Chemical and Thermal Characterization of High- and Low-Density Irradiated Polyethylenes

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ABSTRACT: A comparative study of the dynamic mechanical relaxation spectra of high- and low-density polyethylenes irradiated with γ-radiation from a Co[60] source was performed. The irradiation doses ranged from 0 to 100 Mrad. All the samples were previously characterized by determination of the molecular weight distribution, the number of functional groups, and the crystalline fraction. All the relaxation zones between $-145°C$ and the melt were studied in the frequency range from 0.3 to 30 Hz. The changes observed in the mechanical relaxation spectra were related to modifications in the chemical structure and morphological parameters attributed to the exposure of the samples to the γ-radiation. © 2002 Wiley Periodicals, Inc. J Appl Polym Sci 86: 1953–1958, 2002

Key words: polyethylene; radiation; infrared spectroscopy; differential scanning calorimetry (DSC); mechanical properties

INTRODUCTION

Low- and high-density polyethylenes are used in many applications (nuclear power plants, radiation equipment, sterilization systems, etc.) where exposure to high-energy radiation can occur. In addition, high-energy radiation is used to deliberately modify the chemical and physical structure of polymers.

The effects of high-energy irradiation on polyethylene have been studied by several investigators.[1–10] It is well known that γ-radiation can induce crosslinking and scission in polyethylene chains.[2,3] However, these effects depend on the radiation dose and the morphology of either a single-crystal, bulk, or oriented preparations. The model proposed by Patel and Keller[3] suggests that crosslinking takes place preferentially in the amorphous region rather than in the crystalline region, which coexists in the polymer with the amorphous zone.

On the other hand, dielectric and viscoelastic studies of polyethylenes have been carried out for several decades by many researchers and the general trends are well known. Three relaxation zones (usually designated as α, β, and γ, in order of decreasing temperature) are well established. However, the molecular origin and the morphological assignment of each mechanical relaxation are still a matter of discussion because of the variety of interpretations proposed by different authors.[11]

The aim of this work was to investigate the influence of different radiation doses on the chemical, thermal, and mechanical behavior of polyethylenes. Thus a variety of supplementary measurements were made to accomplish the necessary characterization, that is, to quantitatively determine the structural and chemical parameters that may describe the structural and morphological state of the specimens and that may suggest the molecular origin of the relaxation zones.

EXPERIMENTAL

Material preparation

The three different types of polyethylene were supplied by Dow Chemical Iberica S.A. (Tarragona, Spain). The commercial labels of the polyethylenes are as follows: high-density, PE 10062 ($M_n = 18.8 \times 10^3$, $M_w = 62.7 \times 10^3$); low-density, PE 710 ($M_n = 7.53 \times 10^3$, $M_w = 47.6 \times 10^3$) and PE 980 ($M_n = 6.22 \times 10^3$, $M_w = 46.8 \times 10^3$).

Samples of all the polyethylenes were melted, quenched at 20°C, and annealed for 65 h at 104.6°C. After that, they were irradiated under air atmosphere at a constant temperature of 20°C with γ-radiation from a Co[60] source. The irradiation rate was 1.4×10^{-4} Mrad/s and the total doses were 0, 2, 20, and 100 Mrad, respectively, for the different samples. The thickness of the samples was about 1 mm.

Spectrometry measurements

All samples were characterized by determination of the functional groups vinyl, vinylidene, transvinylene,

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aldehyde, and ketone by means of a Nicolet 510 FTIR spectrophotometer (Nicolet Instruments, Madison, WI). The functional groups were determined by the absorption peak at 1730 cm^{-1} (aldehyde), 1719 cm^{-1} (ketone), 965 cm^{-1} (*trans*-vinylene), 909 cm^{-1} (vinyl), and 888 cm^{-1} (vinylidene). The equations used are those proposed by Sato[12] and have been used in previous works.[9,10]

Differential scanning calorimetry (DSC) measurements

Changes in the crystalline content and the melting temperature caused by irradiation were studied by differential scanning calorimetry using a Perkin–Elmer DSC 4 (Perkin Elmer Cetus Instruments, Norwalk, CT), under nitrogen atmosphere, and previously calibrated with an indium standard. About 6–7 mg of sample were accurately weighed in a standard aluminum pan. The pans were sealed, pierced, and heated from 0 to 180°C at a heating rate of 20°C/min.

