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Photochemical Behavior of Poly(organophosphazenes). 3. Role of the Charge-Transfer Process in the Photolysis of Poly[bis(*p*-tolylamino)phosphazene] in Halogenated Solvents

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ABSTRACT: The photochemical behavior of poly[bis(*p*-tolylamino)phosphazene] in halogenated solvents is the result of two concurrent processes: the homolytic scission of side-chain *p*-tolylamino moieties and the charge-transfer reaction from these groups to the solvent in which the polymer is dissolved. Moreover, three parameters determine the reaction path of the excited polymer in solution: the concentration of molecular oxygen, the presence of species which may supply hydrogen atoms, and the electron affinity of the solvent in which the photolysis is carried out. The relative importance of these parameters to the overall photochemical behavior of poly[bis(*p*-tolylamino)phosphazene] in solution has been evaluated.

Introduction

Since the pioneering work of Allcock on the preparation of poly(organophosphazenes),[1] interest in these polymers with a phosphorus–nitrogen backbone has markedly grown. Due to the fact that poly(organophosphazenes) are prepared by nucleophilic substitution of the chlorines of poly(dichlorophosphazene), a wide variety of substituents can be inserted in the inorganic backbone, and polymers with variable chemical and physical properties are obtainable. Since some of these polymers have high resistance to flammability,[2] commercial application of these materials as fire-resistant coatings and flame-retardant additives is currently being considered.[3] Recently, other research areas, such as biomedical applications,[4] have begun to be explored, so increasing scientific interest in these polymers.

To date, most of the experimental work in the field of poly(organophosphazenes) has been done on the synthesis, characterization, and thermal properties of these polymers. Moreover, several studies on the thermal degradation of poly[(aryloxy)phosphazenes] have been reported[5-8] and their photochemical stability has begun to be explored.[9]

In our laboratory, the activity on poly(organophosphazenes) is mainly focused on the behavior of these polymers in solution under γ and UV irradiation. Irradiation with γ rays of air-saturated solutions of poly[bis(arylamino)phosphazenes] in various solvents leads to degradation of the polymers, induced mainly by the free radicals formed by the action of the γ rays on the solvent.[10] The photochemical behavior of poly[bis(*p*-tolylamino)phosphazene] and poly[bis(β-naphthoxy)phosphazene], as examples of arylamino- and aryloxy-substituted poly(organophosphazenes), has been investigated in previous papers of this series.[11,12] It could be demonstrated that, for both polymers, the primary photochemical act is the homolytic cleavage of the bond between the phosphorus atom of the inorganic backbone and the arylamino or aryloxy substituent. In the absence of oxygen, interchain linkage of the macroradicals formed is the dominant process: this leads to an increase of molecular weight and to gel formation. In air-saturated solutions, a peroxidic intermediate on the phosphorus atom can be formed and the breaking of the O–OH bond induces chain scission of the polymer and a decrease in molecular weight.

In a recent communication,[13] we presented some preliminary results concerning the influence of the solvent on the photochemistry of arylamino-substituted polyphosphazenes. The results were that the electron affinity of the solvent plays an important role in the photoreactivity of poly[bis(arylamino)phosphazenes] and, in this paper, we give a more detailed account of our investigation.

Experimental Section

Poly[bis(*p*-tolylamino)phosphazene] (PTAP) was prepared according to a known procedure[14] and was purified by repeated dissolution in THF and precipitation with CH_3OH. The elemental analysis data of the polymer are as follows (calculated values in

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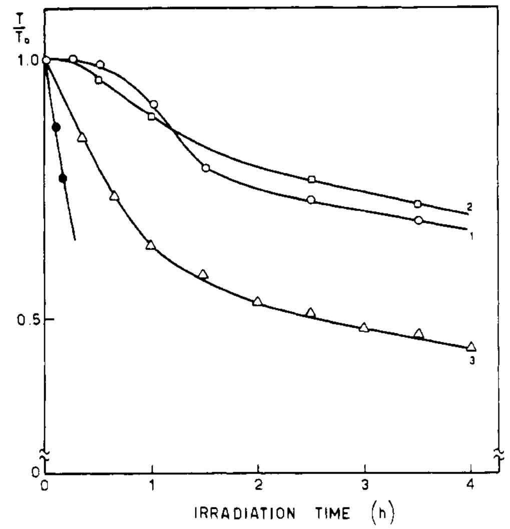


Figure 1. Changes in viscosity of PTAP solutions with irradiation time: (○) THF; (□) CH_2Cl_2; (△) $CHCl_3$; (●) CCl_4.

parentheses): C, 64.7 (65.3); H, 6.1 (6.2); N, 16.0 (16.3); P, 12.1 (12.1); Cl, 0.8 (0.0). The properties of the polymer were $[\eta] = 79$ mL/g at 25 °C in THF, $\bar{M}_n = 3.3 \times 10^5$, and $\bar{M}_w = 1.3 \times 10^6$.

The halogenated solvents were Carlo Erba RS (or RP) grade and were purified from the stabilizing agents following known procedures.[15] When necessary, a known amount of absolute ethanol was added to the proper solvent. Tetrahydrofuran (THF) was a Carlo Erba RP grade product and it was purified by distillation over NaOH and potassium metal immediately before the use. THF-d_8 and $CDCl_3$ were Merck and Carlo Erba products, respectively.

