Relationship between the Mechanical Relaxations in the α Zone and the Calorimetric Transitions in Low Density Polyethylene

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Synopsis

The α-relaxation spectra of LDPE, irradiated and unirradiated, has been compared with their calorimetric thermograms. There exists a correlation between the two mechanical relaxations that appear in the α zone and the two fusion peaks observed in the calorimetric thermograms, confirming that the parameter that governs the temperature of the relaxations α_I and α_{II} is the most probable crystallite thickness, whereas the height of the α-relaxation zone, as measured by means of tan δ_{max}, depends on the total crystalline content of the sample.

INTRODUCTION

The mechanical α-relaxation zone in PE is a complex region, formed by two or more superposed relaxations. As seen from the reviews of McCrum,[1] Popli,[2] and C. Boyd,[3,4] the molecular origin and discussion of physico-chemical variables on which it depends is a controversial topic. Nevertheless, the most recent studies[2,5] point to the idea that the temperature position of the α-relaxation is governed by the mean thickness of the crystallites which form the crystalline phase in PE. This mean thickness also governs the position of the fusion peaks that appear in the thermograms of these polymers. So a relationship between the position of the α-peaks and the calorimetric ones can be presumed.

EXPERIMENTAL

The polymers used were commercial PE 710, 980, 519, 549, and XP5204II from Dow Chemical Ibérica S.A. (Tarragona). Samples of them were irradiated in air at constant temperature of 20°C with γ radiation from a Co^{60} source. The irradiation rate was 1.4×10^{-4} Mrad/s. The total dose was 20 Mrad. The thicknesses of samples were about 1–1.5 cm.

Every sample was characterized by determination of the functional groups ketone, aldehyde, vinyl, vinylidene, and transvinylene,[6] by infrared spectroscopy (IR), of the weight mean values of the molecular weight M_w by steric exclusion chromatography (SEC) (46.8×10^3–82.2×10^3), of the mean molecular weight in number M_N (6.2×10^3–11.2×10^3), and of the polydispersity degree (6.2–7.5).

CCC 0021-8995/87/082819-10$04.00

TABLE I

Annealing temp (°C)	Time (h)
Unirradiated polyethylenes	
75.3	46
82.3	48
89.8	6
99.6	27
102.3	48
107.2	24
Irradiated polyethylenes	
76.1	48
89.8	6
99.6	41
106.9	27

Prismatic bar samples were cut from a plate crystallized from melted polymers. Each sample was subjected to an annealing process which consisted in heating it until a temperature T (given in Table I) keeping T constant from 6 to 48 h, and then cooling it in liquid N_2.

The changes in morphology and in the fusion temperatures caused by the different annealing processes were studied by scanning differential calorimetry in a METTLER TA 3000 thermoanalyzer, with a 10K/min scan velocity. The total crystalline content of each sample was determined through

$$X = (H_a - H_c)/H_m \qquad (1)$$

where H_a and H_c are the enthalpy in the melt state and the crystalline state, respectively, their difference being obtained from the thermogram, and H_m is the change in melting enthalpy of a perfect crystal of infinite size. The value of H_m is 290 J/g.[7]

The mechanical spectra were obtained in a POLYM-LAB Dynamic Mechanical Thermical Analyzer (DMTA), an apparatus which gives directly the storage modulus E' and the loss tangent tan δ. Measurements were carried through at 1Hz and from −80°C to 100°C, with a heating velocity of 1K/min. This last value has been preferred to others proposed,[5] because thermal equilibrium can be better achieved with it; at higher heating velocities, such as 3 K/min, the position of the peaks can be seen to shift towards higher temperatures, probably due to the lack of thermal equilibrium.

