Laser-induced Chemical Vapour Deposition of Polymethanimine

Josef Pola,[a] Antonín Lyčka,[b] Leonid E. Guselnikov[c] and Vera V. Volkova[c]

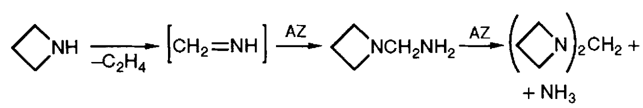
[a] *Institute of Chemical Process Fundamentals, 165 02 Prague, Czechoslovakia*
[b] *Research Institute of Organic Synthesis, 532 18 Pardubice—Rybitví, Czechoslovakia*
[c] *A. V. Topchiev Institute of Petrochemical Synthesis, B-71 Moscow, USSR*

Continuous-wave CO_2 laser photosensitized (SF_6) decomposition of azetidine, dominated by expulsion of ethene and formation of polymethanimine, represents a convenient process for chemical vapour deposition of thin polymeric films.

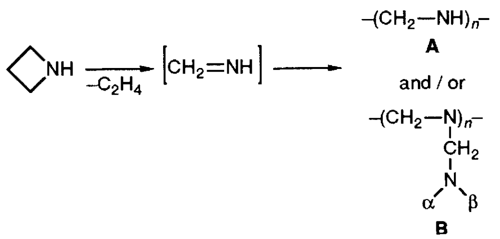
Continuous-wave (cw) CO_2 laser heating of a sensitizer serves as a very efficient means of carrying out truly homogeneous processes. This technique[1,2] was shown[3] to induce many new pathways in gas-phase chemistry owing to the elimination of heterogeneous steps that normally occur in hot-wall reactors. When applied to thermal decomposition of the four-membered silacyclobutanes[4] and 4-silaspiro[3.4]octane[5] the technique is a unique, efficient and selective route to polymers arising from intermediary silenes, although normal thermolysis of the parent compounds yields mostly silene cyclodimer.[6] A specific pathway has also been reported in the laser-powered decomposition (LPD) of spirohexane.[7]

We now report that LPD of another four-membered ring, azetidine, is a source of a new type of polymer, polymethanimine. The experiments were carried out with a cw CO_2 laser by procedures reported previously.[8] Mixtures of azetidine (AZ; 1.3–9.3 kPa) and SF_6 (1.3–8 kPa) were irradiated with a focused laser beam [the P(20) line of the 10.6 μm transition, incident energy density 20 W cm^{-2}] in a glass cylinder equipped with NaCl windows, a valve and a sleeve with a rubber septum. The progress of the decomposition was monitored by IR spectroscopy using absorption bands at 1320 cm^{-1} (AZ), 3140 cm^{-1} (ethene) and 3300 cm^{-1} (ammonia). The mean effective temperature[1] of the AZ decomposition was estimated from the rate of the cw CO_2 laser-photosensitized decomposition of 1-methyl-1-silacyclobutane[4] using the technique for non-interfering systems[1] and log A and E_a parameters from ref. 9. The value, depending on the SF_6 pressure, is in the range 700–760 K, but the maximum temperature within the hot zone where pyrolysis effectively takes place is presumably[2] considerably higher.

The irradiation of AZ results in the formation of gaseous ethene, ammonia and a white solid deposit. The quantities of



Scheme 1



Scheme 2 In **B**, α,β indicate H, CH_2NH_2, or $CH_2N(CH_2N<)_2$

Table 1 The LPD of acetidine AZ[a]

SF_6 (mol %)	Total pressure/ kPa	Conversion (%)	T_{eff}/ K	Gaseous products, p/kPa C_2H_4	NH_3
23	11	83	700	6.5	0.6
50	11	63	740	3.2	0.2
66	4	73	—	1.0	<0.1
75	11	100	760	2.6	0.2

[a] Irradiation times less than 10 s.

the decomposed AZ and ethene formed are almost equal, the ammonia yield being about one tenth that of ethene (Table 1).

This course of AZ decomposition differs remarkably from that occurring under normal conditions[10] (400 °C; glass flow reactor; excess of He) which yields as much as 90% of diazetidinylmethane by a mechanism assumed to follow that in Scheme 1.