Molecular weight determinations, viscosity measurements, UV spectra recording, and identification of the photolysis products are as reported elsewhere.[11]

The solutions were irradiated at room temperature (≃22 °C) in a Desreux-Bischoff-type suspended level viscometer with quartz walls. The exciting source was an HBO 150-W high-pressure mercury lamp whose light was rendered parallel and filtered by a cutoff filter to eliminate radiation below 300 nm.

Fluorescence quenching experiments were performed in aerated solutions, using a Perkin-Elmer MPF 44A spectrofluorimeter. Fluorescence lifetimes were measured by a single-photon-counting apparatus from Applied Photophysics.

The absorption spectra of transient intermediates produced during the photolysis were determined with an Applied Photophysics flash photolysis apparatus (Model KR 10) whose resolution time is about 20 μs.

The concentration of the solutions subjected to steady photolysis was around 10 g/L.

Results and Discussion

Figure 1 shows that UV irradiation of air-saturated solutions of poly[bis(*p*-tolylamino)phosphazene] in THF, CH_2Cl_2, $CHCl_3$, and CCl_4 produced appreciable decreases of viscosity, whose extent depends on the nature of the solvent. More exhaustive information on the nature of the phenomena occurring in the irradiated solutions (chain scission and/or cross-linking processes) comes from the determination of the average molecular weights after a fixed irradiation time. Table I collects the values of $\bar{M}_n$ and $\bar{M}_w$ before and after 4 h of irradiation. It can be seen that, in THF, CH_2Cl_2, and $CHCl_3$, degradation of PTAP is the prevailing process. At the end of the irradiation, the number of breaks per original chain is 0.43 in THF, 0.55 in CH_2Cl_2, and 1.06 in $CHCl_3$. Partial cross-linking is also operative in THF and in CH_2Cl_2 as detectable by the initial increase of $\bar{M}_w$ with the irradiation (see Figure 2) and by the slight increase in $\bar{M}_w/\bar{M}_n$, which, after 4 h of irradiation, rises from the initial value of 3.95 to 4.31 in THF and 4.65 in CH_2Cl_2. Cross-linking is the dominant process in CCl_4 so that, at the end of the irradiation, about 75% of the starting polymer was recovered as a gel. It must be stressed that, in oxygen-free solutions, the importance of cross-linking processes increases, as already found in the case of the photolysis of poly[bis(β-naphthoxy)phosphazene] in CH_2Cl_2 solution.[12]

Table I
Average Molecular Weights of PTAP after 4 h of Irradiation in Air-Saturated and Deaerated Solutions[a]

	air-satd soln		deaerated soln	
solvent	$\bar{M}_n$	$\bar{M}_w$	$\bar{M}_n$	$\bar{M}_w$
THF	2.3×10^5	9.9×10^5	3.2×10^5	1.4×10^6
CH_2Cl_2	2.1×10^5	9.8×10^5	3.4×10^5	1.9×10^6
$CHCl_3$	1.6×10^5	5.0×10^5	3.4×10^5	1.9×10^6
CCl_4	≃75% gel		≃75% gel	
CCl_4 + 1% EtOH	1.1×10^5	3.0×10^5	3.6×10^5	2.1×10^6

[a] Starting polymer: $\bar{M}_n = 3.3 \times 10^5$, $\bar{M}_w = 1.3 \times 10^6$.

Table II
Products of the Photolysis of PTAP in THF and Halomethanes Identified by Gas Chromatographic Comparison with Authentic Samples

solvent	products
THF	*p*-toluidine, toluene
CH_2Cl_2	*p*-toluidine, toluene, *sym*-dichloroethane
$CHCl_3$	*p*-toluidine, *sym*-tetrachloroethane
CCl_4	*p*-toluidine, hexachloroethane
CCl_4 + 1% EtOH	*p*-toluidine, *sym*-tetrachloroethane, pentachloroethane, hexachloroethane

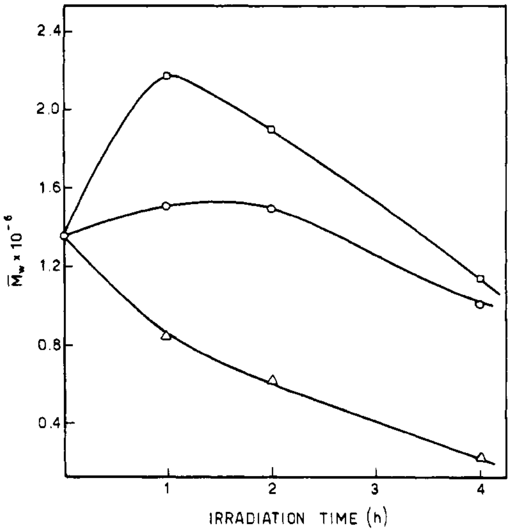


Figure 2. Variations of $\bar{M}_w$ of PTAP solutions with irradiation time: (○) THF; (□) CH_2Cl_2; (△) $CHCl_3$.

