Performance of Crystallization Analysis Fractionation and Preparative Fractionation on the Characterization of γ-Irradiated Low-Density Polyethylene

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ABSTRACT: The effects of γ-radiation on a low-density polyethylene (LDPE) were investigated by novel techniques, such as crystallization analysis fractionation and preparative fractionation, to analyze and compare their performance with other analytical procedures such as DSC, FTIR, and GPC. The LDPE was thus irradiated with four different doses of γ-radiation. Different fractions were obtained from these irradiated materials by preparative fractionation, which were characterized by the above-mentioned analysis techniques. The changes in the morphology and chemical structure of LDPE after the irradiation were analyzed and it was found that both oxidative scission and crosslinking are phenomena related to the exposure of LDPE at high-energy radiation. Crystallization analysis fractionation and preparative fractionation proved to be suitable techniques to characterize the effects of γ-radiation on a low-density polyethylene material. © 2004 Wiley Periodicals, Inc. J Appl Polym Sci 94: 1803–1814, 2004

Key words: polyethylene (PE); irradiation; fractionation of polymers; crystallization analysis fractionation; preparative fractionation

INTRODUCTION

Polyethylene can be exposed to gamma irradiation in a wide range of industrial applications. Also, high-energy radiation can be used to enhance its thermal and chemical resistance. Because of this technological importance, the effects of γ-radiation on the morphology and composition of polyethylene have been widely studied over the years by many investigators.[1–22] However, it is difficult to obtain a full interpretation of the changes that polyethylene undergoes after high-energy radiation exposure because different aspects take part in this process. It is accepted that γ-radiation in an oxygen atmosphere induces many competing reactions, including chain scissions, oxidative reactions, crosslinking, or unsaturations.[5,12,13,17,19] The type of polyethylene, its morphology, the absorbed dose of radiation, and the conditions in which irradiation occurred (temperature, presence of oxygen) will all influence the irradiation process.

The conventional techniques usually used for the characterization of irradiated polyethylene include differential scanning calorimetry (DSC), thermogravimetric analysis (TGA), gel-permeation chromatography (GPC), Raman spectroscopy, and FTIR spectroscopy. With these techniques, the changes on the melting behavior and crystallinity together with the appearance of new functional groups associated with the effects of γ-radiation on polyethylene have been studied. However, new techniques such as semipreparative fractionation by molecular weight or crystallization analysis fractionation (CRYSTAF) could also be used for this characterization. Both techniques share the same operation principle, that is, the fractionation of a polymer solution by its controlled precipitation, although they differ in the way the fractionation is performed and in the purpose of this fractionation.

Semipreparative fractionation by molecular weight with the solvent–nonsolvent approach is used to obtain different fractions that could be characterized by other techniques. The fractionation is achieved by adding an increasing content of a nonsolvent into the polymer solution, which leads to a controlled precipitation of the initial polymer in different fractions of increasing molecular weight.[23] This is a preparative method that does not offer analytical information about the composition or morphology of polymers by itself, but together with other analytical techniques could be a powerful tool to fully characterize their chemical and structural properties.

Crystallization analysis fractionation (CRYSTAF) is a new analytical technique that has been developed in the recent years as an alternative to temperature rising elution fractionation (TREF) to obtain the chemical composition distribution (CCD) of polyolefins. The analytical procedure followed by CRYSTAF equipment has been extensively described in previous publications.[23–25] CRYSTAF, differently from TREF, involves a single-step crystallization process caused by a controlled reduction of temperature, in which the polymer molecules precipitate at different temperatures according to their composition. The analysis is performed by monitoring the concentration of polymer remaining in solution during the crystallization cycle by means of an infrared detector. The first data at high temperatures, where no crystallization has occurred, indicate the initial concentration of polymer in solution. As the temperature decreases, the most crystalline fractions composed of macromolecules with few branches will precipitate first, followed by the molecules with increasing branching content. Finally, at the lowest temperature of the experiment, the remaining fraction in solution indicates the percentage of polymer that has not crystallized, which is composed of highly branched and, in our case, crosslinked material as well. With this procedure, the cumulative curve of the percentage of polymer in solution is directly obtained as a function of the temperature. The first derivative of this curve offers us information about the CCD and the branching degree of the polymeric material, given that the temperature scale can be calibrated and transformed to number of branches/1000 carbons. If a quantitative analysis is required, the calibration of the temperature axis into number of branches/1000 carbons can be performed by a combined application of preparative TREF and characterization of the fractions by nuclear magnetic resonance (NMR) or infrared spectroscopy.[25]

CRYSTAF has been applied to the analysis of the crystallization of polyolefins, such as linear low-density polyethylene (LLDPE) and polypropylene (PP), and to the characterization of polymeric materials such as polyolefins blends and copolymers.[23–27] This technique is suitable for evaluating the crystallization behavior of polyolefins because it is capable of revealing the formation of different morphologies, depending on the crystallization conditions. Moreover, CRYSTAF analysis exhibits high sensitivity to detect the components of polyolefin blends and quantitative information about their composition can be obtained directly from the crystallization curves. However, this technique has not been applied yet to the analysis of the degradation processes that polyolefins may undergo.

The aim of the study was to investigate the performance of novel techniques such as CRYSTAF and preparative fractionation (PREP) to the characterization of irradiated low-density polyethylene (LDPE) samples. The samples were preparative fractionated into a soluble and a nonsoluble part, and the application of CRYSTAF to the analysis of the effect of γ-radiation on LDPE was studied in a comparison with other conventional analysis techniques such as DSC and FTIR. In addition to this, preparative fractionation by molecular weight was used to obtain different fractions of irradiated LDPE samples, which were analyzed by GPC and FTIR to relate the molecular weight of the different fractions with the presence of determined functional groups.

EXPERIMENTAL

Material preparation and irradiation of the samples

The original LDPE was kindly supplied by Dow Chemical Ibérica S.A. (Tarragona, Spain). The commercial label of the polyethylene is LDPE 985 ($M_n = 16 \times 10^3$, $M_w = 75 \times 10^3$, $\rho = 0.9230$ g/cm^3). The samples of polyethylene were prepared by compression molding in an M-Carver press at 170°C and 14 bar for 10 min. After cooling, they were annealed in a forced ventilation oven under air atmosphere at 104.6°C for 65 h. Finally, the samples were quenched in a thermostatic bath with water and ice at 0°C.

The irradiation was performed under air atmosphere with γ-radiation provided by a ^{60}Co source at a temperature of 20°C. The irradiation rate was 1.4×10^{-4} Mrad/s, and the final radiation doses were 2, 20, and 100 Mrad for the different samples. Also, some samples were not irradiated to act as control material.