RESULTS AND DISCUSSION

Figures 1 and 2 show the thermograms of each PE for the different thermal treatments. In each case there are two melting peaks, generally overlapped, one at lower temperatures—labeled as I—and another at higher temperatures —labeled as II. The multiplicity of melting peaks in high and low density polyethylenes has already been noted by other authors,[8-10] and is attributed
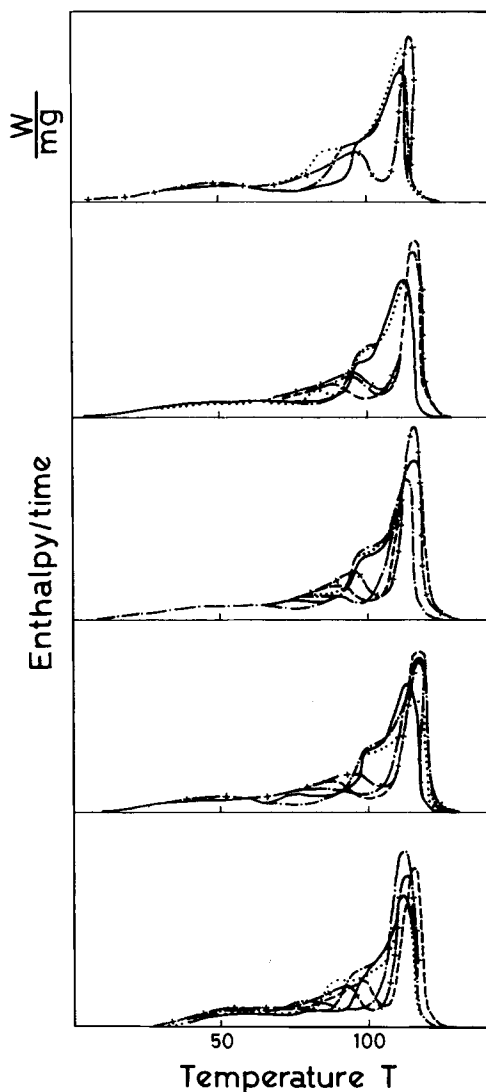
Fig. 1. Calorimetric thermograms of unirradiated polyethylenes. The annealing temperatures were 75.3°C (···), 82.3°C (– ·· –), 89.8°C (——), 99.6°C (— · —), 102.3°C (---), 107.2°C (— + —).

to the distribution of crystallite thicknesses around two typical sizes, which arise during the thermal history undergone by the sample.

When PE plates crystallize from the melt through rapid cooling a distribution of crystallite thickness is obtained, the crystals being bigger in the regions where molecular chains have no defects (branching, unsaturations, ...), and smaller in regions with more defects. Nonetheless, when the sample is subjected to a subsequent annealing process two phenomena take place: On the one hand, there is an increase in crystallite size due to the diffusion of the molecules of the interspherulitic zone into the crystalline zones, and, on the other hand, there is the segregation in two crystalline zones, the one with
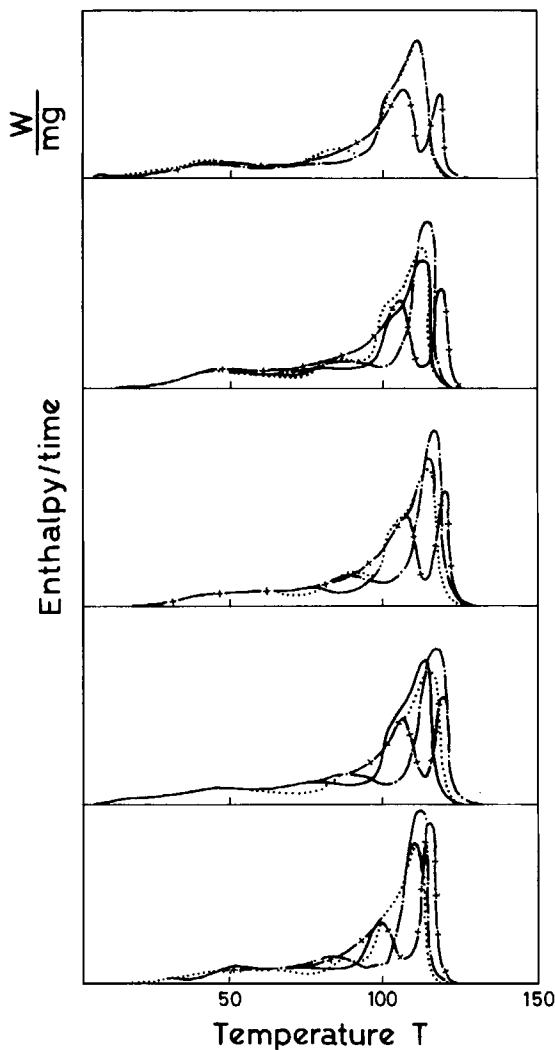
Fig. 2. Calorimetric thermograms of irradiated polyethylenes. The annealing temperatures were 76.1°C ($\cdots$), 89.8°C (——), 99.6°C (— · —), 106.2°C (— + —).

