The role of unsaturations in the Gamma irradiation of crosslinkable polymers

Angel J. Satti [a,b,*], Andrés E. Ciolino [b], Noemí A. Andreucetti [a], Enrique M. Vallés [b]

[a] Departamento de Química, Instituto de Química del Sur (INQUISUR). Universidad Nacional del Sur (UNS) – Consejo Nacional de Investigaciones Científicas y Técnicas (CONICET). Av. Alem 1253, 8000 Bahía Blanca, Argentina
[b] Planta Piloto de Ingeniería Química (PLAPIQUI). UNS – CONICET. Camino La Carrindanga km 7, 8000 Bahía Blanca, Argentina

HIGHLIGHTS

- Terminal vinyls from metallocenic synthesis accelerate radioinduced crosslinking.
- Trans vinyl structures are generated during irradiation, but vinyldenes are reluctant to react.
- The position of the vinyl groups noticeably affects the irradiation process.
- Irradiated vinyl ended PDMS crosslinked more readily than PDMS with 227 main chain vinyls.
- Dose-to-gel is reduced more than 20 times when irradiating vinyl terminated polymers.

GRAPHICAL ABSTRACT

Irradiated PEX # (ethylene copolymers with an # amount of 1-hexene -H- or 1-octadecene -OD) and their non-vinyl containing hidrogenated samples (PEX #h), along with irradiated vinyl functionalized siloxane polymers. Numbers within parentheses correspond to the number of vinyl groups per polymer chain for each irradiated polymer. Note that PDVi have been crosslinked with the lower dose of irradiation, although it has only one vinyl group. However, that is a terminal vinyl, while for the other polydimethylsiloxane derivatives, vinyls are within the main chain.
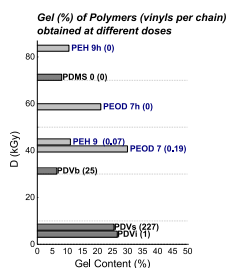
Gel (%) of Polymers (vinyls per chain) obtained at different doses

ARTICLE INFO

ABSTRACT

Nowadays, the understanding of the interaction of ionizing radiations with polymeric materials is becoming increasingly important. It is well known that many parameters regarding the synthesis of the polymers noticeably affect the irradiation process. In this work, an analysis of the effect of the type and the position of unsaturations in the molecular structure of crosslinkable polymers is performed. For such purpose, two solid semycristalline metallocenic ethylene 1-olefin copolymers (mEOC) which contain a low concentration of unsaturations from the synthesis, and their hydrogenated samples, were irradiated along with liquid poly(dimethylsiloxane) (PDMS) homo and copolymers containing different location and concentration of vinyl groups, which were structurally tailored through anionic synthesis. The source of irradiation was ^{60}Co, under vacuum at room temperature, in all the cases. The results indicated that terminal vinyls drastically accelerate the crosslinking to lower doses, even at much lower concentrations than other type and location of unsaturations for both, mEOC and PDMS, type of polymers.

© 2015 Published by Elsevier Ltd.

1. Introduction

Throughout the last 60 years high energy irradiation has been extensively used to modify the molecular structure of commercial polymers in order to improve their properties for specific

* Corresponding author at: Departamento de Química, Instituto de Química del Sur (INQUISUR). Universidad Nacional del Sur (UNS) – Consejo Nacional de Investigaciones Científicas y Técnicas (CONICET). Av. Alem 1253, 8000 Bahía Blanca, Argentina.
E-mail address: angel.satti@uns.edu.ar (A.J. Satti).

applications (Andreucetti et al., 1999; Charlesby, 1960; Dole, 1972; Li et al., 2002; Machi, 1995; Perraud et al., 2003; Satti et al., 2008, 2010a, 2010b, 2010c, 2012; Vallés et al., 1990). The radioinduced effects produce radicals and macroradicals that lead to two principal reactions: crosslinking and scission of polymer chains. Some polymers such as poly(ethylene) (PE) and polydimethylsiloxane (PDMS) are prone to crosslink while other polymers like poly(propylene) and poly(methylmethacrylate) suffer degradation at different levels. Regarding the first group, the molar masses of these polymers increase noticeably, and can even form a crosslinked insoluble material (gel) at certain radiation dose (the gel dose, D_{gel}) (Charlesby, 1960). Therefore, with just a simple post-reactor process, the final properties of this group of polymers can be significantly modified and/or enhanced by using radiation to induce these crosslinking reactions. Just to mention some examples, the viscoelastic properties of PE are increased by irradiation processes (Satti et al., 2010a), and PDMS can go from a liquid polymer to a solid elastomer, giving a wide range of applications through its physicochemical modifications (Charlesby, 1960; Rogero et al., 2005; Mashak and Taghizadeh, 2006; Satti et al., 2008, 2010a, 2010b, 2010c; Woo and Sandford, 2002). Even more: since the medical field is one of the most beneficiated with the application of PDMS derivatives (due to their biocompatibility and biodurability) (Aziz et al., 2003; Birkefeld et al., 2004; Fu and Kao, 2010; Mashak and Rahimi, 2009; Nicolson and Vogt, 2001; Van den Kerckhove et al., 2001), the gamma irradiation of these polymers is also used for sterilization purposes. For such a reason, it becomes clear that an understanding of the changes induced by irradiation along this process is crucial to control the numerous variables that take part in this process.

Although the irradiation of PE and PDMS homopolymers has been largely studied, different types of synthesis or additional functionalization of the original polymers lead to a wide range of derivatives that may influence the way in which the radiation process affects the chemistry of a posterior radioinduced crosslinking process. Since the early 90s, the synthesis of PE and PE derivatives by using metallocenic catalysts has became an important way to obtain polyolefins in a more controlled manner than with the conventional Ziegler-Natta catalysts. Linear or tailor branched PE can be obtained with a polidispersity (PD) around 2, while with other types of conventional catalysts the PD indexes can scale up to 20. For example, instead of the classical high pressure process, the metallocenic catalysts allow to obtain linear low density polyethylene (LLDPE) with low PD by adding different olefins as comonomers (Quijada et al., 1995). Depending on the olefins, the length of the side branches of the resulting LLDPE can be controlled. However, in the synthesis of PE or ethylene/1-olefin copolymers (mEOC) by using metallocenic catalysts there are some side reactions that lead to the formation of unsaturations along or at the end of the resulting polymer chains (Kokko et al., 2000; Kokko, 2002; Quijada et al., 1995). Since unsaturations react more readily with the radioinduced radicals (Dole, 1972; Satti et al., 2010b), it is important to understand the role of these unsaturations in the irradiation process.

