

Gamma-Irradiated Metallocenic Polyethylene and Ethylene-1-Hexene Copolymers

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Received 22 July 2009; accepted 20 December 2009

DOI 10.1002/app.31983

Published online 2 March 2010 in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: The aim of this work is to present a detailed study of the changes introduced by gamma radiation on several metallocenic polyethylene copolymers. Therefore, metallocenic polyethylene and copolymers with 3.3, 9.2, and 16.1 mol % of hexene comonomer content were synthesized and irradiated with ⁶⁰Co gamma radiation under vacuum at room temperature with radiation doses ranging from 0 to 100 kGy. Size Exclusion Chromatography data show that crosslinking reactions predominate over scission, even for the copolymer with the highest tertiary carbon content. Over a certain critical dose, which depends on the molecular weight and molecular structure of the initial polymer, an insoluble gel forms. The irradiated polymers also exhibit complex rheological behavior with increasing melt viscosity and elasticity, consistent with long chain

branching and/or crosslinking. FTIR confirms depletion of terminal vinyl groups and increase of trans unsaturations with dose. The rate at which these two reactions evolve seems to depend on the comonomer content of the irradiated copolymers. Differential scanning calorimetry and Raman spectroscopy analyzes indicate less crystallinity and thicker interphases in irradiated materials. A mathematical model, which accounts for scission and crosslinking reactions, fitted well the evolution with radiation dose of the measured molecular weight data. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 117: 290–301, 2010

Key words: polyethylene copolymers; irradiation; metallocene catalysts; modeling; structure-property relations

INTRODUCTION

Metallocene catalysts made possible the synthesis of Ethylene/ α -olefin copolymers with well-defined structures, homogeneous comonomer composition, and narrow molecular weight distribution. The introduction of a chosen α -olefin during ethylene polymerization induces the insertion of short chain branches of a desired length in the growing chains. As a consequence, the resulting copolymer has a structure similar to that of linear low density polyethylene with a tertiary carbon content directly related to the amount of comonomer incorporation.

On the other hand, crosslinking is commonly used in a number of industrial applications to modify the properties of commercial polyolefins. When these

polymers are irradiated several macroradical reactions are induced producing a network type structure with enhanced mechanical, thermal, and elastic properties.^{1–5} In the case of irradiated PE, crosslinking reactions prevail over chain scissions.^{1,2} This tendency to crosslink has also been observed on metallocenic commercial copolymers of ethylene-1-octene irradiated with γ -rays³ or electron beam (EB).⁴

This work is focused on the characterization of metallocenic ethylene/1-hexene (PEH) copolymers with molar comonomer contents of 3.3, 9.2, 13.9, and 16.1% crosslinked by a wide range of doses of γ -rays under vacuum. Thus, we could analyze the significance of different tertiary carbon contents on irradiated metallocenic polyethylenes. The detailed analysis presented herein for these copolymers extends the range of most of the previous works done on metallocenic commercial copolymers containing lower incorporation of comonomer.^{3,5}

The crosslinking efficiency and the critical gel dose for the different polymers were determined using size exclusion chromatography (SEC) with refractive index detector (RI) combined with multi angle laser light scattering (MALLS) and selective

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Contract grant sponsors: Universidad Nacional del Sur, CONICET and ANPCyT (Argentina), Universidad de Chile, Universidad de Valladolid (Spain), Proyecto CYTED VIII. 11.

TABLE I
Polyethylene and Ethylene/1-Hexene Copolymers Synthesized for This Work

Name	% molar incorporated hexene ^a	$M_w \times 10^{-3}$ [Da] ^b	PD ^c	D_{gel} (kGy) Experimental	D_{gel} (kGy) Model	Vinyl content ($\times 10^4 C = C/1000 C$) ^d	Trans vinylene content ($\times 10^4 C = C/1000 C$) ^d
PE	0	157.6	1.91	28.0	28	184	0
PEH 3	3.3	111.5	1.92	28.0	28	206	36.1
PEH 9	9.2	86.4	2.22	39.6	38	224	96.0
PEH 14	13.9	59.9 ^c	2.03	–	–	248	141
PEH 16	16.1	73.3	2.01	61.8	55	263	154

Obtained by:

^a ¹³C-NMR.

^b SEC-MALLS.

^c SEC-RI.

^d FTIR.

extraction with solvent. Fourier transform infrared (FTIR) spectroscopy was used to study the evolution of the chemical changes induced on the polymer by radiation. Dynamic rheometry measurements were used to study the rheological behavior of the PEH copolymers. Thermal properties and crystalline morphology were also determined using differential scanning calorimetry (DSC) and Raman spectroscopy. To the best of our knowledge, this is the first time that an exhaustive Raman spectroscopy analysis is done on irradiated PEH copolymers. Also, an existing predictive mathematical model that takes account of crosslinking and scission reactions for irradiated PE and PDMS polymers⁶ was successfully used for fitting the evolution of the weight average molecular weight (M_w) and gel fraction (w_g) of the irradiated copolymers with radiation dose.

EXPERIMENTAL

Polymerization

The polymers shown in Table I were synthesized using a 1-L Parr reactor with stirring (500 rpm) at 333 K with an ethylene pressure of 2 bar. The catalyst/cocatalyst used was Et[Ind]₂ZrCl₂/MAO. The reaction was carried in toluene solution for 30 min and stopped with methanol acidified with HCl (2%). The resulting polymers were precipitated and then washed with methanol and acetone. Finally, the product was dried at room temperature.

Characterization

Nuclear magnetic resonance (¹³C-NMR)

The amount of comonomer incorporated in the copolymers was measured by ¹³C-NMR at 80°C using a VARIAN XL-300 spectrometer operating at 75 MHz.⁷ For this purpose, the polymer samples were dissolved in *o*-dichlorobenzene with a 20 vol %

of d₆-benzene as internal lock and chromium (III) triacetylacetonate as paramagnetic substance to reduce the relaxation times. Table I shows the obtained results. The nomenclature used to identify the different copolymers is of the type PEH # where H and # are letters and numbers that identify, respectively, the comonomer used (H = 1-hexene), and the amount of comonomer incorporated on a molar basis. To identify the irradiated samples, when dealing with specimens that were irradiated, a second number is added to indicate the radiation dose applied to the original copolymer. For example PEH 3 40 refers to the copolymer containing 3% molar hexene irradiated with 40 kGy.

Irradiation procedure

All polymers were compression-molded to 1-mm thick flat sheets using a hydraulic press at 180°C for 2 min and a maximum pressure of 10 MPa. Next, the polymer sheets were allowed to cool at room temperature and placed inside Pyrex tubes attached to a vacuum glass line and left under high vacuum for 24 h. The samples were then sealed in those same Pyrex tubes. The irradiation of the samples was performed at room temperature with a ⁶⁰Co γ -source. The applied doses ranged from 7 to 103 kGy. They were measured with a Red Perspex dosimeter. Following irradiation, the polymer samples were annealed for 2 h at 140°C to assure undetectable levels of long-living radicals.⁸

Sol-gel analysis

This analysis was performed to determine the insoluble gel fraction. Weighed samples were 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 was added and nitrogen was continuously bubbled to avoid

oxidation of the samples. Then, the samples were carefully washed with cold methanol and vacuum dried to a constant weight.

