

Dielectric Relaxation Study of Low-Density Polyethylene by Thermally Stimulated Depolarization Currents and Thermal Sampling

J. M. MESEGUER DUEÑAS, J. L. GOMEZ RIBELLES, and
R. DIAZ CALLEJA, *Laboratory of Thermodynamics and Physical
Chemistry, Universidad Politécnica de Valencia, P.O. Box 22012,
Valencia, Spain*

Synopsis

The dielectric relaxation zone of a low-density polyethylene has been studied by thermally stimulated depolarization currents (TSDC) and thermal sampling (TS). Three relaxations have been found in this zone, which have been labeled γ_I , γ_{II} , and γ_{III} in decreasing order of temperature. Samples of different crystallinities were subjected to several thermal treatments in order to study the molecular origin of each relaxation. The γ_I relaxation intensity changes with the thermal treatment, while the intensity of the γ_{II} relaxation is only slightly modified. Using TS it has been proved that the γ_I relaxation fulfils the compensation law with a high level of significance. Nevertheless, the experimental data are not enough to verify the γ_{II} and γ_{III} relaxation.

INTRODUCTION

The study of the dielectric relaxations of polyethylene (PE) is very complex, owing to the number of factors that affect its behavior such as: semicrystalline structure, branching, molecular weight, saturations, polar groups, and thermal treatments that affect crystallinity and crystallite size.

The slight polar character of PE presents experimental difficulties and can necessitate oxidation of the samples in order to increase the intensity of experimental measurements.

In order to study the dielectric relaxation spectrum of PE, three complex characteristic relaxation zones (called α , β , and γ from major to minor temperature) are defined. This nomenclature agrees with that used in dynamical mechanical measurements.

It is generally assumed that the γ relaxation zone of PE is due to molecular motions taking place in the amorphous phase of the polymer.¹⁻⁶ Alternative mechanical and dielectric measurements of the relaxation zone of PE have shown more than one relaxation peak.¹⁻¹⁰

In this work thermally stimulated depolarization currents (TSDC) and thermal sampling (TS) techniques have been used to study the γ relaxation zone of a branched LDPE. Both techniques are appropriate to this objective because of their high resolution, and their mutual complementarity.

EXPERIMENTAL

A Dow Chemical PE710 was used in this work. It is a low-density PE, with a branching degree 1.9 $\text{CH}_3/100 \text{CH}_2$. The average molecular weights were $\bar{M}_n = 7.53 \times 10^3$, $\bar{M}_w = 4.76 \times 10^4$, $\bar{M}_z = 1.35 \times 10^5$.¹¹

Films of 0.35 mm thickness were obtained by melting the PE for 1 h between two plates of glass at 15 K over the melting temperature (383.5 K), and then cooled, without controlling, to room temperature. The films were then subjected to the following thermal treatment: annealing for 1 h at 393 K and quenching to room temperature in water.

Films of about 30 mm diameter were utilized in experimental measurements. They were metalized with colloidal silver and dried in a vacuum.

The crystallinity was measured in a Perkin'Elmer DSC4 calorimeter, assuming a value for the heat of fusion of PE of $H_m = 70 \pm 1$ cal/g.¹² The melting temperature was 383.5 K.

The TSDC and TS experimental equipment, with standard characteristics,¹³⁻¹⁵ was able to scan in the temperature range from 110 to 470 K. A Keithley 642 electrometer, manufactured in the United States (with a sensitivity of 10×10^{-16} A) was used to measure the depolarization currents.

The parameters of all TSDC measurements were: polarization temperature 291 K, depolarization temperature 113 K, polarization time 10 min, electric field applied 5 kV/mm, and heating rate 2 K/min. The depolarizations were performed between 113 K and 330 K.

In the TS measurements, described below, the electric field applied and the heating rate were the same as in TSDC measurements.

