

# Photochemical Behavior of Poly(Organophosphazenes). I. Poly[Bis(*p*-Tolylamino)]Phosphazene

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## Synopsis

The photolysis of poly[bis(*p*-tolylamino)]phosphazene has been studied in methylene chloride solution. The main reactions observed were chain scission and crosslinking. The dissociation into radicals of polyphosphazene is proposed as the primary act of the photolysis. This has been substantiated by the results of the photolysis carried out in the presence of both radical scavengers and some benzophenones as sensitizers.

## INTRODUCTION

The synthesis and characterization of poly(organophosphazenes) have received increased attention since Allcock et al.<sup>1</sup> first prepared uncrosslinked poly(alkoxyphosphazenes) through nucleophilic replacement of chlorine in uncrosslinked  $(\text{NPCl}_2)_n$  with alkoxide ions. In fact, one of the most attractive features of the linear poly(organophosphazenes) is that, by a proper choice of the substituent group, they become suitable for interesting applications.<sup>2-4</sup> A useful characteristic of polyphosphazenes is that they are inherently flame resistant and some serve as flame retardants for other polymers. Since their fabrication into fibers is relatively easy, they have potential application in textile technology for fire-resistant fabrics or for coweaving with conventional organic polymer fibers.<sup>5</sup> For this reason, investigations on thermal and photochemical behavior of polyphosphazenes are worthwhile. The thermal stability of some polyphosphazenes has been investigated both in solution and in bulk phase.<sup>6-8</sup> This paper reports the photochemical behavior of poly[bis(*p*-tolylamino)]phosphazene,  $[\text{NP}(\text{NHC}_6\text{H}_4\text{CH}_3\text{-}p)_2]_n$ , in methylene chloride solution.

## EXPERIMENTAL

### Materials

Benzene, methanol, tetrahydrofuran, and methylene chloride used for the purification of the polymer, were Carlo Erba RP grade distilled immediately before use. Methylene chloride used for photochemical experiments was RS Carlo Erba spectrophotometric grade: it contains  $\approx 0.5\%$   $\text{C}_2\text{H}_5\text{OH}$  as stabilizer. Benzophenone, 4- $\text{CH}_3$ —, 4- $\text{Cl}$ —, 2- $\text{OH}$ —, 2- $\text{NH}_2$ —, and 4-phenyl-benzophenone were purified Aldrich products.

### Procedure

The synthesis and characterization of poly[bis(*p*-tolylamino)]phosphazene (I) have been reported.<sup>9</sup> Its purification was performed by repeated dissolution in benzene and precipitation with methanol. The properties of the recovered polymer were  $[\eta] = 68$  ml/g at 25°C in THF,  $\bar{M}_n = 2.0 \times 10^5$ ,  $\bar{M}_w = 5.5 \times 10^5$ . Analytical data, calculated values in parentheses, were C, 63.85 (65.36); H, 6.30 (6.27); N, 15.90 (16.33); P, 11.45 (12.04); Cl, 2.15 (0.00). The polymer contains some chlorine present either as salification chloride of the NH group and/or residual P—Cl.

Vigorously stirred air-saturated methylene chloride solutions of the polymer ( $c = 16$  g/liter) were irradiated at room temperature ( $\approx 22^\circ\text{C}$ ) in a Desreux-Bischoff-type suspended level viscometer with quartz walls. The parallel light of a HBO 150 W high-pressure mercury lamp was filtered to eliminate radiations of  $\lambda < 260$  nm which photolyze the  $\text{CH}_2\text{Cl}_2$ . In the case of irradiation in the presence of benzophenones, the light was filtered by a cutoff C.S. 052, which eliminates radiations of  $\lambda < 340$  nm, in order to avoid direct photolysis of the polymer. The distance from the light source was 15 cm. Molecular weights were measured by a Hewlett-Packard high-speed osmometer Mechrolab Model No. 502 and by a Sofica photogoniometer using the nonpolarized light of 546 nm. The refractive index increment adopted was 0.180.<sup>10</sup> Solution viscosity was measured in a water thermostat at  $25 \pm 0.5^\circ\text{C}$ . Spectral changes were monitored by means of a double beam UV Perkin Elmer 124 and an IR 225 spectrophotometer.

