RADIATION INDUCED OXIDATIVE DEGRADATION OF POLY[BIS(*p*-TOLYLAMINO)] PHOSPHAZENE IN CHLORINATED HYDROCARBONS

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Abstract—Degradation induced by ionizing radiations on polyphosphazenes, dissolved in chlorinated methanes, is the subject of this investigation. Both steady gamma and pulse radiolysis techniques have been employed.

The labile sites for radical attack in poly[bis(*p*-tolylamino)] phosphazene were identified as the aniline N–H and benzyl C–H bonds of the pendant groups. All the primary radicals, by themselves or after peroxidation, can give rise to macroradicals by hydrogen abstraction from the polymer molecules. Appreciable crosslinking appeared only in the presence of quite a high concentration of oxygen, whereas, in its absence or after it had been consumed, practically no $\bar{M}_w$ changes were detected. Optical spectra of intermediates formed after pulse radiolysis are reported and attributed to radical-polymer charge transfer complexes, anilinium ions and toluidine radicals. *p*-Toluidine is formed as an end-product by hydrogen abstraction from polymer molecules. In solvents where hydrogen chloride can be formed, the amino functional group is affected.

INTRODUCTION

Free radicals, which can be produced in chemical systems by many processes, are responsible for many degenerative reactions undergone by polymeric materials in solution.

Among the initiators of radical chain processes, ionizing radiations are of considerable interest, mainly because of increasing utilization of polymers in nuclear plants, where great stability against high energy radiations is necessary. In this respect, the polyorganophosphazenes form a very interesting class of polymers, for which chemical, physical and technological properties have been extensively investigated [1–9].

In the domain of low energy radiations, the photochemical behaviour of some of these polymers was extensively studied in this Institute, using both steady and pulsed light sources [10–12].

The effects of ^{60}Co gamma rays on poly[bis(*p*-tolylamino)]phosphazene, dissolved in chlorinated hydrocarbons and other solvents, and the role played by radical intermediates were also preliminarily investigated [13].

To obtain spectral and kinetic information on these transient species and to throw more light upon the early steps which control the interaction between radiations and these polymers, pulse radiolysis experiments were also performed, both on polymer solutions and on pure solvents [14]. Pulse radiolysis is invaluable to produce high initial concentrations of free radicals; this technique, coupled with a spectrophotometric detection system, allowed us to monitor directly the process in which radicals are destroyed and to describe the optical spectra of the intermediates subsequently formed.

EXPERIMENTAL

Products and solvents

Poly[bis(*p*-tolylamino)]phosphazene, PTAP ($\bar{M}_w = 2.2 \times 10^6$), poly[bis(anilino)]phosphazene, PAP ($\bar{M}_w = 1.1 \times 10^6$) and poly[bis(phenoxy)]phosphazene, PPP ($\bar{M}_w = 1.7 \times 10^6$) were synthesized, purified and characterized by methods and techniques already described [13, 15].

Methylene chloride, used as a solvent, was an E. Merck "*pro analysi*" grade product; for steady and pulse radiolysis experiments, it was purified by standard methods [16] and stored in the dark in a pure inert gas atmosphere. Carbon tetrachloride (E. Merck "*pro analysi*" grade product) was used as supplied. Deuterated chloroform, triethylamine and tetrahydrofuran (THF) were Carlo Erba RP grade products; tetrahydrofuran was distilled over NaOH immediately before use.

Instrumentation and techniques

Steady gamma irradiations were performed with a 6000 Ci ^{60}Co source of the Atomic Energy of Canada Ltd. The usual polymer concentration was about 8 g/l. Oxygen-free samples were obtained by pumping away the dissolved oxygen with a vacuum system (total pressure = 10^{-6} torr) using the freezing–thawing technique. For viscosity measurements, a Desreux–Bischoff suspended level viscometer was used ($T = 25°$). Molecular weights were measured by a Sofica photogoniodiffusometer. U.V.-visible spectra were recorded with a Perkin–Elmer model 124 spectrophotometer. I.R. spectra were run with a Perkin–Elmer model 399 instrument, by evaporating the solvent from the test solutions on the NaCl window of the spectrophotometer. For pulse radiolysis experiments, the electron source was a Vickers 12 MeV linear accelerator, with pulses ranging from 5 nsec to 5 μsec, and the kinetic analyses were performed with the optical detection system described previously [17]. A Hamamatsu R955 photomultiplier tube was employed to detect the optical signals; waveform traces were stored on Tektronix 7633 oscilloscope, equipped with a 7A16A (~2 nsec rise time) or a

7A22 ($\sim 0.3\,\mu$sec rise time) amplifier. For hydroperoxy groups detection, the iodometric method due to Carlsson and Wiles [18], was used. Yields of irradiation products are reported as G values, where G = number of molecules or ions produced by 100 eV of radiation absorbed.
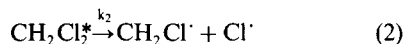
RESULTS AND DISCUSSION

Radiolysis of the solvent

The radiolysis of hydrogen containing halo-methanes results in a wide variety of radical processes, mainly because of hydrogen abstraction from the parent molecule by the primary radicals produced by radiations.