On the other hand, functionalization of certain polymers can be searched deliberately to obtain some specific structure or property. As pointed out in the previous paragraphs, biomedicine is a topic with a growing demand, in which biocompatible polymers like PDMS take part with more complex or functional structures. In some particular cases, the synthesis of the desired polymers must be performed with sophisticated synthetic methods in order to obtain the targeted structures. Anionic polymerization techniques are an example, since monodisperse PDMS with controlled molar masses and level of unsaturations can be obtained. In addition, monodisperse PDMS samples allow the study of radioinduced structural changes in an easier way because the homogeneity of the studied polymer samples leads to a better understanding of the molecular structure modifications that take part along this process (Satti et al., 2010c). For example, Satti et al.

(2010c) studied the effect of the γ-irradiation over anionic PDMS copolymers. The results obtained in that work indicate that the presence of vinyl groups along the polymer main chain significantly decreases the D_{gel} (Satti et al., 2012). With the purpose of extending the results, in this paper it is also studied how the crosslinking process is affected by the position of the vinyl groups in the polymer chain. This can be envisioned by studying the changes induced by radiation on polymers containing dissimilar levels of unsaturations and at different places along the chain.

Taking into account all these facts, in this article we analyze and compare how the presence of unsaturations affects the radioinduced reactions of mEOC and PDMS polymers. For this purpose, hydrogenated and unhydrogenated samples of mEOC were irradiated in order to observe the differences in crosslinking due to the presence or absence of unsaturations. On the other hand, PDMS homopolymers and copolymers with different concentrations of vinyl groups (at the end or along the main chain) were synthesized through anionic polymerization techniques. The analysis of the irradiated samples was performed by using Fourier Transform Infrared Spectroscopy (FTIR), size exclusion chromatography (SEC) and gel extraction.

2. Materials and methods

2.1. mEOC copolymers: synthesis, characterization and hydrogenation

Two mEOC copolymers were synthesized by using a 1 L Parr reactor with stirring (500 rpm) at 60 °C with an ethylene pressure of 2 bar. Et[Ind]$_2$ZrCl$_2$/MAO were the catalyst/co-catalyst used for the synthesis, and toluene (about 500 mL) was employed as solvent. The samples obtained were precipitated in cold methanol; subsequently washed with acetone, methanol and water; and then dried in a vacuum oven until constant weight. The amount of comonomer incorporated in the copolymers was measured by ^{13}C-NMR at 80 °C using a VARIAN XL-300 spectrometer operating at 75 MHz. Cristallinity of these copolymers was obtained from the thermograms obtained by diferential scanning calorimetry (DSC, Perkin Elmer). Additional details regarding the synthesis and characterization of these copolymers are given in previous works (Satti et al., 2010a, 2010b). All mEOC polymers are identified as PEX # as it is shown in Table 1, where X corresponds to the comonomer used (H for 1-hexene, OD for 1-octadecene), and # to the amount of incorporation of the comonomer, respectively.

A convenient quantity of the obtained mEOC samples (about 3 g) was hydrogenated by using Wilkinson's catalyst ([(Ph$_3$)P]$_3$RhCl/(Ph)$_3$P) under hydrogen pressure, at 100 °C during 48 h (Osborn et al., 1966). Briefly, the hydrogenation reactor (Parr®, 2 L capacity) was filled with the polymer sample and

Table 1
Structural description of the polymers used in this work.

Structure	Polymer	Comonomer	Incorporation (% M)
Metallocenic Ethylene Copolymer	PEH 9	1-hexene	9.1
	PEOD 7	1-octadecene	7.1
Hidrogenated Metallocenic Ethylene Copolymer	PEH 9h	1-hexene	9.1
	PEOD 7h	1-octadecene	7.1
Anionic PDMS Homopolymer	PDMS 0	–	–
Anionic PDMS Homopolymer (vinyl ended)	PDVi	–	–
Anionic PDMS Block Copolymer	PDVb	V$_4$	3.7
Anionic PDMS Statistical Copolymer	PDVs	V$_4$	18.1

500 mL of toluene. Hydrogenation proceeds at 100 °C and 300 rpm in toluene, using a final hydrogen pressure of 4,8 atm. The reaction was finished by cooling down at room temperature (RT). The samples obtained were washed in fresh chloroform, under constant stirring, during 24 h in order to eliminate catalyst's residues (Ciolino et al., 2006). Then, they were precipitated in cold methanol, and dried in vacuum oven until constant weight. The hydrogenated products were named with an "h" following their original names (Table 1).

2.2. Synthesis and characterization of PDMS and derivatives

The synthesis of PDMS polymers was performed by using anionic polymerization (high-vacuum techniques), following conventional procedures (Hadjichristidis et al., 2000; Ninago et al., 2009; Uhrig and Mays, 2005). All manipulations were performed under high vacuum in glass Pyrex reactors, equipped with break-seals for the addition of the reagents and constrictions for removal of products at different stages of the reaction (Ninago et al., 2009; Satti et al., 2010c, 2012). All polymerizations were initiated by employing sec-butyl lithium (sec-Bu$^-$Li$^+$, freshly synthesized) as initiator; benzene (Dorwill, Argentina) as solvent; THF (Cicarelli, Santa Fe, Argentina) as promoting agent; and degassed methanol (Química Industrial Bahiense, Argentina) as terminating agent. Two cyclic siloxane monomers were used: 1,3,5-hexamethyl(cyclotrisiloxane) (D$_3$, Sigma-Aldrich), and 1,3,5,7-tetrametil-1,3,5,7-tetravinyl(cyclotetrasiloxane) (V$_4$, Sigma-Aldrich). A linear, hydroxyl terminated PDMS (PDMS 0); and a block (PDVb) and/ or a statistical (PDVs) copolymers were obtained depending on the synthetic strategy employed. Experimental details regarding the synthesis of these copolymers were published in a previous paper (Satti et al., 2012). An extra vinyl terminated PDMS was synthesized in a similar procedure, by using an excess of chlorodimethylvinylsilane (Sigma-Aldrich) as terminating agent instead of methanol. This polymer was purified and separated from acidic residues by multiple extractions (4 times) with a mixture of 10 % NaHCO$_3$ and ethyl ether (Dorwill, Argentina). The remaining polymer in the ether solution was then filtered, redisolved in toluene and precepitated in methanol. This polymer was identified as PDVi. Structure details of all these PDMS derivatives, are also summarized in Table 1.

