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Storage time effect on free charge relaxation of amorphous poly (ethylene terephthalate)

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Using thermally stimulated depolarization currents of PET-a electrets formed by the windowing polarization technique, the effect of the storage time previous to depolarization on the free charge relaxation, ρ, has been studied. It was noted that the temperature at which the relaxation maximum appears increases with the storage time, whereas the intensity of the maximum decreases. This behaviour depends on both the polarization temperature and the polarizing field. It was also observed that there is a polarization temperature, the optimal polarization temperature, for which the relaxation maximum temperature does not depend on the polarizing field.

1. Introduction

When an electric field is applied to a dielectric material at high temperature, and subsequently the material is cooled, it becomes a thermoelectret. In a wide sense, an electret is a dielectric material that produces a permanent external electric field which results from permanent ordering of molecular dipoles (bounded charge), or surface or volume free charge. At room temperature, the decay time of this charge is much larger than the duration of the studies made on them and, because of this, thermal stimulation of these relaxation processes is a very adequate technique for studying those materials. Among these techniques, the one in widest use is thermally stimulated depolarization currents (TSDC). The processes of electret formation, and its ulterior depolarization by TSDC, have been widely described [1, 2].

TSDC discharges of amorphous poly(ethylene terephthalate) (PET-a) electrets show two relaxations in the temperature range between 30 and 100 °C. One is a polar relaxation, α, which presents its maximum at approximately 82 °C and is related to the vitreous transition. The other one, ρ, is due to free charge trapped in the polymeric electret and it appears at temperatures above the glass transition, T_g [3]. This peak is deficiently reproducible, which has been attributed to the high sensitivity of free charge to the different experimental parameters and to the previous treatments that the material has received [4]. A satisfactory reproducibility of ρ relaxation is achieved if the material is kept at the polarization temperature long enough to reach its equilibrium state before polarization, and if the polarization time is long enough for the material to become saturated.

The trapping and relaxation processes of the charge are intimately related to the physical and chemical properties of the material. Because of this, a study of these processes can provide useful information from the materials science point of view [2].

In this work we studied the electret free-charge decay with storage time, t_s, which is the time for which the electret is kept at the final temperature before the TSDC discharge.

2. Experimental procedure

2.1. Material

Experiments were carried out on commercial poly (ethylene terephthalate) (PET). Films of amorphous PET (PET-a) (of approximately 2 cm diameter and 220 μm thickness) were prepared by melting the material in moulds and then quenching them into iced water. These films were conditioned in a vacuum chamber, at 40 °C, for a few days and afterwards the samples were heated up to approximately 90 °C in order to eliminate internal stresses, originated during the manufacture, which could give rise to polarization. In order to check that such polarization had been removed, a TSDC discharge was carried out on a conditioned, but not previously polarized, sample and a null intensity was measured in the temperature range between room temperature and 100 °C.

Density measurements carried out subsequent to the conditioning process described above, gave a degree of crystallinity lower than 2% in all cases. The number average molecular weight ($M_n = 20\,000$) was determin-ed by viscosimetric measurements, using *O*-chlorophenol at 25 °C as solvent and the Marshall and Todd equation [5] as the relation between M_n and $[\eta]$

$$[\eta] = 6.56 \times 10^{-4}\, M_n^{0.79} \qquad (1)$$

which is valid for the molecular weight range between 12 000 and 25 000. Aluminium electrodes (2 cm diameter) were vaporized on both sides of all samples.

2.2. Experimental apparatus

The experimental apparatus consists of a measuring cell placed in an air-forced Heraeus oven, modified to be controlled by a Setaram PID RT-3000 temperature programmer. The temperature was measured by a digital thermometer Mettler TM-15 with a Pt-100 probe located very close to the sample. The current was measured by a Keithley 616 digital electrometer and recorded by an XY recorder HP 7046 A. Data were collected by a Linseis L8500 A/D converter and then computer processed.

2.3. Polarization technique

During electret formation, simultaneous heat and electrical treatments are applied to the dielectric material. The polarization process may be carried out in several ways, the most common of which is conventional polarization (CP). In this work, the polarization technique used is a variation of the windowing polarization method (WP) [6–11].

The thermoelectret conventional and windowing polarization processes are represented in Fig. 1a and b, respectively. In the thermal treatment of these processes, three steps can be differentiated: first, the material is heated from room temperature, T_0, up to the polarization temperature, T_p; then, the material is kept at the polarization temperature for a polarization time, t_p; finally, the sample is cooled to a final temperature, T_f, which can be room temperature or a different one.