### RESULTS AND DISCUSSION

Figure 1 shows the UV spectrum in  $\text{CH}_2\text{Cl}_2$  of poly[bis(*p*-tolylamino)]phosphazene together with that of *p*-toluidine. The long-wavelength band of the polymer ( $\lambda_{\text{max}} = 285$  nm) is attributed to the intramolecular charge-transfer transition of *p*-toluidine ( $\lambda_{\text{max}} = 294$  nm)  $1 \rightarrow a_\pi$ .<sup>11</sup> The hypsochromic shift in the band of the polymer is due to a deviation from coplanarity of the benzene ring and amino group similar to that found for hindered *N,N*-dimethylanilines with *ortho* substituents.<sup>12</sup> Another hypothesis suggests that the deviation from coplanarity of the benzene ring in the polymer is due to hydrogen bonding. In this respect, it should be noted that glass-transition temperatures of poly(arylamino phosphazenes) are higher than those of the corresponding aryloxy compounds. This suggested a lower torsional mobility of the phosphazene backbone in poly(aminophosphazenes) with respect to the alkoxy derivatives due to intermolecular or intramolecular hydrogen bonding.<sup>13</sup> Evidence for hydrogen bonding in (I) could be obtained from its IR spectrum (Fig. 2), which clearly shows the bonded NH stretching frequency at  $3250\text{ cm}^{-1}$  besides the free NH at  $3360\text{ cm}^{-1}$ .<sup>14</sup>

UV irradiation of  $[\text{NP}(\text{NHC}_6\text{H}_4\text{CH}_3\text{-}p)_2]_n$  in  $\text{CH}_2\text{Cl}_2$  causes a decrease in viscosity (Fig. 3) and a rapid browning of the solution due to a structureless absorption in the visible with a shoulder at  $\approx 390$  nm (Fig. 4). After 40 hr of irradiation, the average molecular weights are  $\bar{M}_n = 5.3 \times 10^4$  and  $\bar{M}_w = 1.5 \times 10^5$  compared with the unirradiated polymer where  $\bar{M}_n = 2.0 \times 10^5$  and  $\bar{M}_w = 5.5 \times 10^5$ . No attempt was made to separate and characterize the products of long-term photolysis. The IR spectrum of the end products recovered by

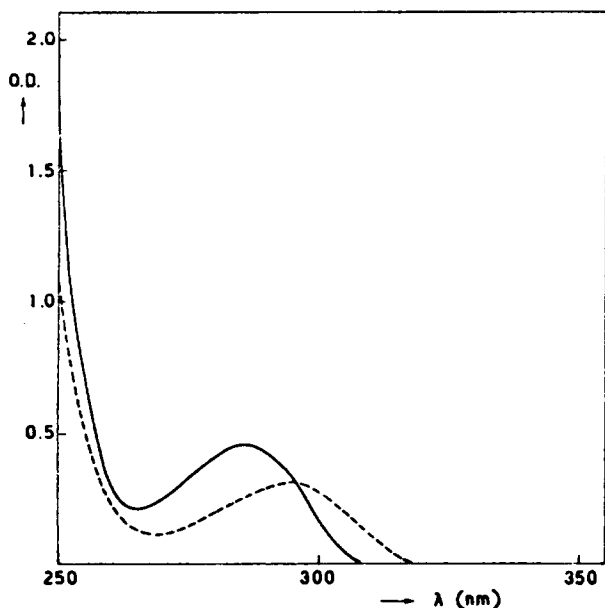


Fig. 1. Absorption spectra of *p*-toluidine (dashed line) and poly[bis(*p*-tolylamino)]phosphazene (full line).  $c = 1.76 \times 10^{-4}$  mole/liter (based on repetitive unit) in  $\text{CH}_2\text{Cl}_2$ , 1 cm cell.

