# Effect of Initial Crystallinity on the Response of High-Density Polyethylene to High-Energy Radiation

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Received 12 January 1998; accepted 14 May 1998

ABSTRACT: Samples of each of two high-density polyethylenes with various initial degrees of crystallinity, but otherwise identical, were exposed under a vacuum to moderate doses of gamma irradiation. The results indicate that, for otherwise initially identical polymer samples, the dose required to reach the gel point increases with increase of the initial degree of crystallinity. Above the critical dose for gelation, the gel content decreases with higher degrees of crystallinity at equal radiation doses. The mechanical behavior of the polymers changed progressively from ductile to brittle as the crystallinity was increased. The extensibility of originally ductile samples decreases with increasing radiation dose. The irradiation of samples having intermediate behavior produces a change to ductile behavior. Mechanical behavior is not modified substantially when brittle samples are irradiated. The initial modulus is little altered by irradiation, while the yield stress shows a slight increase with irradiation. The mechanical properties, such as draw ratio at break and ultimate tensile stress, decrease with dose in ductile samples. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 71: 1375–1384, 1999

**Key words:** high-density polyethylene; morphology; irradiation; mechanical properties

## INTRODUCTION

The treatment of polyethylene with high-energy ionizing radiation is used to control the melt properties and/or to improve the physical properties of the polymer in the solid state.<sup>1-6</sup> The melt properties of polyethylene can be changed and its physical properties in the solid state improved by exposure to ionizing radiation.<sup>1-6</sup> Radiation causes various chemical reactions, mainly involving free radicals, that alter the molecular structure and, consequently, the properties of the irradiated materials. In the case of the linear polyethylene family, the most important reaction that occurs during irradiation is the combination of free radicals that leads to molecular chain linking.<sup>1–10</sup> During the early stage of the irradiation processes, chain linking produces an increase in molecular weight. Then, at a given dose, usually known as the "critical dose for gelation" (CDG), the weight-average molecular weight becomes infinite. At this point, the molecular structure of the polymer is partitioned into two fractions, an insoluble three-dimensional network or gel, and a soluble part composed of isolated molecules. Beyond the CDG, the amount of gel increases with the dose level.<sup>1-3,5,8-10</sup> Studies on the response of polyethylene to irradiation led to the recognition of a set of factors that affect the critical dose for gel formation.<sup>1,3,5,8–10</sup> One of these factors is the morphology of the polymer during irradiation.

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Contract grant sponsor: National Research Council of Argentina (CONICET).

Journal of Applied Polymer Science, Vol. 71, 1375-1384 (1999)

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When the radiation process is carried out at a relatively low temperatures, that is, room temperature, it is generally observed that, in samples with low crystallinity, radiation is much more effective in forming a gel than in samples with highly developed crystallinity.<sup>5,8</sup>

The effect of the levels of crystallinity of polyethylene samples crystallized from the melt on the structural modifications induced by irradiation is an important area of research. Despite the large number of reported studies on the effect of morphology on radiation-induced changes in polyethylene, there are still various factors that remain to be clarified. In particular, the effect of crystallinity on the critical dose required to form an incipient gel and on the amount of the gel at a given dosage are not well understood for specific irradiation conditions.

Mechanical properties constitute an additional point of interest regarding the response of polyethylene to irradiation. It is well known that the tensile properties of polyethylene are notably affected by irradiation.<sup>6,11–14</sup> For polyethylene, the extensibility generally decreases while the elastic modulus grows with increase in the radiation dose. However, there is limited information about the influence of the initial morphology on the changes in tensile properties upon irradiation. The investigation in this field has been mainly done by comparing different morphological systems which were obtained by changing the molecular structure of a polymer.<sup>11,12,15</sup>

To our knowledge, there is as yet no systematic study addressing the effect of the initial morphology on the mechanical properties of a given irradiated polyethylene. In recent studies, it was shown that the initial morphology profoundly affects the tensile behavior, as well as specific mechanical properties, of nonirradiated polyethylene.<sup>16,17</sup> As an example, the change from ductile to brittle behavior has been observed in a small range of crystallinity in linear polyethylene.<sup>16</sup>

