

See discussions, stats, and author profiles for this publication at: <https://www.researchgate.net/publication/230695674>

Structural Changes of Conjugated Pt-Containing Polymetallaynes Exposed to Gamma Ray Radiation Doses

ARTICLE in THE JOURNAL OF PHYSICAL CHEMISTRY A · AUGUST 2012

Impact Factor: 2.69 · DOI: 10.1021/jp3060747 · Source: PubMed

CITATIONS

11

READS

45

11 AUTHORS, INCLUDING:



Augusto Batagin-Neto

São Paulo State University

21 PUBLICATIONS 72 CITATIONS

SEE PROFILE



Enrico Bodo

Sapienza University of Rome

111 PUBLICATIONS 1,538 CITATIONS

SEE PROFILE



Iole Venditti

Sapienza University of Rome

50 PUBLICATIONS 477 CITATIONS

SEE PROFILE



Carlos F. O. Graeff

São Paulo State University

175 PUBLICATIONS 1,521 CITATIONS

SEE PROFILE

Structural Changes of Conjugated Pt-Containing Polymetallaynes Exposed to Gamma Ray Radiation Doses

Ilaria Fratoddi,^{†,‡} Erika S. Bronze-Uhle,^{*,§} Augusto Batagin-Neto,^{||} David M. Fernandes,^{||} Enrico Bodo,[†] Chiara Battocchio,[⊥] Iole Venditti,[†] Franco Decker,[†] Maria Vittoria Russo,[†] Giovanni Polzonetti,[⊥] and Carlos F. O. Graeff[§]

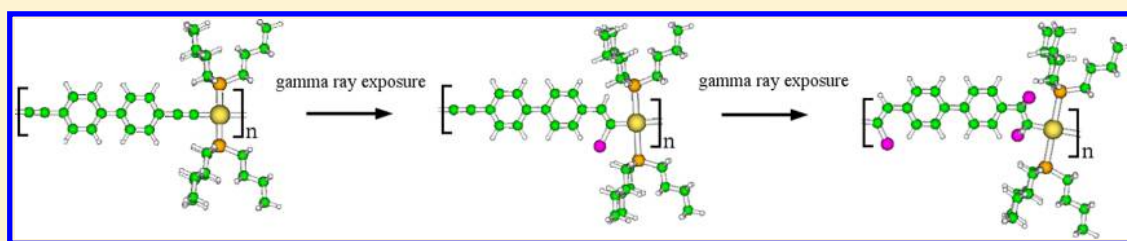
[†]Department of Chemistry, University of Rome "Sapienza", P.le A. Moro 5, 00185 Rome, Italy

[‡]Center for Nanotechnology for Engineering (CNIS), University of Rome "Sapienza", P.le A. Moro 5, 00185 Rome, Italy

[§]Department of Physics, FC-UNESP, Av. Eng. Luiz Edmundo Carrijo Coube 14-01, 17033-360 Bauru, Brazil

^{||}POSMAT-Programa de Pós-Graduação em Ciência e Tecnologia de Materiais, UNESP-Univ Estadual Paulista, Bauru, SP, Brazil

[⊥]Department of Physics, Unità INSTM and CISDiC University Roma Tre, Via della Vasca Navale 85, 00146 Rome, Italy



ABSTRACT: The effect of ^{60}Co gamma rays irradiation on the polymetallayne $[-\text{Pt}(\text{PBu}_3)-\text{C}\equiv\text{C}-\text{C}_6\text{H}_4-\text{C}_6\text{H}_4-\text{C}\equiv\text{C}-]_n$ (Pt-DEBP) of defined chain length corresponding to 10 repeat units, has been studied in detail. The UV-vis absorption spectra of Pt-DEBP have been recorded in solution upon exposure of the polymetallayne at increasing radiation doses in the range up to 90 Gy, with special care to the features related to low doses. Complex modifications of the chemical structure of Pt-DEBP could be accessed through NMR, FTIR, GPC, and XPS characterizations, which support the attack of Cl and H radicals coming from the radiolysis of the solvent, CHCl_3 , to the triple $\text{C}\equiv\text{C}$ bonds of the backbone, leading to the formation of chlorinated double and single $\text{C}-\text{C}$ bonds, with a concomitant increase of the molecular weight due to a recombinant effect of oligomer fragments upon irradiation. The presence of vinyl and single chlorinated moieties has been sustained from the simulation of the UV-vis spectra based on theoretical calculations.

1. INTRODUCTION

The importance of ionizing radiations is recognized in a variety of scientific and technological topics related to human quality of life such as, for example, the medicine and food industries.^{1–6} The drawback of gamma rays is their harmful nature, which may be responsible for some forms of cancer, and therefore, a strict control of their dose is mandatory.⁷ Detection of gamma rays is commonly based on detectors containing inorganic crystals of high atomic number.⁸ Though inorganic materials do present a number of advantages, with special emphasis on sensitivity, there are disadvantages like high costs and/or difficulty in production⁹ or the need for low temperature to operate.¹⁰ Therefore, new dosimeters specially using new materials are in demand.¹¹

In this framework, studies on the optical and electrical properties of conjugated polymers have been reported as promising radiation detectors.^{12–15} In particular, our group has investigated the behavior of poly(2-methoxy-5-(2'-ethyl-hexyloxy)-1,4-phenylene vinylene) (MEH-PPV) in halogenated aliphatic solvents under gamma ray exposure and found that this polymer is sensitive to doses lower than 10 Gy, presenting a blue shift in its main absorption peak proportional to the

applied dose.¹⁶ In the mechanism proposed, the solvent plays a major role in the modification of the polymer chemical structure; in our model, the halide solvents under ionizing irradiation produce radicals, that attack the polymer chain.¹⁷

