

Poly-1,2-azepines by the photopolymerization of phenyl azides. Precursors for conducting polymer films

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Communications to the Editor

Poly-1,2-azepines by the Photopolymerization of Phenyl Azides. Precursors for Conducting Polymer Films

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The photochemistry of phenyl azides (**1**) has been the subject of intensive research since their discovery by Wolff in 1912.¹ Despite numerous reports on the formation of large amounts of intractable tars as main products in this photochemistry,¹⁻⁸ only a few contradictory notes have been made concerning the composition of the tar and its possible mechanism of formation.^{3,4,7} In a variety of other reactions both singlet **2** and triplet **3** phenylnitrenes act as intermediates (Scheme I).⁹⁻¹² By the addition of nucleophiles, including primary and secondary amines, **2** is trapped, furnishing 2-substituted 3H-azepines **4**.^{6,8} Comprehensive chemical and spectroscopic investigations have revealed that this trapping occurs after **2** has been rearranged to azacycloheptatriene **5**, possibly via the azirine **6**; **5** has an estimated lifetime of approximately 1 ms in inert media.^{9,13} We now report our experimental evidence for the formation of poly-1,2-azepines **7** as the primary product of the polymerization of **2**. The ease of oxidation of these polymers is investigated in view of the formation of conducting polymers.

Irradiation of **1a** (neat) with a 500-W high pressure mercury arc at room temperature in an atmosphere of nitrogen, followed by heating at 110 °C in toluene, leads to the precipitation of insoluble dark-brown polymer **7a** in 15% yield.¹⁴ The same polymer, with only a small amount of low molecular weight impurities (<5%), is obtained as a thin film (up to 10 μm) on the fused silica window of the reaction vessel, when gaseous **1a** is irradiated. The polymer is grown in high-resolution patterns when the irradiation is performed through a photomask (Figure 1). Similar results are found for a series of substituted phenylazides (**1b-1g**).

We propose the formation of a (substituted) poly-1,2-azepine (**7a-g**) by the polymerization of **5**, which in turn is formed from **1** via **2** (Scheme II). The virgin poly-1,2-azepines, being antiaromatic poly(ketene)aminals, are easily oxidized when exposed

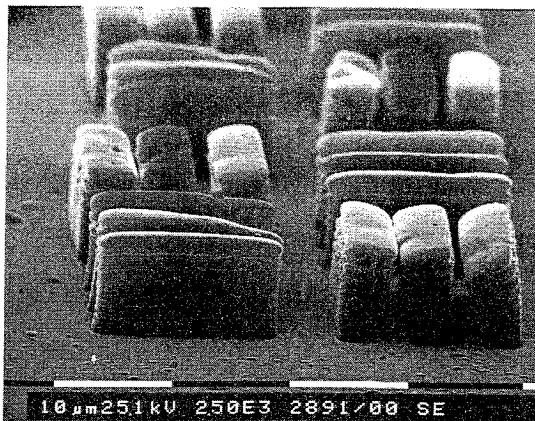


Figure 1. SEM photograph of poly-1,2-azepine **7a** as grown pattern-wise on fused silica with so-called contact illumination. The bars represent 10 microns. The mask used exhibits equal lines and spacers.