lamellae formed by low molecular weight molecules and the other formed by lamellae of higher molecular weight molecules, due to a mechanism of lamellar diffusion, as indicated by several authors.[11–13]

The crystalline content of each sample has been calculated with eq. (1), and the results are given in Table II. Figures 3 and 4 give as example the values of E' and tan δ for the PE 549 samples, irradiated and without irradiation, for the different thermal treatments. Similar representations have been obtained for each PE.[6]

These figures show the β-relaxations around $-20°C$, whose position and height is almost unmodified as a consequence of irradiation or annealing, and the α-relaxation, between 10 and 100°C. This last relaxation zone consists of the α_I and α_{II} peaks, in order of increasing temperature, It is observed that

TABLE II
Crystalline fraction in unirradiated polyethylenes

Sample	Annealing temperature (°C)					
	75.3	82.3	89.8	99.6	102.3	107.2
710	50	79	48	50	49	51
549	49	49	46	50	50	50
519	46	46	45	47	48	48
980	46	48	44	—	—	46
XP5204II	46	46	47	48	48	46

Crystalline fraction in irradiated polyethylenes

Sample	Annealing temperature (°C)			
	76.1	89.8	99.6	106.9
710	47	48	49	49
549	48	45	46	45
519	44	44	45	45
980	44	44	—	44
XP5204II	44	46	45	45

both peaks overlap or separate with the same pattern as do the calorimetric peaks corresponding to the melting of the crystalline zones related to the peaks I and II.

In order to make this effect more apparent, Figures 5 and 6 show the values of tan δ vs. T, for some of the PEs whose samples were subjected to two different annealing temperatures, for which both melting peaks appear overlapped and separated. It was observed that the relaxations here termed as α_I and α_{II} appear also overlapped or separated, respectively.

In order to study quantitatively the temperature dependence of the α_I- and α_{II}-relaxations on the (most probable) crystallite thickness, Figure 7 shows the temperature at which tan δ achieves its maximum vs. the reciprocal of the melting temperature. This magnitude— and not the crystallite thickness calculated from Thomson's formula as suggested by Illers and Hendus[14]—has been chosen for representation because, as stated by Zoepfl et al.[15,16], h_m^0 is independent of dose up to 20 Mrad but both σ_e and T_m^0 increase with increasing dose in a manner they did not quantify. Thus it cannot be assured that the values of σ_e and T_m^0 are applicable to the irradiated PEs.

The α_{II}-relaxation is more prominent in those samples which were subjected to annealing temperatures of 76.1; 89.8; 99.6°C in irradiated PEs and of 75.3; 82.3; 89.8; 99.6; 102.3°C in the unirradiated PEs, thus its temperature position is little affected by the α_I-relaxation. Figure 7 shows the temperature of the maximum in tan δ vs. the melting temperature of the calorimetric melting peak II.