A widely accepted picture, agreeing with the results so far obtained on these substrates, is shown for methylene chloride by the following sequence of reactions, noting that, for the purposes of the present work, only the major processes are considered [19, 20]:
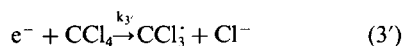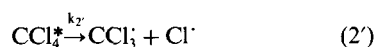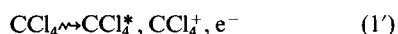
Primary radicals formation

$$CH_2Cl_2 \rightsquigarrow CH_2Cl_2^*, CH_2Cl_2^+, e^- \qquad (1)$$

$$CH_2Cl_2^* \xrightarrow{k_2} CH_2Cl^\cdot + Cl^\cdot \qquad (2)$$

$$e^- + CH_2Cl_2 \xrightarrow{k_3} CH_2Cl^\cdot + Cl^- \qquad (3)$$

Secondary radicals formation

$$Cl^\cdot + CH_2Cl_2 \xrightarrow{k_4} CHCl_2^\cdot + HCl \qquad (4)$$

$$CH_2Cl^\cdot + CH_2Cl_2 \xrightarrow{k_5} CHCl_2^\cdot + CH_3Cl \qquad (5)$$

Reactions (4) and (5), with reported rate constants $k_4 = 6 \times 10^4\,M^{-1}\,sec^{-1}$ [21] and $k_5 = 1.2\,M^{-1}\,sec^{-1}$ [21, 22] at 25° in liquids, are rather slow with respect to the corresponding radical–radical recombinations, which are diffusion controlled processes (i.e. $k \cong 10^{10}\,M^{-1}\,sec^{-1}$ in this solvent). It is deduced that reactions (4) and (5) should be, to some extent, less favoured when high dose rate electron pulses (high electron current in very short times, as 50–200 nsec) are used, as in the present work, whereas radical–radical recombinations should become dominant.

From these basic considerations, it can be concluded that the principal species able to diffuse towards an eventual solute (oxygen and/or polymer) are the primary radicals, formed during the radiation pulse ($CH_2Cl^\cdot$ and $Cl^\cdot$ for methylene chloride; $CHCl_2^\cdot$ and $Cl^\cdot$ for chloroform).

Analogous considerations can be made also for the non-hydrogenated halocarbon CCl_4, the behaviour of which is obviously limited to the first three steps of the general reaction mechanism:

$$CCl_4 \rightsquigarrow CCl_4^*, CCl_4^+, e^- \qquad (1')$$

$$CCl_4^* \xrightarrow{k_{2'}} CCl_3^\cdot + Cl^\cdot \qquad (2')$$

$$e^- + CCl_4 \xrightarrow{k_{3'}} CCl_3^\cdot + Cl^- \qquad (3')$$

so showing that the radical species, which could react with the solute in the very early stages, are the radicals $CCl_3^\cdot$ and $Cl^\cdot$.
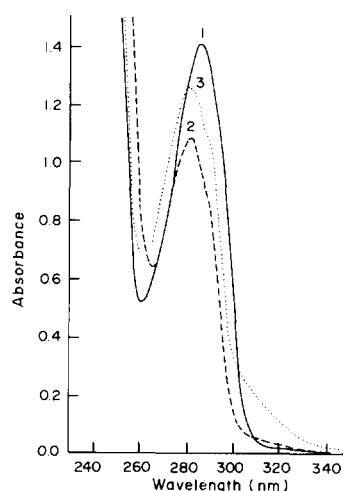

Fig. 1. Gamma irradiation of PTAP in air-saturated CH_2Cl_2: u.v.-visible absorption spectra. $c = 5.64 \times 10^{-2}\,M$ (repeat units), optical path = 10 mm. (1) Before irradiation; (2) 12.0 krad; (3) 24.0 krad (dose rate = 4 rad/sec).

Gamma radiolysis of polymer solutions

The absorption spectrum of an air saturated solution of PTAP in methylene chloride (Fig. 1) shows a band with $\lambda_{max} = 287$ nm, due to the p-tolylamino substituent group, as can be inferred by comparison with the spectrum of p-toluidine in the same solvent, which has a maximum at 294 nm [10]. When such a solution ($c = 5.64 \times 10^{-4}\,M$, expressed in repeat units) was irradiated with a ^{60}Co gamma source with a constant dose rate of 4 rad/sec, an optical density decrease, associated with an ipsochromic shift of this band from 287 to 282 nm, was observed (Fig. 1). Meantime, a new broad absorption, attributed to unidentified degradation products, appeared in the "visible" region, from 300 to 400 nm.