RESULTS AND DISCUSSION

TSDC measurements were conducted on a sample subjected to the thermal treatment described in the Experimental section. Figure 1 shows the results of such a test in the temperature range between 113 and 185 K. Three maxima in

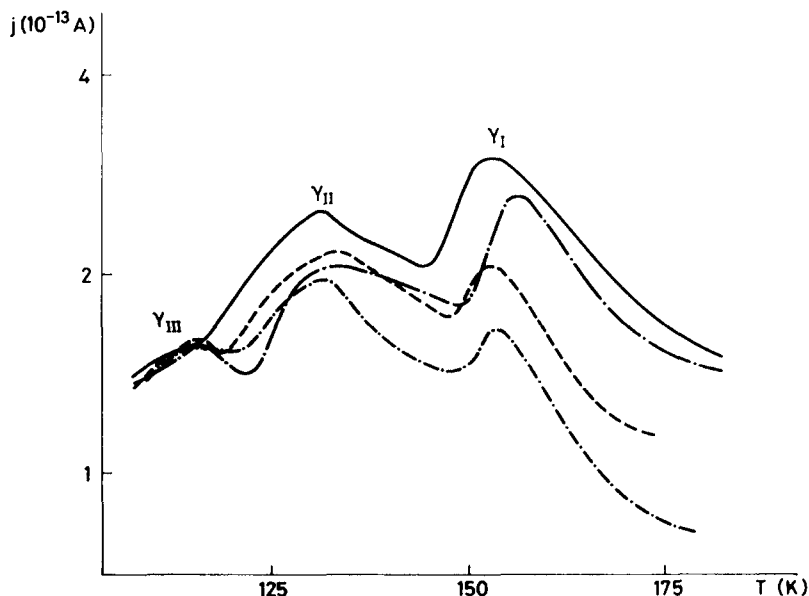


Fig. 1. Depolarization current measured using TSDC technique on a sample subjected to the thermal treatment described in the Experimental section. Annealed at 393 K and quenched to room temperature (—), and on samples recrystallized at different temperatures: 343 K (---), 363 K (-·-·-), and 373 K (·····).

TABLE I
Crystallinity of the Samples Subjected to Different Thermal Treatments

Recrystallization temperature (K)	Melting enthalpy (J/g)
Without recrystallization	138
343	138
363	141
373	139

the depolarization current can be observed at 153, 131, and 116 K. The corresponding relaxation processes will be called γ_I , γ_{II} , and γ_{III} , respectively.

The existence of at least two relaxations in the relaxation zone has been proved from both alternative dielectric⁴⁻⁹ and mechanical^{1-3,10} measurements. The one at the highest temperature appears more clearly. The other one appears as a shoulder. These two relaxations must be related to the γ_I and γ_{II} shown in Figure 1. They appear in TSDC at a lower temperature and less overlapped than in alternative measurements because of the low equivalent frequency of the TSDC measurements (approximately 10×10^{-3} Hz with the experimental conditions of this work). This also allows the γ_{III} peak to emerge from the other two, while in other types of measurements it does not appear.

Several samples prepared from the same original sheet of polymer were recrystallized at different temperatures for 24 h. Thus samples with different melting enthalpy were obtained by differential scanning calorimetry, which are given in Table I. The experimental results of the TSDC scans of each sample is shown in Figure 1. The three relaxations appear in all the samples. The intensity of the γ_I relaxation is strongly dependent on the crystallinity, decreasing when the latter increases (Fig. 2). The changes caused by thermal treatments on the melting enthalpy, that is, on the absolute crystallinity of the samples, are very little. The intensity of the γ relaxation is affected by the treatment, whereas the intensity and temperature of both the γ_{II} and γ_{III} relaxation remains unaltered.

Figure 2 shows the differential calorimetry scans for each one of the treatments. It is observed that the spectrum is a complex one, with the melting process starting at low temperatures. The recrystallization caused by the treatments significantly modifies the spectra or, what amounts to be the same, the crystalline morphology of the polymer. This suggests that, in branched PE, the γ_I relaxation, commonly assumed to originate in the amorphous phase, may be further related to the crystalline morphology of the polymer.

Thermal Sampling Study

The TS technique, initially proposed by Bucci and Fieschi¹⁶ has been used in the study of the γ relaxation of the LDPE because it is an especially appropriate method to the study of distributed dielectric relaxations as well as in complex relaxation processes with several peaks overlapped.