Preparative fractionation by molecular weight

The preparative fractionation by molecular weight of the LDPE samples was performed with PREP mc2 equipment from Polymer ChAR (Valencia, Spain). Xylene, stabilized with Irganox 1010 at 0.3% (w/v), was used as solvent and diethylene–glycol–monobutyl–ether (DGMBE), stabilized with Irganox 1010 at 0.6% (w/v), was used as nonsolvent. The fractionation was carried out in isothermal mode at a temperature of 120°C.

Two different fractionation experiments were carried out. First, the soluble fraction of the irradiated samples was separated from the nonsoluble fraction with xylene at 130°C (starting material 1 g). In a second experiment, the soluble fraction of the samples, irradiated with 2 and 20 Mrad doses, was subjected to PREP, using solutions with different contents of solvent and nonsolvent agents. With this second experiment, different fractions of increasing molecular weight were obtained. Table I shows the nomenclature used for all the LDPE samples obtained after their irradiation and preparative fractionation.

TABLE I
Nomenclature of the LDPE 585 Samples After Irradiation and Preparative Fractionation

s1	LDPE 585 nonirradiated
s2	LDPE 585 after being subjected to 2 Mrad of γ-irradiation
s2SF	Soluble fraction of sample s2
s2SF1	Fractions of increasing molecular weight of sample s2SF
s2SF2	
s2SF3	
s2SF4	
s2NF	Nonsoluble fraction of sample s2
s3	LDPE 585 after being subjected to 20 Mrad of γ-irradiation
s3SF	Soluble fraction of sample s3
s3SF1	Fractions of increasing molecular weight of sample s3SF
s3SF2	
s3SF3	
s3NF	Nonsoluble fraction of sample s3
s4	LDPE 585 after being subjected to 100 Mrad of γ-irradiation
s4SF	Soluble fraction of sample s4
s4NF	Nonsoluble fraction of sample s4

CRYSTAF

The crystallization analysis fractionation was performed with a CRYSTAF 200+ instrument from Polymer ChAR. About 25 mg of each sample was dissolved in a solution of 1,2,4-trichlorobenzene (TCB), stabilized with Irganox 1010 0.3% (w/v), at a temperature of 160°C for 90 min. Afterward, the solution was kept for 45 min at 100°C and then the crystallization process started at a cooling rate of 0.1°C/min from 100 to 30°C. The cumulative curve of the CCD was obtained as a function of the crystallization temperature.

FTIR spectroscopy

FTIR spectroscopic analyses of the different samples were carried out with a Nicolet Avatar 320 (Nicolet Analytical Instruments, Madison, WI), in the transmission mode, at a resolution of 4 cm^{-1}. Thirty-two scans were taken in the range of 400 to 4000 cm^{-1} and averaged. The absorbance spectra of the aldehyde (1739 cm^{-1}), ketone (1715 cm^{-1}), transvinylene (965 cm^{-1}), vinyl (909 cm^{-1}), and vinylidene (888 cm^{-1}) functional groups were recorded and investigated.

GPC

The molecular weight distribution of the samples was obtained by means of a Waters 150CV gel permeation chromatograph (GPC; Waters Associates, Milford, MA) at a temperature of 140°C and eluted with TCB, stabilized with Irganox 1010 at 0.3% (w/v). The flow rate was 1 mL/min and the samples were introduced at a concentration of 0.5% (w/w).

DSC

DSC measurements were performed with a Perkin–Elmer DSC7 differential scanning calorimeter (Perkin Elmer Cetus Instruments, Norwalk, CT), calibrated with indium and zinc standard, under nitrogen atmosphere. The samples of about 7 mg were accurately weighted and encapsulated in aluminum pans with 40 μL of capacity. Under a nitrogen flow of 80 mL/min, the samples were first heated from 10 to 180°C, at a heating rate of 20°C/min, and maintained at that temperature for 3 min. Then, the samples were cooled from 180 to 10°C, at a cooling rate of −20°C/min, maintained at 10°C for 2 min, and heated again until 180°C at a rate of 20°C/min. The melting temperatures, together with the degree of crystallinity, were obtained from these experiments for the two scanning cycles.

RESULTS AND DISCUSSION

The separation of the irradiated samples into a soluble fraction and a nonsoluble fraction was carried out by PREP. Therefore, the original LDPE 985 irradiated samples (s1, s2, s3, and s4), their soluble fractions (s2SF, s3SF, and s4SF), and their nonsoluble fractions (s2NF, s3NF, and s4NF) could be characterized by analytical techniques such as FTIR spectroscopy, GPC, DSC, and crystallization analysis fractionation.

From the quantitative results of the preliminary fractionation of the four original LDPE samples, it is possible to make a first approach to the structure of the materials. Table II shows the percentages of soluble and nonsoluble fractions in each sample. Sample s1 (nonirradiated LDPE) is totally soluble in xylene, which corresponds to a material with low branched and crosslinked structure. Also, the sample irradiated with 2 Mrad (s2) still has a very high soluble content, so it was not possible to obtain enough nonsoluble fraction (s2NF) for further characterization. However, it can be observed that the nonsoluble fraction increases substantially with the irradiation doses as a consequence of the degradation reactions that take place.

TABLE II
Composition of the Soluble and Nonsoluble Fractions

Sample	Soluble fraction (%)	Nonsoluble fraction (%)
s1	100	0
s2	93.72	6.28
s3	34.64	65.36
s4	15.21	84.78

Spectroscopic analysis of the irradiated LDPE samples

The absorbance spectra of the irradiated samples (s1, s2, s3, and s4), of their soluble fractions (s2SF, s3SF, and s4SF) and of the nonsoluble fractions (s3NF and s4NF) were recorded and studied. The peaks corresponding to the aldehyde (1739 cm^{-1}), ketone (1715 cm^{-1}), transvinylene (965 cm^{-1}), vinyl (909 cm^{-1}), and vinylidene (888 cm^{-1}) functional groups were investigated, and their relative absorbance ratios were determined related to the height of a reference peak at 2020 cm^{-1}, to make their results comparable and to eliminate the effect of the thickness of the films.

Figures 1 and 2 represent the spectroscopic results of the analyzed functional groups for the irradiated original samples (s1, s2, s3, and s4), their soluble fractions (s2SF, s3SF, and s4SF), and the nonsoluble fractions (s3NF and s4NF) as a function of the radiation doses. As a whole, for the original irradiated samples before fractionation (s1, s2, s3, and s4), the vinyl and vinylidene ratios decrease with the radiation dose, whereas the transvinylene, ketone, and aldehyde ratios increase. Consequently, γ-radiation promotes the formation of imperfections in the polymeric chains, in agreement with previous works.[20,21]

It can be observed that the main oxidative degradation reactions, here indicated by the production of ketones and aldehydes, occur at a higher rate with low radiation doses, although with higher doses this tendency is slowed down. This phenomenon could be explained because at high radiation doses, an excess production of radicals could be expected, which would recombine before they could be reached by oxygen molecules to propagate the oxidation.[13] This hypothesis may be supported by the fact that the nonsoluble fraction increased remarkably for high radiation doses, as confirmed by the results of preparative fractionation.