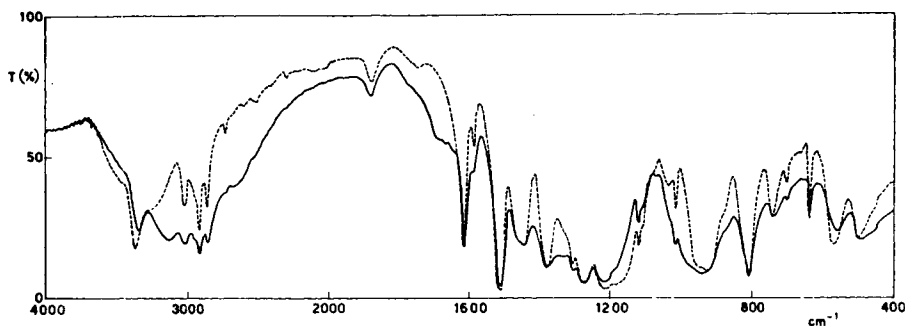


Fig. 2. IR spectrum of poly[bis(*p*-tolylamino)]phosphazene before irradiation (dashed line) and after 40 hr irradiation (full line). KBr pellet.

evaporation of  $\text{CH}_2\text{Cl}_2$  shows a general loss of structure and an increase of absorption around  $1700 \text{ cm}^{-1}$  (carbonyl absorption) and  $3000 \text{ cm}^{-1}$ .

The fact that UV spectra of high-polymeric organophosphazenes are almost identical to those of corresponding cyclic trimers and tetramers provides strong evidence against the occurrence of a high degree of delocalized skeletal bonding.<sup>2,3</sup> As the P—Cl bond does not absorb appreciably above  $240 \text{ nm}$ ,<sup>2</sup> it is reasonable that for our experimental conditions ( $\lambda_{\text{irr}} > 260 \text{ nm}$ ) the photochemical properties of  $[\text{NP}(\text{NHC}_6\text{H}_4\text{CH}_3\text{-}p)_2]_n$  are very similar to those of the *p*-toluidine. In experiments carried out in gas,<sup>15</sup> solution<sup>16</sup> and matrix phase at low temperature,<sup>17</sup> photolysis of aniline and its derivatives led to the formation of arylamino and hydrogen radicals. Using a gas chromatograph coupled with a mass spectrograph, we identified the compounds listed in Table I as products of the early stages of the photolysis (1 hr irradiation) of polymer (I). The *p*-toluidine is by

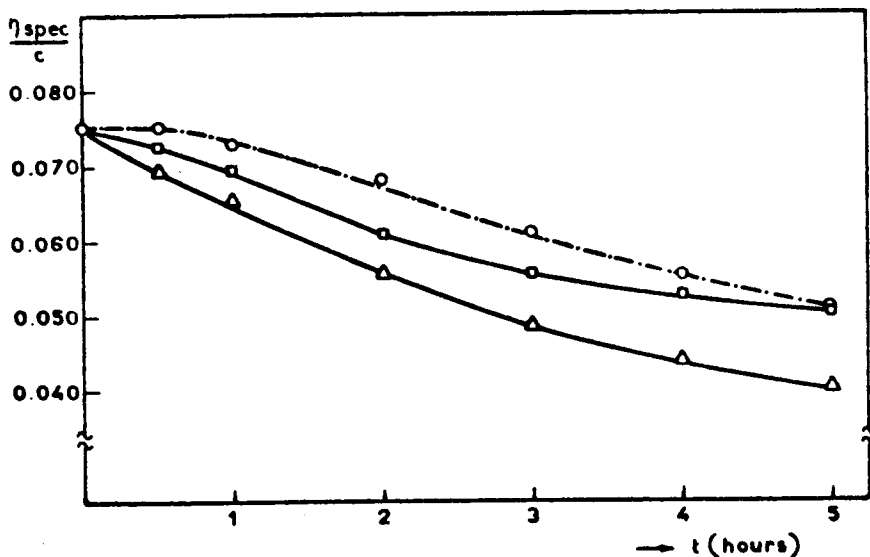


Fig. 3. Changes in viscosity of poly[bis(*p*-tolylamino)]phosphazene solution with irradiation time. (O-O-O) no scavenger added; (□-□-□) in presence of  $5 \times 10^{-3} M$  hydroquinone; (Δ-Δ-Δ) in presence of  $5 \times 10^{-3} M$  phenylthiol.