TS experiments are composed of a polarization and a depolarization step (Fig. 3). In this work, the polarization of the sample did not include an isothermal step. The sample was cooled at a constant rate and the electric

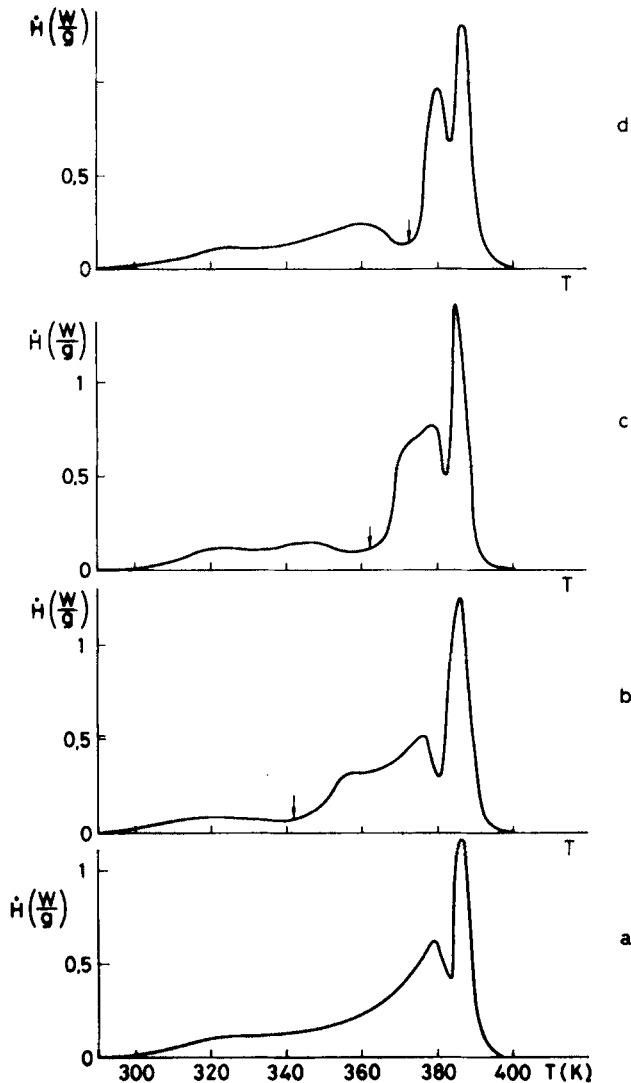


Fig. 2. Heat flux as a function of the temperature on samples with different treatments: (a) Sample annealed at 393 K and quenched at room temperature. (b) Sample recrystallized at 342 K. (c) Sample recrystallized at 363 K. (d) Sample recrystallized at 373 K.

field was applied at a temperature T_p (polarization temperature) and suppressed, short circuiting the sample at the temperature T_d (depolarization temperature), the polarization window being $\Delta T = T_p - T_d = 5$ K in this work. The sample was cooled at the same rate until the temperature T_0 was reached. Then, after an isothermal depolarization step, the sample was heated at 2 K/min measuring the thermostimulated depolarization current.

The current peak thus obtained is approximated to a single Debye peak if the polarization window is narrow enough. The relaxation time corresponding to each polarization window $\tau(T)$ can be obtained from the experimental depolarization current at each temperature as the total polarization divided

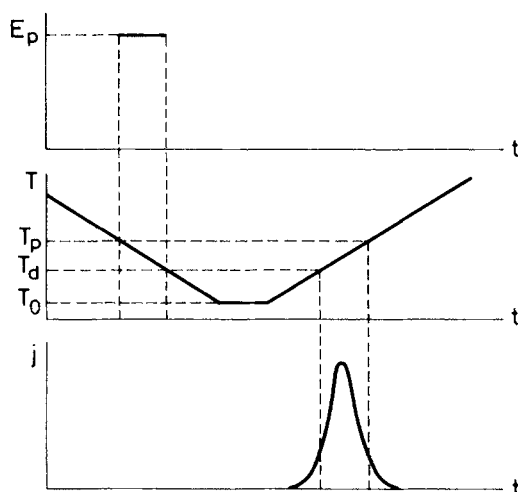


Fig. 3. Schematic representation of the electric field, temperature, and current intensity corresponding to a thermal sampling test. See text.

by the intensity of the current $j(T)$:

$$\tau(T) = (1/q) \int_T^{\infty} j(T) dT / j(T)$$

T is the sample temperature and q the heating rate.