In those cases where the mechanical α_I- and α_{II}-relaxations can be graphically separated (annealing temperatures of 106.9 and 107.2°C) the temperature of the α_I peak has been determined. Figure 7 shows also these values as function of the reciprocal of the temperature of the melting peak I. From this graph it can be observed that the relationship between the temperature of
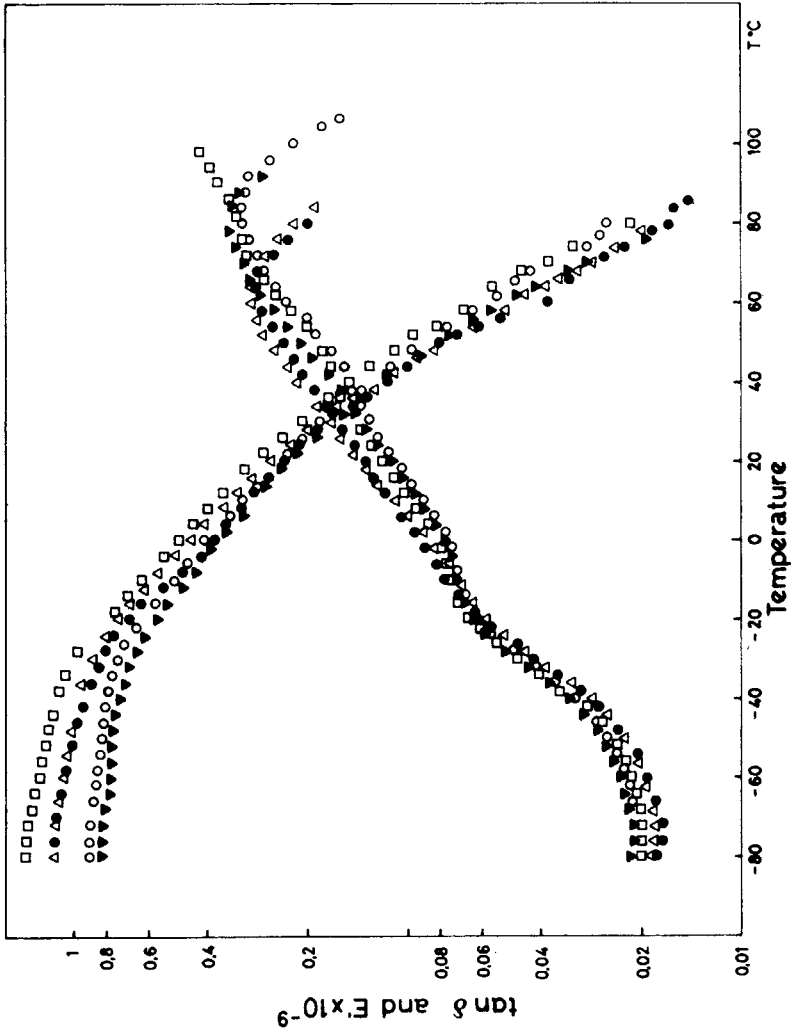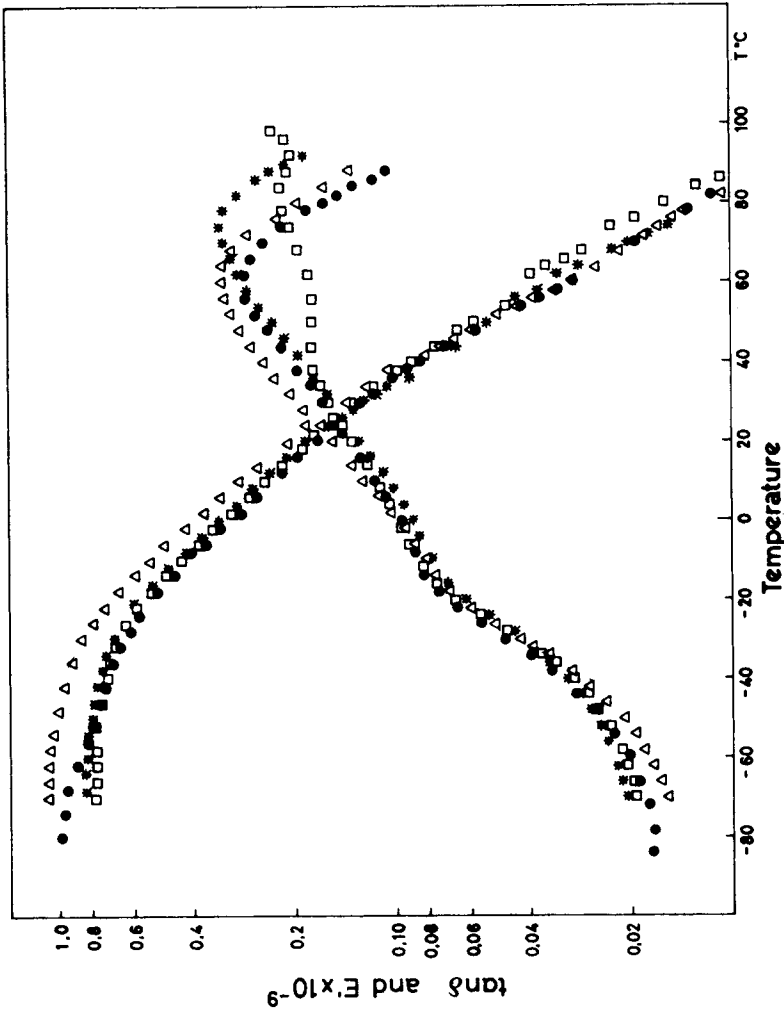
Fig. 3. Values of storage modulus and tan δ vs. temperature $T(°C)$, for the unirradiated polyethylene 549. The annealing temperatures were 75.3°C (△), 89.8°C (●), 99.6°C (▼) 102.3°C (○), and 107.2°C (□).