The purpose of the present work was to provide information about the role played by crystallinity in the response of linear polyethylene to irradiation. To do this, we studied the influence of the initial crystallinity on the evolution of the geldose relation and the tensile behavior and specific mechanical properties over an extended radiation dosage. Samples having different levels of crystallinity were prepared following various wellcontrolled crystallization conditions. These samples were then irradiated with different doses at room temperature under a vacuum. The gel pro-

Sample Codes	Thermal Treatment				
IWQ	Ice-water quenched				
SCA	Slow cooled out of press				
SCP	Slow cooled in press				
I110	Crystallized at 110°C				
I127	Crystallized at 127°C				

Table I Code Used to Identify Samples

portions were determined by the extraction of solubles. The tensile mechanical behavior was studied at room temperature.

## **EXPERIMENTAL**

#### Materials

Two high-density polyethylenes supplied by DuPont de Nemours (Wilmington, DE) and Oxy Petrochemical (Dallas, TX) were used in this study. The polyethylenes, which we call PE1 and PE2, have a weight-average molecular weights  $(M_w)$  of 56,900 and 80,600, respectively. The polydispersity  $(M_w/M_n)$  was about 2.6 for both polymers.

#### **Sample Preparation**

Films of the initial material were prepared by compression molding at 150°C using a hydraulic press with thermostatically controlled platens. The samples were molded between 1.5-mm-thick steel plates held apart by 0.5-mm-thick brass spacers. Crystallization conditions were chosen so as to obtain samples having various levels of crystallinity as follows: (1) The first set of samples called IWQ was obtained by quenching from the melt to ice-water temperature; (2) the second set was obtained by cooling down the mold to room temperature out of the press; these samples were labeled as SCA; (3) the third set was prepared by slow cooling from the melt to ambient temperature keeping the samples between the press platens; these samples were named SCP; (4) the following group of samples was prepared by isothermal crystallization at 110°C of polymer PE1; this set was denominated I110; (5) and, finally, the last group was obtained by isothermal crystallization at 127°C of polymer PE2; these samples were named I127. The sample code is summarized in Table I.

### Sample Characterization

The degree of crystallinity of the samples was determined from the enthalpy of fusion. It was measured in a Perkin–Elmer DSC-2 using a heating rate of 10°C/min. The melting endotherm was defined by drawing a straight line from the onset to the end of melting. The area of each endothermic peak was determined by planimetry. The degree of crystallinity was calculated using 69 cal/g for the enthalpy of fusion of completely crystalline polyethylene.<sup>18</sup> Table II presents the measured crystallinity mean values for the samples prepared following the different crystallization conditions. The tensile behavior of linear high-density polyethylene changes substantially over this crystallinity range.<sup>16</sup> The heat of fusion of irradiated samples was also determined. We have observed no substantial differences in the heat of fusion beyond the experimental uncertainty, with respect to the parent sample.

## **Irradiation Procedure**

Dumbbell-shaped samples with a gauge length of 12 mm, thickness about 0.5 mm, and 4-mm width were cut from the films and inserted into Pyrex tubes. The tubes were evacuated to  $10^{-4}$  Torr for 2 days and then sealed off. Subsequently, these samples were exposed to  $\gamma$ -rays generated by a  $^{60}$ Co source at room temperature. The dose rate was 3.3 kGy/h, determined by dosimetry with a radiochromic thin-film dosimeter.<sup>19</sup> Equal doses of 20, 50, 100, and 200 kGy were applied to all samples. The error in dose is estimated to be  $\pm 10\%$ . After irradiation, samples were stored in a vacuum at room temperature for 1 week before opening the tubes for sample characterization.

#### **Sample Analysis**

The gel fraction was determined by the extraction of solubles with xylene at  $125^{\circ}$ C. The extraction was performed by placing about 30 mg of each sample into a basket made from stainless-steel mesh. Then, the baskets were immersed in hot xylene for periods of 6 h. After each of these periods, the samples were dried in a vacuum oven at 60°C to a constant weight. The extraction was considered complete when, after two consecutive periods of extraction, there was no detectable change of weight in the dried gel. The total time of extraction varied between 36 and 48 h depending on the sample. The solvent was changed to a fresh solvent between each consecutive extraction. Samples below the gel point were analyzed by gel permeation chromatography (GPC) following standard procedures. IR analysis was performed on samples using a Nicolet 520 FTIR spectrometer. The evolution of the 1715-cm<sup>-1</sup> absorption peak attributed to carbonyl stretching was followed to determine the oxidation level in the samples qualitatively.