Size exclusion chromatography (SEC)

The molecular weight of the materials was determined by SEC in a Waters 150C ALC/GPC equipped with three PLgel Mixed-A 300 × 7.5 mm 20 μm columns (Polymer Laboratories) and a set of two detectors: RI- (Waters) and MALLS (Dawn DSP, Wyatt Technology Corporation). 1,2,4-trichlorobenzene was used as solvent. The analyzes were performed at 135°C and 1.0 mL/min. The columns were calibrated with narrow molar mass distribution standards of polystyrene ranging from 980 to 20 × 10⁶ Da (Pressure Chemical). The universal calibration of the columns and the calibration constants of the MALLS detector were tested with polyethylene standards (NIST) of 32,000 and 120,000 Da with polydispersities of about 1.05. The Mark-Houwink calibration constants used with TCB at 135°C were $K_{ps} = 0.000121$, $\alpha_{ps} = 0.707$ for the polystyrene standards, and $K_{pe} = 0.000406$, $\alpha_{pe} = 0.725$ for the polyethylene samples. These constants were provided from a "Working Party on Molecular Characterization of Commercial Polymers" 422/4/98 of the International Union of Pure and Applied Chemistry (IUPAC), where the PLAPIQUI chromatography laboratory participated.

Rheology

The rheological characterization of the melted polymers was carried out in nitrogen atmosphere using a Rheometrics RDA-II rheometer with 25 mm parallel plates geometry. The viscoelastic properties of the polymers were measured in small-amplitude oscillatory shear flow as a function of frequency and temperature. The frequencies ranged from 0.04 s⁻¹ to 400 s⁻¹. The temperature ranges were varied according to the melting point of the different polymers (PE: 120–220°C, PEH 3: 100–200°C, PEH 9: 80–180°C, PEH 16: 60–160°C). To ensure the linear relation between stress and deformation, small strains were used in all the dynamic tests, which were selected from previously performed strain sweeps.

Fourier transform infrared spectroscopy (FTIR)

A Nicolet 520 FTIR Spectrometer was used to determine the concentration of the different saturations present in the original and irradiated polymers. For this purpose, films were prepared by melt pressing the materials at 150°C using a hydraulic press. The spectra were recorded at a 4 cm⁻¹ resolution over the range of 4000–400 cm⁻¹ with air as background.

Quantitative data relating to the vinyl, vinylidene and trans double bonds were calculated using the following equation:

$$\text{Unsaturated groups per 1000 C} = A \cdot (b \cdot k)^{-1} \quad (1)$$

where A is IR absorbance, b is the thickness of the films (in millimeters), and k are: $k = 0.95$ for *trans* unsaturation at 966 cm⁻¹, and $k = 0.97$ for vinyl double bonds at 908 cm⁻¹.^{9,10}

Differential scanning calorimetry (DSC)

The thermal transitions were determined using a Perkin-Elmer Pyris 1 calorimeter under argon atmosphere and calibrated with indium and n-heptane standards. To ensure the same thermal history for all samples, the original and irradiated copolymers were first heated to 150°C, maintained at 150°C for two minutes, and then cooled down to -40°C at 10°C/min. After this treatment, the samples were reheated at 10°C/min. and the corresponding endotherms were recorded between -40 and 150°C. The melting peaks and the corresponding areas were determined to obtain the temperature (T_f) and enthalpy (ΔH_f) of fusion. To estimate the degree of crystallinity of the polymer, we used a ΔH_f value of 288 J/g for the melting enthalpy for 100% crystalline PE.¹¹

Raman spectroscopy

The Raman spectra of the polymers were obtained on a confocal LabRam Dilor S.A. microspectrometer. The amount of crystalline, amorphous and interfacial polymer contents were determined from the analysis of the internal mode region of the Raman spectra ($960 < \Delta\nu < 1550$ cm⁻¹), following the method proposed by Strobl et al.¹² The excitation source was a He/Ne laser (632.817 nm). The scattered light was collected by a microscope, followed by a notch filter. For deconvolution of the overlapping band systems, the curve analysis program Grams (supplied by Galactic Industries Corp.) was used.

Mathematical model

A previously developed mathematical model was used to analyze the experimental data. It is a mean-field model based on probability theory that considers that irradiation of linear polymers induces both crosslinking and scission. The starting material may have any molecular weight distribution (MWD). It is assumed that all bonds are equally likely to react, producing either crosslinking or scission, that there are no substitution effects and no intramolecular

reactions. Only tetrafunctional crosslinks are allowed. Further details may be found elsewhere.⁶

The input parameters for this model are the MWD of the virgin linear polymer, the experimentally measured irradiation dose at the gel point, and the proportion of the applied energy that produces crosslinks or scission. It calculates pregel molecular weights, postgel molecular weights of the soluble fraction, plus the sol and gel fractions.

RESULTS AND DISCUSSION

SEC and extraction Characterizations

The evolution of the molecular weight changes due to scission and crosslinking reactions were determined using a double detection RI and MALLS SEC system. Figure 1(a) presents as an example the chromatograms obtained with the RI detector of the original and modified PEH 16 copolymers irradiated with increasing doses below the critical dose to reach gelation (D_{gel}). For comparison purposes, the chromatograms have been normalized to unit area.

The signal of the RI detector was preferred in this case because RI detectors are more sensitive in the low molecular weight side of the molecular weight distribution. This allows a better appreciation of the changes induced in the molecular weight distribution by scission reactions. On the high molecular weight side of the normalized peaks, a significant rise of the concentration of high molecular weight chains with increasing dose is observed. This is a consequence of the crosslinking reactions induced by macroradical recombination. On the low molecular weight side, the concentration of low molecular weight species rises slightly with radiation as a consequence of the scission reactions [Fig. 1(b)]. From the evaluation of the SEC results at low levels of radiation, the intensity of scission was estimated to be about 2% of the crosslinked material for all the irradiated samples. The intensity of scission was estimated by subtracting from the chromatograms of the irradiated samples the correspondent nonirradiated material sample.²

The onset of D_{gel} is related to the molecular characteristics of the polymer and to the efficiency of the irradiation process. Irradiated samples extracted with boiling xylene were used to calculate the gel content and D_{gel} (Table I) for the PE and PEH polymers. This was achieved by extrapolating the plots of gel fraction (w_{gel}) versus applied dose to zero gel. As expected, an inverse relation between the critical dose to reach gelation and the molecular weight of the initial polymers was found. The sol fractions of the polymer samples (w_{sol}) were calculated as the ratio of the final weight of the soluble portion of a polymer sample to its initial unextracted weight. The evo-