Fig. 4. Values of storage modulus and tan δ vs. temperature $T(°C)$ for the irradiated polyethylene 549. The annealing temperatures were 76.1°C (△), 89.8°C (●), 99.6°C (*), and 106.9°C (□).
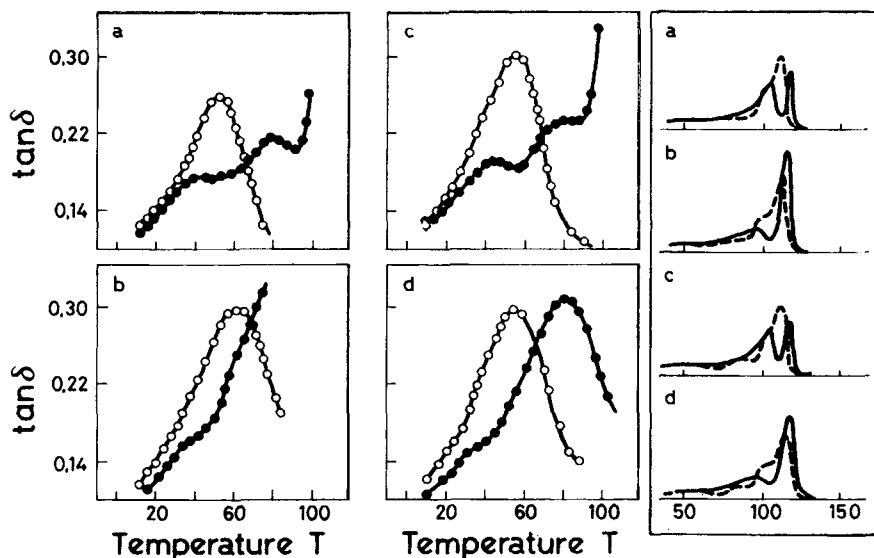
Fig. 5. Correlation between the calorimetric peaks I, II and the α_I and α_{II} mechanical relaxations: (a) irradiated PE 549; (b) unirradiated PE 549; (c) irradiated PE XP5204II; (d) unirradiated PE XP5204II.
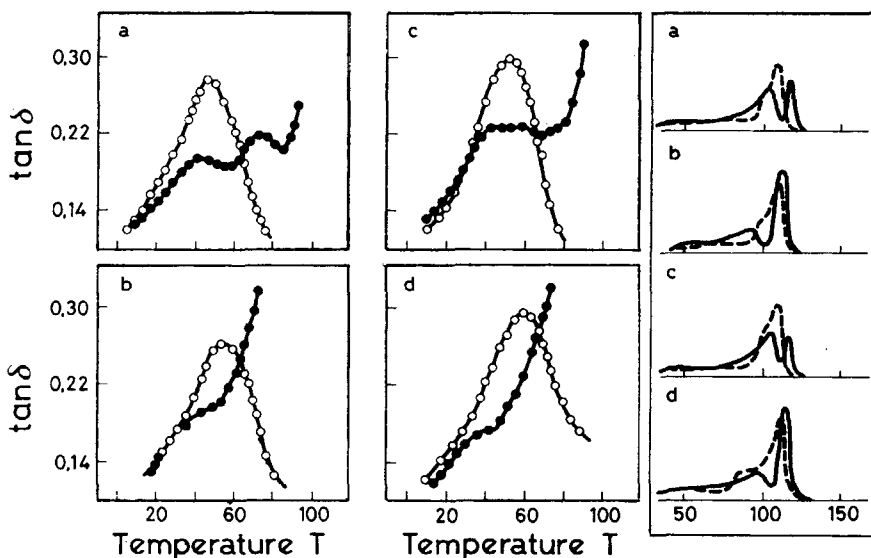

Fig. 6. Correlation between the calorimetric peaks I, II and the α_I and α_{II} mechanical relaxations: (a) irradiated PE 519; (b) unirradiated PE 710; (c) irradiated PE 980; (d) unirradiated PE 980.