## **Mechanical Behavior**

Tensile measurements were carried out using an Instron tester at a crosshead speed of 2 cm/min. The dumbbell-shaped samples had equidistant ink marks placed 2 mm apart in order to facilitate the measurement of the draw ratio after break. The specimens were deformed at room temperature  $(23-25^{\circ}C)$ .

The elastic modulus, yield stress, and ultimate tensile stress were obtained from nominal stresselongation curves. The initial modulus (E) was determined from the slope of the stress-strain curve at 1% strain. The yield stress (YS) was taken from the maximum in nominal stress observed in the curves at low deformation levels. The draw ratio after break,  $\lambda_B$ , was obtained from the relation between the spacing of the fiducial marks immediately after break and their initial spacing. The ultimate tensile stress (UTS) was estimated from the stress at the breaking point  $x\lambda_B$ . The reported data are average values for from five to seven samples. The standard deviation is about 9-10% of the mean for the initial modulus; about 2-7% for the yield stress, about 2-9% for the draw ratio after break, and about 10-20% for the ultimate tensile stress.

## **RESULTS AND DISCUSSION**

The variation of gel content with irradiation dose for polymers PE1 and PE2 is shown in Figure 1. A

Table IIPercentage of Crystallinityof Nonirradiated Samples

Polymer	Sample	Crystallinity (%)
PE1	IWQ	61.4
	SCA	73.0
PE2	III0 IWQ	79.6 57.5
1 112	SCA	67.6
	SCP I127	78.0 82.0



**Figure 1** Gel amount against radiation doses for samples having different crystallinities. Polymer PE1: ( $\bullet$ ) 61.4%; ( $\bullet$ ) 73%; ( $\bullet$ ) 74.0%; ( $\bullet$ ) 79.6%. Polymer PE2: ( $\bigcirc$ ) 57.5%; ( $\square$ ) 67.6%; ( $\triangle$ ) 78.0%; ( $\diamondsuit$ ) 82.0%.

20-kGy dose was not sufficient to produce a gel fraction. With 50 kGy of irradiation, a significant proportion of the gel was observed in all PE2 samples. As expected, an increase of the gel fraction with irradiation dose is observed for all samples. With the low molecular weight polymer PE1, a small amount of gel was formed in samples IWQ (10% by weight) and SCA (5%) at the same dose of 50 kGy. Samples SCP and I110 of the polymer PE1, which have more highly developed crystallinity, are still soluble at that dose.

These data indicate that the gel point for polymer PE1 changes from about 40 to 60 kGy when the degree of crystallinity increases from 60 to 80%. As there are no data points at levels of irradiation between 20 and 50 kGy, it is difficult to determine accurately the gel point for polymer PE2 in Figure 1. However, the same trend of higher gel contents with lower degrees of crystallinity is observed. This effect is clearly confirmed by the changes in the molecular weight distribution of the irradiated samples below the critical dose for gel formation as it is in Figure 2, which corresponds to measurements for PE2 irradiated with 20 kGy. In the plot, the GPC curves were normalized to the same total area. The broadening of the high molecular weight side is evident for all the samples irrespective of the level of crystallinity. This is to be expected when the polymer becomes more branched as species of high molecular weight appear.<sup>20</sup> The GPC curves are ordered according to the level of crystallinity of the initial samples; the mass fraction of high molecular weight species increases as the level of crystallinity decreases. This is a clear indication that the intermolecular linkage is more effective in forming high molecular weight species in samples with lower fractions of crystalline polyethylene. Thus, we would expect that highly developed crystallinity samples require higher irradiation doses to reach the gel point.

At dosage levels higher than the gel point, the plots of Figure 1 indicate that the proportion of gel increases constantly with dose. The rate of



**Figure 2** GPC curves for PE2 samples having different initial crystallinity levels: ( $\bullet$ ) 57.5%; (+) 67.6%; ( $\blacktriangle$ ) 78%; (\*) 82%. The dose was 20 kGy. Full line corresponds to the original PE2 polymer.