Moreover, if we compare the ketone and the aldehyde rates for the soluble and nonsoluble fractions after high radiation doses, it can be confirmed that these groups appear mainly in the soluble fraction. This fact may be an indication that oxidative scission mechanisms prevail at low radiation doses and are particularly evident in the soluble fractions. However, considering the transvinylene group, its production shows a remarkable increase in the nonsoluble fraction, particularly at high radiation doses. Some authors have indicated that the formation of unsaturated transvinylene groups is a basic reaction of polyethylenes when they are irradiated with high doses, and they are usually related to crosslinking mechanisms.[13,18] Thus, all these indications are in agreement with the works of various authors,[5,12,13,17,19] which suggest that, although both oxidative scission and crosslinking are phenomena associated with γ-radia-

tion on polyethylenes, oxidative scission with formation of ketone and aldehyde groups occurs mostly at low radiation doses, whereas for higher doses crosslinking mechanisms acquire remarkable significance.

For a further study of the effects of irradiation on the chemical structure of LDPE, their molecular weight distribution was correlated with the content of some characteristic functional groups. First, preparative fractionation by molecular weight (PREP) was performed on the soluble fractions of the samples irradiated with 2 and 20 Mrads (s2SF and s3SF). With this procedure, four fractions with increasing molecular weight were separated by PREP from sample s2SF, whereas for the case of sample s3SF, there were three obtained fractions. These fractions were afterward analyzed by GPC to study their molecular weight distribution, and with FTIR spectroscopy to record the presence of ketone, aldehyde, vinylidene, vinyl, and transvinylene functional groups.

Figure 3 represents the molecular weight distribution for the analyzed samples and their respective fractions after preparative fractionation by molecular weight. It is shown that the broad molecular weight distribution of the samples s2SF and s3SF leads to narrower shapes for their respective fractions after PREP. Finally, Figure 4 shows the relationship between the average molecular weight and the content of each analyzed functional group. As a whole, it can be stated that the fractions with lower average molecular weight possess higher ratios of the analyzed functional groups, especially aldehydes and ketones. Besides this, the evolution of the functional group ratios shows an asymptotic behavior, given that their values become stabilized for increasing molecular weight values from M_w = 50,000. These results may provide evidence of the performance of oxidative scission mechanisms associated with γ-irradiation of LDPE, which lead to a progressive diminution of the molecular weight of the polymeric chains and an increase of the concentration of carbonyl groups. If we study the case of transvinylene groups, it can be observed that their presence increases with the radiation dose, and their content does not depend on the molecular weight of the fractions. These facts suggest again that their appearance is not related to the scission reactions, but to the crosslinking mechanisms among the polymeric chains, as has been proposed by some authors.[13,18]

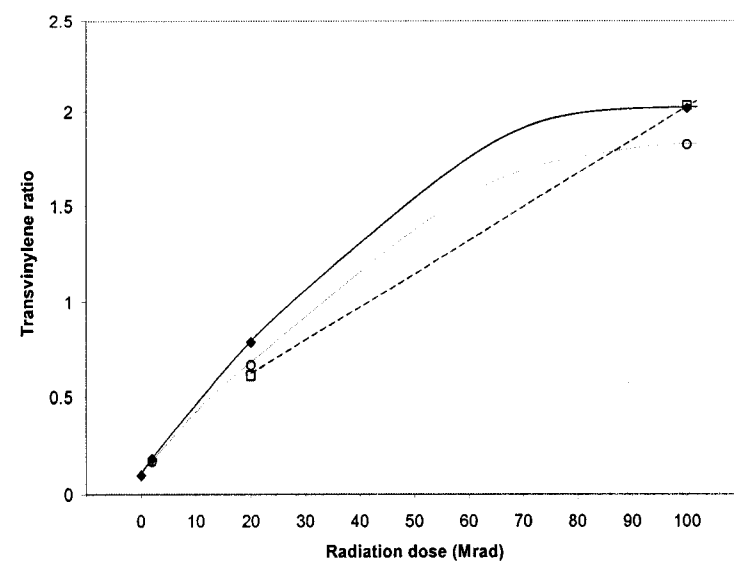## Study of the morphology of the irradiated LDPE samples by DSC and CRYSTAF