$\tan \delta_{max}$ and the temperature of the melting peak is the same for both relaxations. Thus, it can be concluded that the relaxations α_I and α_{II} take place in the crystalline regions, that the molecular origin is the same for both, and that their temperature depends on the most probable crystallite thickness that represents the thickness distribution.
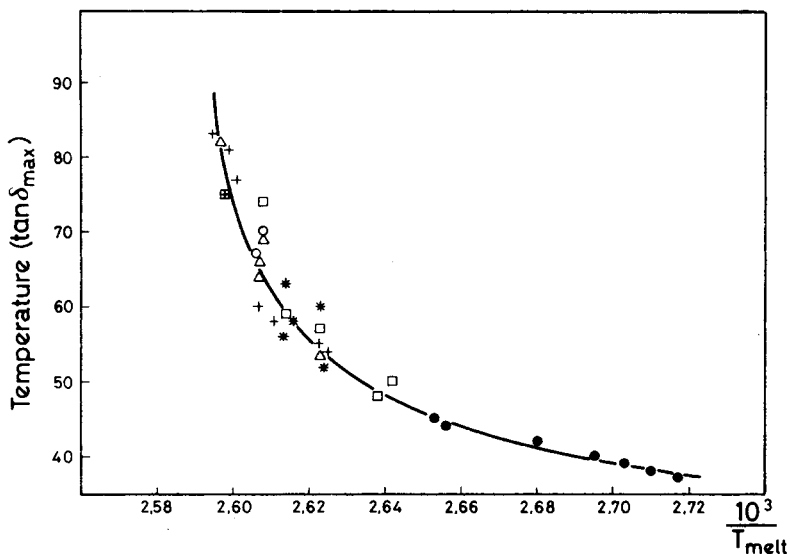
Fig. 7. Relationship between the temperature of tan δ_{max} in the relaxation α_I and α_{II} and the reciprocal of melt temperature of the calorimetric peaks I and II. The symbols corresponding to the α_{II} relaxation in the polyethylenes: (□) 519; (△) 549; (○) 710; (∗) 980; (+) XP 5204II; (●) α_I-relaxation.

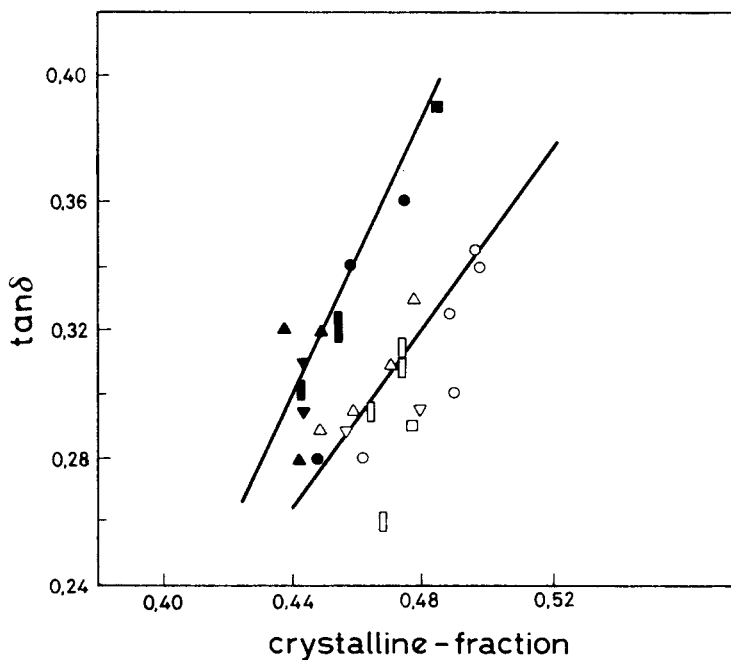Fig. 8. Relationship between the values of tan δ_{max} and the crystalline fraction. Irradiated polyethylenes: (□) XP5204II; (■) 710; (●) 549; (▲) 519; (▼) 980. Unirradiated polyethylenes: (▮) XP5204II); (□) 710; (○) 549; (△) 519; (▽), 980.

Figure 8 shows for each sample the values of $\tan \delta_{max}$ as a function of the respective total crystalline content, the observed relationship being increasing. This fact supports the assignment of the α-relaxation zone to molecular motions in the chains forming the crystalline phase of these PEs.

CONCLUSIONS

The relationship between the different peaks of the α mechanical relaxation zone and the melting peaks that appear in the calorimetric thermograms has been studied for LDPEs, irradiated and unirradiated. The complexity of the mechanical α-relaxation zone is due to the existence of a binodal lamellar distribution, whose presence is caused by the thermal history of the sample.

The temperature of the α_I- and α_{II}-relaxations is governed by the most probable crystallite thickness. This relationship has not been obtained directly, but through the reciprocal of the melting temperatures of regions I and II.

In the LDPEs, irradiated (20 Mrad) and unirradiated, the intensity of the α-relaxation zone as represented by the height of $\tan \delta$ is governed by the total crystalline content of the sample.

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