In the conventional polarization process (Fig. 1a), the polarizing field, E_p, is applied during the second and third steps. Because of this, the charge is activated during both steps and "frozen" over the last one.

In the windowing polarization method, (Fig 1b), the electric field is removed during cooling (the third step). The aim is to activate the charge associated exclusively with a definite temperature, which is the polarization temperature in our case, and to avoid the overlapping of this charge effect with the charge effect that the field may activate during the cooling. Moreover, the application of the polarizing field at a definite temperature allows relaxations to be identified which, because of their similar activation energies, could be mixed up on an only wide relaxation in the case of conventionally polarized electrets.

The WP method proposed by other authors [9] includes an intermediate step in which the sample is kept at a temperature slightly lower than the polarization temperature. The temperature range over which the polarizing field is applied determines the polarization window width. In this work, the applied method is an extreme case of the aforementioned one, corresponding to the case of null window width. In fact, both methods give almost the same results in the case of narrow windows. The difference is related to the fact that in our case the charges activated at T_p (both dipoles and free charge) relax during sample cooling, so that the contribution of the related mechanism during discharge is slightly lower than that obtained if the field is applied during cooling. On the other hand, as the cooling rate, V_c, influences the resulting TSDC curve, it is not sensible to use an excessively low rate, so that the electret does not loose a significant part of its polarization. In this work, a cooling rate of $V_c = 2.2\ ^\circ\mathrm{C\ min^{-1}}$ was used.

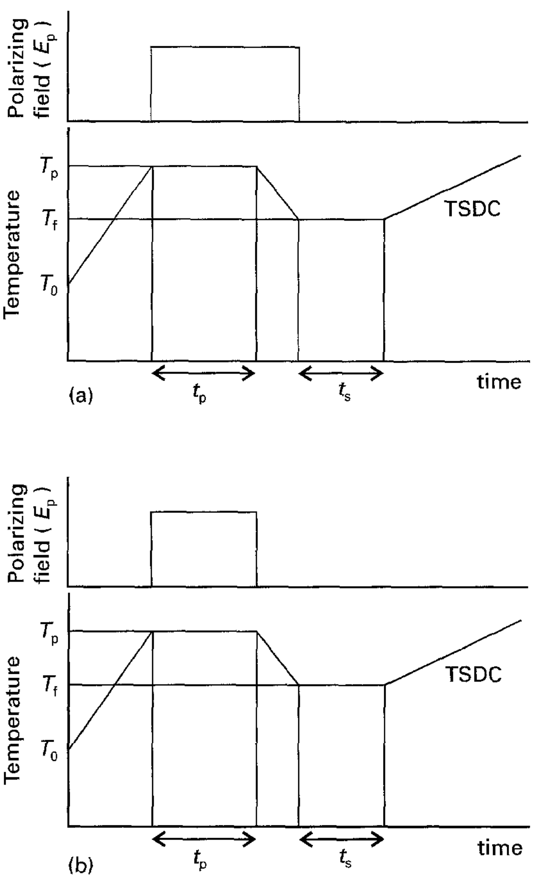

Figure 1 Electret formation processes by (a) conventional polarization and (b) windowing polarization techniques, and their TSDC.

The electrets were formed using the WP technique. The experimental parameters used were polarizing fields $10 < E_p < 100\ \mathrm{kV\ cm^{-1}}$; polarization temperatures $80 < T_p < 95\ ^\circ\mathrm{C}$; polarization time $t_p = 15$ min. The T_p range selected is that over which the ρ relaxation becomes manifest. It is convenient to notice that this peak is activated at polarization temperatures above approximately 70 °C. It appears between 70 and 80 °C, not clearly defined, just above the maximum of the polar peak which is becoming extinguished due to thermal agitation [12]. Because of this the samples were cooled to $T_f = 70\ ^\circ\mathrm{C}$ after polarization.

The depolarization heating rate was $2.2\ ^\circ\mathrm{C\ min^{-1}}$ in all cases. The samples were heated to approximately 100 °C. It is not convenient to heat the sample to higher temperatures because amorphous PET tends to crystallize. If once the sample has been heated up to 100 °C it is cooled immediately, the degree of crystallinity changes are insignificant.

