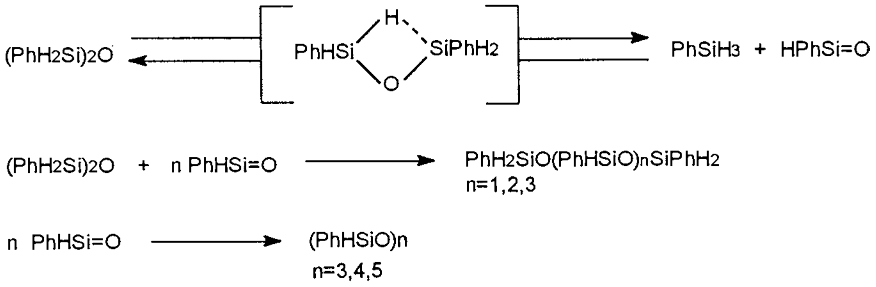


Fig. 2. Parts of the mass spectrum of the regions A, B and C, as indicated in Fig. 1, with the assignment of high ion signals.



Scheme 1. Plausible steps in the laser photosensitised decomposition of DPDS

The CO_2 laser graphite-photosensitised decomposition of DPDS in the liquid phase affording mostly linear poly(phenylsiloxanes) $PhH_2SiO(PhHSiO)_nSiPhH_2$ appears to be a simpler reaction than conventional decomposition of DPDS. Thus, DPDS heated in an ampoule at 300°C for 2 h affords a remarkably more complex mixture of poly(phenylsiloxanes) $(PhHSiO)_n$ ($n = 3,4$), $PhH_2SiO(PhHSiO)_nSiPhH_2$ ($n = 1,2$), $Ph_nH_{6-n}Si_2O$ ($n = 3,4$), $Ph_nH_{8-n}Si_3O_2$ ($n = 4,5$), $H_4Ph_6Si_4O_3$ and of polyphenylsilanes Ph_nSiH_{4-n} ($n = 2$–4). The phenylsilanes Ph_nSiH_{4-n} reveal the occurrence of scrambling of Ph and H substituents in initially formed phenylsilane, while polyphenyldisiloxanes $Ph_nH_{6-n}Si_2O$ ($n = 3,4$) originate by Ph/H scrambling in DPDS. Higher poly(phenylsiloxanes) $Ph_nH_{8-n}Si_3O_2$ ($n = 4,5$) and $H_4Ph_6Si_4O_3$ are in line with insertion of PhHSi=O into Ph_nSiH_{4-n} ($n = 2$–4) or $Ph_nH_{6-n}Si_2O$ ($n = 3,4$), since both insertion of silanone into Si–O and Si–H bonds have been observed [20].

Even though the laser-induced reaction appears to be characterised by temperature gradient (formation of ethyne necessitates higher temperatures than extrusion of phenylsilanone taking place at 300°C), its simpler course is promising for polymerising hydridosiloxanes in the liquid phase in the absence of catalytic amounts of acids or bases. Carbon particles do not seem to exert a specific effect in assisting the DPDS decomposition on graphite surface (and not in the liquid phase), since the same, but a slower course of DPDS decomposition is observed in the absence of graphite.

In summary we emphasise that the laser-induced decomposition of DPDS provides the first example of silanone extrusion from linear-chain disiloxanes. More work is in progress to shed more light on the role of graphite and to explore this reaction with other hydridosiloxanes.

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