It must be pointed out that, at least for our experimental conditions, the "shifted" absorption at 282 nm, after having reached a minimum, underwent a subsequent increase with increasing dose of radiations. The absorption in this spectral region (280–300 nm) can be attributed to degradation products of PTAP, such as p-amino-benzaldehyde or p-hydrazo-toluene [23]. Parallel viscosity and light scattering measurements, carried out always on air-saturated samples, revealed molecular weight changes depending both on radiation dose and dose rate. By plotting $\bar{M}_w$ against radiation dose (Fig. 2) at a dose rate of 4 rad/sec, an increase of molecular weight for doses up to 50 krad was observed, followed by a decrease for higher doses. This behaviour can be explained by an initially prevailing crosslinking process, occurring in the presence of oxygen, while degradation would prevail for higher doses. The dose rate effect, at a constant dose of 79 krad, is shown in Fig. 3: an increase of radiation seems to favour crosslinking up to a maximum value around 40 rad/sec, after which further increase of dose rate results in an inversion of the tendency.

By irradiating with the same dose rate PTAP oxygen-free solutions, the 287 nm bleaching and blue shift, although considerably slower, were also detected; however, no new absorption appeared in the 300–400 nm region.
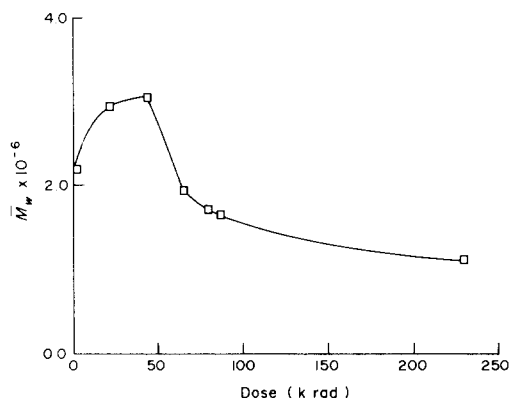
Fig. 2. Gamma irradiation of PTAP in air-saturated CH_2Cl_2: dose effect on $\bar{M}_w$ (dose rate = 4 rad/sec). Molecular weights were measured 90 min after the end of irradiation.

In these oxygen-free conditions, substantial molecular weight changes were not detected. An interesting point was that similar behaviour was noticed by pulsing repeatedly oxygen-saturated samples. Explanation for this finding came from considering that the high doses here employed (20–30 krad/pulse) produced high concentration of radicals. These radicals consumed most of the dissolved oxygen during the first electron pulses and hence further pulses dealt with lower and lower oxygen contents until practically oxygen-free conditions were reached.

All these experimental data suggest that oxygen is the determining factor for any degradative radiation induced process of arylaminophosphazenes in halomethane solution. The formation of oxidized degradation products could explain both the build-up of the "visible" absorption between 300 and 400 nm and the decrease of the 287 nm band.

Some comments are required on the blue shift of this band, which, as reported above, was observed also in deaerated samples. The same phenomenon, i.e. intensity decrease and blue shift of the 287 nm band, was observed when hydrogen chloride was added to unirradiated solutions of PTAP in methylene chloride and tetrahydrofuran. In this case, no new absorption appeared at 282 nm and in the "vis-
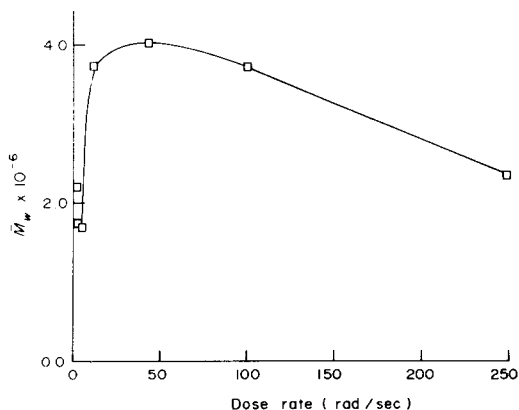

Fig. 3. Gamma irradiation of PTAP in air-saturated CH_2Cl_2: dose rate effect on $\bar{M}_w$ (total dose of radiation = 79 krad). Molecular weights were measured 90 min after the end of irradiation.
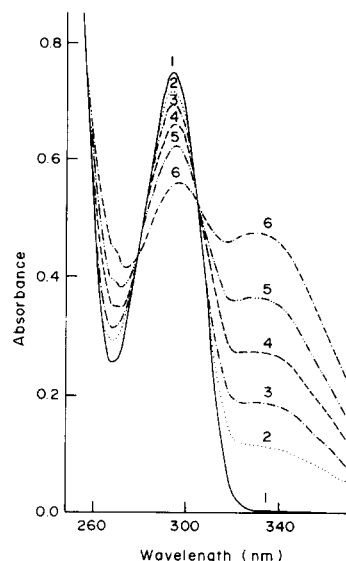