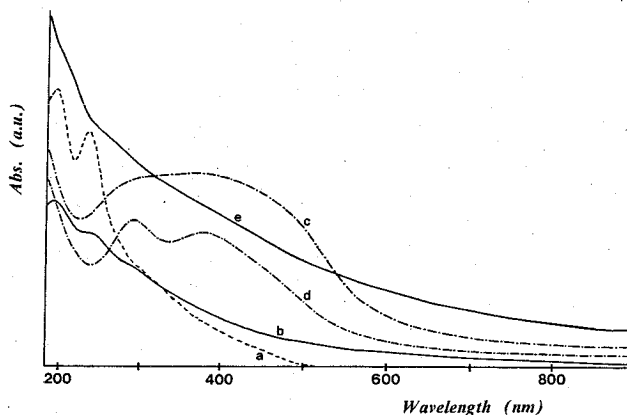
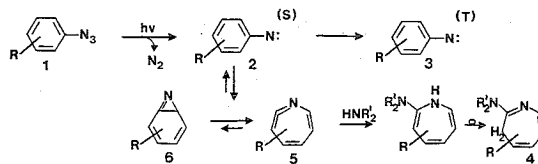
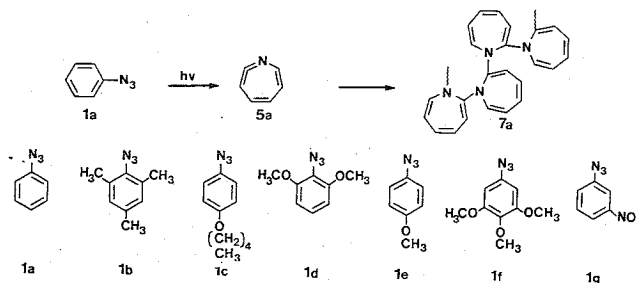


Figure 2. The UV-vis spectra of ultrathin (<0.1 μm) films of **7a**: (a) the virgin polymer, (b) after exposure to air, (c) directly after exposure to I₂ at 80 °C for 30 min, (d) the sample of (c) after 30 min; upon heating for 1 h at 80 °C spectrum (b) returns, and (e) after exposure to AsF₅ at room temperature at 400 Torr for 20 h.

Scheme I



Scheme II



to air. The UV-vis absorption spectrum of a thin film of **7a** as grown in nitrogen shows absorptions typically for azacycloheptatriene units (Figure 2).¹⁵ Upon exposure of **7a** to air, the bands

(1) *Azides and Nitrenes, Reactivity and Utility*; Scriven, E. F. V., Ed.; Academic Press: New York, 1984.

(2) Horner, L.; Christmann, A.; Gross, A. *Chem. Ber.* **1963**, *96*, 399.

(3) Reiser, A.; Leyshon, L. J. *J. Am. Chem. Soc.* **1971**, *93*, 4051.

(4) Abramovitch, R. A.; Challand, S. R.; Scriven, E. F. V. *J. Am. Chem. Soc.* **1972**, *94*, 1374.

(5) Waddell, W. H.; Go, C. L. *J. Am. Chem. Soc.* **1982**, *104*, 5804.

(6) Leyva, E.; Platz, M. S.; Persy, G.; Wirz J. *J. Am. Chem. Soc.* **1986**, *108*, 3783.

(7) Leyva, E.; Young, M. J. T.; Platz, M. S. *J. Am. Chem. Soc.* **1986**, *108*, 8307.

(8) Schrock, A. K.; Schuster, G. B. *J. Am. Chem. Soc.* **1984**, *106*, 5228.

(9) Chapman, O. L.; Le Roux, J. P. *J. Am. Chem. Soc.* **1978**, *100*, 282.

(10) Chapman, O. L.; Sheridan, R. S.; Le Roux, J. P. *J. Am. Chem. Soc.* **1978**, *100*, 6245.

(11) Chapman, O. L.; Sheridan, R. S. *J. Am. Chem. Soc.* **1979**, *101*, 3690.

(12) Chapman, O. L.; Sheridan, R. S.; Le Roux, J. P. *Recl. Trav. Chim. Pays-Bas* **1979**, *98*, 334.

(13) Shields, C. J.; Chrisope, D. R.; Schuster, G. B.; Dixon, A. J.; Poliakoff, M.; Turner, J. J. *J. Am. Chem. Soc.* **1987**, *109*, 4723.

(14) During the photopolymerization the reaction sample is slightly heated (up to 40 °C) due to the 500-W mercury arc irradiation. Heating at 110 °C increased the isolated yield, due to further thermal polymerization. By using the same procedure **7a** is isolated also, when concentrated solutions of **1a** in inert media are irradiated.