The extensive cross-linking in CCl_4 solution can be avoided by adding H-supplying molecules to the reaction medium. In CCl_4 containing 1% (by volume) EtOH, no gel formation was detected after 4 h of irradiation. The molecular weights were reduced to $\bar{M}_n = 1.1 \times 10^5$ and $\bar{M}_w = 3.0 \times 10^5$ (initial values 3.3×10^5 and 1.3×10^6, respectively), the number of breaks per original chain was 2, and $\bar{M}_w/\bar{M}_n$ decreases from the original value of 3.95 to 2.73, so indicating that a random scission of the polymer chain is operative.[16]

It must be pointed out that the addition of 1% C_2H_5OH to THF, CH_2Cl_2, and $CHCl_3$ (hydrogen-containing solvents) does not modify appreciably the behavior of PTAP under irradiation.

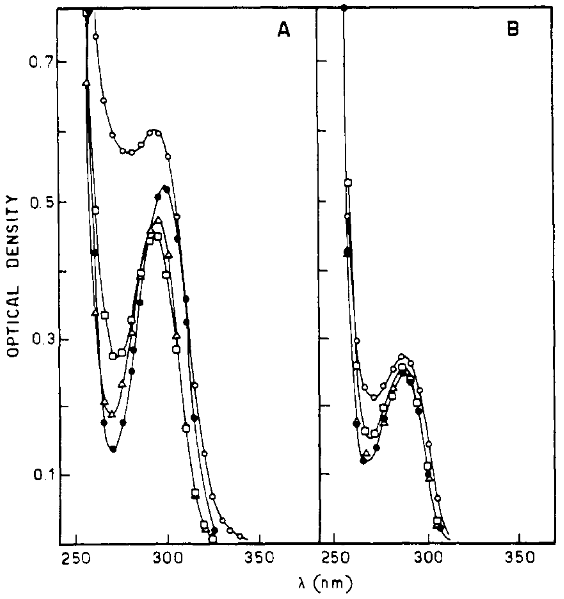


Figure 3. UV absorption spectra of *p*-toluidine (A) and PTAP (B) in (●) THF, (△) CH_2Cl_2, (□) $CHCl_2$, and (○) CCl_4. $c = 0.45$ g/L, cell 0.1-cm thick.

Table II lists the identified low molecular weight products of the photolysis. Free *p*-toluidine is the main product of the photolysis in all the solvents, while toluene was found only when the photolysis was performed in THF and CH_2Cl_2 solutions. When halocarbon solvents were used, polyhalogenated ethanes, coming from combination reactions of radicals of the solvent, are also present in solution. Moreover, an increase of the chlorine content in the polymer recovered after the photolysis was observed; for example, in the polymer recovered after 4 h of irradiation in CCl_4, the chlorine percentage increased from the initial 0.8% to 6.3%.

Looking at the above results, we note that the behavior of solutions of PTAP under irradiation seems to be affected by the following factors: (a) the presence of molecular oxygen in solution; (b) the possibility of the solvent supplying H atoms. When both of the above-mentioned experimental conditions are fulfilled simultaneously, a third factor seems to influence the photochemical behavior of the polymer: (c) the electron affinity of the solvent. The intervention of this latter parameter in determining the photoreactivity of PTAP in solution is supported by UV spectral data, fluorescence quenching studies, and flash photolysis experiments in solvents of different electron affinity.

UV Absorption Spectra

The UV absorption spectra of *p*-toluidine and poly[bis(*p*-tolylamino)phosphazene] in THF, CH_2Cl_2, $CHCl_3$, and CCl_4 are reported in Figure 3. In THF, the spectrum of the polymer and that of the free toluidine are quite similar, indicating that the same electronic transition is involved in the free amine and in the amine bonded to the inorganic backbone. The hypsochromic shift which is observed in the band of the polymer may be due to a deviation from coplanarity of the benzene ring and amino group due to steric crowding or to intramolecular hydrogen bonding.[11] An interesting feature of the spectra of both poly[bis(*p*-tolylamino)phosphazene] and *p*-toluidine is an increase of the absorption in the region 260–280 nm on going from THF to CCl_4. Variations of the absorption spectrum in halocarbon solvents have been already observed for both aliphatic and aromatic amines.[17,18] These variations have been attributed to a sharing of electrons between the amine (the electron donor) and the halogenated solvent (the electron acceptor) with formation of an n,σ-type charge-transfer complex following the scheme

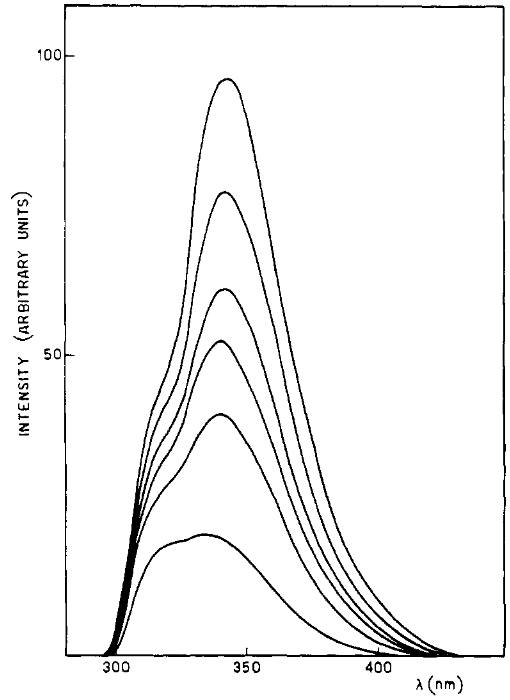


Figure 4. Fluorescence quenching of PTAP in an aerated solution of THF by CCl_4.