Fig. 4. Gamma irradiation of p-toluidine in air-saturated CH_2Cl_2: u.v.-visible absorption spectra. $c = 4.75 \times 10^{-4}$ M, optical path = 10 nm. (1) Before irradiation; (2) 2.9 krad; (3) 5.8 krad; (4) 8.6 krad; (5) 12.0 krad; (6) 16.8 krad.

ible" region. It must be noted that the original spectrum was restored by neutralizing the added HCl with a solution of triethylamine.

Taking into account that high yields of HCl are expected when hydrogen containing chloromethanes are irradiated (for example, in chloroform $G_{HCl} = 4 \div 12$ [20]), it can be assumed that the ipsochromic shift is caused by reaction of amine groups with HCl, generated by radiation or expressly added to the system. Furthermore, experiments carried out under analogous conditions on THF and CCl_4 solutions, where HCl could not be produced by radiations, did not show any ipsochromic shift.

However, when an air-saturated methylene chloride solution of p-toluidine was irradiated, only an intensity decrease of the 294 nm band and development of a strong absorption at 330 nm were observed (Fig. 4). This fact could be explained by assuming that the ipsochromic shift was easily detectable only with arylamino-containing polymers, which remain in solution even after a partial salification, but not with free anilines, the hydrochlorides of which are very slightly soluble in methylene chloride.

An important contribution to the understanding of the oxidative degradation mechanism of PTAP was given by the spectral analysis of irradiated methylene chloride solutions of poly[bis(anilino)]phosphazene (PAP). U.V.-visible spectra of this polymer showed qualitatively the same decreasing trend of the 280 nm band; blue shift of this band and broad absorption in the 300–400 nm region were also observed, as for PTAP.

However, a somewhat different picture was shown by i.r. spectra of irradiated samples of PTAP and PAP in methylene chloride. Spectral changes were observed in both cases in the 3500 cm^{-1} region (O–H stretching). More evident variations appeared, both for PTAP and PAP, between 3400 and 2800 cm^{-1}. In particular, a shift of the 3280 cm^{-1} band, attributed
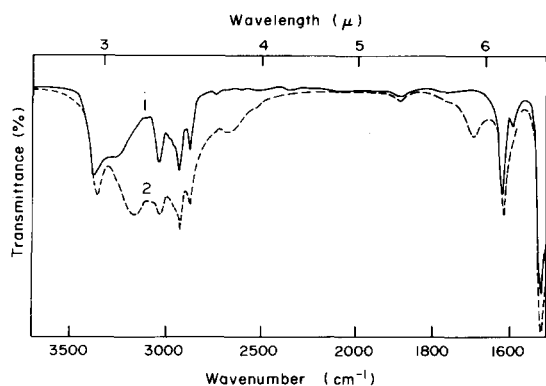
Fig. 5. I.R. spectra of PTAP. (1) Before irradiation; (2) after gamma irradiation in air-saturated CH_2Cl_2 (total dose = 864 krad; dose rate = 4 rad/sec).

to "bonded" N–H stretching vibration, towards lower frequencies was observed. This effect could be due to degradation products, where H bonds have different geometries than in the original polymers. It is noteworthy that only PTAP showed a new band at $1700\,cm^{-1}$, attributed to the carbonyl stretching vibration. In Fig. 5 the i.r. spectra of PTAP, before and after irradiation in methylene chloride, are reported.

This spectrophotometric evidence suggests that one of the probable sites for oxidative attack in this polymer is the carbon atom of the p-methyl substituent group, which is present only in PTAP. On the other hand, the high stability of the aromatic ring against oxidegradation is also supported by preliminary experiments with poly[bis(phenoxy)]-phosphazene (PPP), the i.r. spectrum of which, after irradiation, showed no absorption at 1700 and $3500\,cm^{-1}$.

Besides the spectrophotometric data described above, other relevant analytical results were obtained.

Peroxy groups were found, by standard analytical methods [18], after gamma irradiation of PTAP films. The remarkable post-effect, already observed for irradiated samples stored in the dark [13], agrees with this finding. Oxygen should be involved in the formation of unstable peroxy macrostructures [12], decomposition of which should be responsible for the molecular weight decrease observed at increasing times after irradiation (Table 1). Moreover, among the products of degraded polymer in methylene chloride, as already found in chloroform [13], only p-toluidine was unambiguously identified.

It is noteworthy that, in parallel experiments carried out on PTAP solutions in deuterated chloroform, deuterated p-toluidine was not found.