Table I. Characteristic Data of (Substituted) Poly-1,2-azepines

polymer	GPC ^a	UV ^b	IR ^c
7a	30.0	202, 245, 320 (w, sh)	750, 690
7b	32.0 ^d	200, 240 (w), 340 (sh)	845
7c	33.0 ^d	n.a.	835
7d	30.5	202, 280	780, 730
7e	30.2	n.a.	815
7f	30.5	n.a.	850 (w)
7g	30.5	195, 240, 320 (w, sh)	810, 740, 670 (all w)
emeraldine ^e	30.5		

^aGPC with DMF/0.05 M LiBr, retention time of peak is given. ^bUV-vis spectra of ultrathin films on fused silica. ^cIR out-of-plane vibrations in the region below 900 cm⁻¹. ^dThese Rt's are overshadowed by hydrophobic interactions as proven with the corresponding azides and anilines. ^eEmeraldine and polyanilines have been studied in great detail.¹⁶

are broadened, while a long tail into the near infrared appears, characteristic of the presence of undefined defect levels in the band gap of the virgin polymer. These slightly oxidized poly-1,2-azepines are the main products in the photolysis of **1**, as found in most studies published to date.¹⁻¹³ We have performed most of our analyses on these, inadvertently, slightly oxidized polymers.

The most significant data on the spectroscopic analyses are given in Table I. Independent of their structure, a low average molecular weight for **7a-g** is found with GPC (\overline{DP} about equal to emeraldine, i.e., 8-10). The out-of-plane C-H resonances in the IR fingerprint region indicate that no aromatic substitution of the phenyl azides occurs, thus excluding the formation of substituted polyanilines.^{3,4,16} Additional evidence for ring expansion during polymerization is found from ¹H and ¹³C NMR spectroscopy, although this analysis is hampered by the presence of paramagnetic species.¹⁷ The NMR spectra show very broad and low sensitivity resonances for the atoms of the azepine ring mainly by paramagnetic broadening. Powder ESR spectra of **7a** show a single isotropic Gaussian signal with a *g* factor of 2.0035 and a peak-to-peak line width of 6 G.

In contrast to neutral azepines¹⁸ the slightly oxidized poly-1,2-azepine **7a** is not reduced by H₂ and Pd/C. However, upon exposure of **7** to hydrogen chloride the corresponding HCl salts are isolated from this heterogeneous reaction.¹⁹

The ease of oxidation of **7** prompted us to investigate the possible formation of conducting polymers.²⁰ Upon oxidative doping of the polymer films with I₂ or AsF₅ specific conductivities up to 10⁻² S/cm are found. UV-vis spectra of ultrathin, doped samples (Figure 2) show that the extension of the conjugation is limited and that the conductivity with I₂ is reversible due to evaporation of the dopant.²¹ Polymer **7f** is clearly a much better C-T donor for I₂ than **7g**. These results show again that conductivity can be obtained from precursors lacking delocalization, as shown before.²²

The formation of conducting poly-1,2-azepines suggests that the charged species formed are stabilized by conjugation or even aromaticity. The species to be expected are radical cations and

dications of azepines. Delocalization of these species and 6- π electron aromaticity of the dication is evident both from theoretical studies and from experiments.²³ However, extended conjugation is excluded owing to steric hindrance between the individual azepine rings (ortho-substituted aromatics). Hence, a moderate conductivity is expected and found.

Two remarkable deductions can be drawn from the comparison of polymerizations carried out in nitrogen and in air. Firstly, the rate of polymer formation is identical in both cases, indicating that **2** and not **3** is the intermediate, as already suggested by Platz.⁴ Secondly, the polymerization performed in air is accompanied by simultaneous photooxidation of **7**, furnishing carbonyl-containing polymers (strong IR absorption at 1750 cm⁻¹), presumably by oxidation of the ketene-aminal group. In the case of alkoxy-substituted phenylazides **1c-e** and especially **1f** the photooxidation is most pronounced.²⁴

On the basis of the evidence presented, poly-1,2-azepines are established to be the primary products of the photopolymerization of phenyl azides. The polymers are easily oxidized to delocalized charged species, yielding conducting polymers that can be formed in films with pattern structures.

Acknowledgment. We gratefully acknowledge the valuable discussions with Dr. E. E. Havinga of our laboratories and Prof. Dr. H. Wynberg of the University of Groningen.

