
RADICAL FORMATION ON IRRADIATED POLYCARBONATE

Mauro Cesar Terence*
Selma Matheus Loureiro Guedes**

Abstract

Type II polycarbonate, PC II, manufactured with high purity reagents, as used on medical fabrication was gamma irradiated by a ^{60}Co source with dose of 100 kGy. The formation and decay of PC II radicals ($G_{\text{scission}} = 1$) was investigated by electron spin resonance spectroscopy in the presence and absence of air at room temperature. The air does not interfere in the formation of radicals because they are formed as consequence of direct interaction of gamma radiation, but it interferes in their decays. During irradiation, the air reacts with all isopropyl radicals and with 2/3 of phenoxy-phenyl radicals.

Keywords: Polycarbonate, phenoxy, phenyl.

* Universidade Presbiteriana Mackenzie (UPM).

** Instituto de Pesquisas Energéticas e Nucleares (Ipen).

1 INTRODUCTION

Polycarbonate (PC) is an amorphous polymer containing benzene rings and carbonate groups in its main chain and methyl groups connected to the main chain. Benzene rings give high radiolytic stability to the PC since they decentralize the energy absorbed from the ionization radiations; even so, the main chain scissions when the PC is sterilized with γ rays, which transport around 1.25 MeV (CHRISTOFER; FOX, 1962).

Polycarbonate PC II, a new PC type, has been made available in Brazil; the PC II production process is different from the old process for the PC I (ENCYCLOPEDIA..., 1970). The concentration of additives in PC II is rather smaller than in PC I, but PC II presents better properties and higher molecular radiolytic resistance. G_{scission} is the number of scissions by 100 eV of absorbed energy in the main chain.

The G_{scission} for PC I is 16.7, whereas the G_{scission} for PC II is =1 (ARAÚJO, 1993). This means that, for each 400 eV of energy absorbed by PC I, there are around 67 scissions in the main chain and about 4 scissions for PC II. These PCs are used in the production of medical appliances that can be sterilized with γ rays.

Commercial radio-sterilization of medical appliances is carried out at room temperature in the presence of air, and the ionizing radiation can also favor the polymeric oxidation according to the radiolytic species. Interaction between the ionizing radiation and the air produces ozone, a very strong oxidizing agent. That is the reason why the formation and the decay of radicals in PC II radiolysis have been investigated both in the presence and absence of air.

2 EXPERIMENTAL PART

Processes requiring fewer additives are used in the production of the new PC type, the PC II. The PC II studied here had average molar mass of 22000 g/mol (ENCYCLOPEDIA..., 1970). Two samples of PC II, powder form, were prepared in suprasil tubes, each containing 0.5 g. One of the samples was sealed in the presence of air under atmospheric pressure, and the other was sealed under a 10^{-5} mmHg pressure in a high-vacuum line. Both samples were irradiated with γ rays stemming from a ^{60}Co source and whose dose rate was 1.2 kGy/h with a dose of 100 kGy. The spectrums of electronic paramagnetic resonance (EPR) were obtained at room temperature with the equipment JES-ME-ESR, simultaneously with the Mn^{2+} standard.

3 RESULTS AND DISCUSSION

With a view of studying the formation and decay of radicals in PC II radiolysis, EPR spectrum of samples irradiated in the presence and absence of air have been obtained, as well as samples irradiated in the absence of air and that after irradiation were put in the presence of air and had their radicals observed.

Figure 1 shows the PC II spectrum irradiated in the vacuum with 100 kGy. Figure 1A is made up of a wide singlet, when the equipment yield increases around six times, from 1.8×10 to 1.1×100 .

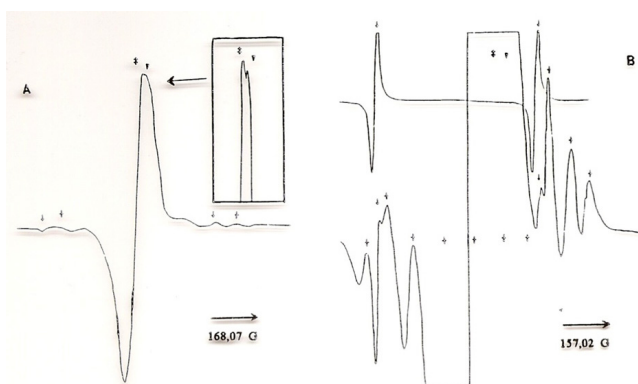
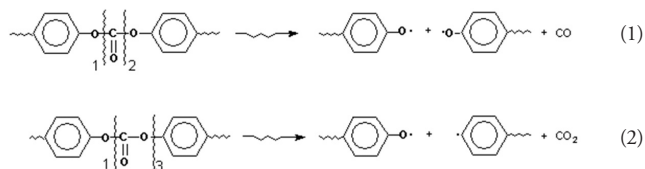


Figure 1 EPR spectrum of the PC irradiated in the vacuum with 100 kGy: a) yield $1,8 \times 10$, b) yield 5.0×100 . Isopropyl radical (+), phenyl radicals (‡), phenoxy radical (∇), standard Mn^{2+} (∩).