**Figure 3** Gel amount against crystallinity level. Dose:  $(\bullet, \bigcirc)$ , 50 kGy;  $(\blacksquare, \Box)$  100 kGy;  $(\blacktriangle, \triangle)$  200 kGy. Filled and open symbols correspond to PE1 and PE2, respectively.

gelation is greater in samples with lower crystallinity.

If the gel fraction is taken as a measure of the effectiveness of the irradiation process, then an increment in crystallinity levels reduces the efficiency of irradiation. For example, Figure 1 shows that in order to produce 40% gel the sample with crystallinity of 82% has to be irradiated to a dose of 200 kGy, while for the sample with crystallinity of 58%, the dose required to produce the same amount of gel is 50 kGy.

A more illustrative way to display the effect of crystallinity is to plot the gel content against the initial crystallinity level of the samples, as shown in Figure 3. These plots clearly show the important effect of the crystallinity level on the response to radiation. The gel content decreases rapidly with crystallinity at a constant dose. It should be observed that there is not a linear relationship between gel amount and crystallinity level. At doses of 100 and 200 kGy, the drop in the gel fraction seems to be more pronounced at crystallinity levels over 70%.

A comparison of the results from the irradiated samples of polyethylenes PE1 and PE2 reveals similarities that can be associated with the differences in molecular weight that exist among the parent polyethylenes. The samples of PE1 irradiated to a dose of 200 kGy lies approximately on the same curve that describes the data points of PE2 samples irradiated with a dose of 100 kGy. A similar situation occurs when samples of PE1 irradiated to dose of 100 kGy are compared with those of PE2 irradiated to 50 kGy.

In the search for an interpretation of the results described above, we found that a combination of different reasons can explain the change in the efficiency of gel formation with crystallinity in the case of melt-crystallized bulk polyethylene. Considering the experimental irradiation procedure adopted here, one plausible alternative is that some of the free radicals produced may not have combined to produce chain linking, thus remaining trapped in the semicrystalline medium. If this is the case, then it is expected that upon exposing the samples to air these free radicals could react with oxygen, producing different oxygenated products in polyethylene.<sup>1,2,5,7,9</sup> In this way, the radicals could have followed alternative reactions to those conducting to chain linking, precluding the formation of higher amounts of gel.

To explore this possibility, we analyzed the samples by IR spectroscopy to detect the presence of oxidized species. Different absorption peaks were observed in the 1730-1700-cm<sup>-1</sup> region. These peaks are associated with the absorption of different species having carbonyl groups, namely, acidic, ketonic, or aldehydic groups.<sup>21</sup>

To compare the samples in terms of the extent of carbonyl formation, we defined a "carbonyl index" as the relationship between the absorption bands of highest intensity observed at  $1715 \text{ cm}^{-1}$ and the 720-cm<sup>-1</sup> band associated with the stretching mode of the —CH2— group. The data are presented by plotting the gel fraction against the carbonyl index as is shown in Figure 4. The absorption peaks for the samples irradiated with 20 kGy were very weak, making impossible the estimation of the carbonyl index. The value of the



**Figure 4** Gel amount against carbonyl index at the following doses:  $(\oplus, \bigcirc)$  50 kGy;  $(\blacksquare, \Box)$  100 kGy;  $(\blacktriangle, \triangle)$  200 kGy. Filled and open symbols correspond to PE1 and PE2, respectively.



**Figure 5** Stress-elongation curves for IWQ samples of PE2, Xc = 57.5%. The dose (kGy) is indicated beside each curve.

carbonyl index for higher doses are relatively low, indicating that the samples are lightly oxidized. The gel fraction decreases continuously with the carbonyl index for different doses. These results suggest that part of the radicals produced during irradiation were trapped by the medium and then scavenged by oxygen. Thus, the differences observed in the gel amount between samples at a given dose may be due, in large part, to those radicals that follow reactions other than those leading to chain linking.

#### **Mechanical Behavior**

There is information concerning the influence of the irradiation process on the mechanical behavior and specific mechanical properties for polyethylene.<sup>2,3,5,11,12,22–26</sup> However, there is limited evidence on the role played by the morphology in controlling the mechanical behavior of irradiated polyethylene.