Since the $\ln \tau(T)$ against $1/T$ can be approximated as a straight line, it is possible to use the Arrhenius model to fit the data of $\tau(T)$:

$$\tau(T) = \tau_0 \exp(E/kT)$$

k is the Boltzmann's constant.

The characteristic parameters E (apparent activation energy) and $\ln \tau_0$ can be determined for each polarization window.

TS experiments were conducted in the temperature range from 113 to 198 K. Table II shows the values of E and $\ln \tau$ for each polarization window. When these values are represented against the polarization temperature T_p (Fig. 4), three relaxation zones can be observed, which appear in the same temperature ranges as the three relaxations γ_I , γ_{II} , and γ_{III} found in TSDC measurements. Both E and $\ln \tau_0$ are distributed in the three relaxations as shown in their change with T_p within the temperature range of each one.

The Eyring equation:

$$\tau = (h/kT) \exp(\Delta G/kT)$$

(h is the Planck's constant and ΔG is the Gibbs free energy) has been used to check if the three relaxations follow the compensation law. ΔS and ΔH (the entropy and the enthalpy of the relaxation, respectively) were calculated by representing $\ln(\tau T)$ against $1/T$ for each polarization window of the TS experiment. Table III shows the calculated values and the linear dependence

TABLE II
Apparent Activation Energy, $\ln \tau_0$ and Polarization Temperature of
Each Thermal Sampling Tests

T_p (K)	E (kcal/mol)	$\ln \tau_0$
113	4.2	-13.5
118	4.2	-13.0
123	3.3	-9.0
128	2.1	-3.0
133	4.4	-12.3
138	5.4	-15.0
143	5.0	-12.7
148	4.6	-10.6
153	5.7	-13.6
158	10.6	-28.8
163	11.8	-31.7
168	11.0	-28.3
173	9.6	-22.6
178	9.1	-20.4
183	10.4	-25.8
188	7.7	-14.9
193	6.6	-11.0
198	6.5	-10.6

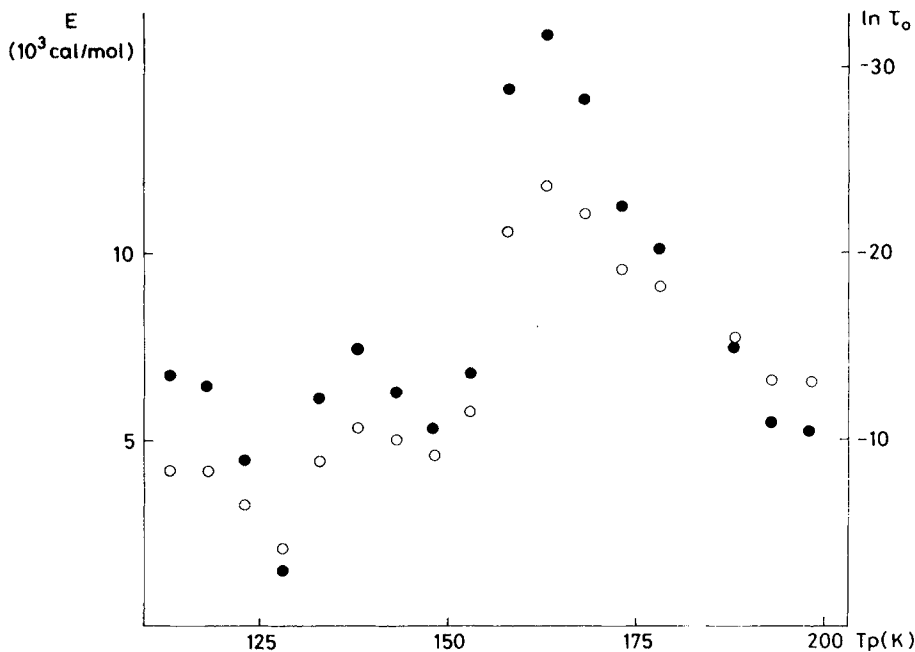


Fig. 4. Characteristic parameters E (○), activation energy, and $\ln \tau_0$ (●), preexponential factor, of the depolarization current measured in different thermal sampling tests, as a function of the polarization temperature.