$$D + A \rightleftarrows D\cdots A \leftrightarrow D^+A^-$$

The free energy change associated with an electron-transfer process may be expressed as

$$\Delta G = IP_D - EA_A - C \qquad (1)$$

where IP_D is the ionization potential of the donor, EA_A is the electron affinity of the acceptor, and C is a term which accounts for the Coulombic change on forming the complex in its equilibrium configuration. Equation 1 shows that an increase of the electron affinity of the acceptor brings about a decrease of ΔG and, consequently, an increase in the value of the association constant of the charge-transfer complex. The electron affinity of halomethanes increases in the order $CH_2Cl_2 < CHCl_3 < CCl_4$, i.e., in the same order of the variations of optical density of both free toluidine and PTAP. The parallel trend of the absorption of free toluidine and PTAP in solvents of different electron affinity seems to justify the hypothesis that a charge-transfer complex is formed between the polymer and the halogenated solvent. The association constant between *p*-toluidine and CCl_4 was measured by applying the Benesi–Hildebrand equation:[19] the estimated value (5×10^{-2} mol^{-1} L) is in fair to good agreement with that reported by Davis[18] for the *N*,*N*-dimethylaniline–CCl_4 complex. Quantitative evaluation of the association constant for the complex between CCl_4 (the strongest electron acceptor in the series of the chloromethanes) and the polymer is not possible. However, the spectral variations due to the presence in solution of a complex suggest for PTAP an interaction about 1 order of magnitude lower than that for the free *p*-toluidine.

Fluorescence Quenching Studies

The fluorescence spectrum of PTAP in THF solution and the effect of small additions of CCl_4 on the emission are reported in Figure 4. A decrease of the fluorescence quantum yield with increasing [CCl_4] is observed. It must

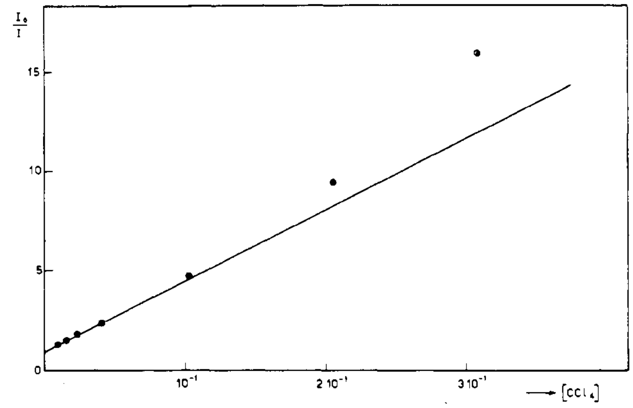


Figure 5. Stern–Volmer plot for the quenching of the fluorescence of PTAP in an aerated solution of THF by CCl_4.

be pointed out that appreciable quenching is observable with CCl_4 concentrations which do not perturb the absorption spectrum of the polymer, so excluding that the formation of the ground-state molecular complex is responsible for the quenching of the fluorescence. Similar effects are also observed in the presence of other halogenated hydrocarbons.

If an electron donor lies in the first electronically excited singlet state, the equation (1) for the formation of a charge-transfer complex modifies, following Weller,[20-22] to

$$\Delta G = \mathrm{IP_D} - \mathrm{EA_A} - C - {}^1\Delta E^{0\text{–}0} \qquad (2)$$

where ${}^1\Delta E^{0\text{–}0}$ is the spectroscopic energy for the 0–0 transition of the donor from the ground state to the first excited singlet state. From a comparison of eq 1 and 2, one sees that the charge-transfer complex between a given electron acceptor and an electronically excited donor is stronger than that formed by the same donor in its ground state by the quantity ${}^1\Delta E^{0\text{–}0}$.

Electron-transfer processes involving excited states occur with quenching of the emission of the donor and may be followed by fluorescence spectroscopy. The fluorescence quenching follows the Stern–Volmer relationship[23]

$$I_0/I = 1 + k_q\tau^0[\mathrm{A}]$$

where I_0 and I are, respectively, the fluorescence intensities in the absence and in the presence of a concentration [A] of halogenated compound, τ^0 is the lifetime of the emitting state in the absence of any quencher, and k_q is the fluorescence quenching rate constant. Figure 5 reports, as an example, the Stern–Volmer plot for the quenching of the fluorescence of PTAP in THF by CCl_4. A good linear plot is obtained up to $[CCl_4] = 10^{-1}$ M, so confirming that complex formation in the ground state is not responsible for the fluorescence quenching. Only at $[CCl_4] > 2 \times 10^{-1}$ M, when variations in the absorption spectrum are also observable, does the Stern–Volmer plot show the upward curvature which is characteristic of an interaction between the quencher and the emitting species in the ground state.[24]

According to eq 2, if the formation of a charge-transfer complex between the electronically excited polymer and the halogenated compound is responsible for the fluorescence quenching, there should be a linear relationship between the ΔG of the process and the electron affinity of the quencher. As demonstrated by Weller,[20-22] the free energy variations in eq 2 are obtainable from the fluorescence quenching rate constants, and the electron affinities, although not readily available, are related to the polarographic redox potentials of the quenchers.[25] Table III lists the quenching constants for the emission of PTAP in THF by several halogenated hydrocarbons with different polarographic potentials as determined by Kolthoff and Lingane.[26] There is a 30-fold change in k_q on going from the poor electron acceptor CH_2Cl_2 to the strong acceptor CCl_4. The correlation between quencher redox potential and quenching rate constant is poor. However, the rather steady increase of log k_q with increasing ease of reduction of the halogenated compounds seems to confirm the charge-transfer nature of the interaction between the electronically excited polymer and the halogenated compound.