Polymetallaynes represent a peculiar class of polymeric materials,^{18,19} which show electro-optical properties for a wide range of applications.²⁰ However, few studies on their behavior under gamma radiation for the dosimeters development has been reported so far. In this context, for a few years, our research has been involved in the synthesis and study of the properties of rod-like polymetallaynes.^{21–23} Recently, we have explored the potential of a polymetallayne, i.e., $[-\text{Pt}(\text{PBu}_3)_2-\text{C}\equiv\text{C}-\text{C}_6\text{H}_4-\text{C}_6\text{H}_4-\text{C}\equiv\text{C}-]_n$, Pt-DEBP, in dosimetry.²⁴ It was found that, after irradiation, Pt-DEBP (in chloroform solution) changes its absorption and emission spectrum similarly to what was found in MEH-PPV. The system proved to be in fact very sensitive, changes in the fluorescence spectrum could be observed even for doses of approximately 1

Received: June 20, 2012

Revised: August 3, 2012

Published: August 17, 2012



Gy. Thus, demonstrating promising dosimetry properties to be used in medical or radiation protection applications. It has been proposed, similarly to what has been described to MEH-PPV that the effect is induced by chlorine radical attack on the polymer chain, but given the complex nature of this organometallic polymer, no detailed mechanism was presented.

In this work, we performed a more detailed investigation on the effects of ionizing radiation on the chemical structure of Pt-DEBP in chloroform solutions. Pt-DEBP samples exposed to gamma ray in the range of 1 to 90 Gy were studied using UV-vis and luminescence spectroscopy as well as NMR, GPC, FTIR, and XPS analysis. The results were compared with theoretical studies in order to assess the chemical structure modifications induced by irradiation.

2. EXPERIMENTAL SECTION

2.1. Materials. All reactions have been performed under an inert argon atmosphere. Solvents have been dried on Na_2SO_4 before use. All chemicals, unless otherwise stated, have been obtained from commercial sources and used as received. The compound 4,4'-diethynylbiphenyl, $\text{H}-\text{C}\equiv\text{C}-\text{C}_6\text{H}_4-\text{C}_6\text{H}_4-\text{C}\equiv\text{C}-\text{H}$ (DEBP), and the complex *trans*- $[\text{PtCl}_2(\text{PBu}_3)_2]$ have been prepared according to literature methods.^{25,26} The organometallic polymer $[-\text{Pt}(\text{PBu}_3)_2-\text{C}\equiv\text{C}-\text{C}_6\text{H}_4-\text{C}_6\text{H}_4-\text{C}\equiv\text{C}-]_n$ (Pt-DEBP) was synthesized from equimolar amounts of dichloride square planar complex *trans*- $[\text{Pt}(\text{PBu}_3)_2\text{Cl}_2]$ in the presence of monomer DEBP in NH_4Et_2 as solvent and base, following a reported method.¹⁷

2.2. Characterization of Pt-DEBP. **2.2.1. Pt-DEBP before Irradiation.** IR (film, cm^{-1}): 2094 ($\nu \text{C}\equiv\text{C}$), 1602 ($\nu \text{C}=\text{C}$), 401, 393. UV (CHCl_3): 372.2 nm. ^1H NMR (CDCl_3 , δ ppm): 0.93 (t 18H $-\text{CH}_3$ $J = 9.00$ Hz), 1.45 (q 12H $\text{P}-\text{CH}_2-\text{CH}_2-\text{CH}_2-$), 1.62 (m 12H $\text{P}-\text{CH}_2-\text{CH}_2-$), 2.15 (m 12H $\text{P}-\text{CH}_2-$), 7.29 (d, 4H, $\text{Ar}-\text{H}$), 7.44 (d, 4H, $\text{Ar}-\text{H}$). ^{31}P NMR (δ ppm, CDCl_3 ($J^{195}\text{Pt}-^{31}\text{P}$) Hz): 3.72 (2358), 7.52 (2371) with intensity ratio 4/1, corresponding to a 10 metal unit oligomer. Elemental analysis (%) found (calculated for the $\text{Pt}_{10}\text{P}_{20}\text{Cl}_2\text{C}_{240}\text{H}_{612}$): C = 58.61, (60.06); H = 7.84 (7.81).

2.2.2. Pt-DEBP after Irradiation (90 Gy). IR (film, cm^{-1}): 2094 ($\nu \text{C}\equiv\text{C}$), 1730 ($\nu \text{C}=\text{C}-\text{Cl}$), 1602 ($\nu \text{C}=\text{C}$). UV (CHCl_3): 332.0 nm. ^1H NMR (CDCl_3 , δ ppm): dd 7.369 + 7.246, ($J = 8.02$ Hz) ($\text{Ar}-\text{H}$), m 2.086 (internal $\text{P}-\text{CH}_2$), m 1.950 (terminal $\text{P}-\text{CH}_2$), m 1.557 ($\text{P}-\text{CH}_2-\text{CH}_2$), q 1.401 ($J = 7.10$ Hz) ($\text{P}-\text{CH}_2-\text{CH}_2-\text{CH}_2$), t 0.867 ($J = 7.20$ Hz) ($\text{P}-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_3$), q 4.114 ($J = 7.00$ Hz). ^{31}P NMR (δ ppm, CDCl_3 ($J^{195}\text{Pt}-^{31}\text{P}$) Hz): 3.55 (2359), 7.31 (2375) with intensity ratio 10/1.

2.3. Methods. Fourier transform infrared (FTIR) spectra have been recorded by nujol mulls or films deposited from CHCl_3 solutions by using KRS-5 cells, on a Bruker Vertex 70 Fourier Transform spectrometer. ^1H and ^{31}P nuclear magnetic resonance (NMR) spectra have been recorded in CDCl_3 on a Bruker AC 300P spectrometer at 300 and 121 MHz, respectively; the chemical shifts (ppm) have been referenced to TMS for ^1H NMR assigning the residual ^1H impurity signal in the solvent at 7.24 ppm (CDCl_3). ^{31}P NMR chemical shifts are relative to H_3PO_4 (85%). UV-vis spectra have been recorded in CHCl_3 solutions at room temperature on a Varian Cary 100 or on a Shimadzu (UV mini 1240) instrument. All measurements have been carried out at room temperature using solutions of the polymers in CHCl_3 .