2.3. Irradiation procedure

The mEOC samples were compression molded to 1 mm thick flat sheets using a hydraulic press at 180 °C, during 2 min and employing a maximum pressure of 10 MPa. These samples together with the liquid PDVb, PDVs and PDVi samples were enclosed in sealed glass vials, which were evacuated under a conventional vacuum-line equipped with a mechanical oil pump, a mercury diffusion pump, liquid nitrogen traps, upper and lower glass tube rigs, and stopcocks during 4 h. The sealed tubes obtained were treated with gamma radiation at the Centro Atómico Ezeiza (CAE), Argentina, using a ^{60}Co source, at RT. The gamma radiation doses applied to the polymers ranged between 3 and 100 kGy, at a dose rate of 10 kGy/h. The applied doses were measured with a Red Perspex dosimeter. After irradiation, the polymer samples were annealed for 2 h at 140 °C to assure undetectable levels of long-living radicals (Rijke and Mandelkern, 1971).

2.4. Characterization

2.4.1. Fourier transform infrared spectroscopy (FTIR)

The analysis of the different unsaturations present in the irradiated polymers and their precursors was determined using a Nicolet$^®$ 520 FTIR Spectrometer. For this purpose, films of mEOC were prepared by melt pressing the materials at 150 °C using a hydraulic press. Quantitative data on the vinyl groups and trans-double bonds in the mEOC samples before and after radiation

treatment were calculated from the FTIR spectrum (Chum, 1992; Dole, 1979; Satti et al., 2010b). Chemical changes in the irradiated PDMS samples were followed by FTIR, using a Micro-FTIR Thermo Nicolet$^®$ equipment, working on reflection mode. Spectra were obtained from a drop of the treated materials taken without further conditioning from the ampoules where they had been irradiated. All the spectra were recorded at a 4 cm^{-1} resolution over the range of 4000–400 cm^{-1}, with air as background.

2.4.2. Size exclusion chromatography (SEC)

The molecular weight of the materials was determined by SEC in a Waters$^®$ 150C ALC/GPC with three PLgel Mixed-A 300 × 7.5 mm^2, 20 µm pore size, columns (Polymer Laboratories). Two detectors were used: refractive index (RI) (Waters$^®$) and multi-angle laser light scattering (MALLS) (Dawn DSP, Wyatt$^®$ Technology Corporation). The solvent used was 1,2,4-trichlorobenzene at 135 °C for mEOC, while for PDMS derivatives was toluene at RT. Both solvents were eluted at 1.0 mL/min. The columns were calibrated with narrow standards of polystyrene (Pressure Chemical) and polyethylene (NIST).
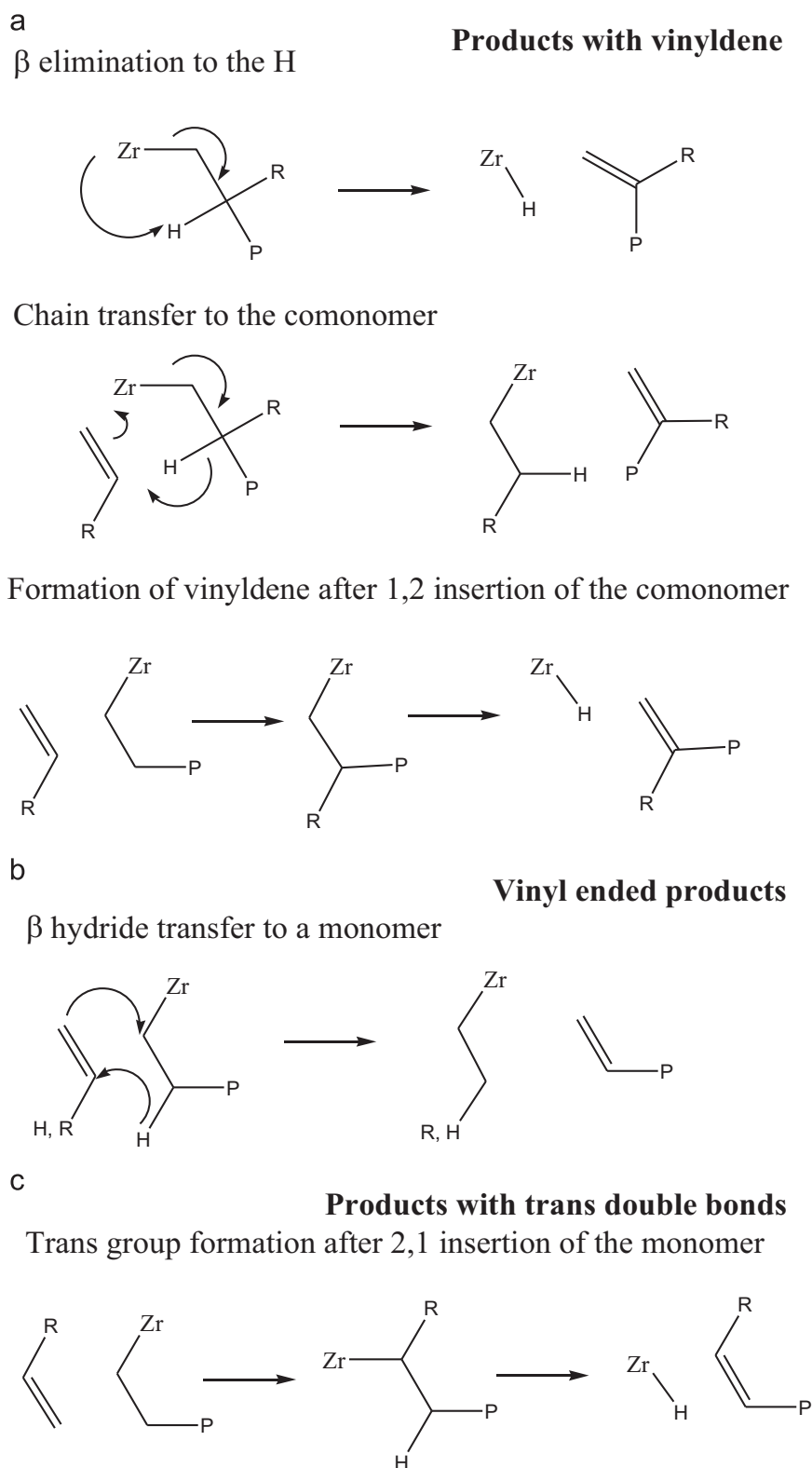
2.4.3. Gel extraction

After annealing the irradiated polymers, the Pyrex glass tubes were cut open. Gel extraction was performed to measure the insoluble gel fraction. For this purpose, the samples of mEOC were weighed, packed in paper cartridges, placed inside round bottom flasks, immersed in an oil bath at 130 °C and extracted five times with fresh xylene for 24 h. About 0.5 wt% Irganox 1010 antioxidant was added, and nitrogen was bubbled continuously during extraction to avoid oxidation processes. After the extraction cycle was completed, the samples were precipitated, washed with cold methanol and vacuum dried to a constant weight. A similar but simpler procedure was also used for the PDMS samples. The main difference was that they were weighed and extracted five times with toluene at RT for a week. The mass percentage of the gel fractions of the samples was calculated by gravimetry.