Table III
Rate Parameters for the Quenching of the Emission of PTAP in THF Air-Saturated Solution by Halogenated Compounds[a]

compound	$-E_{1/2}$, V	K_{SV}, M^{-1}	k_q, $M^{-1}\ s^{-1}$	log k_q
CH_2Cl_2	2.33	1.5 ∓ 0.2	2.6×10^8	8.41
$CCl_2{=}CHCl$	2.14	9.9 ∓ 0.2	1.7×10^9	9.22
CH_3CH_2Br	2.08	2.6 ∓ 0.2	4.4×10^8	8.64
$CH_2{=}CHCH_2Cl$	1.91	6.0 ∓ 0.1	1.0×10^9	9.00
$CHCl_3$	1.67	15.5 ∓ 0.5	2.6×10^9	9.42
CH_2BrCH_2Br	1.52	13.5 ∓ 0.1	2.3×10^9	9.36
CCl_4	0.78	32.5 ∓ 0.2	5.5×10^9	9.74
$CHBr_3$	0.64	41.5 ∓ 1.0	7.0×10^9	9.85
CCl_3CCl_3	0.62	20.5 ∓ 2.5	3.4×10^9	9.53

[a] Calculated by using $\tau^0 = 5.6$ ns as the fluorescence lifetime of PTAP in THF air-saturated solution. Fluorescence decay monitored at 340 nm; excitation wavelength 290 nm.

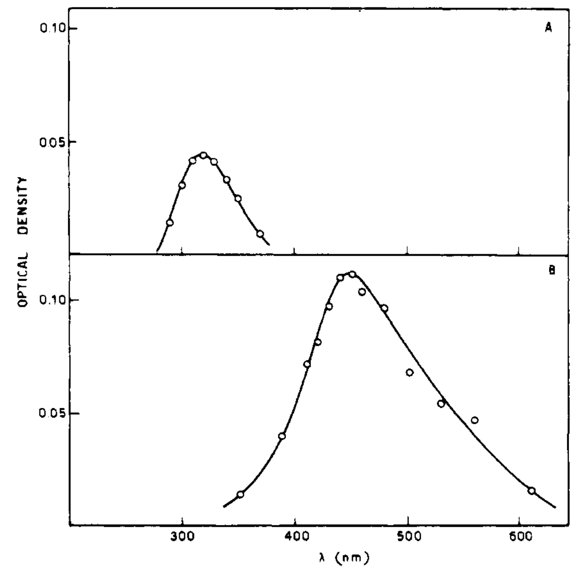
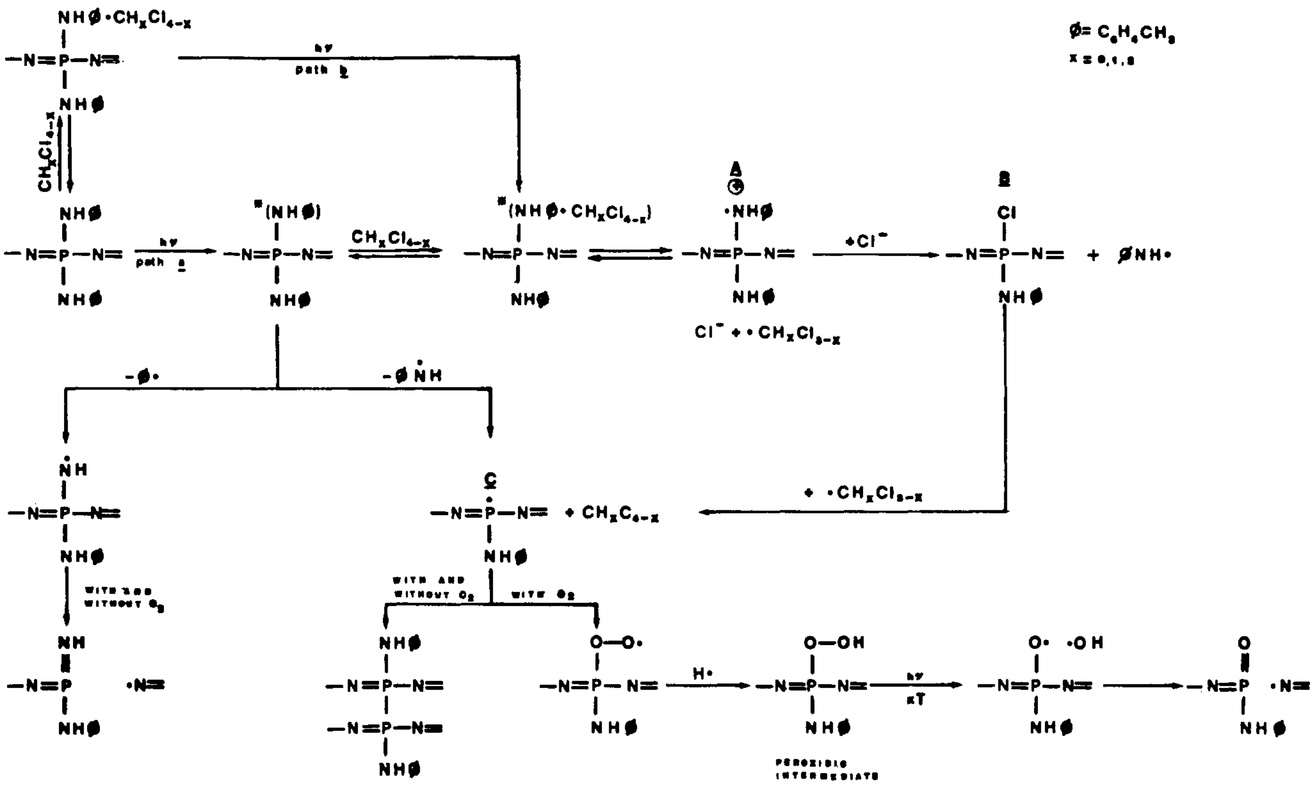