3. Results and discussion

TSDC curves of PET-a electrets formed by windowing polarization at polarization temperatures from 82–100 °C show only ρ relaxation. In Fig. 2, TSDC discharges of windowing polarized PET-a electrets, formed under the same conditions, are plotted for different storage times. It can be noted that the maximum peak intensity, I_m, and the area enclosed below the curve diminish as t_s increases. This behaviour reflects the remanent charge decrease after storage, although the trapped charge and peak area correlation is not clearly established [2]. It can also be noted that the temperature at which the peak maximum appears, T_m, increases with t_s.

The values of I_m versus log (t_s) are plotted in Fig. 3 for several values of E_p and T_p. It can be noted that in the case of the shortest storage time used ($t_s = 1$ min), I_m increases with E_p for all the polarization temperatures studied. This result is a consequence of the increase in the carriers activated by the field. For the lowest value of T_p studied ($T_p = 82.7\,°$C, Fig. 3a–c), a practically linear dependence can be seen between I_m and log (t_s) in the storage time and polarizing field ranges used. For higher values of T_p, it can be noted that this linear dependence ceases for successively lower polarizing fields (Fig. 3f–h). For a fixed T_p value, the slope increases with E_p, which is associated with an increase in the carriers recombination rate. The increase in polarizing field seems to be related to an increase in the number of carriers which are located in traps, the depth of which increases with T_p. When the field is removed, and in the time period before the discharge, shallowly trapped carriers recombine quickly, and the deeply trapped carriers seem to be responsible for the more regular behaviour.

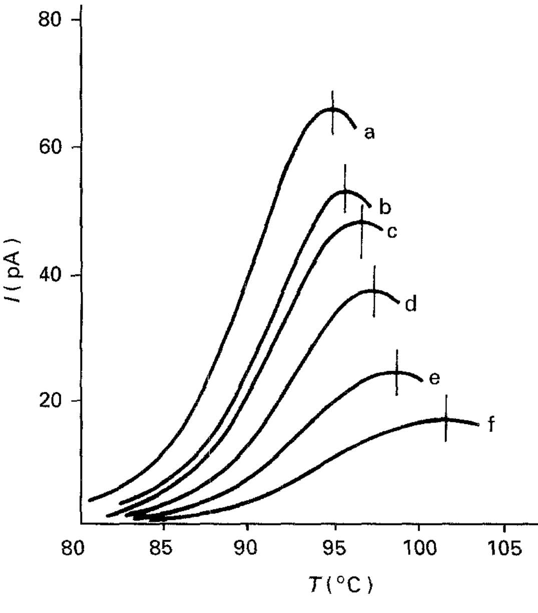

Figure 2 Windowing polarized electrets TSDC curves for several storage times. $T_p = 82.7$ °C, $E_p = 80$ kV cm^{-1}, $t_p = 15$ min; t_s (min): (a) 1, (b) 3, (c) 5, (d) 15, (e) 30, (f) 60.

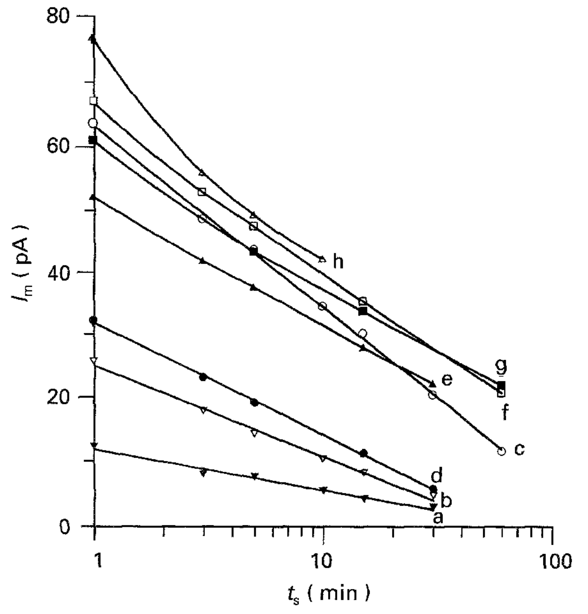

Figure 3 ρ relaxation maximum intensities versus storage time for several polarization temperatures and polarizing fields. $t_p = 15$ min.
$T_p = 82.7\,°$C, E_p (kV cm^{-1}): (a) 12, (b) 24, (c) 80.
$T_p = 88.5\,°$C, E_p (kV cm^{-1}): (d) 24, (e) 48, (f) 80.
$T_p = 91.0\,°$C, E_p (kV cm^{-1}): (g) 60, (h) 90.