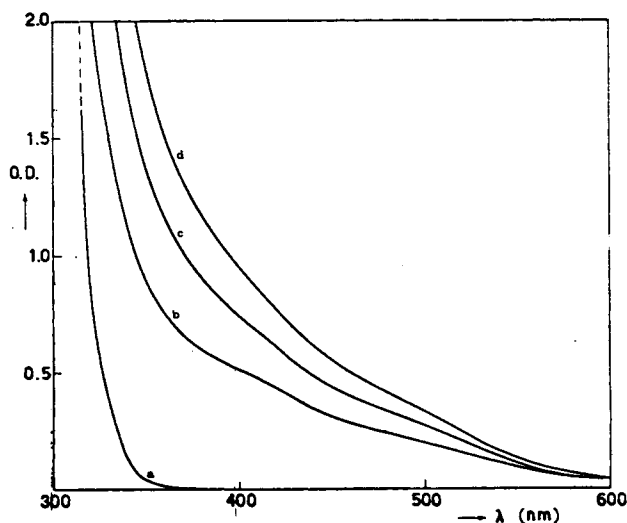


Fig. 4. Changes in UV absorption spectrum of poly[bis(*p*-tolylamino)]phosphazene with irradiation time. (a) Before irradiation, (b) after 15 min irradiation; (c) after 30 min irradiation; (d) after 45 min irradiation.

far the most abundant product; this suggests the following mechanism for the primary act of the photolysis of poly[bis(*p*-tolylamino)]phosphazene:

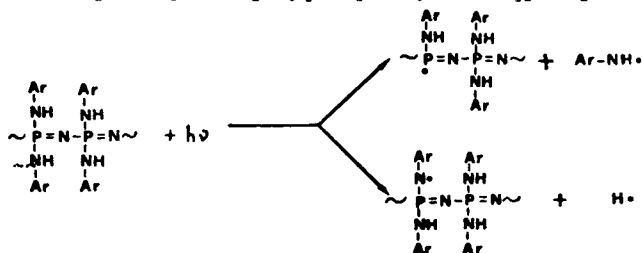


TABLE I  
Mass Spectra of Products Formed in Early Stages of the Photolysis of Poly[Bis(*p*-Tolylamino)]-Phosphazene in Methylene Chloride Solution

<i>m/e</i>	Relative intensity	Assignment
90.5	6	1-Cl-butene-2 <sup>a</sup>
107	100	<i>p</i> -toluidine <sup>a</sup>
160	2	—

<sup>a</sup> By comparison with an authentic sample purchased from Aldrich.

1-chloro-2-butene should be a product of reactions of the radical  $\cdot\text{CHCl}_2$  formed by abstraction of a hydrogen from the solvent by *p*-tolylamino radical.<sup>18</sup> The third compound is the product of the reaction of free toluidine with the chloro-butene.

The reactions of *p*-tolylamino radicals are responsible for the color of the irradiated solution: benzidine, diphenylamine derivatives, azobenzene, and *p*-benzoquinone imine derivatives have been identified as end products of the photolysis of aniline and related molecules.<sup>16,19</sup> In fact, solutions of (I) containing  $5 \times 10^{-3} M$  hydroquinone or phenylthiol, typical radical scavengers,<sup>20</sup> show an increase in absorption, due to irradiation, in the region 350–550 nm lower than that of solutions of (I) without scavenger added (compare Figs. 4 and 5). The variations in viscosity are greater in the presence of radical scavengers (Fig. 3): this should be attributed to a lower internal-filter effect of the colored photolysis products. *p*-Benzoquinone imine is probably responsible for the IR absorption at  $1700 \text{ cm}^{-1}$ :  $\text{CH}_2\text{Cl}_2$  solutions of  $[\text{NP}(\text{NHC}_6\text{H}_4\text{CH}_3\text{-}p)_2]_n$ , evacuated at  $10^{-6}$  Torr by several freeze-pump-thaw cycles and then sealed, showed no trace of the band at  $1700 \text{ cm}^{-1}$  even after a very long irradiation (100 hr).