Dynamic mechanical thermal analysis (DMTA)

Mechanical spectroscopy was performed in a dynamic mechanical thermal analyzer (DMTA) Mark II of Polymer Laboratories (Poole, UK), in the double-cantilever flexure measuring mode. Measuring scans were performed between −140 and 130°C at a heating rate of 1°C/min for five different frequencies: 0.3, 1, 3, 10, and 30 Hz. The DMTA software converts the measured force/displacement ratio to the storage (E') modulus through a "geometric constant" of the sample. The values of the storage modulus depend multiplicatively on the value of this factor, but the damping factor (tan δ) is independent of it. To obtain accurate values of the storage modulus, a geometric factor based on a free length calculated from an equation proposed by Read[14] was used.

RESULTS AND DISCUSSION

The comparative results of the effects produced by irradiation on the functional groups of polyethylenes aldehyde, ketone, *trans*-vinylene, vinyl, and vinylidene are shown in Figures 1 and 2. It was not possible to obtain acceptable spectroscopic results for PE 10062 irradiated with 100 Mrad because it was partially crosslinked and it was not possible to prepare films thin enough. The increase in concentration of ketonic and aldehydic groups was greater for high-density than for low-density polyethylenes. The concentration of vinyl and vinylidene groups did not show significant tendencies. The increase in concentration for the *trans*-vinylene group was similar for the three polyethylenes.
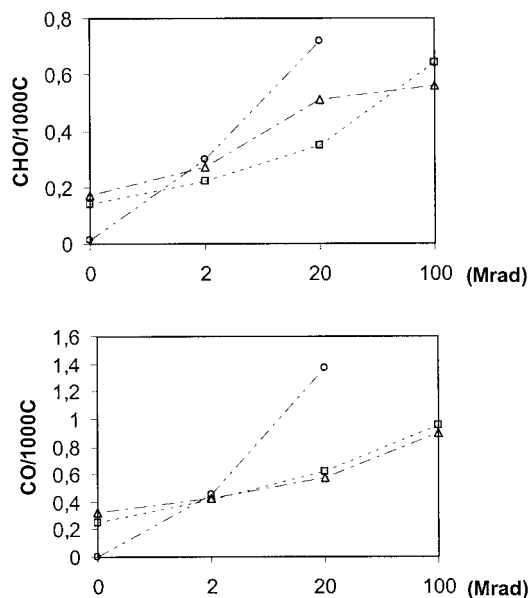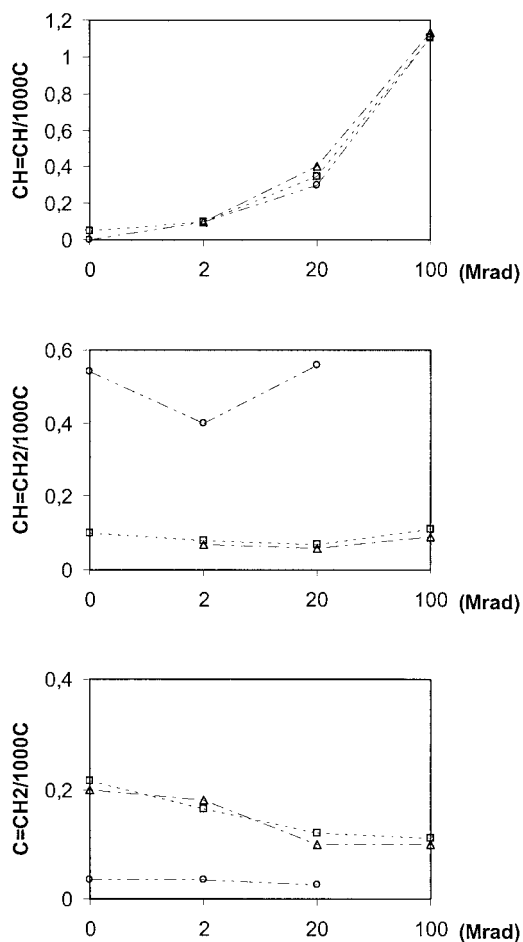

Figure 1 Variation of concentration of carbonyl groups: aldehyde (CHO) and ketone (CO), in PE 710 (△), PE 980 (□), and PE 10062 (○).