The structural changes described above were found to affect noticeably the mechanical properties of the polyethylenes. The tensile behavior at room temperature for some of the irradiated samples is shown as a function of the dosage in Figures 5–7. These plots show stress-elongation curves for a selected set of polymer PE2 samples. They were chosen as examples to illustrate the mechanical behavior observed as a function of dose.

In coincidence with other studies, we observed that the initial morphology has a profound influence on the character of the plastic deforma-



**Figure 6** Stress-elongation curves for SCP samples of PE2, Xc = 78%, demonstrating the effect of dose. The dash line indicates all plausible elongation levels that can sustain the same sample. The dose (kGy) is indicated beside each curve.

tion.<sup>27,28</sup> In the nonirradiated polymer, there is a change in the failure mode from ductile to brittle passing through a transitional mode, when going from samples with a low crystallinity level to those with highly developed crystallinity. We considered, as a transitional mode, that behavior when the neck formed after yielding does not propagate over all the deformation zone of the tested specimen.

At low deformation levels, the irradiated specimens show the typical drop in stress associated with yielding. The stress level at which each sample yields shows a tendency to increase with dose. These results are in accord with those reported by



**Figure 7** Stress-elongation curves for I127 samples of PE2, Xc = 82%, demonstrating the effect of doses. The dose (kGy) is indicated beside each curve.

other authors.<sup>6,15</sup> At high deformation levels, above the yield point, the stress-strain character of these samples depends largely on the irradiation dose and initial morphology. Figure 5 shows stress-strain curves displayed by an irradiated sample of PE2 having the lowest crystallinity level. The same characteristic curves, not shown here, were observed in the IWQ and SCA of PE1 and PE2, respectively. It can be seen that the slope at the end of the curve increases and the stress at failure passes through a maximum as the dose increases. This feature bears a close similarity with the strain-hardening pattern that is observed when the molecular weight increases in linear polyethylene.<sup>17,29</sup>

In contrast with this, Figures 6 and 7 show that the deformation pattern after yielding is very different for samples with higher crystallinity. The irradiation of a sample with a transitional behavior, such as the SCP samples in Figure 6, produces a change from transitional to ductile when irradiated at the lowest dose: 20 kGy. In this case, the formation of chain linking helps in a certain way to stabilize the cold-drawing process, allowing the propagation of the neck throughout all the length of the deformation zone until the samples break apart. When the irradiation dose is increased further, the samples again show a transitional behavior. The sample irradiated to a dose of 200 kGy breaks right after necking, in such a way that it can be considered to be a brittle fracture.

Figure 7 shows the deformation curves corresponding to the sample with a crystallinity level of 82%. The original sample displays a brittle behavior with ductile fracture: It breaks right after yielding. The irradiation of this sample does not alter the general shape of the deformation curves; there is just a slight reduction in the deformation level that the sample can sustain. The notable effect here is that the yielding phenomenon occurs at higher stress levels as the dose increases.

The set of samples studied here also allows us to make some comparison of the mechanical behavior between samples having about the same gel fraction obtained from a different initial morphology. As an example, we compared samples IWQ, SCP, and I127 of the PE2 polymer that were irradiated to a total dose of 50, 100, and 200 kGy, respectively. Figure 8 shows the stress-strain curves for these samples that have about 40% of the gel. From these figures, the differences that exist in mechanical behavior among the samples



**Figure 8** Comparison of nominal stress-elongation curves for PE2 samples having about 40% of gel. The crystallinity and dose are indicated beside each curve.

are evident. The deformation process occurs at notably higher stress levels when the crystallinity of the initial polymer increases. A notable feature is that the relative difference in the stress level at which the deformation of the initial material takes place is not modified by the irradiation process. All these results indicate that the initial morphology of the semicrystalline state is a very important factor in controlling the mechanical deformation characteristics of the material after being irradiated at room temperature.