These results involve the breaking off of the phosphorus–nitrogen side bonds; afterwards, p-tolylamino radicals would abstract hydrogen atoms from the polymer molecules themselves, rather than from the solvent.

Pulse radiolysis of polymer solutions

To clarify the early steps of the overall degradation process, polymer solutions were also irradiated with pulsed electron beams.
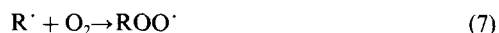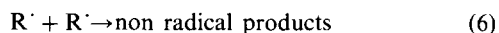
Kinetic studies of the processes afterwards induced revealed a complex mechanism, in which at least 5 different transient species are formed and consumed during the first tenth of a second after the absorption of the radiation by the sample.

Furthermore, we must note that a short and intense pulse of radiation, by creating a high concentration of radicals, may trigger a reaction mechanism quite different from that operating when steady gamma irradiation (i.e. low dose rate) is employed. These facts and considerations, in our opinion, remove any possibility of formulating a detailed mechanism to explain the essentials of the degradation process. Nevertheless, one can try to clarify the first reactions taking place before any intervention of adventitious impurities. In fact, the low concentrations of these materials would locate their reactions in the millisecond time region, so that they do not disturb other processes occurring in the first $200\,\mu sec$, where our observations have been confined.

As Fig. 6A shows, PTAP solutions in oxygen-saturated methylene chloride revealed a transient absorption, following a 50 nsec pulse, in the 250–500 nm spectral region. The spectral variations have been resolved during the first $170\,\mu sec$; one can thus observe that major changes occur between 270 and 400 nm, while minor changes are detectable in the 400–500 nm region. Very similar initial transient spectra in the u.v., i.e. from 6 to $170\,\mu sec$, were also detected by irradiating with the same dose (5 krad) and dose rate ($10^8\,krad/sec$) samples of PTAP in CCl_4, either O_2-saturated or Ar-deaerated (Fig. 6B–D), and PAP in Ar-deaerated CH_2Cl_2 (Fig. 6C).

In our opinion, this result means that the radicals induced by ionizing radiations from chlorinated solvents, either in the presence of oxygen or in its absence, can promote the same initial modifications to the polymer.

The first steps of the degradation process can vary according to the concentration of oxygen. In fact, bearing in mind the reaction scheme reported above (reactions 1–5) and the considerations made therefrom, the fate of the primary radicals (R·) can be recombination or reaction with oxygen and/or polymer (PH).

$$R\cdot + R\cdot \rightarrow non\ radical\ products \tag{6}$$

$$R\cdot + O_2 \rightarrow ROO\cdot \tag{7}$$

$$\begin{array}{l} \qquad\qquad \nearrow RH + P\cdot \tag{8a}\\ R\cdot + PH\\ \qquad\qquad \searrow R\text{-}\dot{P}H \tag{8b} \end{array}$$
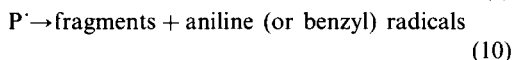
With low irradiation intensity (relatively low dose rate), the recombination process can be minimized

Table 1. Molecular weight changes after gamma irradiation of PTAP in air-saturated CH_2Cl_2: $c = 3.1 \times 10^{-2}\,M$, expressed in repeat units; total dose = 79 krad; dose rate = 44 rad/sec

	Before irradiation	Immediately after irradiation	90 min after irradiation	180 min after irradiation	18 hr after irradiation
$\bar{M}_w \times 10^{-6}$	2.20	4.52	4.00	3.30	2.65

and one can expect that, by altering the O_2 to PH ratio, the balance between (7) and (8) is modified. Although reaction (7) is itself a combination of two radicals (O_2 is a diradical in its ground state) and its absolute rate constant is $k = 5 \times 10^9 \, M^{-1} \, sec^{-1}$ [14] (i.e. at the diffusional limit), some of the chloromethyl radicals can still reach the polymer chain and directly attack both the aromatic ring and the labile bonds C–H and N–H. On the other hand, halomethyl peroxy radicals, because of their lower reactivity [24], are expected to be more selective and to give rise mainly to aniline and benzyl radicals:

$$ROO^{\cdot} + PH \rightarrow ROOH + P^{\cdot} \qquad (9)$$

$$P^{\cdot} \rightarrow \text{fragments} + \text{aniline (or benzyl) radicals} \qquad (10)$$

Hence, a simplified picture of the initial mechanism in chlorinated hydrocarbons, such as CCl_4 and CH_2Cl_2, can be represented in Scheme 1 below ($R^{\cdot} = Cl^{\cdot}$ and/or CH_nCl_{3-n}, where $0 \leqslant n \leqslant 2$):

Referring to Scheme 1, experimental support for an intermediate of the type (Ia) comes from the observation of a typical absorption spectrum with λ_{max} centered at 305–320 nm, always appearing before any other spectral variation takes place ($t \lesssim 1 \, \mu sec$), when pulsing each of the following aromatic substrates: aniline, toluidine, PTAP and PAP dissolved in either methylene chloride or carbon tetrachloride (Fig. 6). Furthermore the shape of this spectrum is unaffected by the presence of oxygen (Fig. 6B–D).