3. Results and discussion

3.1. Effects of the presence of double bonds in irradiated mEOC

Metallocenic copolymerization of ethylene with 1-olefins leads to the formation of unsaturations, as it is shown in Scheme 1 and confirmed in the FTIR of Fig. 1, in which spectra bands located at 894, 908 and 966 cm^{-1} are related to vinyldene, terminal vinyl and trans double bonds respectively. It is well established that these unsaturations are generated by termination or side reactions (Kokko et al., 2000; Kokko, 2002; Quijada et al., 1995). In order to know up to what extent these unsaturations affect the radioinduced reactions, the mEOC were hydrogenated and the resulting materials were then irradiated along with the original mEOC copolymers in order to analyze their differences. The success of the hydrogenation reaction was confirmed by the FTIR spectra of Fig. 2. According to the data obtained, the hydrogenation reaction was effective for the vinyl and trans groups (since their bands disappeared after the process), while vinyldene groups remained unchanged. The same unreactive behavior was observed for the intensity of this band even after the irradiation of the samples, as it can be seen in both Figs. 1 and 2. This fact might indicate a poor reactivity for this kind of double bond, usually attributed to steric hindrance factors.

A plot for the evolution of the number of trans and terminal double bonds per 1000 carbon atoms [C=C/1000 C] in the polymer chain against the intensity of the irradiation dose is shown in Figs. 3 and 4, respectively. As it can be appreciated, Fig. 3 shows an increase in the amount of trans double bonds, while Fig. 4 shows a decrease in the quantity of terminal vinyl groups. Palmlof and Hjertberg (2000)

a

Products with vinyldene

β elimination to the H

Chain transfer to the comonomer

Formation of vinyldene after 1,2 insertion of the comonomer

b

Vinyl ended products

β hydride transfer to a monomer

c

Products with trans double bonds

Trans group formation after 2,1 insertion of the monomer

Scheme 1. Unsaturations formation during metallocenic synthesis of ethylene copolymers. Zr is zirconium, R is comonomer rest, and P is the rest of the polymer.

proposed a mechanism that explained some radical inner transfer after reaction with a radioinduced radical, that would turn vinyls into trans groups. This could explain the appearance of radioinduced trans groups. However, the analysis of the irradiated samples of this work clearly show that trans double bonds arise with dose in the hydrogenated samples without the presence of terminal vinyl groups, as it can be seen in Fig. 2. Comparing the increase of trans groups in mEOC

and hydrogenated mEOC (Figs. 1–3), it can be concluded that this increase should not be attributed to the decay of terminal vinyl groups, but also to other mechanism such as the simultaneous dehydrogenation of two neighbored carbons.

The dissapearence of vinyl double bonds observed in the irradiated samples should be related to radical scavenging, that leads to macroradical entrapment and prolongation of the main chain
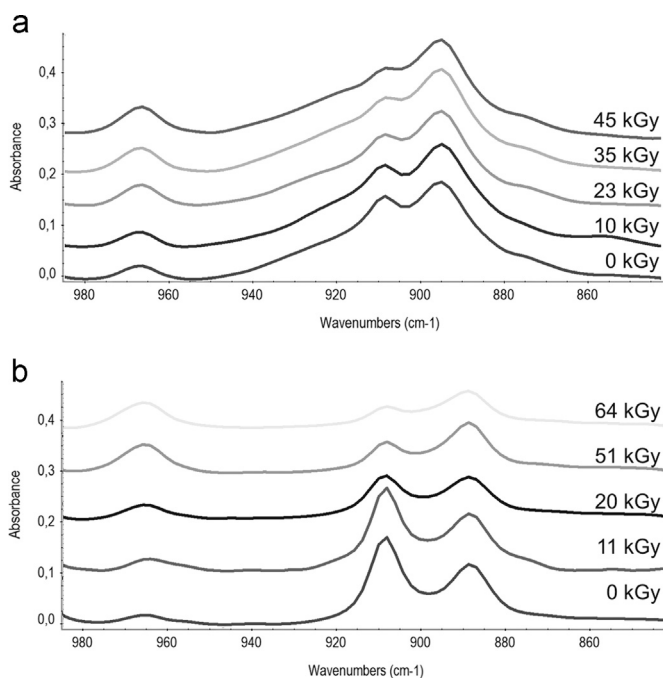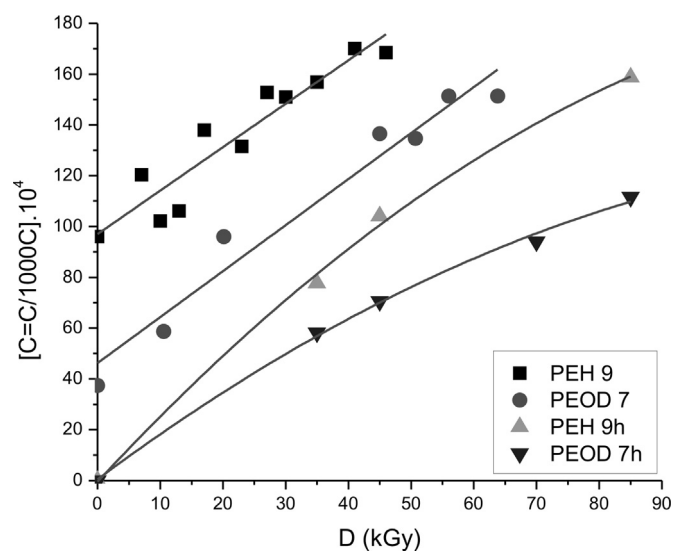
Fig. 1. Unsaturations bands around 894 cm^{-1} (vinyldenes), 908 cm^{-1} (vinyls) and 966 cm^{-1} (trans double bonds) from the FTIR spectra for (a) ethylene –-1-hexene copolymer (PEH 9) and b) ethylene –-1-octadecene copolymer (PEOD 7), along with their irradiated samples. Original values of the Y axis were moved in order to avoid overlapping of the spectra.
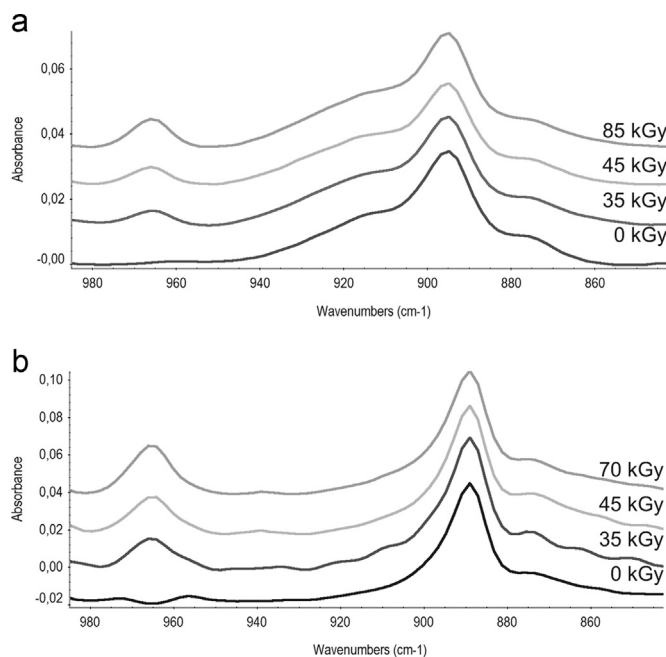