The LPD, affording large amounts of ethene and a solid non-evacuable deposit as major products, can be assumed to be dominated by methanimine polymerization. The low ammonia yields show that the sequence of reactions presumed in the conventional pyrolysis (CP) is unimportant during LPD.

The modest solubility of the polymer in tetrahydrofuran, benzene and chloroform is consistent with a non-crosslinked structure. Two alternative routes for its formation can be assumed; one results in a linear $-(CH_2-NH)-$ structure (**A**), and the other involves reaction of $CH_2=NH$ with polymer **A** yielding branched polymer **B** (Scheme 2).

The latter reaction is analogous to that of methanimine with piperidine.[11] The ^1H NMR spectrum of the deposit (Fig. 1) consists of one slightly broadened singlet at δ 4.70 and broad signals in the range δ 0.8–4.5. The ^{13}C NMR spectrum showed a singlet at δ 74.9 due to CH_2. The intensities of the carbon signals corresponding to the protons resonating at δ 0.8–4.5 must be comparable to the noise. NMR data are in line with the assumption that the deposit consists of one predominant product and a variety of byproducts present in low concentrations. The lack of any N–H ^1H NMR signals is consistent with the preponderance of polymer **B** although some minor contributions of polymer **A** cannot be excluded because of the slightly broadened signals in the ^1H and ^{13}C NMR spectra. For comparison, the ^1H and ^{13}C chemical shifts of the $N-CH_2-N$ fragment in hexamethylenetetramine are similar δ (^1H) 4.69;[12] δ (^{13}C) 74.8[13] to our data. However, the pattern of the IR spectrum of hexamethylenetetramine[14] and of the polymeric deposit (absorption at ν/cm^{-1} 750vw, 840w, 870w, 950s, 980s, 1080s, 1180s, 1198s, 1280m, 1330s, 1420m, 2790vs, 2100s and 2140s) noticeably differ.

Gel-permeation chromatography [polystyrene standards, tetrahydrofuran (THF) as eluent] shows that the deposit is a high-molecular polymer having a weight average M_w of *ca.* 100000 with the low-molecular part of the distribution starting from above 10000 (Fig. 2).

The polymer shows excellent adhesion to aluminium, glass and sodium chloride surfaces, and scanning electron microscopy (SEM) reveals its compact structure (Fig. 3). Thermal decomposition of the polymer in the direct inlet of a mass spectrometer starts only at about 100 °C and results in the formation of an insoluble brown material and the evolution of a gaseous portion with a mass spectrum: m/z (relative intensity) 140(5), 112(2), 85(3), 83(2), 71(4), 70(43), 69(4), 57(5), 56(5), 47(4), 43(10), 42(100), 41(23), 40(4), 39(4), 30(8), 29(8), 28(24) and 27(14), that is somewhat similar to that of hexamethylenetetramine.

The intermediary methanimine can also be obtained by thermolysis of *N*-chloromethanamine,[15] azetidine,[10,11] 2-azabicyclo[2.2.4]alkenes[15] or methyl azide;[16] methanimine is known to decompose[16] upon heating (>720 K, 2.5 Pa) into H_2 and HCN. At temperatures above −80 °C it yields[15] hexamethylenetetramine together with a polymer whose structure has not been elucidated.

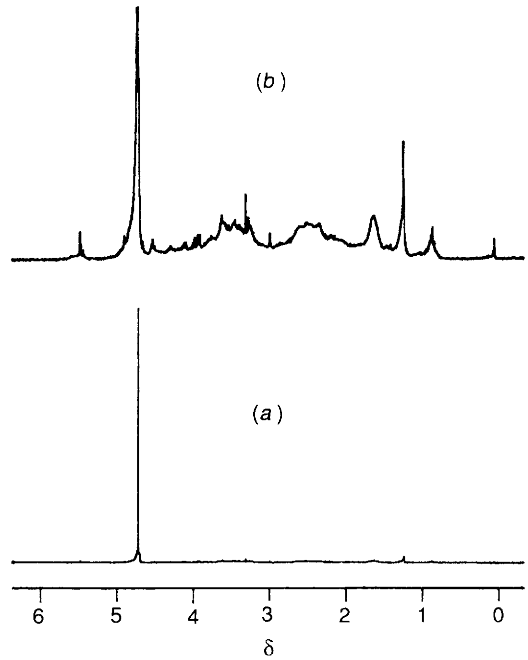


Fig. 1 Standard (*a*) and amplified (*b*) 400.13 MHz ^1H NMR spectrum of the deposit in $CDCl_3$ at 300 K