To acquire a better understanding of the complex phenomena that LDPE samples undergo after high-energy radiation, further investigation about how these chemical changes affect the morphology and
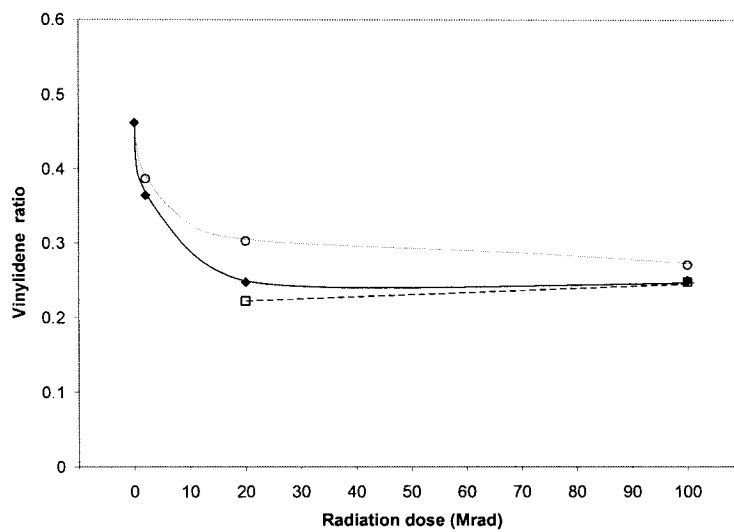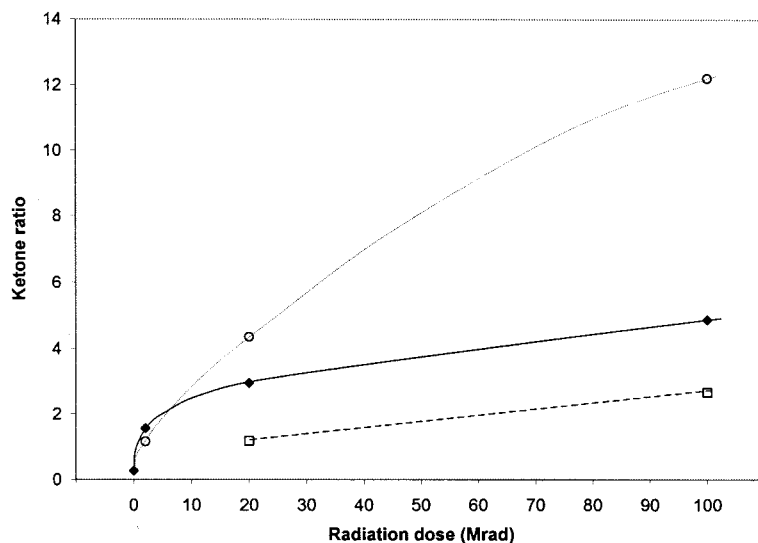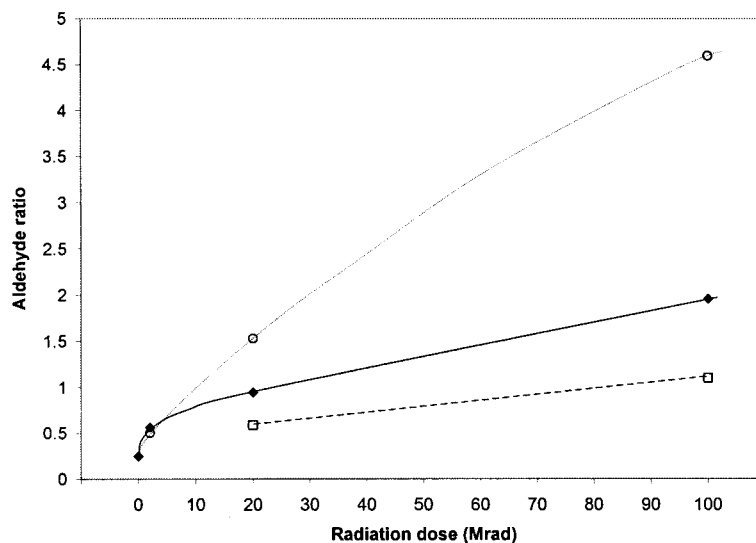
(a)
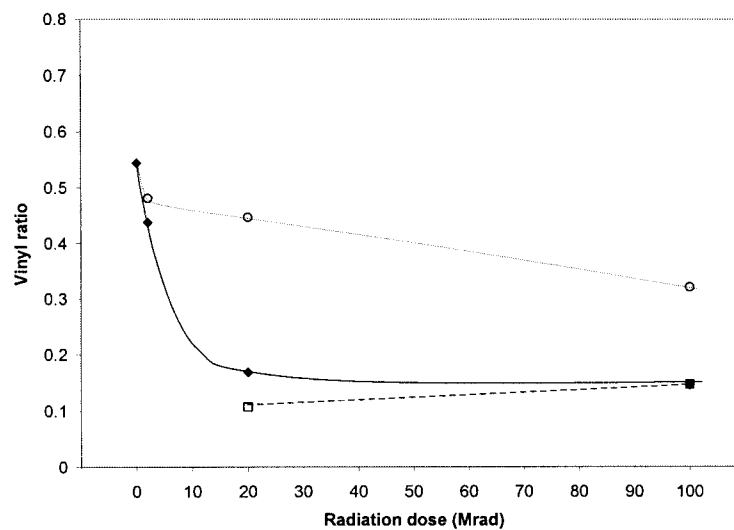
(b)

(c)

Figure 1 Variation of the ratios of some functional groups, (a) vinylidene ratio, (b) vinyl ratio, and (c) transvinylene ratio, with the radiation dose: (◆) original LDPE 985 samples before fractionation; (○) soluble fractions; (□) nonsoluble fractions.

(a)

(b)

Figure 2 Variation of the ratios of carbonyl groups, (a) ketone ratio and (b) aldehyde ratio, with the radiation dose: (◆) original LDPE 985 samples before fractionation; (○) soluble fractions; (□) nonsoluble fractions.

structure of the irradiated samples was performed. DSC and crystallization analysis fractionation were used for this purpose, so the performance of the novel CRYSTAF technique could be discussed.

DSC

Differential scanning calorimetry was used to study the fusion and crystallization behavior of the irradiated LDPE samples and their respective soluble and nonsoluble fractions. The melting temperature and the

crystalline content were determined to investigate the morphological changes introduced by irradiation. The melting temperature was directly obtained from the DSC thermograms as the temperature of the main endotherm. On the other hand, the crystalline content was calculated for all the samples from the following equation:

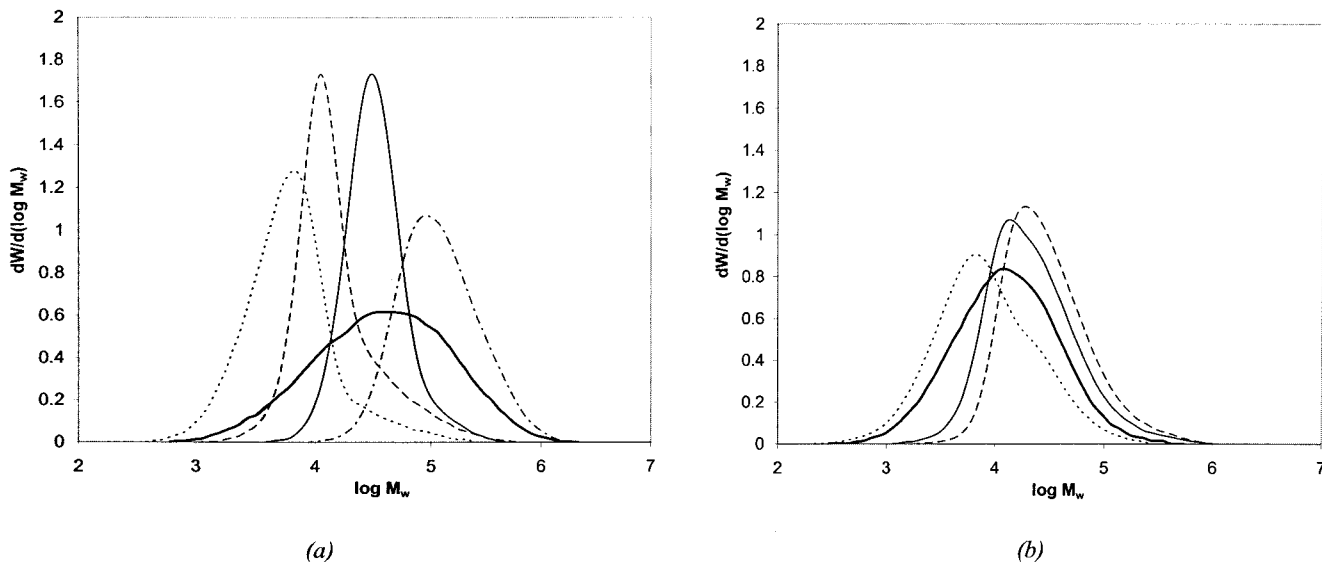$$X_c = \frac{H_m - H_c}{\Delta H_m^{\circ}} \quad (1)$$