TABLE III
 Enthalpy Increment, Entropy Increment, and Polarization Temperature of
 Each Thermal Sampling Test

T_p (K)	ΔH (kcal/mol)	ΔS (cal/mol · K)
113	3.8	-33.3
118	3.9	-33.4
123	3.0	-41.8
128	1.8	-53.0
133	4.2	-34.8
138	4.9	-30.5
143	4.6	-34.3
148	4.2	-38.4
153	5.6	-31.4
158	10.7	0.8
163	11.5	3.8
168	10.1	-6.5
173	9.7	-11.5
178	8.6	-20.0
183	10.3	-6.4
188	7.2	-30.5
193	6.2	-35.5
198	6.3	-38.0

between ΔH and ΔS within the temperature range of each relaxation is shown in Figure 5. Thus the three relaxations seem to follow the compensation law. It is important to note that the compensation temperature for each relaxation (126 K for the γ_I , 88 K for the γ_{II} , and 103 K for the γ_{III} relaxation) is higher than the temperature range in which the relaxation appears both in TSDC or TS measurements, an unusual fact in this kind of measurements. Ronarc'h et al.¹⁷ found only one relaxation in the γ relaxation zone of LDPE using the same technique than that used in this work, but with a heating rate of 10 K/min. The compensation law is shown to be satisfied by this relaxation with a compensation temperature of 258 K. Probably the relaxation found by Ronarc'h et al. corresponds to the overlapping of the three relaxations found in this work because of the high heating rate used. Berticat et al.¹⁸ have shown by calculating relaxation spectra as a function of frequency from the CDT experimental results that as the heating rate increases the fine structure of the relaxation disappears. In fact, the LDPE measured by Berticat in CDT at 12 K/min gives a single maximum γ , although this maximum shows evidence of two subrelaxations in the form of shoulders in the peak. In fact, if an average value of ΔH and ΔS is calculated for each relaxation reported here, the three corresponding points are aligned in a ΔH versus ΔS plot, leading to a compensation temperature of 235 K, very similar to that found by Ronarc'h's group.

The tests of Exner and Johnston-Lyons¹⁷ have been used to check the consistency of the experimental results, leading to a correlation coefficient of 0.99 for the three relaxations. The hypothesis test proposed by Krug et al.¹⁹ was used to reject the hypothesis of a purely statistic linear dependence of ΔS and ΔH . The γ_I relaxation satisfies this test with a significance of 90%, but