A charge transfer complex ($P^{\delta+}$, $Cl^{\delta-}$), involving the aromatic ring and the chlorine atom, was also suggested by other authors [25, 26], on the basis of similar spectral observations, either after flash photolysis or pulse radiolysis of aromatics dissolved in chloromethanes.

Aniline cationic intermediates can also be formed (Ib–Ic), partly as the result of a complete electron transfer from the nitrogen doublet to the electrophilic halo radicals or peroxyhalo radicals, and partly as a
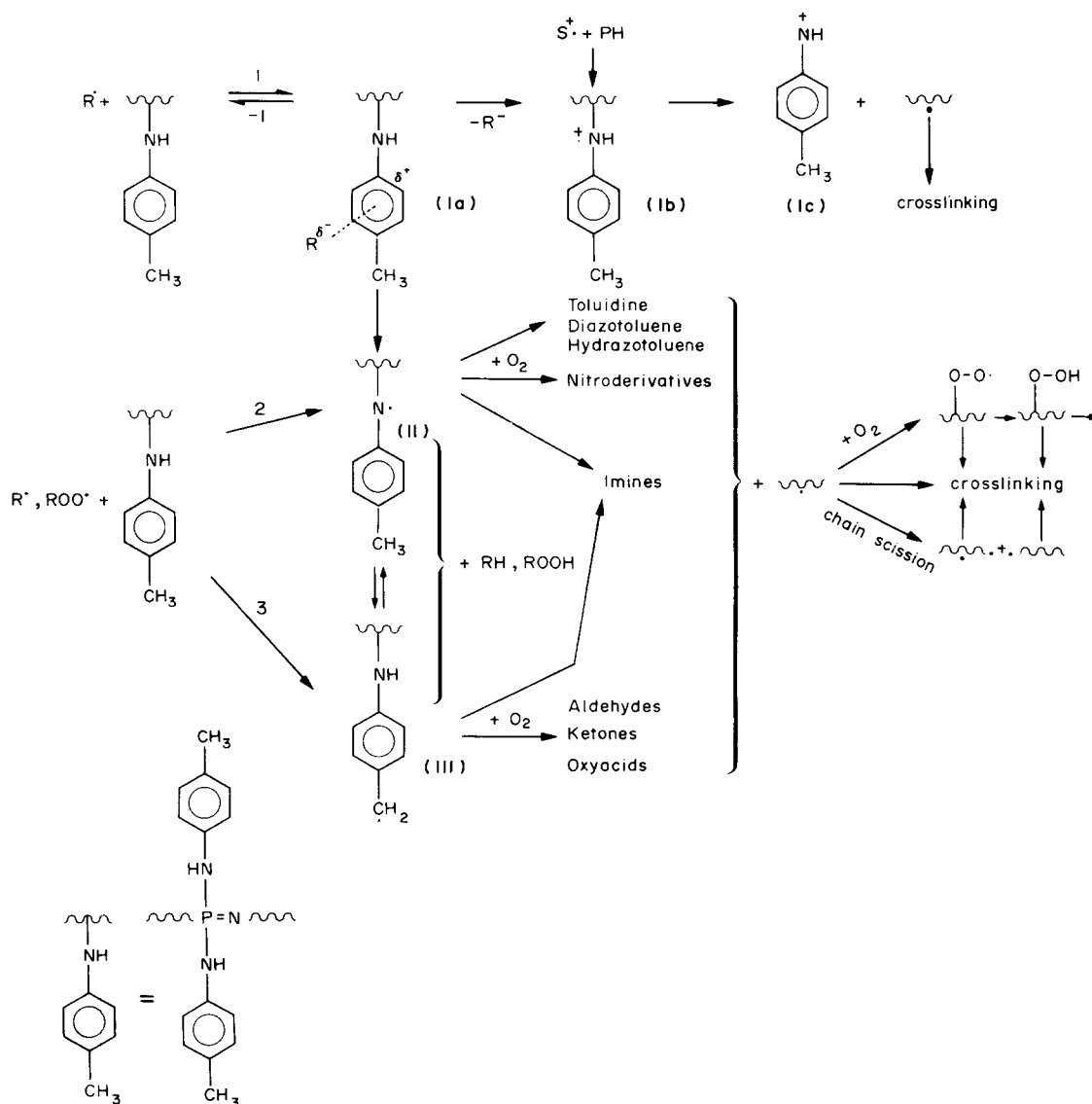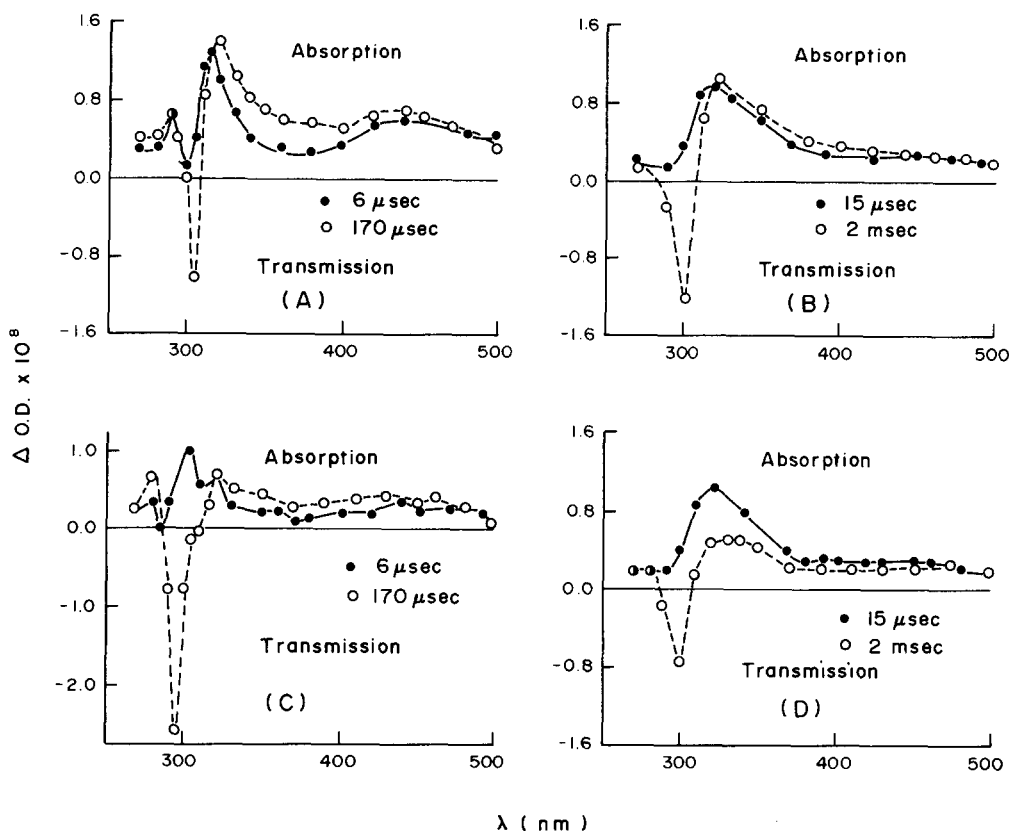