Number-average molecular weight (M_n), weight-average molecular weight (M_w), and molecular weight dispersity ($\bar{D} =$

M_w/M_n)²⁷ were determined by gel permeation chromatography (GPC) on a Perkin-Elmer instrument thermostatted at 30 °C and equipped with a UV detector set at 370 nm. Chloroform (HPLC grade) was used as eluent, pumped at a flow-rate of 0.8 mL/min by a binary LC pump, and monodispersed polystyrene standards were used for calibration. According to the IUPAC recommendation, the term molecular weight dispersity (\bar{D}) is used throughout the article to indicate the ratio of the mass-average to the number-average molecular weights M_w/M_n .

X-ray photoelectron (XPS) spectra were recorded using a custom designed spectrometer, consisting of a preparation and analysis chamber, equipped with a 150 mm mean radius hemispherical electron analyzer, with a four-elements lens system with a 16-channel detector, giving a total instrumental resolution of 1.0 eV, as measured at the Ag 3d_{5/2} core level. A nonmonochromatized Mg K α X-rays source (1253.6 eV Pass Energy = 25 eV, step 0.1 eV) was used in order to acquire core level spectra. The pressure was maintained at 1×10^{-9} Torr throughout the measurements. The spectra were acquired on films casted or spin deposited from CHCl_3 or CH_2Cl_2 solvents. The spectra were energy referenced to the C1s signal of aliphatic C atoms having a binding energy BE = 285.00 eV. Atomic ratios were calculated from peak intensities using Scofield's cross-section values, and λ factors were used.²⁸ Curve-fitting analysis of C1s, P2p, Pt4f, and Cl2p spectra was performed using Gaussian profiles as fitting functions, after subtraction of a Shirley-type background. For quantitative data, the BE values were referred to NIST data.²⁹

2.4. Irradiations. Pt-DEBP solutions were prepared at room temperature, under weak illumination conditions, to avoid polymer photodegradation. Chloroform (CHCl_3) was purchased from ACROS and used as received. Solutions were kept in glass recipients (4 mL, Wheaton 13-425) and irradiated with a ^{60}Co gamma ray source (1.25 MeV, CGR-Model Alcyon II) with appropriate acrylic build-ups (thickness of 0.5 cm). The Pt-DEBP concentrations in the solutions varied from 0.0113 mg/mL to 0.0500 mg/mL. Samples were irradiated with doses ranging from 1 to 90 Gy at room temperature, in the dark (to avoid photodegradation), at a rate of 0.5 Gy/min.

2.5. Electronic Structure Calculations. The calculations have been performed with Gaussian09.³⁰ For the energy calculations and geometry searches, the DFT method with the B3LYP functional³¹ has been used employing a 6-311+G(d)³² basis on the first atoms and the 6-311+G(df) on chlorine. The Pt atom has been treated with the LANL effective core potential (ECP) and triple- ζ (TZ) basis.³³ Excited state calculations have been performed by means of the time-dependent density functional theory (TD-DFT) method.³⁴ Calculations have been developed on the model bimetallic complex with hydrogen substituted phosphines (PH_3) because of the structural complexity of Bu_3 chains in PBu_3 ligands.

3. RESULTS AND DISCUSSION

Figure 1 shows the typical optical absorbance spectra before and after gamma ray irradiation for Pt-DEBP in chloroform at 0.0113 mg/mL. The principal absorption peaks are due to $\pi \rightarrow \pi^*$ absorption localized mainly on the conjugated part of the molecule.²⁰

Similar to what has been observed in MEH-PPV,¹² the main peak position of the absorption spectra shifts to lower wavelengths (blue-shifted), from 374 to 332 nm, after irradiation with 90 Gy. The absorption feature reveals also a reduction in the amplitude of the absorption band. As discussed

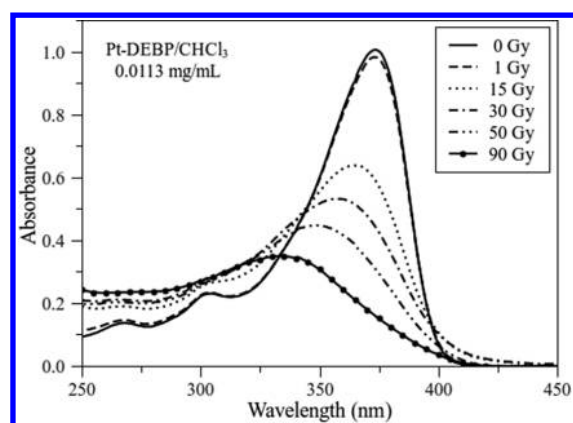


Figure 1. UV-vis absorption spectra of Pt-DEBP sample in CHCl_3 (0.0113 mg/mL) exposed at different irradiation doses (0–90 Gy).

in the introduction, the observed changes are promoted by the attack of radicals, from the radiolysis of the solvent, on the polymer backbone.^{35,13}

However, changes observed in the fluorescence spectrum, not shown here,²⁰ displayed that the observed effect, in Pt-DEBP based system, is distinct from that reported for MEH-PPV. Contrary to what was observed in MEH-PPV, a new signal is observed in the fluorescence spectrum from Pt-DEBP after irradiation, red-shifted with respect to the band found in the nonirradiated material, which dominates the fluorescence signal, for doses above 15 Gy.²⁰

The changes in the emission spectrum indicates the formation of a new emissive center after irradiation.