The changes in the characteristics of the stress-strain curves can be associated with the modification in the topological details that affects the noncrystalline regions. It is generally recognized that the structure of noncrystalline regions solely is affected by the events that occurs during irradiation.<sup>30</sup> The crystal core is not affected to any extent at low irradiation doses, like those used in this work.<sup>5,30</sup>

The combination of molecular bonding and the presence of bulky oxided species alter the manner that molecular segments interact in the noncrystalline region. The mobility of the chain segments could be severely restricted, leading to an important reduction in elastic extensibility when a stress is applied. The chemical junctions formed after irradiating ductile samples contribute to reduce the final extension and to increase the maximum tensile stress which the molecular network is capable of sustaining. In samples that show a transitional behavior, there is an initial contribution of chain linking to the deformation in the early stage of the irradiation process. The chemical junctions could provide additional molecular

Polymer	Dose (kGy)	Modulus (MPa)			Yield Stress (MPa)				
		Sample				Sample			
		IWQ	SCA	SCP	I110	IWQ	SCA	SCP	I110
PE1	0	436	592	594	574	21.7	26.7	26.0	27.0
	20	444	522	536	570	23.4	27.3	28.3	29.3
	50	464	501	527	558	23.0	25.6	28.4	30.6
	100	455	546	544	646	23.7	28.5	28.2	29.0
	200	400	505		649	22.0	28.2		31.4
		IWQ	SCA	SCP	I127	IWQ	SCA	SCP	I127
PE2	0	432	551	594		20.8	25.2	27.4	28.0
	20	475	581	591	579	22.3	28.6	27.8	27.7
	50	371	486	523	574	18.6	25.9	27.9	29.8
	100	443	523	537	662	22.5	27.2	29.0	29.7
	200	452		590	655	24.4	27.9	31.1	33.4

Table III Initial Modulus and Yield Stress of Nonirradiated and Irradiated Samples

connections to the structure that favors a stable drawing process after yielding. The creation of additional chain linking, above the gel point, together with an increase in oxidation limits the extensibility of the structure. Material failure occurs at decreasing deformation levels as the dose increases.

The differences in mechanical behavior between samples having about the same amount of gel may be explained by a combination of at least two factors: If we assume that the sample could have about the same number of effective intermolecular links in order to have similar gel proportions, then these links should be localized in the noncrystalline regions that decrease in proportion with the crystallinity. Thus, the density of molecular unions would increase in samples with higher crystallinity and also its spatial distribution could be altered in a way that reduces the capability of the noncrystalline region to sustain large deformation. The other factor is the increase in the concentration of oxygenated species with both the crystallinity and the doses. The presence of this species could also change the density of that region and modify the interaction between chain segments in a way that reduces the deformability of the structure. We will now examine some specific mechanical properties such as initial modulus, yield stress, draw ratio after break, and ultimate tensile stress.

The measured values of the initial modulus are presented in Table III. The difference in the mod-

ulus among the original samples can be related to the distinctness in crystallinity levels. These results are consistent with studies on different polyethylenes.<sup>17,29</sup> The irradiation process does not seem to alter in a noticeable manner this property. The small differences in modulus values for the samples are within the variation normally observed for this property obtained from the mechanical test used here. The relative difference that exists in the value of the modulus between samples having different structures seems to be maintained over all the dose ranges studied here.

The elastic modulus of semicrystalline polymers depends in a complex way on the morphological factors.<sup>17,30</sup> The relative amount of crystalline and noncrystalline regions and their elastic properties contribute to the values of this property.<sup>17,27–29</sup> The noncrystalline structure is affected mainly by irradiation at the moderate dosage used here which may affect its elastic response.<sup>30</sup> These effects may be reflected in some way by the value of the measured macroscopic modulus. Other studies have reported that the initial modulus increases with dosage for irradiated polyethylene.<sup>22,25,31</sup> However, we have not observed such an effect in our samples. This is likely due to that the crystalline regions make the major contribution to the modulus value in these highly crystalline samples at room temperature.<sup>17</sup> Thus, the slight expected changes in the properties of the noncrystalline region might not



**Figure 9** Draw ratio after break,  $\lambda_B$ , against dose. **T** identifies transitional samples. For brittle samples  $\lambda_B$  = 1. For symbols, see Figure 1.

be detected by the mechanical test performed here.