The crystalline content (X) and the melting temperature (T_m) of all the samples are shown in Tables I and II, respectively. The melting temperature was determined directly from the thermograms as the main endothermic peak. The crystalline content of each sample was determined by $X = (H_0 - H_c)/\Delta H_m$,[10] where H_0 and H_c are the enthalpies in the melt and crystalline states, respectively, per mass unit. Their difference was determined from the area of the endothermic peak ΔH. The enthalpy of melting ΔH_m of an infinite crystal per mass unit is 288 J/g.[13]

In all cases the melting temperature and the crystalline content decreased with the increase in the irradiation dose. Nevertheless, the effect of ionizing radiation depends on the type of polyethylene, given that the changes are more significant in high-density polyethylene.

These results provide evidence that irradiation increases the number of imperfections in molecular chains, which essentially constitute the amorphous region. When the dose of γ-radiation is high enough, not only the amorphous but also the crystalline regions may be attacked. Scissions of chains may be produced, which may be accompanied by crosslinking. The considerable shift of the main peak toward lower temperatures and the decreasing intensity of the endothermic peak in the high-density polyethylene are apparently attributed to this phenomenon.

To analyze the effect of irradiation on the crystalline and amorphous regions, dynamic mechanical spectra of the irradiated and unirradiated polyethylenes were obtained. The most important results obtained for each relaxation zone were analyzed separately.

Figure 2 Variation of concentration of functional groups: *trans*-vinylene (CH═CH), vinylidene (CH═CH₂), and vinylene (C═CH₂), in PE 710 (△), PE 980 (□), and PE 10062 (○).

γ-Mechanical relaxation zone

The γ-mechanical relaxation zone was observed between −140 and −90°C at the frequencies studied in this work. It was observed that the effect of the ionizing radiation on the γ-mechanical relaxation zone is more important for high-density polyethylene. The γ-mechanical peak changes its shape, its height, and its position on the temperature axis. These effects are less pronounced for low-density polyethylenes.

The first issue was to determine how many subrelaxations can be observed in this relaxation zone and

TABLE I
Variation of the Crystalline Content X (%) with the Radiation Dose

| Sample | Unirradiated | Irradiated (Mrad) | | |
		2	20	100
PE 710	—	61.87	—	61.32
PE 980	51.00	49.83	49.16	48.39
PE 10062	84.75	82.22	81.71	79.42

TABLE II
**Variation of the Melting Temperature T_m (°C) with the Radiation Dose**

| Sample | Unirradiated | Irradiated (Mrad) | | |
		2	20	100
PE 710	112.2	111.9	111.6	109.4
PE 980	111.5	111.3	110.3	110.4
PE 10062	136.6	133.5	—	132.7

to analyze the way the ionizing radiation affects each one of these subrelaxations. Aschcraft and Boyd[16] presented the values of E''/E''_{max} versus temperature and interpreted the peak symmetry as an indication of the existence of a single relaxation. Thus, Figure 3 illustrates the values of E''/E''_{max} versus temperature for all polyethylenes, both unirradiated and irradiated. These representations show the presence of a shoulder at lower temperatures, which is more evident in low-density polyethylenes. These results are in agreement with other results found in the literature[10,17] and confirm that this relaxation zone is formed by at least two overlapped relaxations, $γ_I$ and $γ_{II}$, in order of decreasing temperature. The $γ_I$ mechanical relaxation is more prominent than the $γ_{II}$. For high-density polyethylene the shoulder becomes more prominent when the irradiation dose increases. This result suggests that the $γ_{II}$ relaxation may be more important when the scissions and imperfections of the main chain increase.

To analyze in detail this relaxation zone the relationship between the relaxation times and the temperature has been adjusted to an Arrhenius equation,