Scheme 1

Fig. 6. Pulse radiolysis of phosphazene polymers in chlorinated methanes: transient absorption spectra following a 50 nsec electron pulse (dose normalized to 5 krad, optical path = 20 mm). (A) = PTAP in oxygen-saturated CH_2Cl_2, $c = 2.2 \times 10^{-3}$ M; (B) = PTAP in oxygen-saturated CCl_4, $c = 3.0 \times 10^{-4}$ M; (C) = PAP in oxygen-saturated CH_2Cl_2, $c = 2.3 \times 10^{-3}$ M; (D) = PTAP in argon-deaerated CCl_4, $c = 3.0 \times 10^{-4}$ M (concentrations expressed in repeat units).

product of a charge transfer between the solvent cation (S^+) and the amine. Aromatic amine cations are known to have their absorption spectra centered between 400 and 500 nm [27–29], where we detected a broad and structured absorption lasting several hundreds of microseconds. An anilinium ion intermediate was also invoked in a previous paper on the flash photolysis of PTAP to explain a transient absorption having $\lambda_{max} = 455$ nm in methylene chloride [12].

Intermediates (II) and (III) are expected on the basis of the negative enthalpic balance between the R–H and ROO–H bonds of the products and the aniline N–H or benzyl C–H bonds of the polymers. Equilibrium between (II) and (III) is not an uncommon situation, in which the radical centre is transferred from one atom to another, because of a conjugated system. Anyhow u.v. bleaching of the polymer solutions goes on for several hundreds of microseconds; it appears as a sharp increase in transmission, peaking around 295–305 nm (Fig. 6). This behaviour is shown only by amine-containing aromatics (aniline, toluidine and related polymers) and not by others (e.g. toluene). Hence this bleaching marks out the process during which the typical absorption of toluidine is being subtracted and aniline radicals ($\lambda_{max} = 320$ nm) [30] and benzyl radicals

($\lambda_{max} = 290$ and 320 nm) [31] are being generated. The intervention of oxygen in the first step of the degradation process would be distinguishable from that of a direct attack by primary radicals, only in that it would convert these highly reactive species into oxygen radicals. These, in their turn, are highly selective [24] in their bond breaking action, preferring the labile C–H and N–H bonds and thus improving the efficiency of the initiation step, as shown by the bleaching intensities at 300 nm in Fig. 6B and 6D.