In order to assess polymer structural changes induced by irradiation, NMR, GPC, FTIR, and XPS studies were performed out on a Pt-DEBP sample irradiated with 30 Gy. Figure 2a presents the aliphatic region in the ^1H NMR spectrum of Pt-DEBP solutions irradiated with 30 Gy. The peaks of the irradiated compound are found in the aromatic region as a double doublet, as expected in Pt-DEBP based polymers.¹⁷ In addition, a small peak at about 4.1 ppm has been observed (not shown herein), consistent with a vinyl proton of a double bond with a Cl substituent, which suggests radical incorporation in the polymer chain. However, the aliphatic region shows the resonances arising from butyl chains on phosphorus ligand, and the signals centered at about 2.09 and

1.95 ppm are indicative of the chain length; these signals are attributed to internal and to terminal phosphine groups, respectively, and the integral calculated on these peaks indicates an increased chain length in comparison to the pristine sample. In fact, in the pristine sample, the integral ratio between internal/terminal CH_2 on the phosphine ligand is equal to 4/1, whereas in the irradiated sample, this value is 7/1. The corresponding number of repeating units then increases from 10 to about 16 units, in fairly good agreement with ^{31}P NMR and GPC analysis discussed below.

These data can be compared with the ^{31}P NMR of the irradiated sample (Figure 2b) where the signals due to terminal and internal phosphines on platinum(II) units were found at about 7.31 and 3.55 ppm, respectively, with an integral ratio of about 1:10 corresponding to a 22 unit oligomer. The coupling constant J (about 2370 Hz) is in agreement with a square planar Pt(II) center in *trans* configuration. This spectrum has been compared with the ^{31}P NMR of the pristine polymer. In the pristine sample, an integral ratio between terminal and internal phosphine groups equal to 1:4 has been calculated, corresponding to a 10 units oligomer. These results (^1H NMR and ^{31}P NMR) suggest that polymer molecular weight increases after irradiation. In order to evaluate this, GPC analyses were performed on pristine and irradiated samples.

Figure 3 shows the GPC results on pristine and irradiated samples, and it can be observed that the pristine sample contains a major fraction corresponding to about $M_n = 7360$ g/mol together with a minor component with higher M_n (see Table 1). The feature of the chromatogram changed upon irradiation, and the sample showed a single component corresponding to an increased M_n , i.e., 18 000 g/mol. The number of repeating units varied from 9–10 to 22–29, respectively, suggesting a gamma ray induced chain growth, as observed in the literature for aryl alkynes.³⁶

These results prompted us to further investigate the structure of the irradiated sample, and a FTIR analysis was carried out on samples with a concentration of 0.0375 mg/mL, exposed to different irradiation doses (1–90 Gy) (Figure 4). The spectra are normalized to the Ph stretching band at 2954 cm^{-1} to remove the influence of small differences in the baseline.³⁷

The main bands and their assignments for the nonirradiated polymer are in accordance with the literature.^{19,20} However, changes can be observed after irradiation, suggesting that

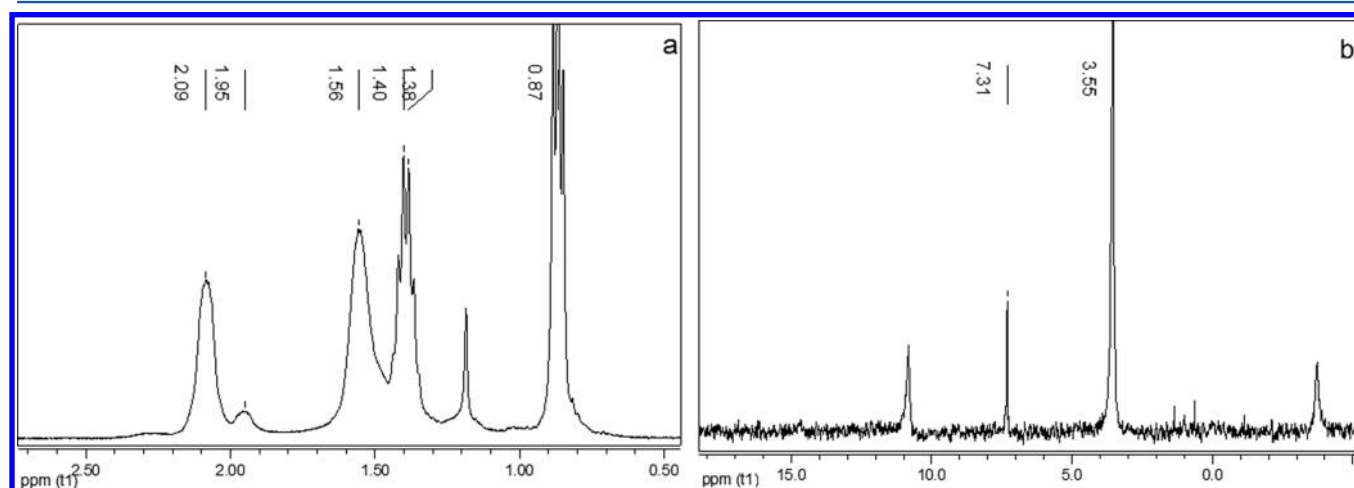


Figure 2. NMR spectra of 30 Gy irradiated Pt-DEBP sample in CDCl_3 : (a) ^1H NMR and (b) ^{31}P NMR.