$$f = f_0 \cdot \exp\left(\frac{-E_a}{RT_{max}}\right)$$

which allows the apparent activation energy E_a for this relaxation process to be calculated. The relaxation was characterized by means of the tan δ results, where T_{max} is the temperature of the maximum of tan δ in the range of −140 to 90°C, for each frequency f. The values obtained are shown in Table III. In all cases these values are slightly higher than those found in the literature.[17,19] The reason is primarily related to the method of measure. The values of E', E'', and tan δ were obtained at a low heating rate (1°C/min), although not strictly isotherm, and as demonstrated in previous studies,[9,10] the heating rate affects the position of the peaks. Nevertheless, the obtained values have to be interpreted as the conjugated value of the overlapped activation energies of both $γ_I$ and $γ_{II}$ relaxations. In high-density polyethylene, either unirradiated or submitted only to low doses of radiation, the most prominent relaxation is $γ_I$, which presents a higher activation energy; however, in low-density polyethylenes or in high-density polyethylene submit-
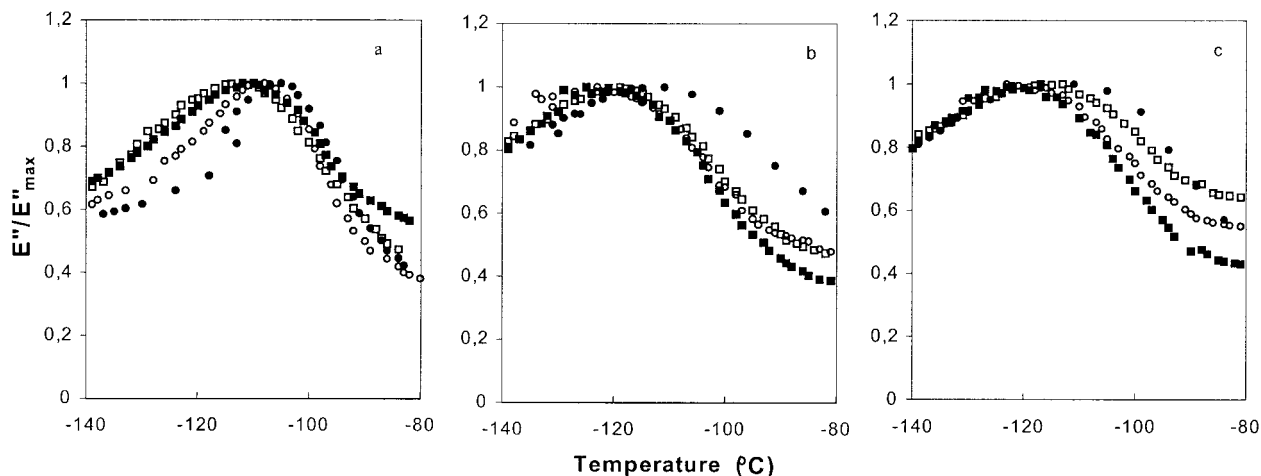
Figure 3 E''/E''_{max} at 10 Hz frequency versus temperature of polyethylenes: (a) PE 10062 unirradiated (●), irradiated 2 Mrad (○), irradiated 20 Mrad (■), and irradiated 100 Mrad (□); (b) PE 710 unirradiated (●), irradiated 2 Mrad (○), irradiated 20 Mrad (■), and irradiated 100 Mrad (□); (c) PE 980 unirradiated (●), irradiated 2 Mrad (○), irradiated 20 Mrad (■), and irradiated 100 Mrad (□).

ted to 100 Mrad irradiation the γ_{II} relaxation is more important and the total activation energy decreases.

Another interesting parameter to be analyzed is the height of the γ-peak. As can be seen in Table III, the height of the γ-peak increases in samples submitted to low doses of irradiation and the opposite effect can be observed for higher doses. These results are similar to those obtained for the same polyethylenes whose crystallinity indexes are lower as a result of irradiation (20 Mrad dose) followed by remelting, recrystallization, and annealing.[10] The reason for the decrease in the γ-peak cannot be attributed to the decrease of amorphous content because the total amorphous content increases, as shown in Table I.

β-Mechanical relaxation zone

The β-mechanical relaxation is a low relaxation zone located between the α- and γ-relaxations. As can be seen in Figures 4, 5, and 6, this relaxation zone is defined in both low- and high-density polyethylenes, although its position on the temperature axis is related to the polyethylene type. In lineal and high-density polyethylene the temperature peak at 10 Hz of frequency is about −40°C and in branched and low-density polyethylenes is about −10°C.

The effect of irradiation on the β-relaxation zone is different in both types of polyethylenes. In low-density polyethylenes the irradiation shifts the position on the temperature axis to lower temperatures and the height of the peak is similar for all irradiation doses. In high-density polyethylene the irradiation increases the height of the peak for low doses (2 and 20 Mrad) but the β-peak disappears for high irradiation doses (100 Mrad). The relationship between relaxation time and temperature has been adjusted again to the Arrhenius equation. The apparent activation energies, in case they could be calculated, are shown in Table III. The calculated values are similar to those obtained for similar polyethylenes[17] and the irradiation doses have not modified the obtained values.