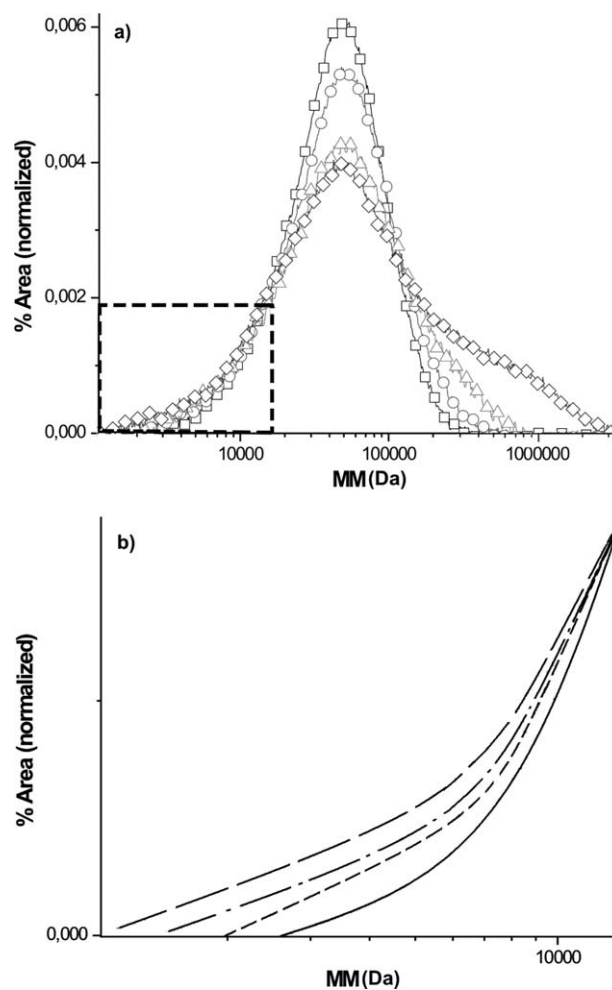


Figure 1 SEC-RI chromatograms of virgin and irradiated PEH 16 (a). Second image is an expansion of the low molecular weight area indicated in the first image (b). — 0 kGy, - - - - 13 kGy, - • - • 30 kGy, and - - - - 41 kGy.

lution of this parameter with the radiation dose for all the irradiated polymers is presented as a function of the normalized radiation parameter D/D_{gel} in Figure 2. Beyond $D/D_{gel} = 1$, all the polymers exhibit a continuous decay in the amount of extractable solubles with increasing doses of radiation. We tried to model this decay with the mathematical model described in the experimental section. To do that, the gel point dose had to be estimated. An optimization was performed to find the value of gel dose that would allow the best fitting of the experimental data on sol fraction. The optimization used Marquardt's method¹³ to minimize the objective function

$$F = \sum_{i=1}^{N_{exp}} \left(w_{s,i}^{exp} - w_{s,i}^{mod} \right)^2 \quad (2)$$

where the superscripts "exp" and "mod" refer to experimental or modeled values, respectively. As suggested by the SEC results, a scission level of 2% was

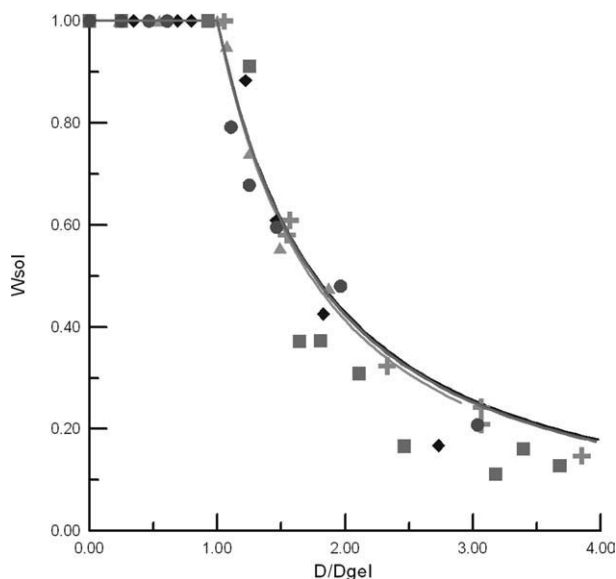


Figure 2 Experimental sol fraction vs. D/D_{gel} compared with the theoretical predictions (lines). ● PE (PD = 1.91), ■ PEH 3 (PD = 1.92), ◆ PEH 9 (PD = 2.22), ▲ PEH 16 (PD = 2.03) and + PEO from literature.

assumed on the calculations for all polymers. The critical gel doses obtained in this way are also reported in Table I and compared with those found by extrapolation to zero of the experimental gel fraction. The agreement between the experimentally measured gel doses and those obtained from the model is very good; the differences are below 5% in all but one polymer, where it is 11%. As all virgin polymer samples had different molecular weights, different gel doses were found on this optimization. It was then possible to simulate the evolution of the soluble fraction with irradiation dose. We show in Figure 2 the result of the optimization. The agreement is very good, at least up to doses slightly higher than twice the critical gel dose, indicating that the model is suitable for these polymers. At higher doses, the model seems to overestimate somewhat the soluble fraction. However, at these levels of radiation the extractable fractions are quite small and the errors made in the estimation of the soluble fraction by weighting the remaining gel fraction could well account for those differences. The different lines shown in the figure correspond to the theoretical predictions for the evolution of the soluble fraction of polymer samples having different initial polydispersities. Results from the literature⁴ were also analyzed with the model to test its capacity to fit other data. They correspond to a PE-co-octene copolymer (Affinity EG 8200 from Dow). The evolution of the sol fraction with irradiation reported for this data is included in Figure 2. Again a good agreement between the experiments and the

prediction of the model was obtained. D_{gel} in this case was 65 kGy.

A simulation using the same model and the gel point values found in the optimization step, produces the predictions of the evolution of the weight average molecular weights with radiation dose shown in Figure 3. The results from the model are compared with the experimentally measured values obtained from SEC. It is well known that this technique separates the polymer molecules according to their hydrodynamic volume in the dissolved state. Molecules with long chain branches have denser structures than linear molecules do at the same molar mass. Therefore, the conventional SEC employing a RI detector and calibrated with linear polymer standards is not accurate to evaluate the weight average molecular weight of irradiated samples containing long chain branches. With the standard universal calibration and the RI data the calculated molar mass averages would be lower than the true values. For this reason, the weight average molecular weight of the samples, M_w , was determined by coupling the SEC with a multiangle laser light scattering (MALLS) detector from Wyatt Technology (Dawn DSP). In this case, the average molecular mass was determined utilizing the commercial program ASTRA developed by Wyatt Technology Corp. Molar mass versus elution plots, as obtained from the MALLS detector, are shown in Figure 4. In this figure, the relation between molar mass against elution volume is presented for the original PEH 9 and the sample irradiated with 30 kGy. It can be clearly