Fig. 2. Unsaturations bands around 894 cm^{-1} (vinyldenes) and 966 cm^{-1} (trans double bonds) from the FTIR spectra for hydrogenated (a) ethylene –-1-hexene copolymer (PEH 9h) and b) ethylene –-1-octadecene copolymer (PEOD 7 h), along with their irradiated samples. Original values of the Y axis were moved in order to avoid overlapping of the spectra.

Fig. 3. Trans double bonds formation and increase with dose for PEH 9(■), PEOD 7 (●), PEH 9h(▲) and PEOD 7h(▼).
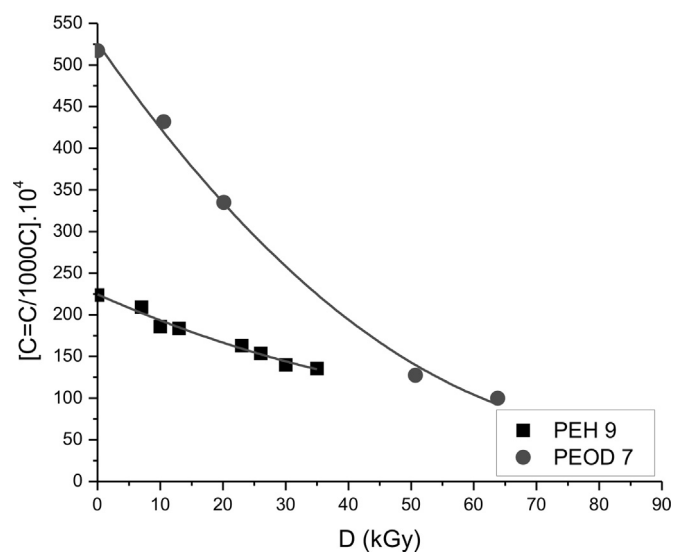
Fig. 4. Terminal vinyl decay with dose for PEH 9(■) and PEOD 7(●).

Scheme 2. Radical entrapment and prolongation of the main chain by vinyl end groups.
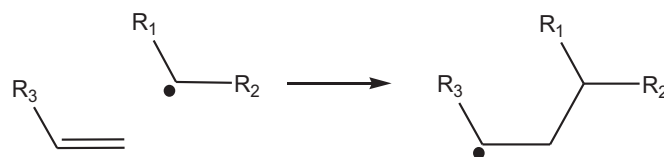
(Scheme 2). This should help to enlarge the molecular weight and accelerate the gelation process. SEC and gel extraction analysis were performed to confirm this. The data obtained of these characterizations are shown in Table 2. Molar masses increased with dose as a consequence of crosslinking reactions, as it was expected. At a certain dose, the degree of crosslinking was high enough to reach the gel point, generating a three-dimensional network. After this, the amount of gel raises by attaching more radioinduced macroradicals to its structure. Nevertheless, other macromolecules do not attach to the gel. These molecules constitute the soluble fraction of the sample, which was extracted and characterized by SEC. The results from the soluble fraction are typed in bold and italics in all the tables to distinguish them from the pre-gel data. As the soluble chains with higher molar mass are more susceptible to form macroradicals that eventually will join the gel fraction, the average molecular weight of the soluble fraction decays with the magnitude of the radiation dose.

The data from Table 2 shows that the increase in Mw was lower for the hydrogenated mEOC. Moreover, the % gel for PEH 9 is about

Table 2
Increase of weight molar mass and gel content in the irradiated mEOC and their hydrogenated samples. The results from the soluble fraction are typed in bold and italics.

| Polymer	D (kGy)	Mw (Da)	% gel
PEH 9 (PD=2,1)	0	86,400	–
	35	*447,300*	*–*
	45	*394,000*	*11.0*
	60	*222,400*	*40.0*
	85	*113,700*	*63.0*
	100	*61,730*	*83.2*
PEH 9h (PD=2,1)	0	86,400	–
	35	148,200	–
	45	152,500	–
	85	*116,700*	*10,5*
	100	*Nd*	35,4
PEOD 7 (PD= 1,76)	0	89,500	–
	42	*Nd*	*30.0*
	51	*726,800*	*37.0*
	57	*372,000*	*62.5*
	83	*137,200*	*77.5*
PEOD 7h (PD= 1,76)	0	89,500	–
	35	161,400	–
	45	169,600	–
	60	*208,600*	*21,1*
	85	*171,400*	*40,8*

Nd: no data.

40 % at 60 kGy, while for PEH 9h, such gel content is almost obtained at 100 kGy. Thus, the same polymer without vinyls need at least 1.7 times more irradiation dose to reach the same gel percentage. Similarly, PEOD 7 reaches 37.0 % gel at 51 kGy, while PEOD 7 h has 40.8 % gel at 85 kGy. Once more, the hydrogenated sample need almost 1.7 times more dose to reach the same gel percentage. The mechanism proposed in Scheme 2 seems to fit well with these results. The presence of vinyl groups helps to crosslink more efficiently, even when these solid semi-crystalline copolymers were irradiated at RT. Moreover, following the molar masses of the copolymers and their original vinyl concentration, PEOD 7 has about 19 % vinyl ended chains, while PEH 9 about 7%. This higher vinyl concentration in PEOD 7 could explain, to some extent, the higher gel content found when comparing these mEOC at different doses, since other parameters like Mw and cristallinity (about 30 % according to DSC) are similar.