Nevertheless, the participation of oxygen in the degradation process becomes determinant only after the loss of the side-substituent; it can react, in fact, with both benzyl and aniline radicals and/or the macroradical fragments, preventing their recombination. A neat proof for this process is shown in Fig. 7a–b, where the upper traces show the bimolecular bleaching of the optical signal due to the radicals formed in an oxygen-free system, whereas the lower traces show, on the same time scale and at the same wavelengths, a build-up of optical absorption when oxygen is present.

Therefore, it can be said that, if oxygen is present, the radicals do not recombine immediately; they are first oxidized and then transformed into the end-products (carbonyls, hydroperoxides), as revealed by the analytical methods described above.
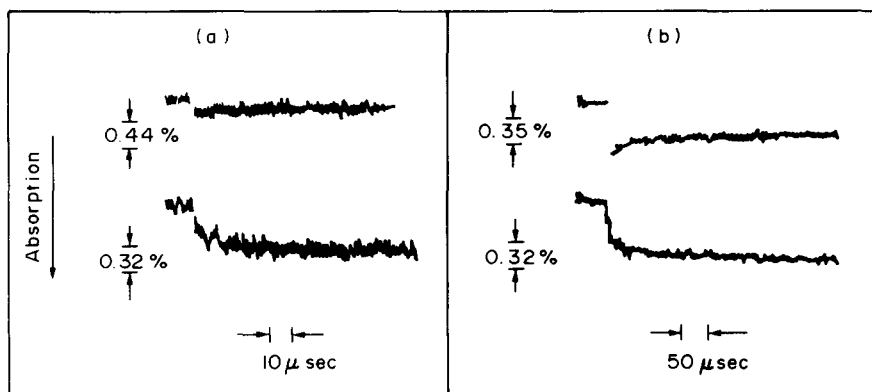
Fig. 7. Typical oscilloscope traces monitoring optical density changes in samples of PTAP dissolved in chloromethanes after a 200 nsec electron pulse. Upper traces: argon-deaerated solutions; lower traces: oxygen-saturated solutions. (a) = PTAP in CH_2Cl_2, $c = 6.0 \times 10^{-4}$ M, $\lambda = 410$ nm, total dose = 4.3 krad; (b) = PTAP in CCl_4, $c = 3.0 \times 10^{-4}$ M, $\lambda = 400$ nm, total dose = 5.0 krad (concentrations expressed in repeat units).

CONCLUSIONS

High energy radiations induce detectable molecular weight changes for PTAP dissolved in chlorinated hydrocarbons, only in the presence of oxygen.

Pulse radiolysis experiments suggest that all the primary radicals (chlorine atoms or chlorosubstituted radicals) can initiate the chain degradation process, either by themselves or after peroxidation. In the former case, the product appears to be a charge transfer intermediate, fast equilibrium of which with the reagents causes some decrease of primary radicals recombination. In the latter case, the process is driven with higher efficiency towards the obligatory pathway for any subsequent degradation, i.e. abstraction of hydrogen atoms, either from the amine sites or from the methyl sites. This fact triggers the detachment of p-toluidine from the polymer backbone. The macroradicals so formed will have many simultaneous chances: (a) crosslinking; (b) fragmentation; (c) abstraction of hydrogen atoms again from other toluidine groups; (d) peroxidation, followed by processes (a) and (b).

The factors favouring one or other of the mentioned paths are: oxygen concentration, dose rate and total dose of radiation delivered to the system. The last two parameters will determine, respectively, the time in which oxygen is consumed and the amount of oxygen consumed. Hence, until O_2 is at sufficient concentration, the process seems to be driven mainly towards crosslinking whereas, when oxygen is nearly consumed, PTAP shows small variations of $\overline{M}_w$, at least in methylene chloride. Further study in this Institute will deal with the effects of ionizing radiations on various phosphazene polymers when the concentration of oxygen is being continuously restored.

Furthermore, some other conclusions can be drawn:

labile sites of the polymer molecule are p-methyl and amino groups, for which there is spectral evidence of oxidation;

hydrochloric acid, coming from the irradiated solvent, attaches to the amino function of the side groups;

p-tolylamino radicals give p-toluidine by extracting hydrogen from polymer molecules.

From the end-products analysis and polymer molecular weight measurements, it can also be inferred that other crosslinking or degradation processes can occur, on a longer time scale, by internal energy transfer, leading to nitrogen–phosphorus bond scission, both in the side and in the main polymer chain.

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