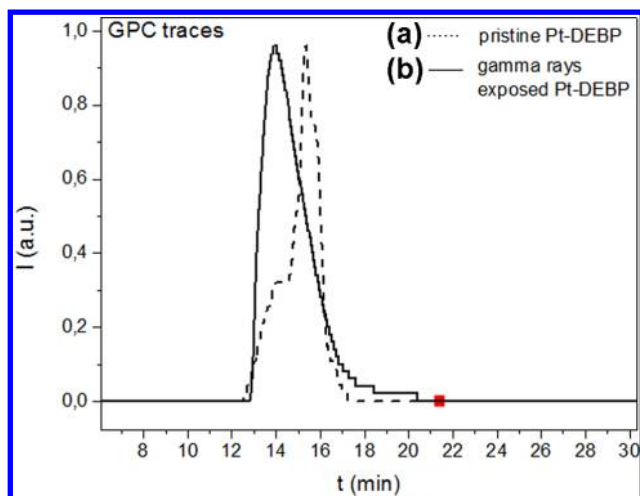


Figure 3. GPC traces of pristine (a) and 30 Gy irradiated (b) Pt-DEBP samples.

Table 1. GPC Data on Pristine and Irradiated Pt-DEBP (30 Gy) Samples

sample	M_n^a (g/mol)	M_w^a (g/mol)	\bar{D}^b	N^c
pristine Pt-DEBP	7360	7960 (80%)	1.08	9–10
	18 280	19 306 (20%)	1.10	
Pt-DEBP after gamma ray	18 000	22 990	1.28	22–29

^aDetermined by GPC in chloroform and based on polystyrene standards. ^b $\bar{D} = M_w/M_n$. ^cNumber of repeating units.

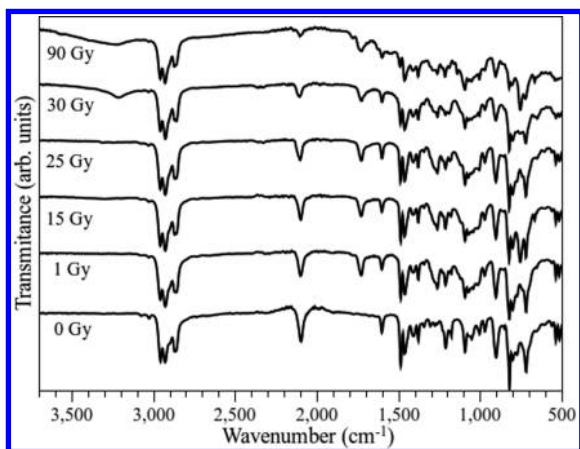


Figure 4. FTIR spectra of Pt-DEBP sample exposed to different radiation doses.

halogen atoms could be added to the polymer chain. After irradiation with 1 Gy, a decrease of the $\text{—C}\equiv\text{C—}$ stretching mode at about 2098 cm^{-1} is observed; concomitantly, it can be observed that the 1728 cm^{-1} band increases after irradiation as previously reported.²⁴ This band can be interpreted either as arising from oxidation of the triple bond, and/or from a stretching mode of the —C=C—Cl or —C=C—Cl_2 double bond, produced upon irradiation in the presence of CHCl_3 . The band at 1261 cm^{-1} and the band at 770 cm^{-1} increase after irradiation and are attributed to —ClC=CCl— (polychlorinated compounds) and C—Cl or —C—Cl_2 stretching modes.³⁸ The presence of $\text{Pt—C}\equiv\text{C}$ stretching mode at about 540 cm^{-1} shows a marked decrease, whereas a band at about 1500 cm^{-1} appeared. This band can be attributed to a Pt—C=C moiety.

Further irradiation doses (after 30 Gy) evidenced that the signals due to double bonds begin to decrease, which indicates the formation of saturated C—C bonds.

XPS signals of irradiation samples are presented in Figure 5. XPS analysis was carried out at C1s , P2p , Pt4f , and Cl2p core levels, and the results were compared with the data on the pristine Pt-DEBP reported in a previous paper.¹⁷ In Table 2, the binding energy (BE), full width at half-maximum (fwhm), and intensity ratio values for Pt-DEBP pristine and 30 Gy irradiated sample are reported. The C1s spectrum collected on the irradiated sample (Figure 5a) appears structured, and peak fitting individuates three components. The main peak at 285.00 eV is associated to C atoms of the main chain, also used to calibrate all spectra; the component at low BE values (283.68 eV) is attributed to C atoms bonded to metals, as in the pristine Pt-DEBP sample. The component at higher BE values (286.26 eV) is not observed in pristine oligomer and is consistent with C atoms bonded to chlorines in $\text{—CH}_2\text{=CHCl—}$ (vinyl) moieties, as reported in the literature; moreover, this signal is consistent with C—Cl fragments in single bonds.^{39,40} The presence of vinyl-like C—Cl groups is confirmed by the Cl2p spectrum (Figure 5b): for this signal, two pairs of spin–orbit components can be individuated. The first spin–orbit pair ($\text{Cl2p}_{3/2}$ BE = 198.21 eV) corresponds to the only signal observed for the pristine sample and is assigned to chlorine atoms bonded to metals (Cl—Pt) in terminal position.¹⁷ The spin–orbit pair at higher BE values ($\text{Cl2p}_{3/2}$ BE = 200.08 eV) is indicative for Cl—C groups and fully consistent with literature data reported for Cl atoms in $\text{—CH}_2\text{—CHCl—}$ moieties either in double and single bonds.^{34,35} The Pt4f signal was found at 72.61 eV , consistent with the presence of Pt(II) square planar centers, arising from the organometallic chain. In Figure 5c, the Pt4f spectrum is reported.

Furthermore, the atomic ratios reported in the fifth column of Table 2 confirm the increased amount of Cl atoms upon the gamma ray treatment; $N(\text{Cl})/N(\text{Pt})$ increases from 0.26 in the pristine sample to 0.49 in the irradiated sample. The amount of Cl atoms bonded to Pt remains almost stable ($N(\text{Cl})/N(\text{Pt}) = 0.26$ in pristine Pt-DEBP; $N(\text{Cl})/N(\text{Pt}) = 0.22$ in gamma ray exposed Pt-DEBP); the increase in $N(\text{Cl})/N(\text{Pt})$ is due to the formation of new vinyl-like or C—Cl groups in double or single bonds belonging to the organic moiety of the oligomer. The applied gamma ray dose induces a radical pathway probably involving the solvent and the polymeric chain and leads to the structural modification of the organic moiety, i.e., an attack to the triple bonds, as depicted in Figure 6.