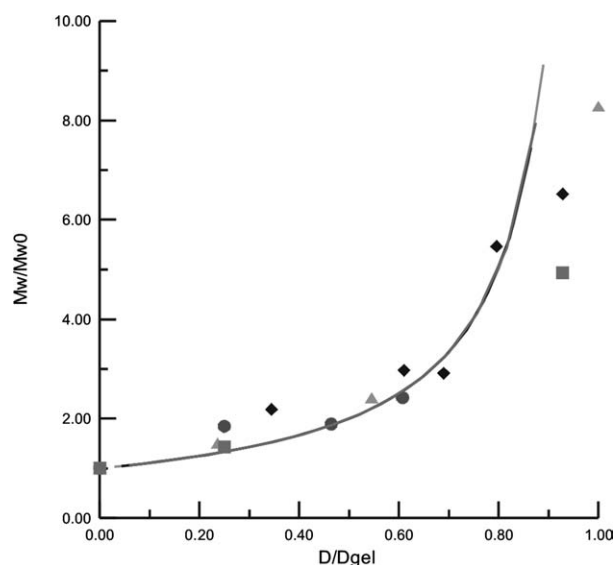


Figure 3 Evolution of normalized M_w with D/D_{gel} compared with the theoretical predictions (lines). ● PE, ■ PEH 3, ◆ PEH 9, and ▲ PEH 16.

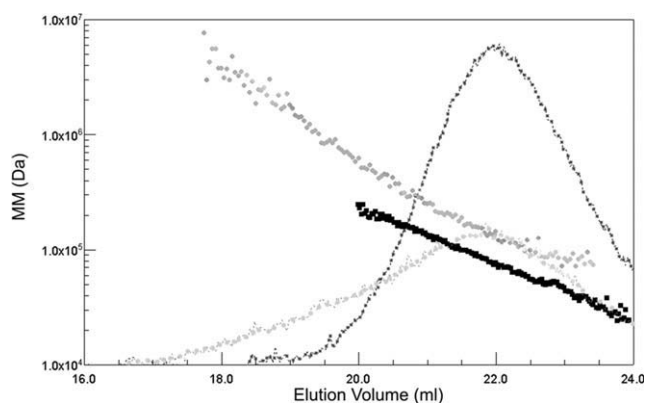


Figure 4 Molar mass against elution volume plots as obtained from MALLS detector, with correspondent overlay chromatograms for ■, original PEH 9 nonirradiated sample and ●, PEH 9 irradiated at 30 kGy.

seen that higher molecular weight fractions elute first.

In Figure 3, the reported molecular weights of all the polymers have been normalized by dividing the molecular weight of each sample at a given radiation dose (M_w) by the molecular weight of the unirradiated material (M_{w0}). Again, very good agreement between the model and the experimental measurements is found up to doses in the vicinity of $D/D_{gel} = 1$, where the evaluation of M_w by SEC becomes inaccurate. In this case, the lines that correspond to predictions for samples with different initial polydispersities are practically superimposed.

The number of long chain branches per 1000 monomer units (λ) for the irradiated samples was also estimated employing the ASTRA software from Wyatt Technology. This requires assuming the functionality of the branch points. As it was established that the theoretical model with tetrafunctional crosslinks fitted well the experimental data, all branch points were considered to be four-armed. Although the calculation of λ is based on a number of assumptions, the results in Figure 5 show that the original unirradiated PEH 9 and PEH 16 copolymers behave as linear polymers with $\lambda = 0$, while PEH 3 and PE have LCB incorporation of about $\lambda = 0.04$ and $\lambda = 0.26$, respectively. This confirms previous results which clearly indicate that considerable levels of LCB can be found in some metallocenic syntheses of polyethylene or polyethylene- α olefin copolymers with low concentration of comonomer.⁷ The results from MALLS also show an approximate linear increase of λ with the radiation dose for all polymers. This is to be expected, as conversion is proportional to dose and each crosslinked site should be considered a branch point. The increase of the number of long chain branches with dose was confirmed as well by the rheological measurements reported in the following section.

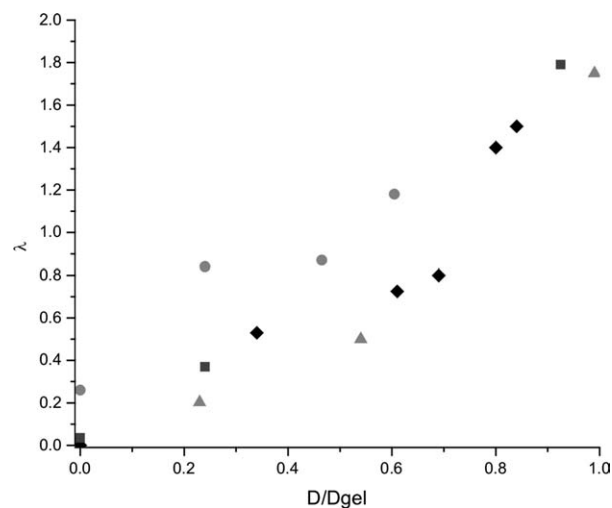


Figure 5 Evolution of λ with D/D_{gel} . ● PE, ■ PEH 3, ◆ PEH 9, and ▲ PEH 16.

Rheology

The viscoelastic properties of the original PE and PEH polymers and the changes induced by increasing doses of applied radiation were studied making use of sinusoidal dynamic oscillation experiments at different temperatures. Reduced van Gurp-Palmen (rvGP) plots, employed for the analysis of the rheological and structural characteristics of the original polymers are shown in Figure 6. For this purpose, the phase angle δ was plotted against the reduced complex modulus G^* divided by the value of the rubbery plateau modulus for linear polyethylene taken as $G_N^0 = 2.0$ MPa at 190°C.¹⁴

A qualitative estimation of the amount of branches present in a given polymer may be obtained from this type of plot by locating the position of a characteristic point, P_c , which was defined as the onset of an inflection point in the curvature of the line

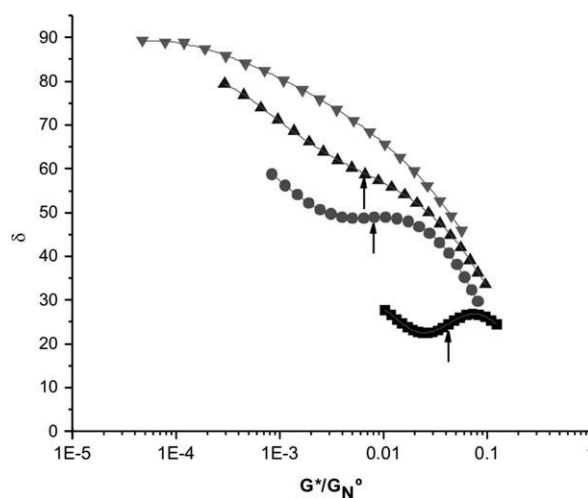


Figure 6 Reduced van Gurp-Palmen (rvGP) plots for: ■ PE, ● PEH 3, ▲ PEH 9, and ▼ PEH 16.