Values of yield stress are also presented in Table III. The differences of yield stress between nonirradiated samples are in concordance with the differences in their crystallinity level. This is in good agreement with the results obtained in different studies.<sup>17,27,29</sup> The yield stress of irradiated samples shows a slight tendency to increase with the dose. Other reported results coincide with these observations.<sup>6,22,25</sup>

Yielding has been associated to different phenomenon involving crystalline and noncrystalline regions.<sup>6,17,29</sup> There is a proportional relation between the yield stress and crystallinity level for unirradiated polyethylene. We have not observed appreciable changes in the crystallinity level in the irradiated sample with respect to the original ones. Thus, the slight increment in the yield stress values may be associated with the modification that occurs in the noncrystalline regions.

Ultimate properties are affected at large extension by irradiation as can be deduced from Figures 9 and 10. The draw ratio after break,  $\lambda_B$ , decreases continuously with the irradiation dose as can be seen in Figure 9. For samples that show brittle behavior, we assigned a value of 1 to  $\lambda_B$ . Transitional samples display  $\lambda_B$  values which have a large error because they represent the average of a broad distribution of values.

The draw ratio after break decreases continuously with dosage for samples that were initially ductile. When samples at doses above the gel point are measured, all data points seem to describe the same general curve. Moreover, the data point for samples from both polymers having different crystallinity fall on the same curve. The data points at 100 kGy have been shifted slightly along the *y*-axis in order not to superposed data. The change in  $\lambda_B$  with dose agrees quite well with those results reported for linear polyethylene as a function of molecular weight in the range from  $10^5$  to  $10^6$ .

The irradiation of samples that display transitional behavior leads, initially, to an increment in  $\lambda_B$ . Then,  $\lambda_B$  decreases until it reaches a value of 1, corresponding to a brittle sample.

The ultimate tensile stress at break (UTS) for ductile samples is plotted against the dose in Figure 10. This property is defined as the ultimate engineering stress times  $\lambda_B$ .<sup>17,29</sup> The UTS shows similar dependence on the dose as does  $\lambda_B$ . The changes in the values of these ultimate properties with dose are consistent with those observed for  $\lambda_B$ . Also, as occurs with  $\lambda_B$ , the UTS value compares very well with those reported for linear polyethylene in the range of molecular weight from about 10<sup>5</sup> to 10<sup>6</sup>.<sup>17,29</sup>

The effect of radiation on the ultimate properties for different polyethylenes has been reported by others.<sup>2,6,11,12,22–24</sup> It has been suggested that there is an equivalence of the network obtained by irradiation and the physical network produced by molecular entanglements in nonirradiated polyethylene in respect to its mechanical response to an applied stress.<sup>6</sup> The dependence of the ultimate properties with dose observed here compares with the effect of molecular weight reported for linear polyethylene which gives support to that point of view.



**Figure 10** Ultimate tensile stress against dose. For symbols, see Figure 1.

# **CONCLUSIONS**

The results obtained from this study demonstrate that the initial morphology becomes of great significance in determining the structural characteristics and the tensile behavior of irradiated highdensity polyethylene. As crystallinity increases, the gel point shifts to higher doses and the gel proportions at a given dose level decrease noticeably. This suggests that the increased amount of crystallinity is preventing the combination of free radicals, reducing the gel proportion.

The irradiation of ductile samples limits the extensibility of the material. The ductility is improved when transitional samples are irradiated at a dose below or just above the gel point. At higher dose levels, there is a trend to brittleness. The irradiation of brittle samples does not modify substantially the characteristics of the deformation pattern.

The initial modulus is not altered to a great extent by irradiation, but the yield stress shows a tendency to increase with dose. The ultimate properties, such as draw ratio after break and ultimate tensile stress, are substantially modified by irradiation. Although the samples show signs of oxidation that may have some effect on the mechanical behavior and related properties, we believe that the molecular bonding is the overriding factor responsible for the changes in the deformation patterns and the specific mechanical properties observed in this study.

The results observed here are governed by the experimental conditions under which the mechanical tests were performed. Changes in the mechanical behavior and properties are expected if the mechanical tests are performed at other temperatures and/or draw rates.

This work was supported by the National Research Council of Argentina (CONICET). The authors thank CNEA (Comisión Nacional de Energía Atómica) for making available their irradiation facility.

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