Figure 6. Transient absorption spectra of PTAP in THF (A) and CH_2Cl_2 (B).

Flash Photolysis Experiments

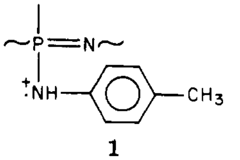
Flash photolysis was used to elucidate the earlier steps of the photolysis processes of PTAP. The spectra of the transient intermediates produced by flash photolysis of PTAP in THF and CH_2Cl_2 aerated solutions are reported in Figure 6. The transient in THF has an absorption maximum at 320 nm, attributable to the *p*-tolylamino radical. The spectrum of the *p*-tolylamino radical reported by Land and Porter[27] has two absorption maxima, at 320 and 405 nm, whose intensity ratio (I_{320}/I_{405}) is about 10. We were not able to detect any absorption at 405 nm in THF, probably because of the low intensity of the flash lamps of our apparatus. The spectrum in CH_2Cl_2 exhibits a maximum at 455 nm. It is interesting to note that a

Scheme I



transient absorption at 455 nm, practically identical with that obtained in CH_2Cl_2, can be induced in THF solutions of the polymer by adding 10^{-1} M CCl_4. No transient spectra of PTAP could be obtained in pure $CHCl_3$ or CCl_4 because of the photolability of the solutions under the analyzing light of the flash photolysis apparatus.

The absorption of the transient in CH_2Cl_2 is attributed to the presence of the radical cation 1, formed by the



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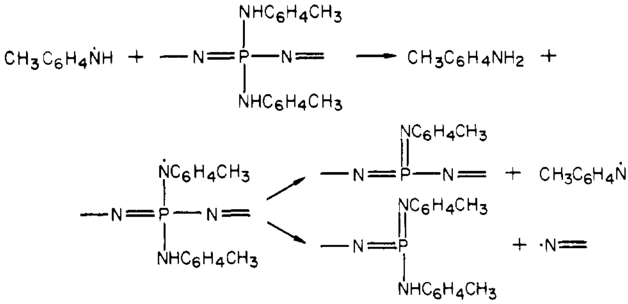
complete transfer of an electron from an electronically excited tolylamino group to the halomethane, which behaves as an electron acceptor. This is supported by the charge-transfer nature of the interaction between halogenated compounds and PTAP, as revealed by the variations of the UV absorption spectra in halomethanes, by the fluorescence quenching studies, and by the strong similarity of the transient spectra in CH_2Cl_2 and in THF containing CCl_4 to the spectrum of the radical cation of *N*-methylaniline reported by Shida and Hamill.[28] At any rate, it is clear that different transient intermediates are found in flash photolysis experiments of PTAP, depending on the nature of the solvent. Moreover, it is sufficient to add a small amount of CCl_4 to the THF solution of the polymer to obtain the same transient species observed in CH_2Cl_2.

Taking into account the previously mentioned results, we suggest that the photochemical behavior of PTAP in THF and in halogenated solvents may be explained on the basis of Scheme I. According to this scheme, the primary act in the photolysis of the polymer in THF solution is the homolytic scission of the $P\text{-}NHC_6H_4CH_3$ and $PNH\text{-}C_6H_4CH_3$ bonds in the excited *p*-tolylamino moiety. This hypothesis is in agreement with the presence in the reaction mixture of a ≃100:1 ratio of free *p*-toluidine to toluene as the main, low molecular weight, products of the irradiation. Further support for this interpretation comes from flash photolysis experiments: the spectrum of the transient intermediate observed in the flash photolysis of PTAP in THF (see Figure 6A) is identified as that of the *p*-tolylamino radical.[27] The toluene radical, produced in the primary photochemical act together with $CH_3C_6H_4\text{-}NH\cdot$, could not be detected by flash photolysis experiments due to its low concentration.

Irradiations performed in THF-d_8 and $CDCl_3$ showed that the *p*-tolylamino radical stabilizes itself by abstraction of an H atom from other tolylamino groups bonded to the phosphazene backbone.[29] In fact, no trace of deuterated toluidine was found in the products of the photolysis carried out in deuterated solvents when analyzed by gas chromatography–mass spectroscopy.