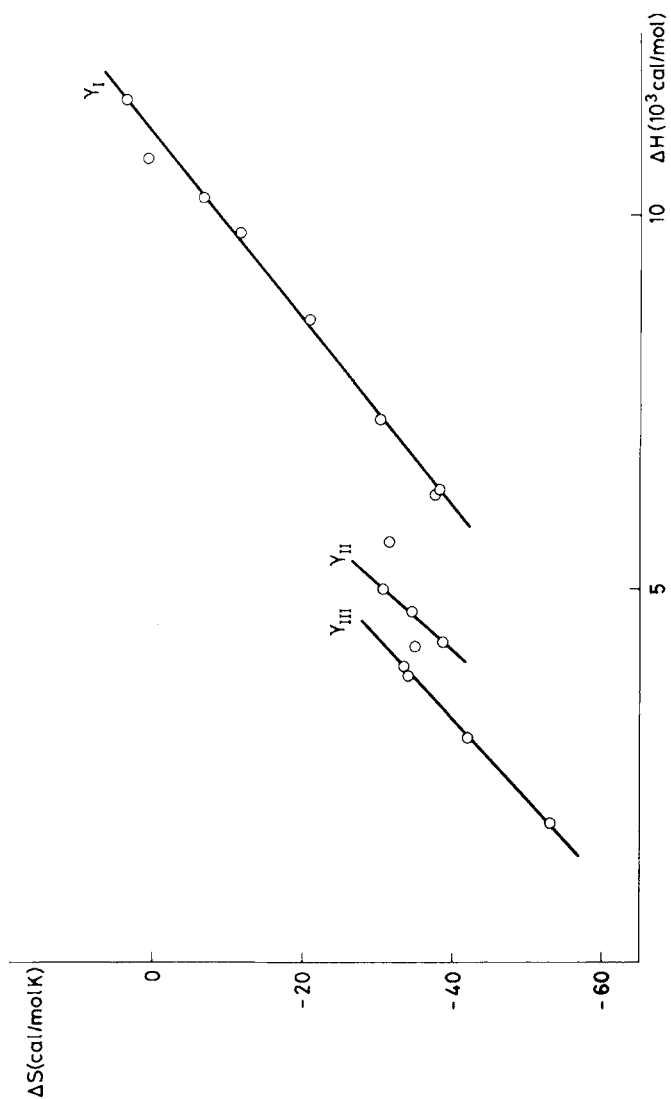


Fig. 5. Diagram representing the entropy increment against enthalpy increment of the relaxation, as calculated, using Eyring equation, from each thermal sampling tests. The straight lines link the points corresponding to the same relaxation (i.e., obtained from experimental TS tests with polarization windows in the range temperature of this relaxation).

the γ_{II} and γ_{III} relaxations have not enough significance due to the scarce number of experimental data points.

CONCLUSIONS

The existence of three relaxations in the γ zone of LDPE has been proved by TSDC and TS. The intensity of the relaxation appearing at the highest temperature (γ_I), ascribed to molecular motions taking place in the amorphous phase of the polymer, depends on thermal treatment. The compensation law is fulfilled by this relaxation.

References

1. K. H. Illers, *Koll. Z. Z. Polym. Sci.*, **251**, 394 (1973).
2. K. H. Illers, *Coll. Polym. Sci.*, **252**, 1 (1974).
3. K. H. Illers, *Koll. Z. Z. Polym. Sci.*, **231**, 622 (1969).
4. M. Kakizaki and T. Hideshima, *J. Macromol. Sci. Phys.*, **8**, 367 (1973).
5. S. Fukui and T. Hideshima, *Jap. J. Appl. Phys.*, **16**, 159 (1977).
6. S. Fukui and T. Hideshima, *Jap. J. Appl. Phys.*, **16**, 497 (1977).
7. W. Pechhold, *Koll. Z. Z. Polym.*, **228**, 1 (1968).
8. W. Pechhold and B. Stoll, *Ber. Busengs Phys. Chem.*, **74**, 887 (1970).
9. W. Pechhold, *J. Polym. Sci.*, **32**, 123 (1971).
10. R. N. Gray and N. G. McCrum, *J. Polym. Sci. A-2*, **7**, 1329 (1969).
11. J. M. Salla, thesis, Barcelona, Spain (1979).
12. K. H. Illers, *Makromol. Chem.*, **113**, 1 (1968).
13. J. Vanderschueren, Thesis, Lieja, Belgium (1974).
14. J. Van Turnhout, "Thermally Stimulated Discharge of Electrets," in *Electrets*, G. M. Sessler, ed. Springer-Verlag, Berlin, 1980.
15. M. Zielinski and M. Kryszewski, *J. Electrostatics*, **3**, 69 (1977).
16. C. Bucci and R. Fieschi, *Phys. Rev. Lett.*, **12**, 16 (1964).
17. D. Ronarc'h, P. Andreu, S. Haridoss, and J. Herron, *J. Appl. Phys.*, **54**, 8 (1983).
18. P. Berticat, B. Ai, H. The Ciam, D. Chatain, and C. Lacabanne, *Makromol. Chem.*, **177**, 1583 (1976).
19. R. R. Krug, W. G. Hunter, and R. A. Criegee, *J. Phys. Chem.*, **80**, 2335 (1976).

Received July 28, 1987

Accepted February 17, 1988