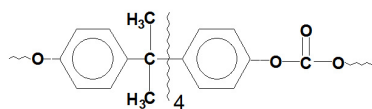
Source: Elaborate by the authors.

Two different peaks can be noticed, one corresponding to the phenyl radical, in a lower magnetic field, and the other peak corresponding to the phenoxy radical, in a higher magnetic field. Other researchers have also observed these radicals (ARAÚJO, 1993; HAMA; SHINOHARA, 1970; JANG; WILKIE, 2005). The phenoxy and the phenyl radicals are formed as consequence of the direct interaction of the radiation with the polymer and according to reactions 1 and 2, with CO and CO₂ escape. Radiation makes the polymeric molecule scission in three different positions: positions 1 and 2, in the carbonyl group, and position 3 between the carbonate group and the benzene ring.

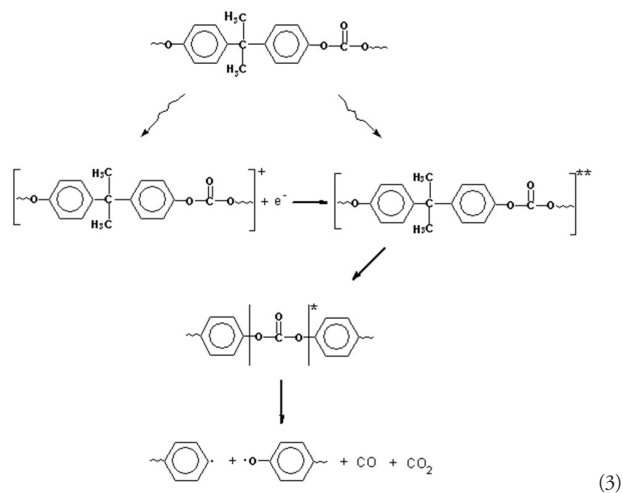


It is important to mention that, according to Hama and Shinohara (1970), when the PC (without process stabilizers) is irradiated with a dose of 54 kGy, at room temperature, there is more formation of CO than of CO₂, observed by mass spectrometry. The relative concentrations of CO and CO₂ are respectively 65.4% and 33.8%, that is, CO/CO₂ ≈ 2; the formation of the other 0.8% of gases has not been identified (HAMA; SHINOHARA, 1970). Therefore, the expected quantity of phenoxy will be around 5 times the quantity of phenyl. However, it is not possible to determine the quantity of radicals through the EPR spectrum, once the phenoxy and phenyl singlets are overlaid.

Figure 1A also shows that low-intensity lines appear next to Mn²⁺ signals when compared to the singlet signal. When the equipment yield is increased around thirty times, from 1.8 × 10 to 5.0 × 100, six lines, out of the ten lines estimated with coupling constant of 1.17 × 10⁻³ T, can be clearly noticed; these lines are associated to an alkyl radical, as for example the isopropyl radical $\sim\text{C}\cdot(\text{CH}_3)_2$ (HAMA; SHINOHARA, 1970), also formed as consequence of the direct interaction between radiation and the polymer, scission the polymer molecule in position 4, between the isopropylidene and the benzene ring. Based on the intensity of radicals bands, it is possible to observe scission predominance between the carbonate group and the benzene ring, as it is mentioned in literature (ARAÚJO, 1993; HAMA; SHINOHARA, 1970).



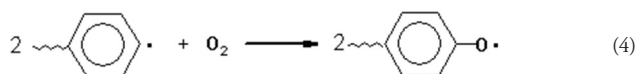
Connection scission is more frequently observed in the carbonate group positions 1, 2 and 3, and it occurs due to the energy absorbed by the carbonyl group, the same way it occurs in the photolysis (GUILLET, 1985), i.e., in carbonyl compounds, non-shared electrons of orbital-*n* shift to non-bonding π orbitals (π^*) and to $\pi \rightarrow \pi^*$ transitions, which are responsible for energy absorption in the carbonyl group (GUILLET, 1985; BETTINI, 1992). Highly excited molecules can be formed by direct interaction of the radiation and the polymer or free electrons, formed during the polymer ionization through interaction of radiation, are re-combined with cations, resulting in excited molecules, as follows:



The exciting energy can be quickly relaxed to lower levels and migrate to any particular connection of the polymer, resulting in homolytic scission. On the other hand, the isopropylidene group is protected by the presence of two aromatic rings in its surrounding area, and therefore it suffers a reduced number of scissions. This protection does not occur in the carbonyl group due to its energy absorption characteristics (MORT; PFISTER, 1982; MONTAUDO; CARROCCIO; PUGLISI, 2002). Formation of the hydrogen atom from the connection C-H of the CH_3 is also expected. However, these radicals can only be observed at low temperatures (around 77 K).