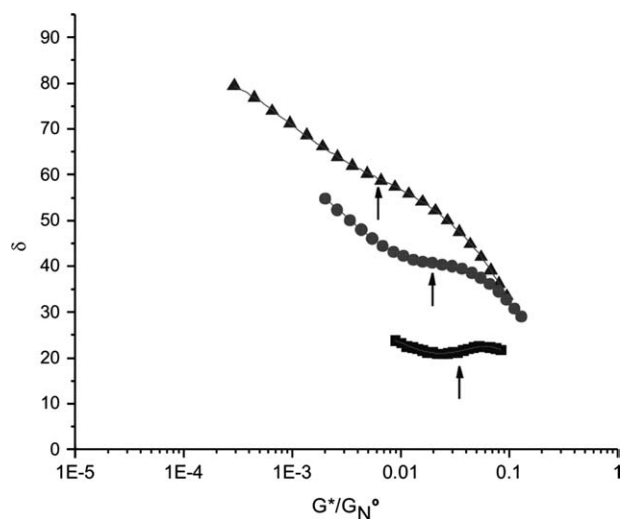


Figure 7 Reduced van Gorp-Palmen plot for PEH 9 irradiated with different doses of γ radiation: \blacktriangle 0 kGy, \bullet 11 kGy, and \blacksquare 42 kGy.

described by the evolution of the experimental data. The concept of the characteristic point to typify the structure of branched polymers was introduced by Trinkle et al. (2002).¹⁵ By studying the rheological response of different sets of model branched polymers, they were able to build a topology map which allows the classification of polymers according to their branch content depending on the position of Pc on that map.

On Figure 6, the evolution of the data for PEH 16 can be described by a single curve free of inflection points, which is the expected behavior for a thermorheologically simple, truly linear polymer. In contrast, the viscoelastic data of the other three polymers develops a progressive change in the type of curvature which allows the location of a clearly defined Pc, indicated by arrows on the plot. The displacement of the Pc locus towards lower phase angles and higher values of G^*/G_N^0 is more pronounced as the concentration of comonomer in the copolymers diminishes: PEH 9 < PEH 3 < PE. This is typical of samples with increasing contents of long chain branches. The location of Pc for PEH 9, PEH 3, and PE on the topology map built by Trinkle et al. corresponds to the region of dilute mixtures of molecules containing long-branches in linear polymer chains. This result is in accordance with the previously reported evaluation of the parameter λ through the SEC-MALLS analysis that allowed the detection of increasing amounts of long chain branches on PEH 3 and PE. The incipient branching revealed by the rheological data from PEH 9 was not detected by SEC-MALLS. This is not surprising, since it is well known that rheological measurements are much more sensitive to the presence of long chain branches than size exclusion chromatography.¹⁶

After irradiation, the original copolymers presented a more complex rheological behavior. This behavior can be attributed to increasing branching and polydispersity induced by the crosslinking reactions. Figure 7 shows as an example of the general trend exhibited by all the irradiated copolymers, the evolution of the Van Gorp-Palmen plots for PEH 9 at 120°C irradiated with different doses. As expected, as the amount of applied radiation grows, the location of Pc moves towards lower δ and higher G^*/G_N^0 values revealing the increasing concentration of branching points generated by the crosslinking process.

The evolution of G' and G'' with frequency at different irradiation doses for the PEH 9 copolymer at 160°C is shown as an example in Figure 8(a,b), respectively. An increment in both elastic (G') and loss moduli (G'') in the terminal zone with increasing radiation dose was observed for the pregel irradiated sample at 11 kGy, but only mild changes appear in the transition to the rubbery plateau. This is a clear indication that the formation of long chain

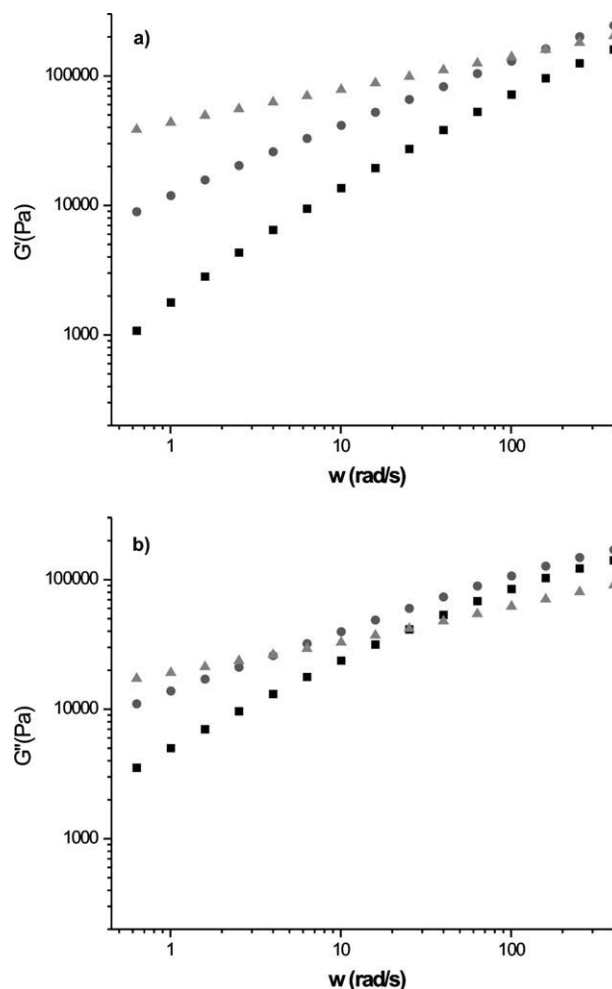


Figure 8 (a) increase of G' and (b) G'' with radiation dose for PEH 9 at 160°C. \blacksquare 0 kGy, \bullet 11 kGy, and \blacktriangle 42 kGy.

branches is the main structural change induced by the irradiation process. Long chain branching affects long time relaxations, but does not modify notably the local behavior of short segments of the polymer chains that are the ones that dominate the viscoelastic performance at high frequencies. A shift of the crossover modulus G_{co} ($G' = G''$) toward lower frequencies is also observed. Close to the gel dose, at 42 kGy, the slopes of G' and G'' remained similar for the entire frequency range analyzed, with G' higher than G'' . This kind of behavior was entirely similar to some of our previous results on irradiated model polyethylene-butene copolymers obtained by hydrogenation of anionically polymerized butadiene.¹⁷ Similar results were found for the changes on the viscoelastic properties of PE, PEH 3, and PEH 16 with increasing doses of radiation. At doses above the critical dose to reach the gel point, G'' values tend to diminish in value with increasing doses while G' evolves at low frequencies, towards a low frequency plateau corresponding to the equilibrium modulus.