3.2. Effects of the presence of double bonds in irradiated PDMS

The effect of vinyl groups during the irradiation process of PDMS was also followed by FTIR. Fig. 5 shows the FTIR spectra of the samples studied between 2800 and 3100 cm^{-1}. There are two bands related to methyl groups ($-CH_3$) at 2900 and 2960 cm^{-1}, and also two bands related to the vinyl groups ($-CH=CH_2$) at 3017 and 3057 cm^{-1} on the PDVb and PDVs copolymers (Alexandrova et al., 1998). This bands cannot be seen for PDVi because this polymer has only one terminal vinyl per chain, while the others have around 25 (PDVb) and 227 (PDVs). However, even for PDVb the intensity of these bands is too low. Consequently, the low intensity of these bands prevents quantitative measurements but it does allow us to perform a qualitative analysis.
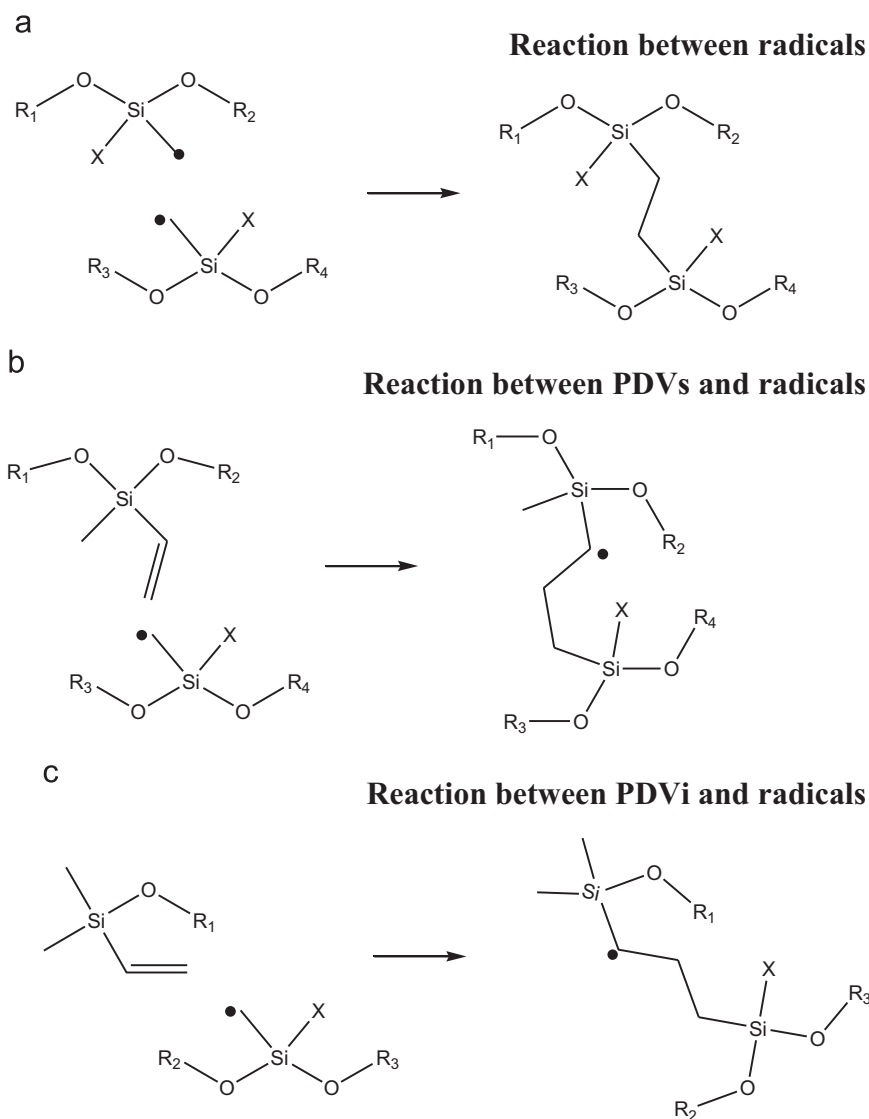
After the irradiation of PDVb, PDVs and PDVi, two other bands arise near 2850 and 2920 cm^{-1} that can be related to the formation of methylene ($-CH_2-$) groups. The presence of these new bands can be explained as follows. Scheme 3a–c shows three possible reactions that may explain the appearance of methylene
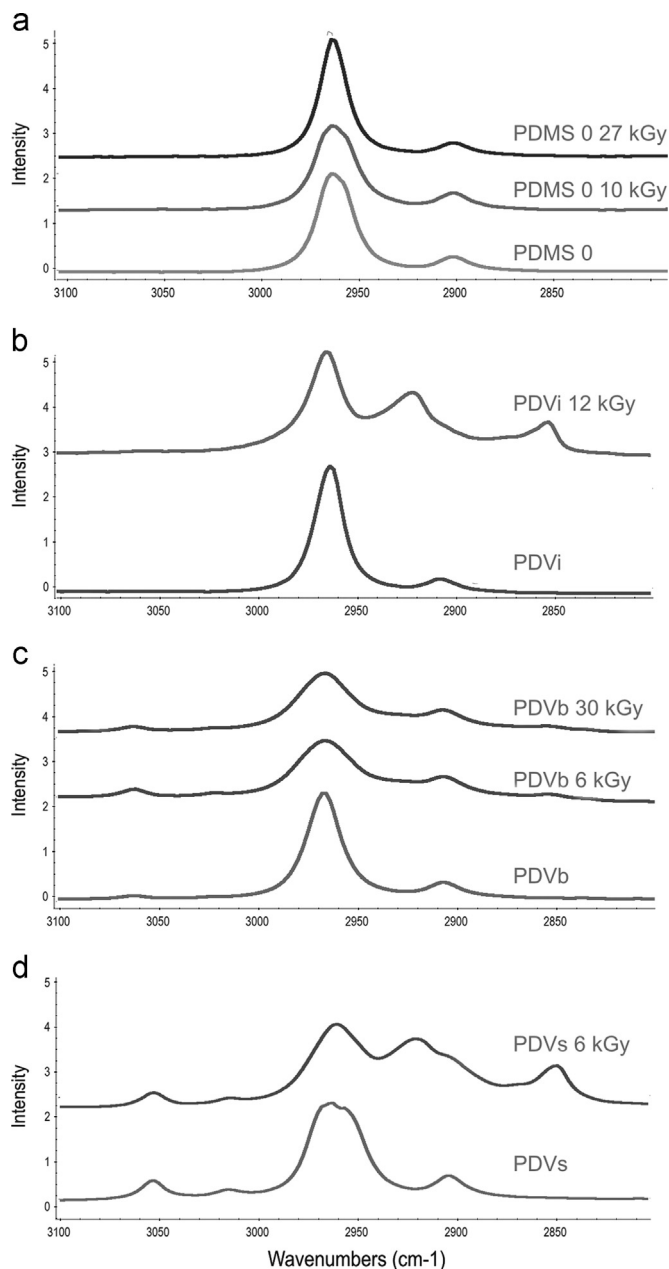
Fig. 5. FTIR spectra for PDMS derivatives and their irradiated samples. Original values of the *Y* axis were moved in order to avoid overlapping of the spectra.

groups after the irradiation of PDMS samples. Reaction (a) is a common H-type crosslinking between two lateral methylene functionalized radicals (R–CH$_2$), that would happen in any type of PDMS (Satti et al., 2008, 2010c). Reaction (b) is proposed to the statistical copolymer and implies the reaction between a radical and a vinyl group. The result is a macroradical containing a methylene group that still can react with another radical site. The third reaction (c), is similar to the second one, but specifically for vinyl ended chains. As it can be seen, $-CH_2-$ groups are generated in all of the reactions proposed in the Scheme.