With the aim of finding an interpretation and proof of the consistency of these results, we have reinvestigated the simulation of the absorption spectra by means of theoretical studies, starting from the model compound already used in our previous paper.²⁰ The model consists of two Pt-containing units terminated by each side by a chlorine atom, i.e., $[\text{Cl—Pt}(\text{PH}_3)_2\text{—DEBP—Pt}(\text{PH}_3)_2\text{Cl}]$. The PBU_3 units are substituted with the more easily tractable PH_3 ones. The model is reported in Figure 6 at the top. We have simulated the saturation of the triple bonds by initially inserting one or two chlorine atoms in each triple bond. We have obtained three compounds: one has two Cl atoms that are in beta position to the phenyl ring, another one has two Cl in α position to the phenyl ring, and the third has 4 Cl atoms. The simulated UV spectra of these compounds together with the one obtained for the original molecule are reported in Figure 7. The substitution of the triple bonds with double ones and the insertion of Cl

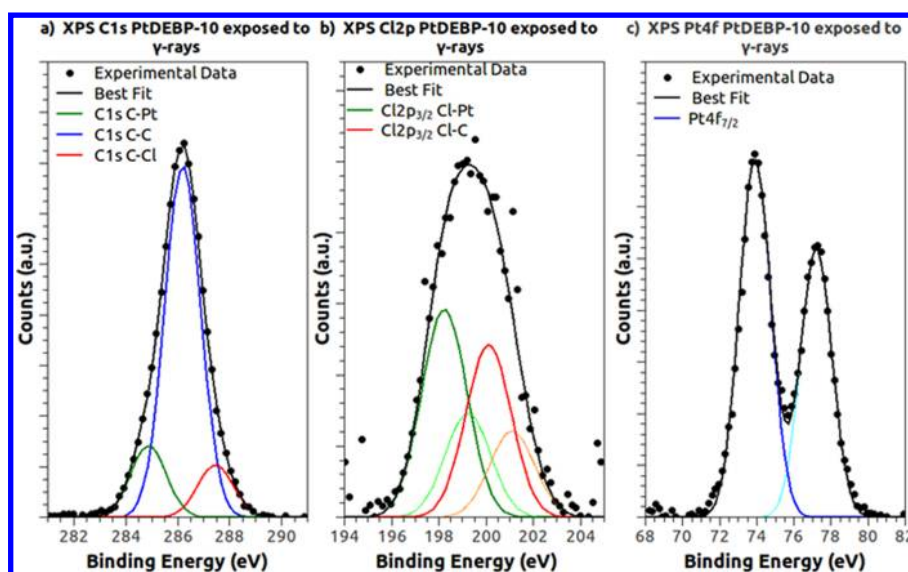


Figure 5. XPS signals in Pt-DEBP gamma ray exposed sample (30 Gy): (a) C1s, (b) Cl2p, and (c) Pt4f spectra.

Table 2. XPS Data for Pristine and Gamma Ray Irradiated Pt-DEBP Sample (30 Gy):

sample	signal	BE ^a (eV)	fwhm ^b (eV)	N _i /N _{Pt} ^c	assignment
gamma ray irradiated Pt-DEBP	C1s	283.68	1.62	5.9	C–Pt
		285.00	1.62	29.0	C–C
		286.26	1.62	4.5	C–Cl
	P2p _{3/2}	131.18	2.10	2.1	Pt–PBu ₃
	Pt4f _{7/2}	72.61	2.00	1	Pt
pristine Pt-DEBP	Cl2p _{3/2}	198.21	2.26	0.27	Pt–Cl
		200.08	2.26	0.22	C–Cl
	C1s	283.59	1.60	Tot:	C–Pt
		285.00	1.60	40.23	C–C
	P2p _{3/2}	131.28	1.84	2.2	Pt–PBu ₃
	Pt4f _{7/2}	72.84	2.00	1	Pt
	Cl2p _{3/2}	198.22	2.16	0.26	Pt–Cl

^aBinding energy. ^bFull width at half-maximum. ^cNumber of atoms versus Pd atom.

atoms do not seem to produce the blue-shift upon irradiation noticed by experiments. Furthermore we do not see such marked weakening of the main absorption band except for the 4 Cl model system (dotted blue line) that, however, has been ruled out by the considerations made in the previous section.

We have repeated the simulation of the UV absorption, therefore, on two more saturated model systems where two additional H atoms have been inserted on one or on both the double bonds for the structures with 2 Cl atom. This substitution finally leads to the spectra reported in Figure 7 (red line). Here, a more dramatic change of the main spectral feature that is compatible with the experimental data is seen: the main absorption shifts from 350 to 270 nm when the double bonds are transformed completely into single bonds (magenta line in the figure), and this shift goes along with a substantial decrease in absorption intensity. When only a partial substitution of a single double bond occurs (red line in the figure), we still have a significant blue shift of the band, albeit we notice only a moderate depletion of the absorption intensity.