Figure 3 Molecular weight distribution curves from GPC of the LDPE 985 samples after preparative fractionation by molecular weight: (a) samples irradiated with 2 Mrads: (—) sample s2FS, (· · ·) sample s2SF1, (– – –) sample s2SF2, (—) sample s2SF3, (– · –) sample s2SF4; (b) samples irradiated with 20 Mrads: (—) sample s3FS, (· · ·) sample s3SF1, (—) sample s3SF2, (– – –) sample s3SF3.

where H_m and H_c are the enthalpies per mass in the melt and crystalline states, respectively, whose difference is given directly by the DSC instrument as the area of the endothermic peak ΔH_m. ΔH_m° is the melting enthalpy per mass of a perfect crystalline polyethylene, which has a value of 288 J/g.[28]

Two scans were carried out for all the analyzed samples. The first scan indicated the direct effect of the γ-irradiation on the structure of the LDPE samples. On the other hand, the shape of the second scan is a consequence of the realignments of the polymeric

chains that occurred after the reactions caused by the irradiation.

The effect of the radiation dose on the melting temperature and the crystalline content is shown in Figure 5 for the irradiated samples before fractionation (s1, s2, s3, and s4). If we analyze the results from the first scan, it can be observed that for low radiation doses (up to 20 Mrads), the crystalline content and the melting point decrease, but for higher radiation doses they tend to level off or even slightly increase. Considering the second scan, both the melting point and the crys-
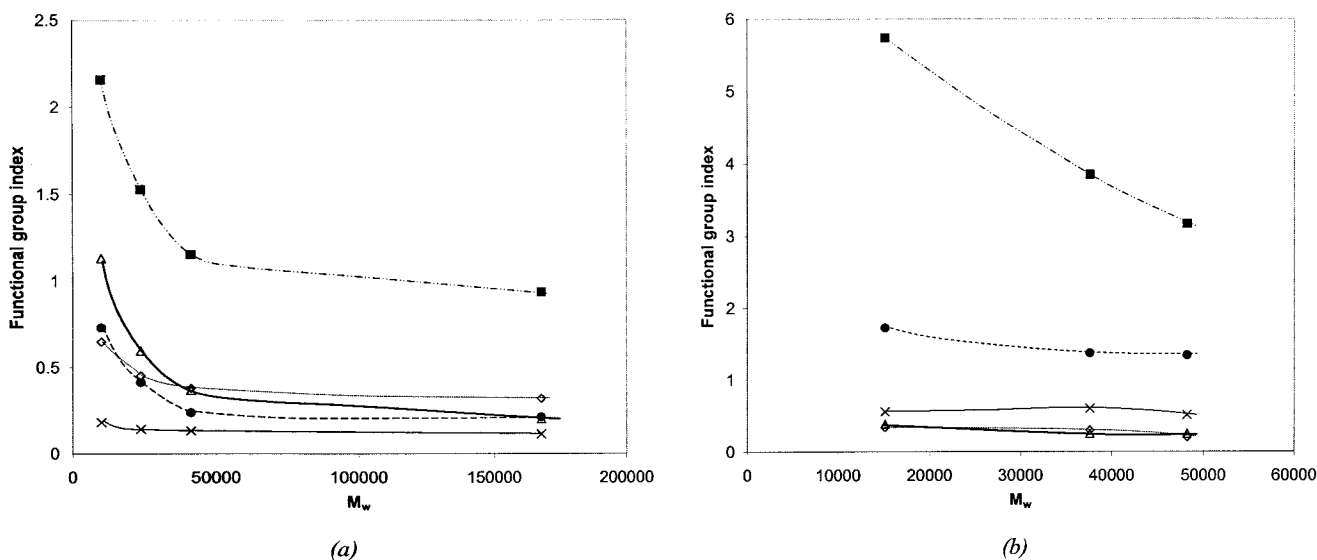

Figure 4 Dependency of the (◇) vinylidene ratio, (△) vinyl ratio, (×) transvinylene ratio, (■) ketone ratio, and (●) aldehyde ratio, with the average molecular weight: (a) samples irradiated with 2 Mrads; (b) samples irradiated with 20 Mrads.
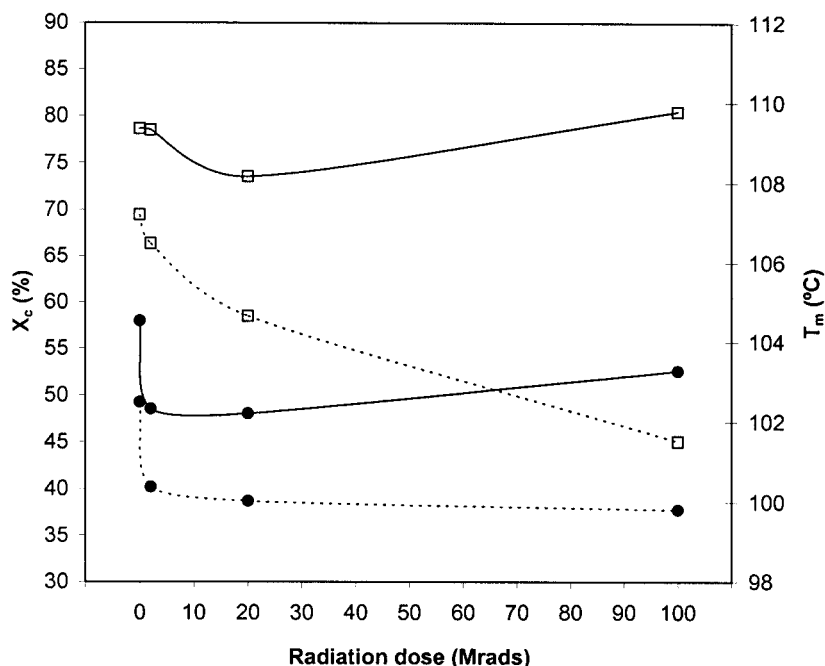
Figure 5 Characterization of the (□) melting temperature and (●) crystalline content of the original LDPE 985 samples before fractionation, for the (—) first and (· · ·) second scans.

talline content decrease with the radiation dose, although this effect is more prominent for lower radiation doses. These results are in agreement with the works of some authors,[2,5,8,10,11,20,21] which have suggested that the decrease of the crystalline content and the melting point could be atributable to the increase of the imperfections in the polymeric chains originated by the radiation. These defects of the polymeric chains could inhibit the crystallization process, leading to smaller and less-perfect crystallites.