Crosslinking may occur by recombination of two macroradicals. No appre-

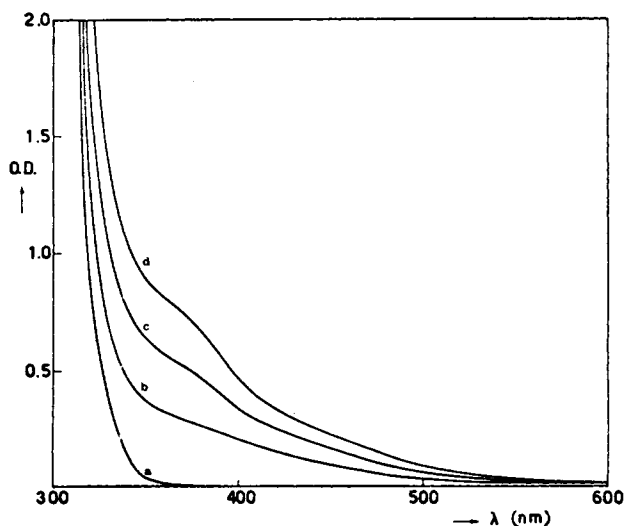
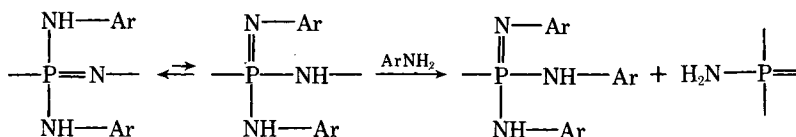


Fig. 5. Changes in UV absorption spectrum of poly[bis(*p*-tolylamino)]phosphazene, in presence of  $5 \times 10^{-3} M$  phenylthiol, with irradiation time. (a) Before irradiation; (b) after 15 min irradiation; (c) after 30 min irradiation; (d) after 45 min irradiation.

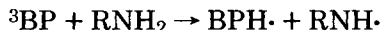
cial gel formation has been observed in our experimental conditions. However, the viscosity of the solution decreases very slowly during the initial irradiation (Fig. 3). Experiments carried out with samples of polymer, subjected to further purification cycles using different solvent/precipitant pairs, showed the same behavior. Hence, the hypothesis of an inhibition of the photolysis by impurities is eliminated. Such a behavior could result from simultaneous degradation and crosslinking, since the gel formation is easily detected by increasing the number of photochemical events (radical formation) per unit volume. Crosslinking, being a bimolecular process, is enhanced by experimental conditions which increase the concentration of reactive species.

Backbone scission during the photolysis occurs by a disproportion of macro-radicals formed by light absorption or by the following aminolysis process:



Such a process, suggested by White et al.<sup>13</sup> to explain the fact that the molecular weights of poly(arylamino)phosphazenes are significantly lower than those of poly(aryloxyphosphazenes), could be responsible for an observed post-effect: irradiated solutions of polymer (I), kept in the dark, show a slight, but significant, decrease in viscosity; such a phenomenon is not observed in unirradiated solutions.

Further support to the mechanism proposed for the photolysis of poly[bis(*p*-tolylamino)]phosphazene comes from irradiation carried out in the presence of benzophenones ( $c = 5 \times 10^{-3}M$ ) as sensitizers. Photolysis in the presence of benzophenone (BP), 4-CH<sub>3</sub>-, 4-Cl-, and 4-phenyl-benzophenone show features very similar to those described for direct irradiation: a decrease in viscosity and a browning of the solutions; the rates of these processes are practically the same for the first three sensitizers and about  $1/5$  lower for 4-phenyl-benzophenone. Solutions containing 2-OH- or 2-NH<sub>2</sub>-benzophenone show no decrease in viscosity and no variation in the UV spectrum even after 40 hr irradiation. These results support the hypothesis that direct photolysis of (I) occurs *via* the radical mechanism of scheme I. Benzophenone and its 4-CH<sub>3</sub>- and 4-Cl-derivatives in their  $n, \pi^*$  triplet excited state, efficiently abstract hydrogen from amines<sup>21</sup> according to



whereas 2-OH- and 2-NH<sub>2</sub>-benzophenone are inefficient as hydrogen abstractors because of an intramolecular ketoenolic equilibrium existing between carbonyl and the hydrogen atom of the substituent group.<sup>22</sup> 4-phenyl-benzophenone has an intermediate behavior because the  $\pi, \pi^*$  nature of its lowest triplet state,<sup>23</sup> in which the excitation energy is delocalized on the whole molecule, greatly reduces the abstractive power of the carbonyl group.

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