The reactions of the two macroradicals formed, which lead mainly to degradation of the polymer in air-saturated solutions and to cross-linking in the absence of oxygen, have been discussed elsewhere.[11,12] The reaction of the *p*-tolylamino radical, which likely is[30]



$$CH_3C_6H_4\dot{N}H + -N{=}\overset{NHC_6H_4CH_3}{\underset{NHC_6H_4CH_3}{P}}-N{=} \longrightarrow CH_3C_6H_4NH_2 + -N{=}\overset{\dot{N}C_6H_4CH_3}{\underset{NHC_6H_4CH_3}{P}}-N{=}$$

$$-N{=}\overset{\dot{N}C_6H_4CH_3}{\underset{NHC_6H_4CH_3}{P}}-N{=} \longrightarrow -N{=}\overset{NC_6H_4CH_3}{\underset{NC_6H_4CH_3}{\overset{\|}{P}}}-N{=} + CH_3C_6H_4\dot{N}H \quad\text{or}\quad -N{=}\overset{NC_6H_4CH_3}{\underset{NHC_6H_4CH_3}{\overset{\|}{P}}} + \cdot N{=}$$

opens to the macromolecule another degradation path.

As far as the photochemical behavior of PTAP in halogenated solvents is concerned, the reaction mechanism seems to be more complicated than that proposed when

THF is the solvent. The photolyzing light can promote to the excited state, besides the *p*-tolylamino groups bonded to the polymer skeleton (path a), the charge-transfer complex between the amino group and the halogenated compound (path b). In fact, the presence of a ground-state charge-transfer complex in solution is indicated by the UV spectra of PTAP in halomethanes (see Figure 3B). Moreover, in halogenated solvents, the uncomplexed, electronically excited, *p*-tolylamino moiety can also form charge-transfer complexes with halo derivatives, as evidenced by the emission quenching experiments (Figure 4). The formation of a charge-transfer complex in the excited state can lead to the production of the radical cation (A), as result of the transfer to the solvent of an electron of the lone pair of the arylamino nitrogen and of the production of a halide ion and of the radical $\cdot CH_xCl_{3-x}$ from the radical anion of the halomethane.[31] The formation of the radical cation is suggested by the flash photolysis experiments, since the spectrum of the transient intermediate produced in the halomethanes (Figure 6B) is practically identical with that reported by Shida and Hamill[28] for the radical cation of substituted *N*-methylaniline. Furthermore, the presence, in the photolysis products, of haloethanes (see Table II), resulting from the combination reactions of the radicals $\cdot CH_xCl_{3-x}$ (where $x = 0, 1, 2$), is a further confirmation that a charge-transfer mechanism is operative in the photochemistry of PTAP in halogenated solvents.

The successive fate of the macroradical A may be rationalized as follows: the difference in electronegativity (0.9) between phosphorus and nitrogen atoms and the presence of the radical cation $-^{+\cdot}NHC_6H_4CH_3$ may induce a partial positive charge on the backbone phosphorus atom. Therefore, it may be conceivably expected that nucleophilic attack on the phosphorus by the chloride ion produced in the charge-transfer step will occur, with formation of P–Cl bonds and release of the radical $CH_3C_6H_4NH\cdot$. This fact may account for the presence of free *p*-toluidine in all the halogenated solvents used for the photolysis and is supported by the found increase of the chlorine content in the PTAP recovered after the photolysis (see Results and Discussion). ^{31}P NMR spectra of the starting and irradiated polymer are consistent with the hypothesis of an insertion of Cl atoms in the polymer backbone. The ^{31}P NMR spectrum of the starting polymer dissolved in $CHCl_3$ has a high-intensity sharp peak at −15.3 ppm, attributed to the phosphorus bonded to the tolylamino group, and a low-intensity broad peak at −8.7 ppm, which may indicate the existence in the polymer of a variety of species[32] among the other residual P–Cl groups. After 4 h of irradiation, the spectrum shows a large decrease in intensity of the peak at −15.3 ppm, and the peak at −8.7 ppm further broadens and increases in intensity. This indicates a partial substitution of the amino groups originally bonded to the phosphorus atom. This fact and the simultaneous increase in the Cl content of the photolyzed polymer seem to justify the hypothesized presence of species B in solution. The formation of such P–Cl bonds during the photolysis of PTAP in halogenated solvents is quite an important fact, since the P–Cl bonds are reported[5-8] to be "the weak points" from which the thermal degradation of poly(organophosphazenes) may start, and it seems reasonable to infer that a similar function may be accomplished by P–Cl bonds during the photochemistry of these polymers. After this step, the presence or the absence of H-supplying agents in solution is the factor driving the overall process to degradation or to cross-linking. Irradiation in H-containing solvents (CH_2Cl_2, $CHCl_3$, CCl_4 + 1% EtOH) allows the macroradical and $\cdot CH_xCl_{3-x}$ radicals to be stabilized. The radical $\cdot CH_xCl_{3-x}$ may also react with species B and induce the homolytic cleavage of the P–Cl bond, giving a molecule of the original solvent and the same macroradical (C) formed when the photolysis is carried out in THF, where the charge-transfer mechanism is not operative. It is worthwhile remembering that the homolytic scission of the P–Cl bond is reported to occur in the photolysis of hexachlorocyclotriphosphazene in organic solvents.[33] As seen before, cross-linking or degradation of the polymer may occur from the macroradical C, depending on the absence or the presence of molecular oxygen in solution.