Figure 6 shows the influence of the radiation dose on the melting point and the crystalline content for the irradiated original samples (s1, s2, s3, and s4) compared to their respective soluble fractions (s2SF, s3SF, and s4SF), and their nonsoluble fractions (s3NF and s4NF). It can be observed that the soluble fractions possess higher crystalline content but lower melting temperatures than those of their respective original samples.

This fact suggests that these soluble fractions may be composed of shorter chains because of the scission reactions originated by the radiation. These short chains crystallize at a higher degree, but giving smaller and less-perfect crystallites, which would explain the lower melting temperature. Moreover, the crystalline content of the soluble fractions increases with the radiation doses, contrary to what occurs with the original irradiated samples. If the nonsoluble fractions are considered, it can be observed that they possess lower crystalline content and melting points. These fractions may be composed of highly branched and crosslinked material, which makes the crystalliza-

tion processes more difficult by generating fewer crystallites with smaller size. This hindering effect is strengthened by the increase of the radiation dose.
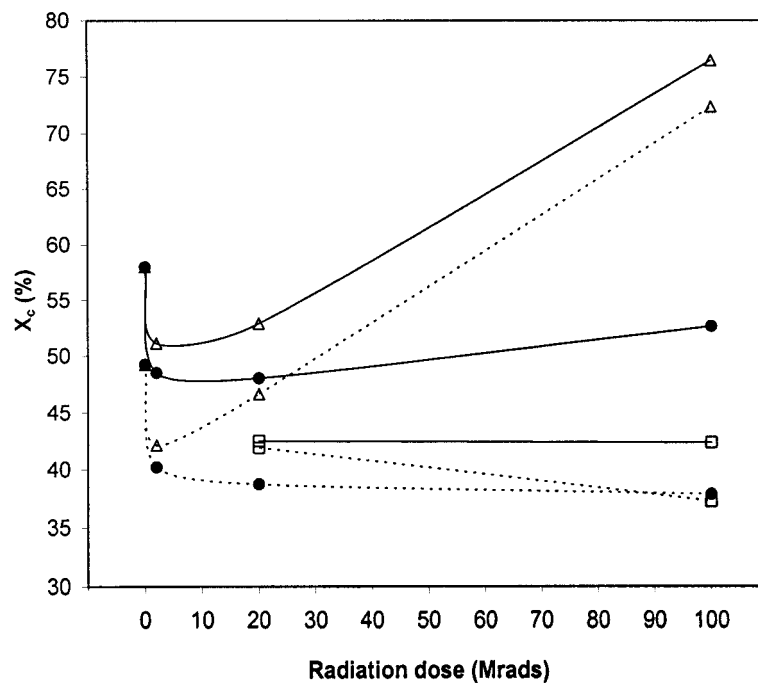
CRYSTAF

Crystallization analysis fractionation allows the determination of the CCD of polyolefins, by monitoring the solution crystallization of the polymer when it is subjected to a controlled decrease of temperature. With this procedure, the cumulative curve of the CCD is obtained as a function of the crystallization temperature. The first derivative of this curve offers us information about the branching degree of the polymeric material.

Figure 7 shows the cumulative and derivative curves for the nonirradiated LDPE sample (s1). It can be observed that the CCD of the sample shows a uniform curve centered at a crystallization temperature of 59.9°C with wide shape, attributed to the fact that the material is a low-density polyethylene that possesses intrinsically a certain branching content. The main crystallization process for the nonirradiated sample ends at around 46°C, when approximately 87% of the sample has crystallized. Therefore, for a further characterization of the irradiated samples, this temperature will be chosen as a reference, and the percentage of the fractions that have crystallized above and below this limit temperature will be calculated for all the analyzed samples. Also, the noncrystallized fraction, which can be easily obtained from the
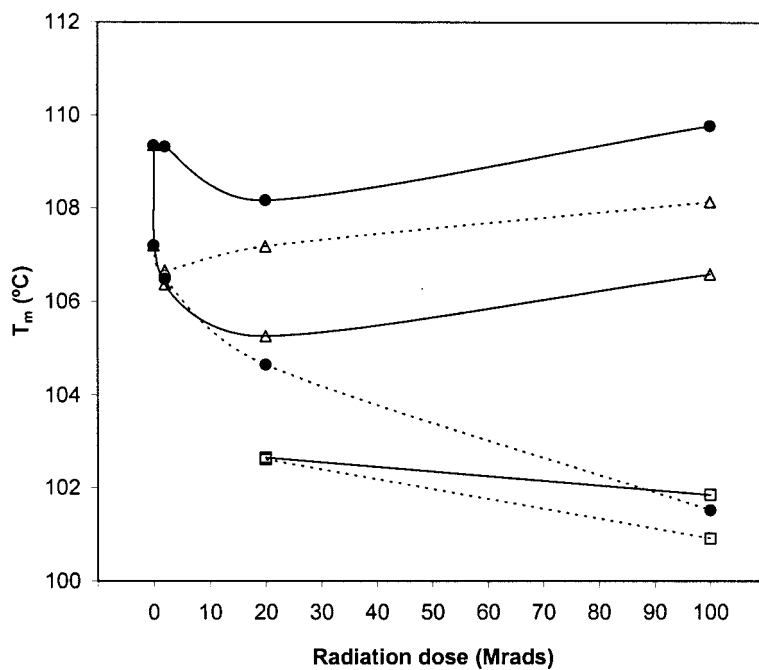
(a)

(b)