FTIR characterization

To analyze the amount and type of unsaturations present in the original and irradiated polymers FTIR absorption spectra were performed between 890 and 990 cm^{-1} .

Terminal vinyl groups (908 cm^{-1} : $\text{P}-\text{CH}=\text{CH}_2$) are present in all the original polymers. As it is evident from the peak at 908 cm^{-1} shown in Figure 9, as the content of 1-hexene in the synthesis of the original copolymers increased, higher concentration of terminal vinyl groups was obtained. The concentration of this group ranged from $184 \times 10^{-4} \text{ C}=\text{C}/1000 \text{ C}$ in PE to $263 \times 10^{-4} \text{ C}=\text{C}/1000 \text{ C}$ in PEH 16. This is a consequence of the incorporation of higher percentages of comonomer during the polymerization that increases the probability of this type of unsaturations.^{18,19} The FTIR spectra of Figure 9 also provides information on the content of the trans-vinyldene (966 cm^{-1} : $\text{CH}=\text{CH}'$) and the vinyldene

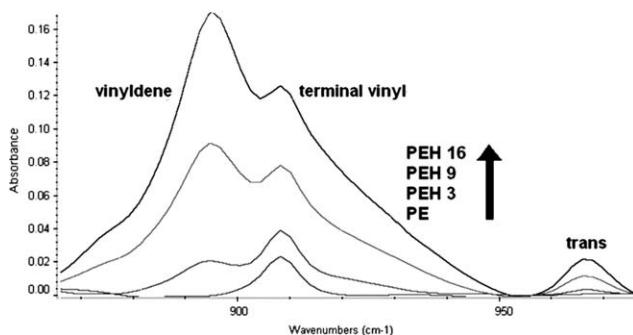


Figure 9 FTIR spectra corresponding to the C=C double bonds of PE and PEH copolymers.

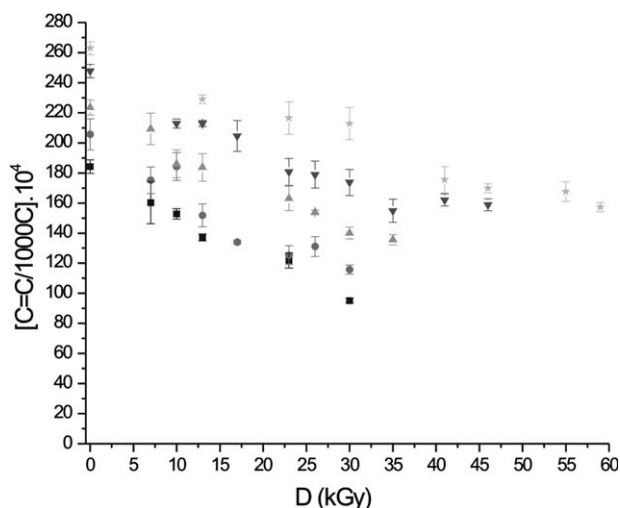


Figure 10 Plot of terminal vinyl group concentration as a function of radiation dose. ■ PE, ● PEH 3, ▲ PEH 9, ▼ PEH 14, and * PEH 16.

groups (894 cm^{-1} : $>\text{C}=\text{CH}_2$). Both groups are produced during metallocenic polymerization and, as before, both types of unsaturations increase their concentration as more comonomer content is present in the reaction.¹⁸⁻²⁰

After the PE and PEH copolymers were irradiated, significant differences in the unsaturation absorption bands with respect to those of the original materials were observed. The evolution of the concentration of the different unsaturations with the radiation dose on the irradiated PE polymer and PEH copolymers are shown in Figures 10 and 11. Within the range of radiation doses studied in this work, the terminal vinyl concentration decreases almost linearly with the applied radiation dose in PE and in each of the PEH copolymers. The rate of decay of the vinyl

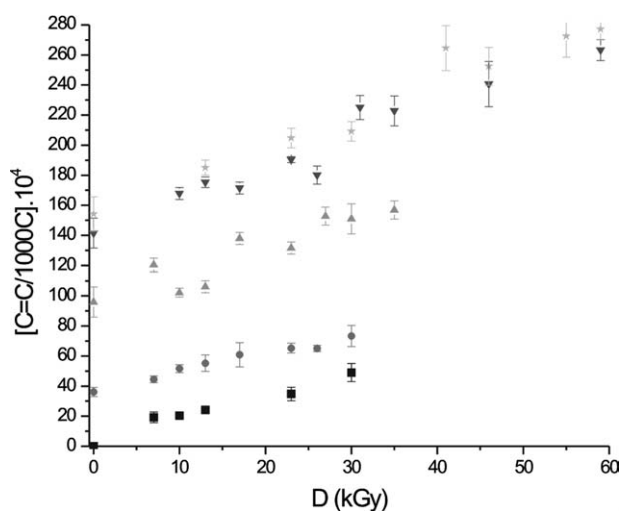


Figure 11 Plot of trans-vinyldene double bond concentration with radiation dose. ■ PE, ● PEH 3, ▲ PEH 9, ▼ PEH 14, and * PEH 16.

groups seems to be similar for PE and the PEH copolymers with up to 9.2% hexene and slightly lower for the copolymers containing 13.9 and 16.1% hexene (Fig. 10).

The evolution of the trans-vinylene double bond with radiation dose was also followed through the peak located at 966 cm^{-1} as shown in Figure 11. The original polymers had different contents of trans-vinylene groups, ranging from zero in the synthesized polyethylene to $154 \times 10^{-4}\text{ C=C}/1000\text{ C}$ in PEH 16. This implies that the concentration of trans-vinylene groups in the original copolymers grew as the concentration of hexene was increased in the copolymerization reaction. The rate of trans-vinylene double bonds formation with radiation was similar in PE, PEH 3 and PEH 9, and slightly superior in PEH 16. The formation of trans-vinylene double bonds on the irradiated polyethylenes is attributed to the dehydrogenation of two nearby main chain carbons with the successive liberation of gaseous hydrogen molecules from the polymers.^{4,7,9,21,22} FTIR analysis also showed that the concentration in vinylidene double bond (894 cm^{-1}), originally produced during the metallocenic polymerization of the PE polymer and the PEH copolymers, was not significantly affected by the irradiation treatment.