Table 3 shows the results of SEC and gel extraction for the PDMS derivatives. These polymers had polydispersities around 1,1, as it is typical for successful anionic synthesis. For PDVi, it is somehow higher, and this fact could be explained as follows. For the ended vinyl PDMS, an excess of chlorodimethylvinylsilane is added during 24 h before killing the polymerization to ensure the functionalization. During this lapse of time, HCl could be produced

a

Reaction between radicals

b

Reaction between PDVs and radicals

c

Reaction between PDVi and radicals

Scheme 3. Possible reactions that may explain the appearance of the methylene groups. $X=CH_3$ or $CH=CH_2$.

leading to some degradation of the polymer, and thus, increasing the disperisty of chains. This is the reason why the remaining HCl must be extracted with $NaHCO_3$ before its final purification.

Once again, the irradiation process promoted crosslinking reactions in all the cases. As it was observed previously for the polyolefins, the copolymers containing vinyl groups suffer crosslinking reactions in a more efficiently way. Their increase in Mw with dose is faster, and the gel content due to crosslinking reactions was reached at lower doses compared to PDMS 0. Between the two copolymers, crosslinking reactions are more noticeable in PDVs than on PDVb. PDVs has almost the double of Mw value. Consequently, this material needs half of the irradiation energy needed for PDVb to reach the same level of crosslinking. However, PDVs also has four times vinyl groups than the block copolymer and this fact is the main cause of the crosslinking differences between both copolymers. In effect, less than 3 kGy are needed to reach almost 14 % gel in PDVs. In contrast, for PDVb, half of this percentage is not reached even at ten times that dose. Moreover, more than twenty times the dose is needed to reach 10 % gel when comparing PDMS 0 and PDVs (Satti et al., 2012).

However, the higher crosslinking was observed for the vinyl functionalized PDMS, even when it has only one vinyl group per chain. In Scheme 3c, the proposed crosslinking mechanism

Table 3
Increase of weight molar mass and gel content in the irradiated PDMS derivatives. The results from the soluble fraction are typed in bold and italics.

Polymer	D (kGy)	Mw (Da)	% gel
PDMS 0 (PD=1,06)	0	49,000	–
	10	61,400	–
	35	124,000	–
	70	*399,900*	*8.1*
PDVi (PD=1,35)	0	92,730	–
	3	*44,930*	*26.6*
	12	*38,420*	*46.0*
PDVb (PD=1,14)	0	42,750	–
	6	111,900	–
	30	*434,600*	*6.5*
PDVs (PD=1,08)	0	82,620	–
	3	*240,000*	*13.9*
	6	*113,760*	*25.5*

through the end vinyl groups gives a product that only differs in the structure of the new latent macroradical. Though, this macroradical is less steric hindered compared to the one obtained for the PDVs, which is located between two large polymer chains (Scheme 3b). Indeed, .H, .CH$_3$, or radicals from smaller chains should be more situable to react under this steric condition. Evenmore, some vinyl groups did not react since the bands related to them at 3017 and 3057 cm^{-1} still appear after irradiation (as it can be appreciated in Fig. 5d). This steric hindrance reminds the lack of reactivity of the vinyldenes in the mEOC polyolefins, although in that case they were practically non-reactive.

Taking into account both types of polymers analyzed on this work, it can be noted that the increase in crosslinking was more noticeable for PDVi than for both mEOC. However, the mEOC have about 7–19 % vinyl ended chains, while every chain in PDVi has a vinyl end group.

4. Conclusions

The effects of the presence of double bonds in the vacuum gamma irradiation of mEOC and PDMS derivatives were analyzed. For mEOC, different kind of unsaturations are present as a consequence of their synthetic mechanism. Vinyldenes are reluctant to react, while trans double bonds are mainly generated with the irradiation process. The terminal vinyl groups are strongly related to an increase in the radioinduced crosslinking process with a factor of about 1.8 with only a level of 7–19 % vinyl ended chains. For PDMS derivatives, the position of the vinyl groups noticeably affects the irradiation process. PDVb (25 vinyl groups along the main chain) needed almost half the value for D$_{gel}$ than PDMS 0, while PDVs (227 vinyl groups along the main chain) needed about 20 times less dose for similar crosslinking than PDMS 0. However, irradiated PDVi, with only one vinyl group at the end of the chain, had more gel at similar doses than the other PDMS derivatives. Once again, it seems that a terminal unsaturation is more efficient for crosslinking reactions since it is not sterically hindered as in other positions of the polymer chain.

References

Alexandrova, L., Diaz, F., Canseco, M., Likhatchev, D., Vera-Graziano, R., 1998. Bulk polymerization of 1,3,5,7-tetravinyltetramethylcyclotetrasiloxane induced by gamma radiation. Radiat. Phys. Chem. 51, 101–106.

Andreucetti, N.A., Fernández Lagos, L., Curzio, O., Sarmoria, C., Vallés, E.M., 1999. Model linear ethylene–butene copolymers irradiated with gamma-rays. Polymer 40, 3443–3450.

Aziz, T., Waters, M., Jagger, R., 2003. Analysis of the properties of silicone rubber maxillofacial prosthetic materials. J. Dent. 31 (1), 67–74.

Birkefeld, A.B., Eckert, H., Pfleiderer, B., 2004. A study of the aging of silicone breast implants using ^{29}Si, ^{1}H relaxation and DSC measurments. Biomaterials 25 (18), 4405–4413.

Hadjichristidis, N., Iatrou, H., Pispas, S., Pitsikalis, M., 2000. Anionic polymerization: High vacuum techniques. J. Polym. Sci. Part A: Polym. Chem. 38, 3211–3234.

Charlesby, A., 1960. Atomic Radiation and Polymers. Pergamon Press, London.