Figure 6   Variation of the calorimetric parameters of the (●) original LDPE 985 samples before fractionation, (△) soluble fractions and (□) nonsoluble fractions, with the radiation dose, for the (—) first and (· ·) second scans: (a) melting temperature; (b) crystalline content.
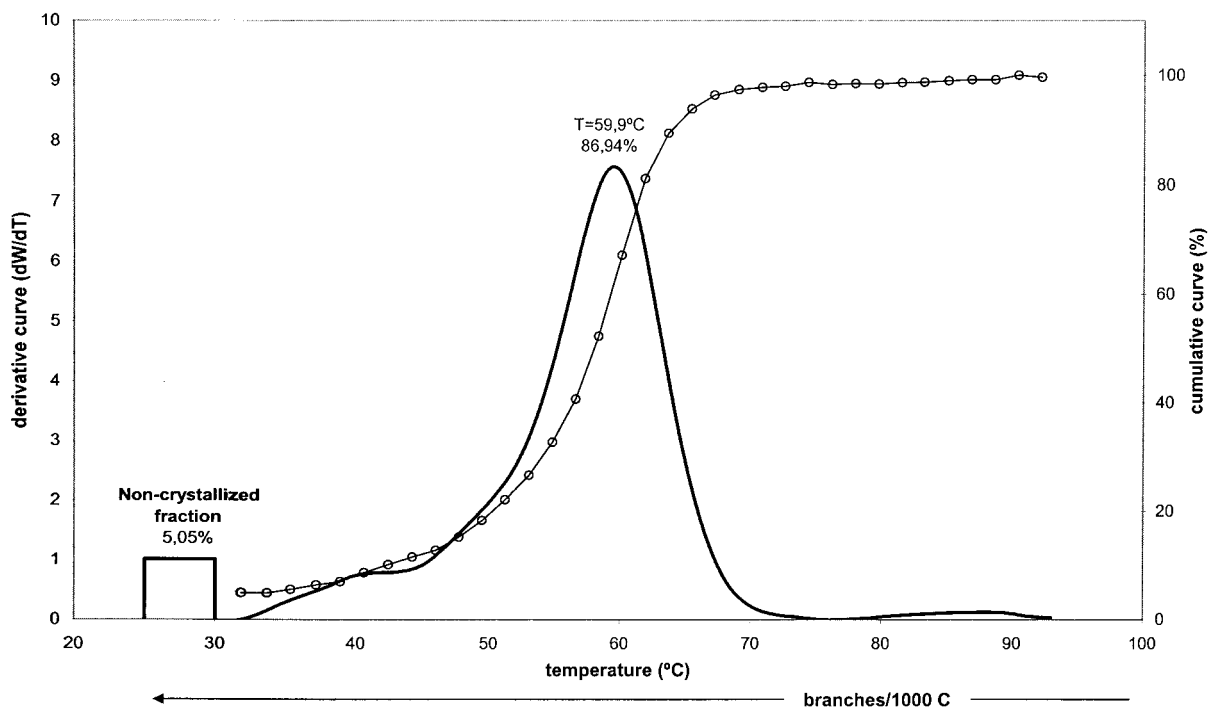
Figure 7 Analysis of the nonirradiated LDPE 985 sample by crystallization analysis fractionation: (–O–) cumulative curve; (—) derivative curve.

cumulative curve, will be another referent parameter for the discussion. These results are shown in Table III.

The derivative curve of the CCD for the four LDPE irradiated samples (s1, s2, s3, and s4) is represented in Figure 8. If we compare samples s1 and s2, it can be observed that low radiation doses do not substantially modify the chemical composition distribution. The main peak shifts slightly toward higher branching content, and even the noncrystallized fraction decreases slightly for the sample irradiated with 2 Mrad. This fact suggests that chain scissions at the LDPE material have occurred at low radiation doses. However, for higher irradiation doses (20 and 100 Mrad), the performance of the degradative processes motivated by the high-energy radiation is clearly evidenced by the considerable modification of the chemical composition distribution curves. For samples s3

and s4, the main crystallization peak has disappeared, leading to a variable CCD with other secondary peaks, which exhibit higher branching content as a result of the combined oxidative scission and crosslinking. Moreover, the exceptional increase of the noncrystallized fraction with highly branched and crosslinked structure indicates the importance of crosslinking reactions for high-radiation doses.

Figure 9 shows the comparison of the derivative curves for some irradiated samples (s2 and s3) and their respective xylene soluble fractions (s2SF and s3SF), obtained after preparative fractionation. The soluble samples present a CCD with lower branch content and the noncrystallized fraction also shows a minor value compared to that of their respective original samples. Nevertheless, for the high-irradiated sample s3, the differences between the soluble fraction

TABLE III
Content of the Crystallized and Noncrystallized Fractions After CRYSTAF Measurements for the Analyzed LDPE 585 Irradiated Samples

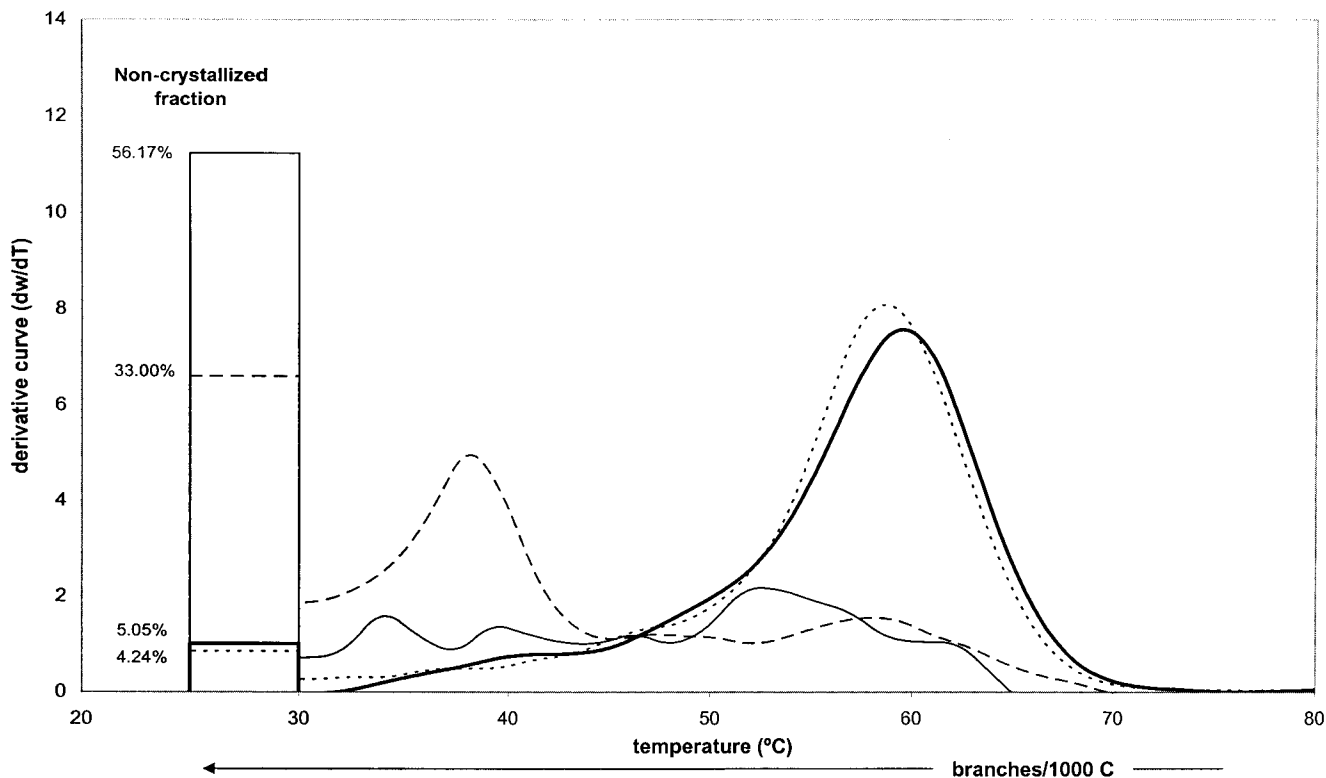| Sample | Radiation dose (Mrad) | Crystallized fraction | | Noncrystallized fraction (%) |
		$T > 46°C$ (%)	$T < 46°C$ (%)	
s1	0	86.94	8.01	5.05
s2	2	86.88	8.88	4.24
s2SF		88.21	8.61	3.18
s3	20	23.71	43.29	33.00
s3SF		37.31	44.66	18.03
s4	100	25.98	17.85	56.17