Raman characterization

It is well known that the radioinduced crosslinking and main chain scission reactions can modify the proportion of crystalline and amorphous phases in the polymers.²¹ To study the evolution of these changes, we used Raman Spectroscopy, a technique that has proven to be helpful for this purpose. To quantitatively evaluate the phase structures, we analyzed the Raman CH_2 twisting and bending internal regions of the unirradiated and irradiated materials. Then, we applied a deconvolution method that uses a combination of Gaussian and Lorentzian functions so as to give the best fit to the observed spectra.²³⁻²⁵

The mass fractions of the three PE phases, namely, the orthorhombic crystalline phase, the liquid-like amorphous phase, and the disordered anisotropic interfacial phase are calculated from the measured integrated intensities of three bands: the CH_2 bending band at 1419 cm^{-1} which is due to the crystalline portions alone, a CH_2 twisting band located between 1303 and 1307 cm^{-1} belonging to the amorphous portion, and another component of the same mode at 1298 cm^{-1} which can be attributed to both the crystalline phase and the interphase.¹² Curve analysis performed in the twisting 1250 to 1350 cm^{-1} region and 1400 to 1500 cm^{-1} bending region shows the mentioned component bands in the spectrum of the polyethylene samples as can be seen in Figure 12(a,b), respectively. According to Strobl and Hage-

dorn,¹² the total integrated intensity in the twisting region between 1250 cm^{-1} and 1350 cm^{-1} , I_t , is independent of the chain conformation, i.e. the amorphous and crystalline content. It therefore provides an internal intensity standard. The amorphous content, α_a (i.e. the mass fraction of the amorphous material), is then calculated by using the twisting bands (subscript t) simply as

$$\alpha_a = I_{1304}/I_t. \quad (3)$$

The crystalline content, α_c , is proportional to the intensity of the 1419 cm^{-1} band^{20,26}:

$$\alpha_c = I_{1419}/(0.47 \times I_t) \quad (4)$$

The interfacial content is then obtained from the relation:

$$\alpha_b = 1 - \alpha_a - \alpha_c \quad (5)$$

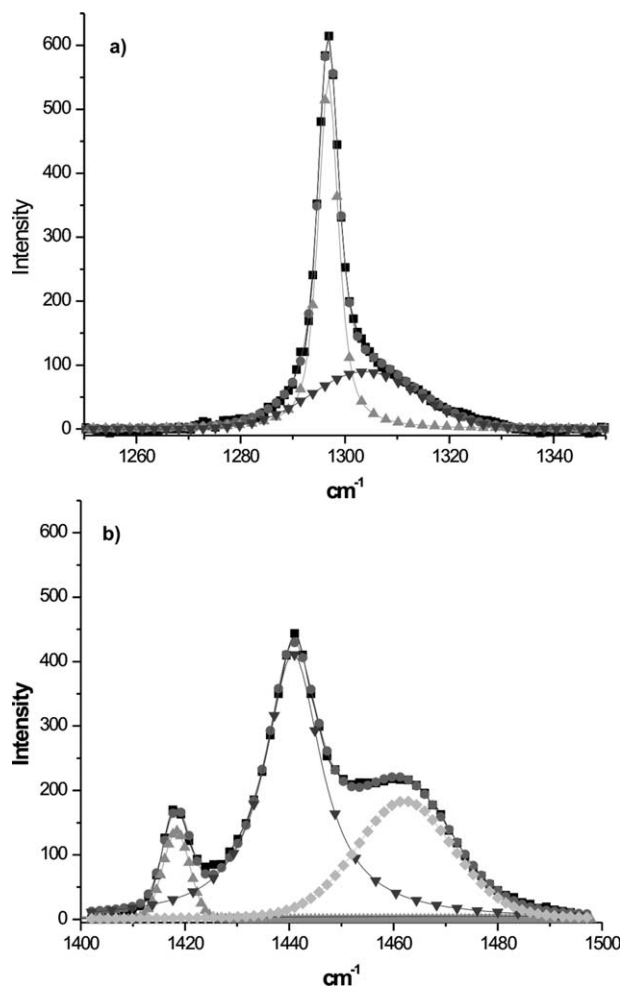


Figure 12 Deconvolution of bands on PEH 3: (a) ▲ 1298 cm^{-1} and ▼ 1304 cm^{-1} , (b) ▲ 1419 cm^{-1} , ▼ 1440 cm^{-1} and ◆ 1460 cm^{-1} . In both (a) and (b), ■ is the original spectrum and ● is the curve fit.

As indicated earlier, the band used for the calculation of the content of the purely crystalline phase belongs to the bending mode. The constant 0.47, used in eq. (4), was experimentally determined from the spectra of fully crystalline PE.^{12,23-25} This band is located in the CH₂ bending modes between 1400 and 1500 cm⁻¹. The literature also reports that the other band assignments (1440 and 1465 cm⁻¹) of the bending mode result in some uncertainties, although these bands are not relevant to the calculations reported herein.²⁷

The analysis of the Raman spectra for the unirradiated PEH copolymers indicates a decrease in α_c and an increase of α_a as the comonomer incorporation increases, while the interfacial phase remained fairly constant (Fig. 13). Moreover, the interfacial region did not exceed 25% of the total composition of the unirradiated samples. Similar results were reported in the literature for random 1-butene, 1-hexene, and 1-octene PE copolymers (PD = 2, Mw around 90,000 Da),²⁸ suggesting that a saturation value is reached for α_b when the chain branching becomes higher than about 3.3 mol %. At those concentrations of comonomer, the lamellar crystallite structure is lost and very small crystallites are formed under the conditions employed.

The Raman spectra of irradiated samples were also analyzed. In the particular case of PE [Fig. 14(a)], we observed a gradual decrease of the initial crystallinity (α_c : 68.1% to 55.0%) in the 0–55 kGy radiation dose range. This behavior has been explained in the literature as being consequence of the growth of branches due to crosslinking.²² In the same dose range, the PE amorphous content remains almost constant, while the interfacial content grows

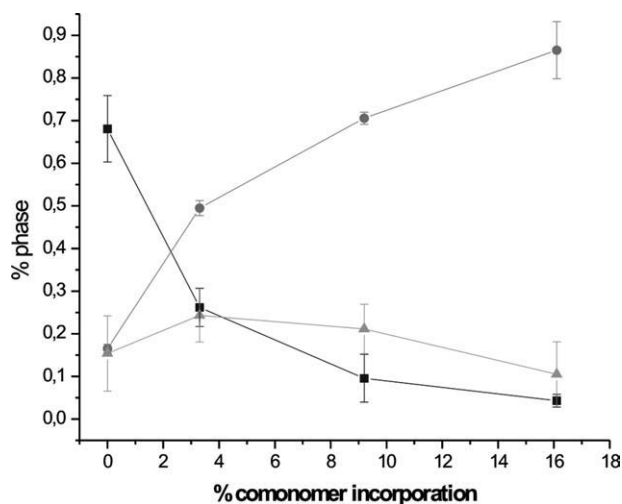


Figure 13 Percentage phase as a function of comonomer incorporation in 1-hexene-polyethylene comonomers. Parameters α_c , α_a , and α_b are represented by ■, ●, and ▲, respectively.