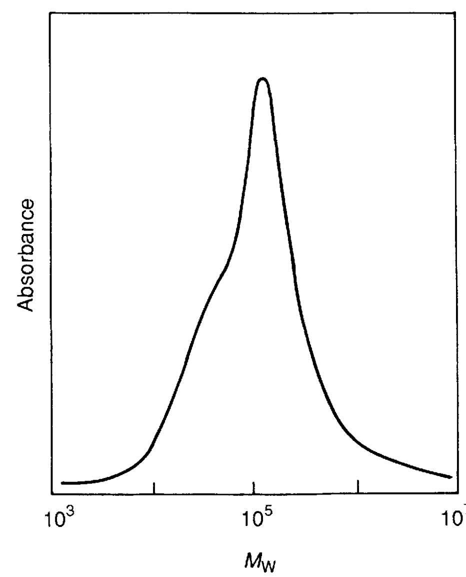


Fig. 2 Elution profile of the deposit from gel permeation chromatography

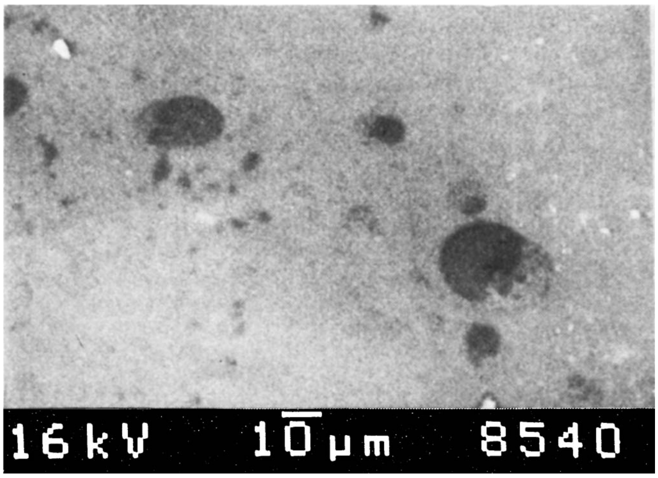


Fig. 3 SEM image of deposit

The principal reasons for the apparently different reaction pathways under LP and CP are: (*i*) heterogeneously catalysed contributions occurring on the hot vessel surface during CP are avoided in LP;[3] (*ii*) less volatile reaction products are condensed (or deposited) on the cold cell walls, where they cannot be further pyrolysed. These two differences alone, however, can hardly explain the fact that LP is dominated by the formation (deposition) of polymer **B** (Scheme 2) and that CH_2=NH is not decomposed. We believe that methanimine polymerization is favoured by the generation of high concentrations of methanimine in the hot reaction zone in LPD. The prevalence of this species increases the importance of its recombination (polymerization) and makes reactions which are of first order in it (reaction of CH_2=NH with AZ) less probable. We point out that the earlier observed[16] decomposition of the intermediary methanimine at temperatures above 770 K occurs at pressures of the CH_2=NH precursor which are three orders of magnitude lower than those used in this work. We also assume that the very low amounts of ammonia observed lend support to the minor formation of diazetidinylmethane according to Scheme 1, which undergoes elimination of ethene and then participates in the polymerization. This is strongly supported by the structure of the deposit inferred from the NMR analysis.

The laser-photosensitized (SF_6) decomposition of azetidine reported now is thus not only proved to be a convenient source of methanimine, but can also serve as a very efficient procedure for polymerizing this intermediary species into high-molecular adhesive layers.

Although the hypothesis that the efficiency of the laser-induced gas-phase decomposition for the deposition of polymer is due to the generation of a high concentration of the reactive monomer needs to be further tested, the reported laser chemical vapour deposition of polymethanimine adds to the potential of laser assisted deposition of thin films important in microelectronics and materials production.[17]

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