Registry No. **1a** (homopolymer), 115483-22-2; **1b** (homopolymer), 115483-23-3; **1c** (homopolymer), 115483-25-5; **1d** (homopolymer), 115483-27-7; **1e** (homopolymer), 115483-28-8; **1f** (homopolymer), 115483-30-2; **1g** (homopolymer), 115483-31-3; **7a** (SRU), 115483-32-4; **I**₂, 7553-56-2; AsF₅, 7784-36-3.

(23) Mass spectra of the radical cation of 1-H-azepine: Rinehart, K. L., Jr.; Buchholz, A. C.; Van Lear, G. E. *J. Am. Chem. Soc.* **1968**, *90*, 1073. MNDO and Gaussian80 calculations on azepines: Dewar, M. J. S.; Trinajstić, N. *Tetrahedron* **1970**, *26*, 4269. Staring, E. G. J.; Meijer, E. W., manuscript in preparation.

(24) The increased reactivity versus photooxidation by alkoxy substitution is well-known: Schaap, A. P.; Zaklika, K. A. In *Singlet Oxygen*; Wasserman, H. H., Murray, R. W., Ed.; Academic Press: New York, 1970; p 287.

Ruthenium(II)-Polypyridine Cage Complexes: Luminescence and Photochemical Properties

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Ruthenium(II)-polypyridine complexes have long since attracted the attention of many researchers because of a unique combination of ground and excited state properties and in the last 10 years have extensively been used as mediators in the interconversion of light and chemical energy.²⁻⁵ A quite important property for luminescent compounds or photosensitizers is their

(1) (a) Istituto FRAE-CNR and University of Bologna. (b) University of Fribourg. (c) University of Bonn.

(2) Kalyanasundaram, K. *Coord. Chem. Rev.* **1982**, *46*, 159.

(3) Seddon, E. A.; Seddon, K. R. *The Chemistry of Ruthenium*; Elsevier: Amsterdam, 1984; Chapter 15.

(4) Krause, R. *Struct. Bonding* **1987**, *67*, 1.

(5) Juris, A.; Balzani, V.; Barigelletti, F.; Campagna, S.; Belser, P.; von Zelewsky, A. *Coord. Chem. Rev.* **1988**, *84*, 85.

(15) Paquette, L. A. In *Nonbenzenoid Aromatics*; Snyder, J. P. Ed.; Academic Press: New York, 1969; Vol. 1, p 249.

(16) See, for polyanilines: Green, A. G.; Woodhead, A. E. *J. Chem. Soc.* **1910**, 101, 1117. Macdiarmid, A. G.; Chiang, J.-C.; Huang, W.; Humphrey, B. D.; Somasiri, N. L. D. *Mol. Cryst. Liq. Cryst.* **1985**, *125*, 309.

(17) NMR data for **7a**: ¹H NMR (DMSO-*d*₆) δ 6.2-8.2 ppm (br m); ¹³C NMR (DMSO-*d*₆) δ 129, 119, 115 ppm (all br).

(18) Elemental analysis shows an average of approximately 0.7 Cl⁻ per monomeric unit. No clear-cut analyses were obtained for the polymers, neither succeeded mass spectroscopy, by using LD-MS and FAB-MS.

(19) Doering, W. von E.; Odum, R. A. *Tetrahedron* **1966**, *22*, 81.

(20) See, for conducting polymers: *Handbook of Conducting Polymers*; Skotheim, T. A., Ed.; Marcel Dekker: New York, 1986; Vol. 1 and 2.

(21) The maximum conductivities found are 0.015 S/cm (**7a** and **I**₂), as measured with the four-point method. Typically, the conductivities are in the order of 10⁻³-10⁻⁴ S/cm. The conductivity is mainly electronic, since it is nearly independent with time when a voltage is applied. Details will be published elsewhere: Meijer, E. W.; Nijhuis, S.; Vroonhoven, F. C. B. M. van; Havinga, E. E.

(22) Swager, T. M.; Grubbs, R. H. *J. Am. Chem. Soc.* **1987**, *109*, 894 and references therein.