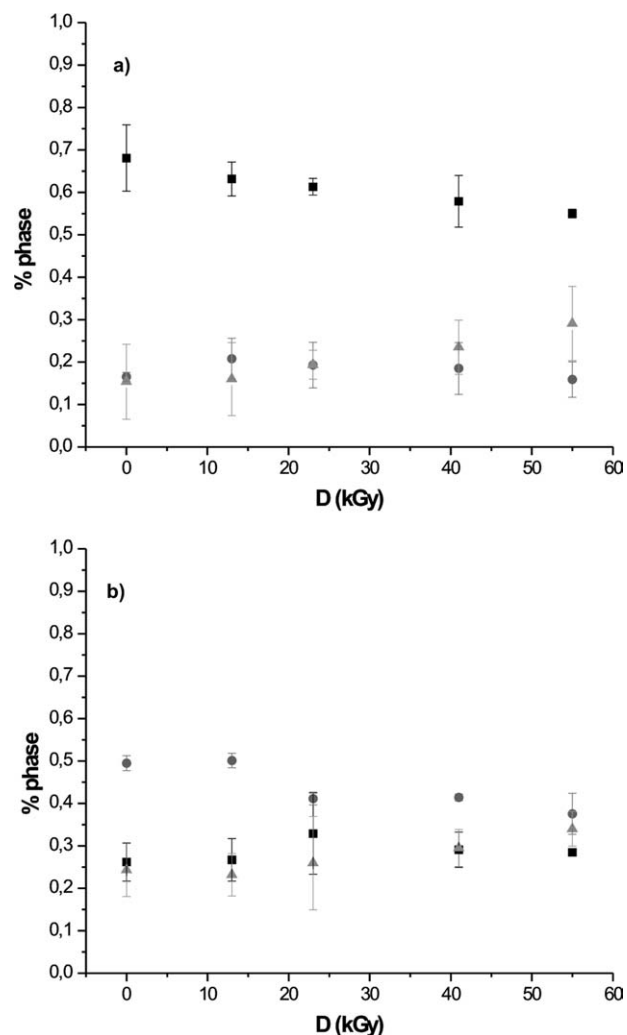


Figure 14 Percentage phase in PE (a) and PEH 3 (b) as a function of radiation dose. Parameters α_c , α_a , and α_b are represented by ■, ●, and ▲, respectively.

from 15 to 30%. This increment seemed to occur mainly at the expense of the crystalline phase.

On the other hand, as we may observe in Figure 14(b), the amorphous content for PEH 3 diminishes somewhat while the interphase content seems to increase slightly with applied radiation dose. The determination of changes in α_c for polymers PEH 9 and PEH 16 is less precise than in the other polymers, because of their low crystallinity. The latter polymer also had a very complex Raman spectrum, which made the deconvolution procedure inaccurate.

Determinations made by many authors^{29,30} on the morphology changes on irradiated single crystals of polyethylene showed that terminal vinyl groups are excluded from the crystalline core and that secondary alkyl radicals tend to be produced at the chain folds at the surface of the crystals before their subsequent reactions. These observations suggest that radioinduced reactions may take place preferentially in the amorphous and interfacial regions. Our results

TABLE II
DSC Values for Polyethylene and Ethylene/1-Hexene Copolymers

Sample	<i>D</i> (kGy)	<i>T_m</i> (°C)	<i>X_c</i> (%)
PE	0	134.73	85
PE 12	13	134.46	82
PE 20	23	134.13	81
PE 40	41	134.21	65
PEH 3	0	108.86	37
PEH 3 30	30	107.71	36.5
PEH 3 40	41	107.19	35
PEH 3 60	59	106.45	34
PEH 9	0	82.11	28
PEH 9 70	69	74.62	28
PEH 16	0	55.39	19
PEH 16 20	23	50.87	185
PEH16 80	82	49.78	18

from FTIR and Raman techniques are consistent with this hypothesis. If the terminal vinyl groups on our copolymers are located in the noncrystalline regions and react preferentially with the radioinduced radicals, we can expect most of the morphological changes in the regions close to the crystal surfaces.

DSC characterization

The morphology of all samples was also analyzed by DSC. These results are shown on Table II. As expected, polymers with higher hexene comonomer content exhibit lower melting temperatures and lower degrees of crystallinity. This is associated with a reduction in the concentration of segments with a length suitable for crystallization.³¹

The degree of crystallinity and the melting point of the original polymers decrease after irradiation because the crosslinks induced by radiation are excluded from crystallites. As a consequence of this, defects arise that lead to smaller crystallites. The observable changes are more evident in the original PE and the copolymers containing lower concentrations of hexane as in this case the crystalline content of the original polymers was higher.

CONCLUSIONS

The effect of gamma irradiation on four different polyethylene copolymers synthesized with an Et[Ind]₂ZrCl₂/MAO metallocene catalyst was explored.

The effect of crosslinking and scission reactions induced by irradiation on the molecular structure of the different polymers was evaluated by SEC and extraction techniques. Very little scission was observed for polyethylene and its copolymers with 1-hexene. These results indicate that, within the range of hexene incorporation covered by this work, scission is not significantly affected by the increment

of tertiary carbons in the main chain. Moreover, the evolution of the amount of gel and that of the weight average molecular weight with the applied doses was well fitted with a theoretical model that does not take into account the presence of the hexene side chains in the original copolymers.

The rvGP-plots were used to study the structural complexity of the unirradiated samples. Only PEH 16, with the highest comonomer content, showed a simple rheological behavior. PE and PEH 3 behaved as polymers containing highly branched structures, while PEH 9 behaved as a mostly linear polymer containing some branches. The presence of long chain branches on the original PE and PEH 3 polymers was also corroborated by the SEC-MALLS analysis. This confirms previous results obtained for different metallocene copolymers prepared with the same Et[Ind]₂ZrCl₂/MAO catalyst.⁷

All polymers exhibited significant changes on their rheological behavior with radiation. At pregel doses the evolution of *G'* and *G''* with frequency was compatible with that typical of highly branched structures. Close to the gel point, *G'* and *G''* curves straighten and become parallel over the entire frequency range covered by our experiments. In the postgel region, *G'* showed higher values than *G''* with no cross over point and tended to evolve towards a low frequency plateau corresponding to the equilibrium modulus.

A decrease in the concentration of the terminal vinyl groups with increasing radiation was observed in the FTIR spectrum for all materials. Two different rates of vinyl decay were observed, a higher one for copolymers containing up to 9.2% of hexene incorporation and a slightly lower one for the copolymers containing higher concentrations of comonomer. An increase of the concentration of trans double bonds with the radiation dose was found. In this case, the rate of formation of double bonds with radiation was slightly superior in the copolymers containing concentrations of hexene higher than 9%. In the original PE, there were not trans double bonds, but they were induced by gamma radiation at a rate similar to that of PEH 3 and PEH 9.

Irradiated PE and ethylene-1-hexene copolymers showed an increase in the interfacial phase volume with the applied dose, as determined by Raman spectroscopy. This effect may be attributable to radioinduced effects on the interphase. A significant decrease in the crystalline phase volume with irradiation was only observed for the samples of polyethylene by both DSC and Raman techniques.

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