According to the suggested reaction scheme, the increase of the degradation rate on going from CH_2Cl_2 to CCl_4 + 1% EtOH is accounted for by the increasing electron affinity of the solvent. In solvents of high electron affinity (CCl_4) the radical cation A is produced in a larger amount than in $CHCl_3$ and CH_2Cl_2 (a solvent which is poorly reduced).

As shown in Table I, the presence in the solvent of H-supplying species is a basic condition for the degradation of the polymer. In fact, in pure CCl_4, $\simeq$75% of the original polymer was recovered as a gel after 4 h of irradiation, either in the presence or in the absence of molecular oxygen in solution. In this solvent, no H-supplying agent is available: consequently the radicals formed both in photochemical and in thermal steps of the reaction sequence can be stabilized by hydrogen abstraction only from the tolylamino groups bonded to the phosphazene backbone. As shown by the experiments carried out in deuterated solvents, this is the path followed by the tolylamino radical. However, the extensive cross-linking observed in pure CCl_4 shows that macroradical combination is the prevailing process. It seems, therefore, reasonable to infer that solvents with an abstractable hydrogen are needed to stabilize the polymeric macroradicals. In this case, the presence or the absence of the molecular oxygen in solution is not important in determining the photochemical behavior of the polymer: the only parameter which drives the photoreaction is the absence of H-supplying species in solution.

Let us consider the photochemical behavior of PTAP in CH_2Cl_2 solution. In the previous papers,[11,12] we proposed a mechanism of homolytic scission of the $P-NHC_6H_4CH_3$ bond as the most important photochemical act of the photodegradation process. The presence of toluene, in addition to *p*-toluidine, among the low molecular weight products of the photolysis in CH_2Cl_2 as well as in THF strongly supports the mechanism of homolytic scission of the bonds $CH_3C_6H_4-NHP$ and $PNH-C_6H_4CH_3$. On the other hand, the spectrum of the transient intermediate produced in CH_2Cl_2 solution during the flash photolysis experiments is that of the radical cation of the *p*-toluidine moiety bonded to the phosphazene backbone. This confirms that the radical cation A is produced as result of a charge-transfer process from the tolylamino group of the solvent. It is probable that both the mechanisms proposed, i.e., homolytic scission and charge transfer to the solvent, are simultaneously operating during the photolysis of PTAP in CH_2Cl_2. This seems quite reasonable in view of the low value of the electron affinity of the CH_2Cl_2. In solvents of increasing electron affinity, such as $CHCl_3$ and CCl_4, the contribution of the charge-transfer mechanism to the overall photochemical behavior of PTAP should increase. In agreement with this, no detectable amounts of toluene were found among the photolysis products, while haloethanes, coming from combination reactions of the radicals $\cdot CH_xCl_{3-x}$ formed from the solvent in the charge-transfer process, are present in considerable amount.

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Laser Flash Photolysis Study of Polymers Containing Benzoyl and Naphthalene Groups

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ABSTRACT: The photochemistry of copolymers of phenyl vinyl ketone, 2-vinylnaphthalene, and methyl methacrylate has been examined by laser flash photolysis techniques. Triplet energy transfer from the initially excited benzoyl chromophores to the naphthalene groups occurs by two distinct mechanisms which reflect static transfer and dynamic transfer. The former occurs between close neighbors along the chain, as well as when loops in the polymer bring together donor and acceptor molecules. Dynamic processes involve the diffusion of segments within the polymer and take place in the 10^{-6}–10^{-7}-s time scale at room temperature.

Introduction

The photodegradation and photooxidation of many common polymers, as well as the photocuring of organic coatings, are frequently controlled by chromophores which absorb in the near-ultraviolet or visible region. The importance of this spectral region is also reflected in the area of polymer stabilization, where many photostabilizers work by either screening the near-ultraviolet light or scavenging the intermediate (usually excited states or radicals) produced on excitation.[4] Since those chromophores are usually a minor component in the polymer system, their efficiency is largely determined by the probability that the mobility of the macromolecule and/or energy migration will bring the excited chromophore and the reactive site together. In order to examine both energy transfer and the mobility of excited states in macromolecules, we have studied the photochemistry of a series of copolymers of phenyl vinyl ketone, 2-vinylnaphthalene, and methyl methacrylate. In these systems the light from a nitrogen laser (337.1 nm) is absorbed virtually exclusively at the benzoyl site, which can then transfer the energy to yield the easily detectable naphthalene triplet.[5]

The transfer of triplet energy from aromatic carbonyls in polymers to bound and free naphthalene moieties has been examined before in solution[5-8] and at 77 K,[9-11] but the kinetics of the intramolecular energy transfer process had not been examined directly.[12] Our study reveals the importance of static and dynamic phenomena in the energy transfer process. Energy migration between carbonyl chromophores, which plays an important role in many other systems,[13-18] does not seem to contribute significantly in the copolymers examined in this study.

Results

All the results reported in this paper have been obtained under oxygen-free conditions, using laser flash photolysis

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