Figure 8 Derivative curves from crystallization analysis fractionation of the LDPE 985 irradiated samples before fractionation: (—) s1, nonirradiated sample; (· · ·) s2, sample irradiated with 2 Mrads; (– – –) s3, sample irradiated with 20 Mrads; (—) s4, sample irradiated with 100 Mrads.

and the original sample are much more evident than those for the low-irradiated sample s2 because of the increasing effect of radiation.

Table III shows the percentage of the fractions that crystallize above and below the reference temperature of 46°C, together with the noncrystallized fraction, for
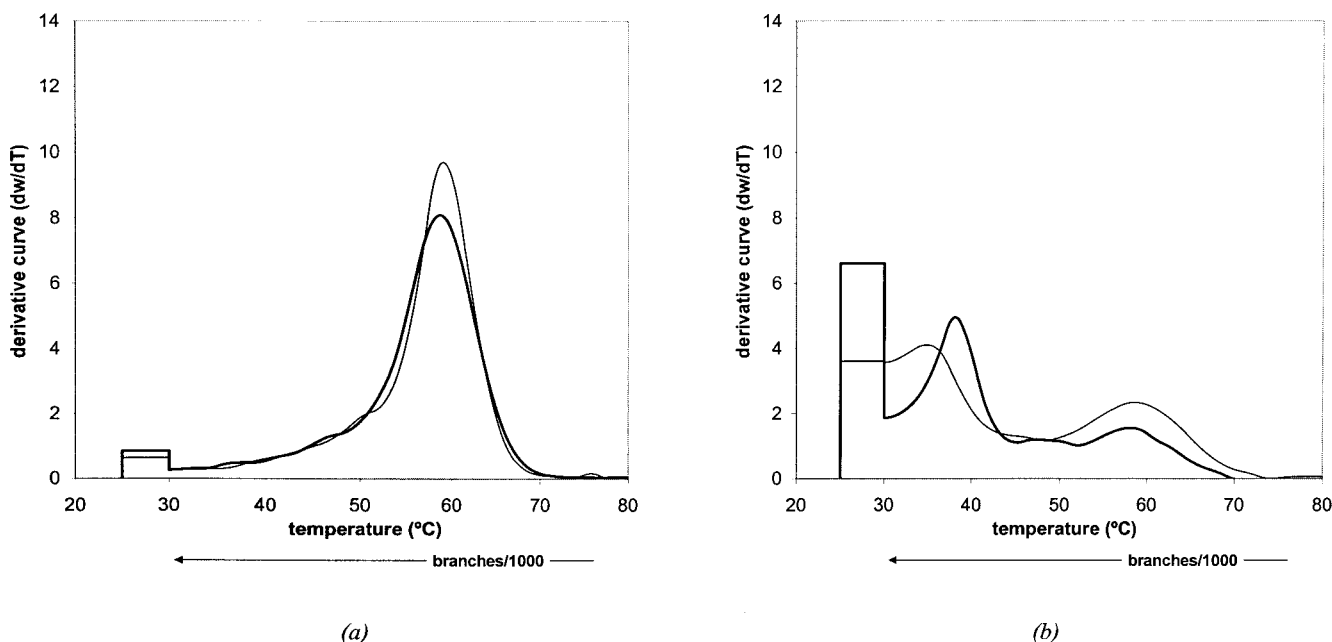

(a)

(b)

Figure 9 Comparative between the derivative curves from crystallization analysis fractionation for the (—) soluble fractions and the (—) samples before fractionation: (a) samples irradiated with 2 Mrads; (b) samples irradiated with 20 Mrads.

all the samples analyzed with CRYSTAF. As it can be observed, samples s1 and s2 show similar contents of the three fractions. However, for sample s3, irradiated with 20 Mrad, the fraction with lower branching degree (the one that crystallizes above 46°C) decreases dramatically, whereas the fraction that crystallizes below 46°C, which possesses higher branching degree, becomes especially important. The noncrystallized fraction increases substantially with the radiation dose, especially for sample s4, irradiated with 100 Mrad. These results are thus in agreement with the features that have been detailed before for Figures 8 and 9.

CONCLUSION

Preparative fractionation by molecular weight (PREP) was used as a preparative procedure to obtain different fractions of the analyzed irradiated samples. The application of this method, together with other conventional analytical techniques such as FTIR, DSC, or GPC, showed excellent performance to characterize in an extended way the effects of irradiation on LDPE materials.

In addition to this, crystallization analysis fractionation (CRYSTAF) proved to be a suitable analytical technique for the study of complex phenomena undergone by polyolefins, such as the effects of γ-irradiation on low-density polyethylene. The information about the branching content and the noncrystallized fraction directly obtained from CRYSTAF measurements could complement the results from other conventional techniques, to obtain further knowledge about the structural and morphological changes that different doses of γ-radiation produce on low-density polypropylene.

It has been observed that oxidative scission and crosslinking are competitive processes that occur simultaneously associated with high-energy radiation exposure. Oxidative scission was shown to prevail at low radiation doses, whereas for higher doses both phenomena show equal tendencies. Some of the analyzed effects of γ-radiation on LDPE include an increase in the quantity of imperfections and in the branching degree of the polymeric chains, a decrease of the crystalline content, and an alteration of the melting behavior.

The soluble fractions of the irradiated samples proved to be mostly affected by oxidative scission because of the high ketone and aldehyde ratio, by the higher crystalline content, and by the lower branching degree. On the other hand, the nonsoluble fractions showed a significant content of transvinylene functional groups and lower crystalline content, which could be attributed to the performance of crosslinking mechanisms.

Moreover, preparative fractionation by molecular weight allowed the correlation of the incidence of a number of functional groups (ketones, aldehydes, vinylidenes, vinyls, and transvinylenes) with the molecular weight distribution. These results suggested the performance of oxidative scission, given that the ketone and aldehyde content was remarkable for lower molecular weight fractions.

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