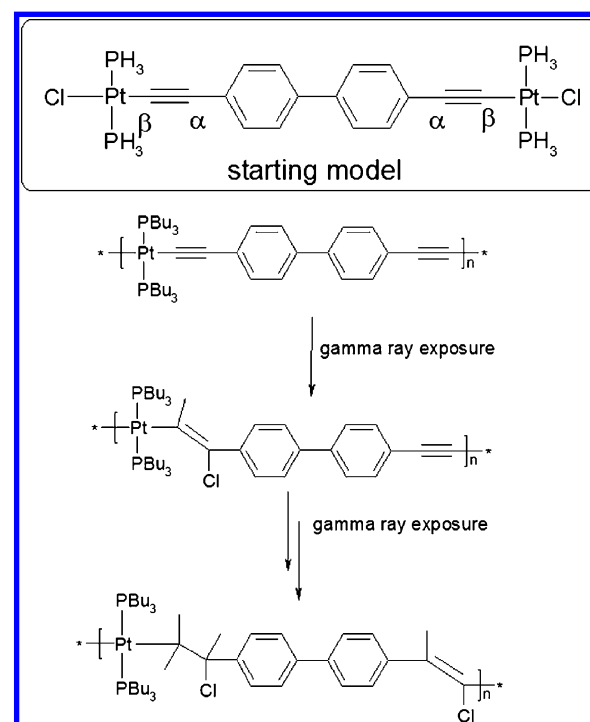


Figure 6. Possible pathway of the polymer chain modification upon attack of chlorine radicals.

These calculations clearly show that the experimental features are compatible with the hypothesis of structures reported in Figure 6 and provide a support for the interpretation of the rather complex reaction pathways taking place in the real system. In particular, we believe that the spectral features noticed during irradiation are compatible with a progressive saturation of the original triple bonds due to the H and Cl radicals and that the resulting compound, although retaining its polymeric length and structure, has changed its nature by incorporating both single and double, partially chlorinated bonds.

In summary, the results indicate two main structural changes after irradiation: chlorine incorporation in the polymer chain,

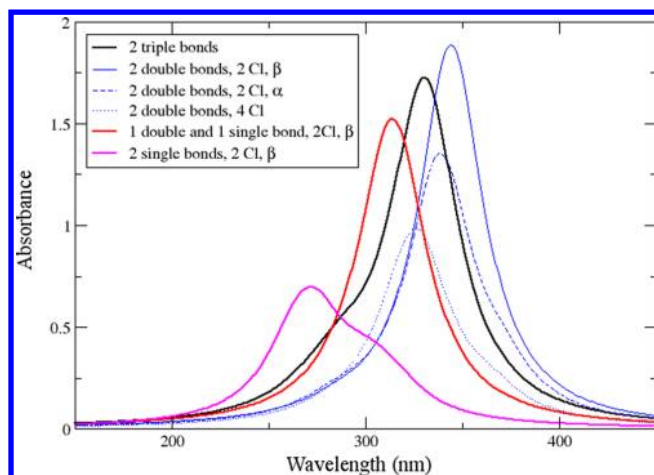


Figure 7. Simulation of UV-vis spectra for the model structures containing triple, double, or single chlorinated bonds.

mainly in the triple bond, and a polymer weight increase. The last effect is probably due to coupling of distinct polymer chains. The coupling hypothesis is reinforced by the qualitative observation of an increase in viscosity of the solutions after irradiation with doses greater than 30 Gy. The solutions did also become darker, indicating platinum decomplexation of the polymer chain. If Pt decomplexes, free radicals are formed in the main chain facilitating interchain reactions, which promotes molecular weight increase. However, at this point, we are not able to describe in detail the mechanism of molecular weight increase.

Regarding the alterations observed in the emission spectrum, it is known that substituents in the polymer chain alter the optical characteristics of these complexes.²⁰ In addition, electron withdrawing groups, like chlorine atoms, can reduce the spin density on the metal resulting in an increase of the quantum efficiency of the fluorescence and blue-shift in the UV-vis spectra. The same effect is observed when the polymer chain is increased, what can be related to changes observed in fluorescence;⁴¹ however, detailed studies about this subject are being conducted.

5. CONCLUSIONS

The changes in the chemical structure of the polymetallayne Pt-DEBP upon irradiation to increasing doses of gamma rays has been investigated. Spectral changes in the UV-vis absorption, detectable at radiations as low as near 1 Gy, suggest the feasibility of low dose dosimeters. The chlorine and hydrogen radicals that are formed upon the radiolysis of the solvent attack the triple carbon bonds give double and single carbon moieties. A chain length increase is then observed as a consequence of the radical formation and rearrangement. Theoretical simulation of the optical spectra of irradiated samples support the experimental results.

AUTHOR INFORMATION

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

We acknowledge the financial support of Ateneo Sapienza 2011/C26A11PKS2, MAE-MIUR Progetti di Ricerca Scientifica e Tecnologica Bilaterale 2008-2010, CNPq (Brazil),

FAPESP (Brazil), CAPES (Brazil), and CNEN (Brazil) for their financial support and Marco A. R. Fernandes (UNESP-Botucatu) for the ⁶⁰Co irradiations.