These results are in agreement with those of Popli et al.,[18] who assigned this relaxation to segmental motion that occurs within the interfacial regions associated with the lamellar crystallites. Thus when the molecular chains that constitute the interfacial regions cannot move by the crosslinking effect, the β-relaxation disappears.

α-Mechanical relaxation zone

The α-relaxation occurs between 10 and 100°C at 10 Hz of frequency for the polyethylenes studied. It is a

TABLE III
Mechanical Characterization of Polyethylenes

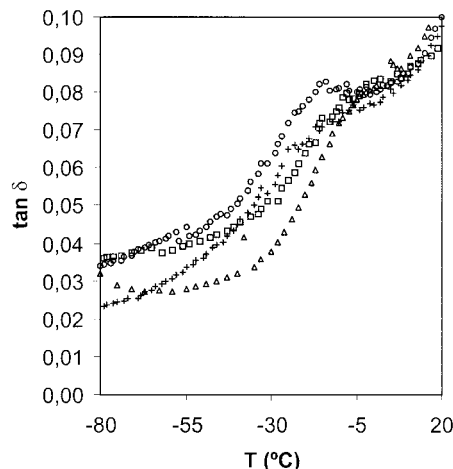| Sample	PE 710 Dose (Mrad)				PE 980 Dose (Mrad)				PE 10062 Dose (Mrad)			
	0	2	20	100	0	2	20	100	0	2	20	100
E_a (γ peak), kcal/mol	13	17	15	12	16	18	17	15	25	22	21	20
tan δ_{max} (γ peak), $\times 10^3$	42	43	39	40	40	44	40	36	40	45	44	29
E_a (β peak), kcal/mol	51	55	50	—	57	55	57	—	—	—	—	—
E_a (α peak), kcal/mol	—	—	—	—	—	—	—	—	29	29	29	28
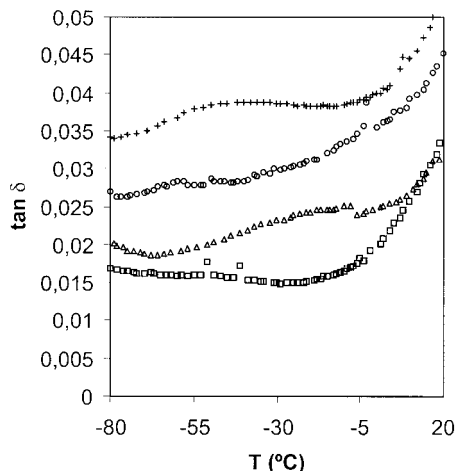
Figure 4 Values of damping factor (tan δ) versus temperature in the β-mechanical relaxation zone at 10 Hz frequency for PE 10062 unirradiated ($\triangle$), irradiated 2 Mrad ($\bigcirc$), irradiated 20 Mrad ($+$), and irradiated 100 Mrad ($\square$).

Figure 6 Values of damping factor (tan δ) versus temperature in the β-mechanical relaxation zone at 10 Hz frequency for PE 710 unirradiated ($\triangle$), irradiated 2 Mrad ($\bigcirc$), irradiated 20 Mrad ($+$), and irradiated 100 Mrad ($\square$).

complex process that may be formed by one, two, or more overlapped relaxations according to the complexity of crystalline morphology.[18]

The mechanical spectra of high-density polyethylene, represented by the values of E'' versus temperature, show a wide α-relaxation zone and only in unirradiated samples can a weak shoulder be observed. The irradiation decreases the height of the α-peak and the position on the temperature axis shifts to lower temperatures. On the other hand, when the values of loss modulus are plotted for low-density polyethylenes, the α-mechanical relaxation is shown as a shoulder of the more prominent β-relaxation.