When the PC II is irradiated with 100 kGy in the presence of air, low-intensity lines related to the isopropyl radical cannot be observed (Figure 2). These radicals formed as direct consequence of the interaction of the radiation with the polymer react with the oxygen in the air. However, there is a singlet, with its half-height width slightly smaller than the one in Figure 1A, moving from higher magnetic fields until approximately six hours after the end of irradiation. It is not possible to observe the two peaks in Figure 2 when the core singlet is enlarged.

The reason is that the peaks are probably overlaid when one of them gets smaller and therefore it is impossible to see them in the EPR. This information suggests that the phenyl radical reacts with oxygen forming the phenoxy radical, according to equation 4.



The radicals may keep stable in the polymer matrix and this makes color show up; this condition is not desirable in a few applications of the PC when the polymer is submitted to radiation. The radicals can also react among themselves by means of twinning recombination or not. The smaller the radical mass, the larger its migration through the polymer matrix can be; this way, there is a non-twinning recombination in a place of the polymer chain distant from its formation place. Twinning recombination occurs when low-mobility radicals are formed and the reason for that may be their larger molar mass and the fact that they recombine in their own formation place or nearby.

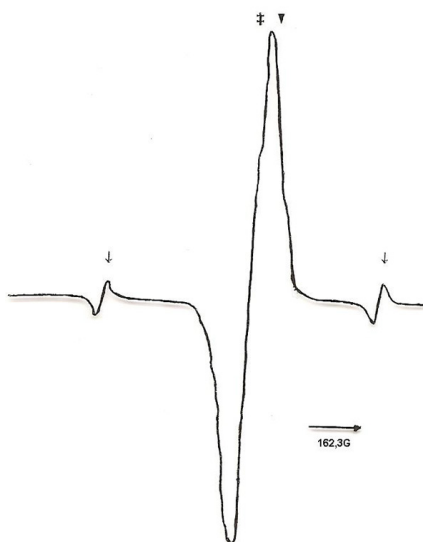


Figure 2 EPR spectra of PC II irradiated in the air with 100 kGy. Phenyl radical (\ddagger), phenoxy radical (∇), standard Mn^{2+} (\downarrow).

Source: Elaborate by the authors.

Through the results it can be ended that: EPR spectrum obtained both, at room temperature and in the vacuum, indicates the presence of three radicals: phenyl and phenoxy, formed in larger quantities, and Isopropyl; these radicals are formed as consequence of the preferential scission of the carbonyl group. In the presence of air, the Isopropyl reacts with O_2 , that is, the O_2 in the air interferes in the decaying process of the radicals, but not in their formation, since they are formed out of the direct interaction of the radiation with the polymer. Formation of phenoxy-phenyl in the vacuum is three times larger than in the air. These radicals react with the O_2 in the air during irradiation, which lasted for 100 hours.

The phenoxy-phenyl radicals decay at room temperature by means of recombination reactions. There are three possible reactions between these two radicals; the RMN ^1H spectrum has shown that the phenoxy-phenyl recombination, with formation of diphenyl ether, a colorless compound, is the most common recombination (MONTAUDO; CARROCCIO; PUGLISI, 2002; WILSK, 1987; TERENCE, 1996).

Scission of the PC II main chain mainly forms phenyl and phenoxy radicals, responsible for the color aspect. Once radio-sterilization occurs in the presence of air, the phenyl radicals are transformed in phenoxy radicals originating a colorless product. Therefore, the yellow color is explained by the phenoxy radical that is stable in the polymeric matrix at room temperature. PCI and PCII have the same chemical structure, but the purity levels of the reagents used in the synthesis are different. PC I reagents are not so pure and, therefore, it is necessary the addition of optical whiteners to disguise the yellow color caused by impurities of the reagents. PC II reagents are purer and, therefore, do not require any optical whitener; for this reason, PC II yellowish index, in sterilization doses, is almost half the yellowish index of PC I, although its G_{scission} is 17 times smaller than the one of PC I. These facts indicate that the use of optical whiteners in PC II is necessary when PC II is used in the manufacturing of medical appliances that are going to be radio-sterilized and for which the yellow color is not desired.

FORMAÇÃO DE RADICAIS NO POLICARBONATO IRRADIADO

Resumo

Polycarbonato tipo II, PC II, manufaturado com reagentes de alta pureza, usado na fabricação de materiais médicos, foi irradiado com raios gama provenientes de uma fonte de ^{60}Co com uma dose de 100 kGy. A formação e o decaimento dos radicais do PC II com ($G_{\text{cisão}}=1$) foram investigados por ressonância paramagnética eletrônica, na presença e ausência de ar e em temperatura ambiente. O ar não interfere na formação dos radicais porque eles são formados como consequência da interação direta da radiação gama com o polímero, mas o ar interfere no decaimento deles. Durante a irradiação, o ar reage com todos os radicais i-propil e com 2/3 dos radicais fenóxi/fenil.

Palavras-chave: Polcarbonato, fenóxi e fenil.

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Contato

Mauro Cesar Terence
e-mail: mauroterence@yahoo.com.br