REFERENCES

- (1) Waksman, R.; Ajani, A. E.; White, R. L.; Chan, R. C.; Satler, L. F.; Kent, K. M.; Pichard, A. D.; Pinnow, E. E.; Bui, A. B.; Ramee, A.; et al. *N. Engl. J. Med.* **2002**, *346*, 1194–1199.
- (2) Brans, B.; Bodei, L.; Giammarile, F.; Linden, O.; Luster, M.; Oyen, W. J. G.; Tennvall, J. *Eur. J. Nucl. Med. Mol. Imaging* **2007**, *34*, 772–786.
- (3) Bryan, R.; Jiang, Z.; Friedman, M.; Dadachova, E. *Fungal Biol.* **2011**, *115*, 945–949.
- (4) Stabin, M. G.; Brill, A. B. *Semin. Nucl. Med.* **2008**, *38*, 306–307.
- (5) Aziz, N. H.; Moussa, L. A. A. *Food Control* **2002**, 281–288.
- (6) Caulfield, C. D.; Cassidy, J. P.; Kelly, J. P. *J. Am. Assoc. Lab. Anim. Sci.* **2008**, *47*, 61–66.
- (7) Smith, D. M. Hard X-ray and Gamma-Ray Detectors. In *Photons in Space*; Huber, M. C. E., Pauluhn, A., Culhane, J. L., Timothy, J. G., Wilhelm, K., Zehnder, A., Eds.; ISSI Scientific Report SR-009, 2010; pp 345–364.
- (8) Knoll, G. F. *Radiation Detection and Measurement*, 3rd ed.; John Wiley and Sons: New York, 2000.
- (9) Owens, A. J. *Synchrotron Radiat.* **2006**, *13*, 143–150.
- (10) Webster, J. G. *The Measurement, Instrumentation and Sensors Handbook: Electrical Engineering Handbook*, 1st ed.; CRC Press: Boca Raton, FL, 1998.
- (11) Chen, Q.; Hajagos, T.; Pei, Q. *Annu. Rep. Prog. Chem., Sect. C: Phys. Chem.* **2011**, *107*, 298–318.
- (12) Graham, S. C.; Friend, R. H.; Fung, S.; Moratti, S. C. *Synth. Met.* **1997**, *84*, 903–904.
- (13) Croonenborghs, B.; Smith, M. A.; Strain, P. *Radiat. Phys. Chem.* **2007**, *76*, 1676–1678.
- (14) Zhong, H.; Zhao, Y.; Li, Y.; Pei, Q. *Nanotechnology* **2008**, *19*, S05503.
- (15) Rogers, T.; Han, C.; Wagner, B.; Nadler, J.; Kang, Z. *MRS Proc.* **2011**, *1312*, 1312, mrsf10-1312-ii10-10.
- (16) Silva, E. A. B.; Borin, J. F.; Nicolucci, P.; Graeff, C. F. O. *Appl. Phys. Lett.* **2005**, *86*, 131901–131902.
- (17) Bronze-Uhle, E. S.; Batagin-Neto, A.; Lavarda, F. C.; Graeff, C. F. O. *J. Appl. Phys.* **2011**, *110*, 073510–073510–9.
- (18) Wong, W.-Y.; Ho, C.-L. *Coord. Chem. Rev.* **2009**, *253*, 1709–1758.
- (19) Abd-El-Aziz, A. S.; Shipman, P. O.; Boden, B. N.; McNeil, W. S. *Prog. Polym. Sci.* **2010**, *35*, 714–836.
- (20) Eloi, J. C.; Chabanne, L.; Whittel, G. R.; Manners, I. *Mater. Today* **2008**, *11*, 28–36.
- (21) Fratoddi, I.; Battocchio, C.; La Groia, A.; Russo, M. V. *J. Polym. Sci., Part A* **2007**, *45*, 3311–3329.
- (22) Fratoddi, I.; Gohlke, C.; Cametti, C.; Diociaiuti, M.; Russo, M. V. *Polymer* **2008**, *49*, 3211–3216.
- (23) Battocchio, C.; Fratoddi, I.; Russo, M. V.; Polzonetti, G. *J. Phys. Chem. A* **2008**, *112*, 7365–7373.
- (24) Batagin-Neto, A.; Bronze-Uhle, E. S.; Fernandes, D. M.; Fratoddi, I.; Venditti, I.; Decker, F.; Bodo, E.; Russo, M. V.; Graeff, C. F. O. *J. Phys. Chem. B* **2011**, *115*, 8047–8053.
- (25) Takahashi, S.; Kuroyama, Y.; Sonogashira, K.; Hagihara, N. *Synthesis* **1980**, 627–630.
- (26) Kauffman, G. B.; Teter, L. A. *Inorg. Synth.* **1963**, *7*, 245–249.
- (27) Stepto, R. F. T. *Polym. Int.* **2010**, *59*, 23–24.
- (28) Scofield, J. M. *J. Electron Spectrosc. Relat. Phenom.* **1976**, *8*, 129–137.
- (29) NIST Standard Reference Database 20, version 3.5; <http://srdata.nist.gov/xps/>.
- (30) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A. et al. *Gaussian 09*, revision A.1; Gaussian, Inc.: Wallingford, CT, 2009.

- (31) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648–5652.
- (32) McLean, A. D.; Chandler, G. S. *J. Chem. Phys.* **1980**, *72*, 5639–5648.
- (33) Hay, P. J.; Wadt, W. R. *J. Chem. Phys.* **1985**, *82*, 299–310.
- (34) Casida, M. E.; Jamorski, C.; Casida, K. C.; Salahub, D. R. *J. Chem. Phys.* **1998**, *108*, 4439–4449.
- (35) Bronze-Uhle, E. S.; Borin, J. F.; Batagin-Neto, A.; Graeff, C. F. *O. Mater. Chem. Phys.* **2012**, *132*, 846–851.
- (36) Bassetti, M.; Fratoddi, I.; Lilla, L.; Pasquini, C.; Russo, M. V.; Ursini, O. Synthesis of Polyarylacetylenes by Gamma-Ray Induced Polymerization of Terminal Alkynes. Nanostructures of *ortho*-Substituted Derivatives. *J. Polym. Sci., Part A: Polym. Chem.* **2012**, accepted.
- (37) Yang, B. D.; Yoon, K. H.; Chung, K. W. *Mater. Chem. Phys.* **2004**, *83*, 334–339.
- (38) Socrates, G. *Infrared Characteristic Group Frequencies*, 2nd ed.; John Wiley & Sons: New York, 1994.
- (39) Clark, M. B., Jr.; Burkhardt, C. A.; Cordella, J. A., Jr. *Macromolecules* **1989**, *22*, 4495–4501.
- (40) Beamson, G.; Briggs, D. *High Resolution XPS of Organic Polymers: The Scienta ESCA 300 Database*; John Wiley & Sons: New York, 1992.
- (41) Kohler, A.; Wilson, J. S.; Friend, R. H.; Al-Suti, M. K.; Khan, M. S.; Gerard, A.; Bassler, H. *J. Chem. Phys.* **2002**, *116*, 9457–9463.