The mechanical spectra represented by the values of tan δ versus temperature show a wide relaxation zone for unirradiated and irradiated polyethylenes (Figs. 7

and 8 for PE 710 and PE 10062, respectively). The radiation modifies the morphology of the samples and these processes affect the α-mechanical relaxation zone in the same way. The position of the α-relaxation shifts to lower temperatures when the calorimetric peak also shifts to lower temperatures. These results are in agreement with those of other investigators found in the literature[9,10,18] and confirm that the parameter that governs the position of the α-mechanical relaxation in the temperature axis is most probably the thickness of the crystallites. The apparent activation energy was calculated from the Arrhenius equation and the values obtained are presented in Table III. These values are in agreement with those obtained for similar polyethylenes and the radiation does not modify them.
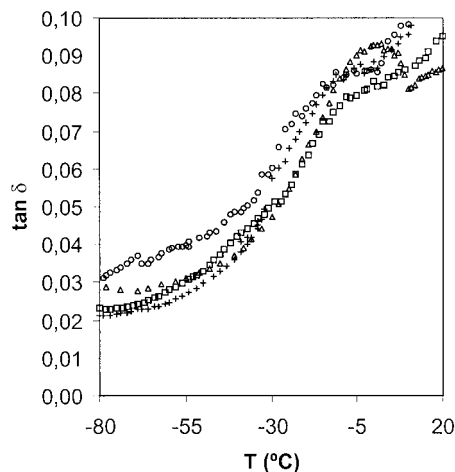
Figure 5 Values of damping factor (tan δ) versus temperature in the β-mechanical relaxation zone at 10 Hz frequency for PE 980 unirradiated ($\triangle$), irradiated 2 Mrad ($\bigcirc$), irradiated 20 Mrad ($+$), and irradiated 100 Mrad ($\square$).
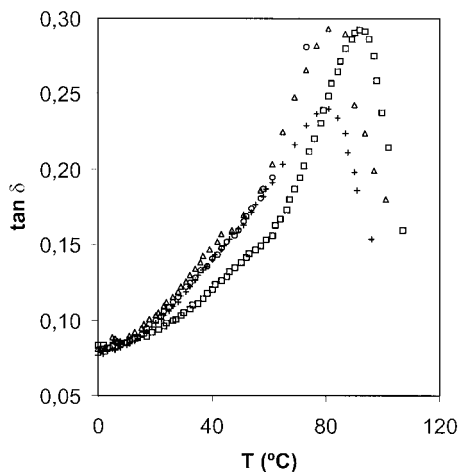
Figure 7 Values of damping factor (tan δ) versus temperature in the α-mechanical relaxation zone at 10 Hz frequency for PE 710 unirradiated ($\triangle$), irradiated 2 Mrad ($\bigcirc$), irradiated 20 Mrad ($+$), and irradiated 100 Mrad ($\square$).
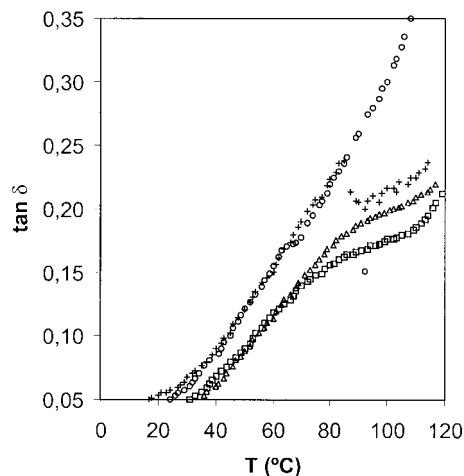
Figure 8 Values of damping factor (tan δ) versus temperature in the α-mechanical relaxation zone at 10 Hz frequency for PE 10062 unirradiated (△), irradiated 2 Mrad (○), irradiated 20 Mrad (+), and irradiated 100 Mrad (□).

ular origin of this relaxation zone instead of the amorphous content.

The height and the position of the α-mechanical relaxation are affected in the same way as are the calorimetric peaks, suggesting that it likely depends on the thickness of the crystallites.

CONCLUSIONS

Irradiation modifies the chemical structure and the morphology of polyethylenes. However, these changes are different according to the type of polyethylene and the radiation dose. It has been found that, in all cases, the melting temperature and the crystalline content decrease with the increasing irradiation dose, which effects are more significant in high-density polyethylene.

The height of the γ-mechanical relaxation zone increases in the irradiated polyethylenes with low irradiation doses, perhaps because of internal defects, but higher doses cause the opposite effect, suggesting that the crosslinking resulting from irradiation makes motion of the molecular chains more difficult.

The height of the β-mechanical relaxation decreases in all the irradiated polyethylenes. Again, the molecular defects (internal insaturations) govern the molec-

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