Chum, S.P., 1992. Effects of vinyl chain-ends on the melt viscoelastic properties of radiation crosslinked polyethylene. J. Plast. Film Sheet 8, 37–47.

Ciolino, A., Sakellariou, G., Pantazis, P., Villar, M.A., Vallés, E., Hadjichristidis, N., 2006. Synthesis and characterization of model diblock copolymers of poly(dimethylsiloxane) with poly(1,4-butadiene) or poly(ethylene). J. Polym. Sci. Part A: Polym. Chem. 44 (5), 1579–1590.

Dole, M., 1972. The Radiation Chemistry of Macromolecules, Vol. I–II. Academic Press, New York.

Dole, M., 1979. Cross-linking and crystallinity in irradiated polyethylene. Polym. Plast. Technol. Eng. 13, 41–64.

Fu, Y., Kao, W.J., 2010. Drug release kinetics and transport mechanisms of non-degradable and degradable polymeric delivery systems. Expert. Opin. Drug. Deliv. 7 (4), 429–444. http://dx.doi.org/10.1517/17425241003602259.

Kokko E., 2002. Metallocene-catalyzed ethene polymerization: Long-chain branched polyethene. Acta Polytechnica Scandinavica Chemical Technology Series 290. Espoo 2002, 52 pp. Published by the Finnish Academies of Technology.

Kokko, E., Malmberg, A., Lehmus, P., Löfgren, B., Seppälä, J.V., 2000. Influence of catalyst and polymerization conditions on long-chain branching of metallocene-catalyzed polyethenes. J. Polym. Sci. Part A: Polym. Chem. 38, 376–388.

Li, J., Peng, J., Qiao, J., Jin, D., Wei, G., 2002. Effect of irradiation on ethylene–octene copolymers. Radiat. Phys. Chem. 63, 501–504.

Machi, S., 1995. Radiation technology for sustainable development. Radiat. Phys. Chem. 45, 399–410.

Mashak, A., Taghizadeh, S.M., 2006. In vitro progesterone release from γ-irradiated cross-linked polydimethylsiloxane. Radiat. Phys. Chem. 75, 229–235.

Mashak, A., Rahimi, A., 2009. Silicone polymers in controlled drug delivery systems: a review. Iranian Polym. J. 18 (4), 279–295.

Nicolson, P.C., Vogt, J., 2001. Soft contact lens polymers: an evolution. Biomaterials 22 (24), 3273–3283.

Ninago, M.D., Satti, A.J., Ressia, J.A., Ciolino, A.E., Villar, M.A., Vallés, E.M., 2009. Controlled synthesis of poly(dimethylsiloxane) homopolymers using high-vaccum anionic polymerization techniques. J. Polym. Sci. Part A: Polym. Chem. 47, 4774–4783.

Osborn, J.A., Jardine, F.H., Young, J.F., Wilkinson, G., 1966. The preparation and properties of tris(triphenylphosphine)halogenorhodium(I) and some reactions thereof including catalytic homogeneous hydrogenation of olefins and acetylenes and their derivatives. J. Chem. Soc. A, 1711–1732. http://dx.doi.org/10.1039/J19660001711.

Palmlof, M., Hjertberg, T., 2000. Crosslinking of poly(ethylene-co-1,9-decadiene) by electron beam irradiation. Polymer 41 (17), 6481–6495.

Perraud, S., Vallat, M., Kuczynski, J., 2003. Radiation crosslinking of poly(ethylene-co-octene) with electron beam radiation. Macromol. Mater. Eng. 288, 117–123.

Quijada, R., Dupont, J., Lacerda Miranda, M.S., Scipioni, R.B., Galland, G.B., 1995. Copolymerization of ethylene with 1-hexene and 1-octene: correlation between type of catalyst and comonomer incorporated. Macromol. Chem. Phys. 196 (12), 3991–4000.

Rijke, A.M., Mandelkern, L., 1971. Irradiation of linear polyethylene Partitioning between sol and gel. Macromolecules 4, 594–599.

Rogero, S.O., Sousa, J.S., Alário Jr., D., Lopérgolo, L., Lugao, A.B., 2005. Silicone crosslinked by ionizing radiation as potential polymeric matrix for drug delivery. Nucl. Instrum. Meth. B 236, 521–525.

Satti, A.J., Andreucetti, N.A., Ressia, J.A., Vallat, M.F., Sarmoria, C., Vallés, E.M., 2008. Modelling molecular weight changes induced in polydimethyl siloxane by gamma and electron beam irradiation. Eur. Polym. J. 44, 1548–1555.

Satti, A.J., Andreucetti, N.A., Quijada, R., Sarmoria, C., Valles, E.M., 2010a. Effect of DBPH and vacuum gamma radiation on metallocenic ethylene - 1-hexene and ethylene - 1-octadecene copolymers. Radiat. Phys. Chem. 79 (1), 9–15.

Satti, A.J., Andreucetti, N.A., Quijada, R., Sarmoria, C., Pastor, J.M., Valles, E.M., 2010b. Gamma-irradiation of a metallocenic polyethylene and ethylene - 1-hexene copolymers. J. Appl. Polym. Sci. 117, 290–301.

Satti, A.J., Andreucetti, N.A., Ciolino, A.E., Vitale, C., Sarmoria, C., Vallés, E.M., 2010c. Molecular weight changes induced in an anionic polydimethylsiloxane by gamma irradiation in vacuum. Radiat. Phys. Chem. 79, 1137–1143.

Satti, A.J., Nador, F., Vitale, C., Radivoy, G., Andreucetti, N., Ciolino, A.E., Vallés, E.M., 2012. Synthesis, characterization, and gamma radiation effects over well-defined poly(vinylsiloxanes) copolymers. J. Appl. Polym. Sci. 124, 832–839.

Uhrig, D., Mays, J., 2005. Experimental techniques in high-vacuum anionic polymerization. J. Polym. Sci. Part A: Polym. Chem. 2005 (43), 6179–6222.

Vallés, E.M., Carella, J.M., Winter, H.H., Baumgaertel, M., 1990. Gelation of radiation crosslinked polyethylene. Rheol. Acta 29, 535–542.

Van den Kerckhove, E., Stappaerts, K., Boeckx, W., Van den Hof, B., Monstrey, S., Van der Kelen, A., De Cubber, J., 2001. Silicones in the rehabilitation of burns: a review and overview. Burns 27, 205–214.

Woo, L., Sandford, C.L., 2002. Comparison of electron beam irradiation with gamma processing for medical packaging materials. Radiat. Phys. Chem. 63, 845–850. http://dx.doi.org/10.1016/S0969-806X(01)00664-8.