On the other hand, in relation to the maximum temperature, Figs 4 and 5 show TSDC curves for several T_p and E_p values and storage times of 1 and 30 min. For $T_p = 82.7$ °C (Fig. 4) it can be noted that T_m shifts to higher values with t_s (c, d) and to lower values with the applied field (a, b). For $T_p = 88.5\,°$ C (Fig. 5) the observed value of T_m does not depend on the applied field, but just on t_s.

The fact that T_m shifts to higher values with t_s suggests that remanent charge is located at deeper levels.

In Fig. 6, T_m is plotted as a function of log (t_r) for several T_p and E_p (t_r is the normalized time t_s/t_0, and $t_0 = 1$ min is the shortest storage time used). For all the E_p and T_p values studied, T_m depends linearly on log (t_r). These straight line slopes increase with T_p, which indicates that the carrier recombination rate increases because of the carrier mobility increase with the temperature (Table I). It can be noted that at a fixed T_p, the slope does not depend on the polarizing field. It can be seen that, at a determinate T_p, these plots are parallel straight lines, so that the maximum temperature decreases with the polarizing field; but at a certain polarization temperature ($T_p \approx 88.5$ °C), the maximum temperature does not depend on the polarizing field (the straight lines which correspond to this temperature overlap). This temperature is the optimal polarization temperature (T_{po}) [12], that is, the polarization temperature at which the TSDC curves obtained from windowing polarized electrets show the highest I_m value as can be seen in Fig. 7. This figure shows TSDC discharges of electrets polarized at several T_p, with all other parameters kept constant. The maximum I_m value is obtained for $T_p = T_{po} = 88.5$ °C.

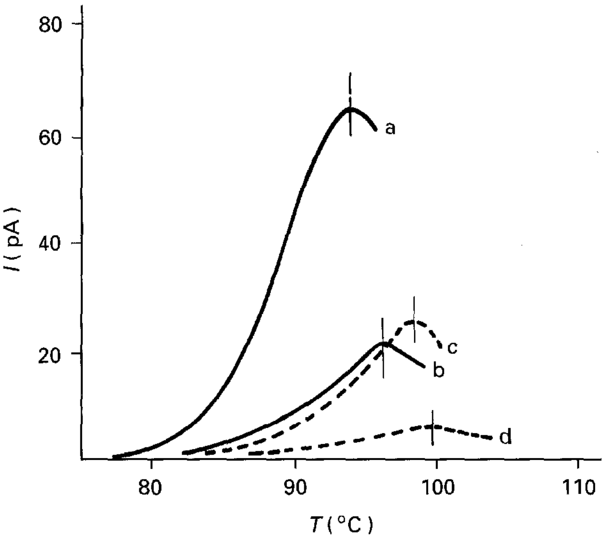

Figure 4 TSDC curves of windowing polarized electrets. $T_p = 82.7\,°C$, $t_p = 15$ min. $t_s = 1$ min, E_p (kV cm^{-1}): (a) 80, (b) 24. $t_s = 30$ min, E_p (kV cm^{-1}): (c) 80, (d) 24.

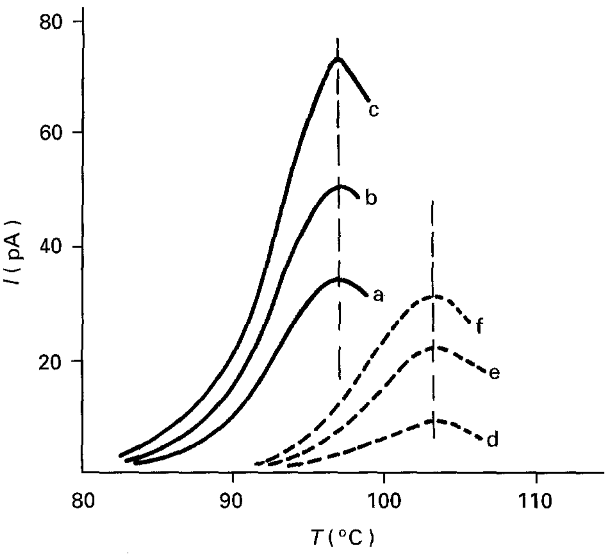

Figure 5 TSDC curves of windowing polarized electrets. $T_p = 88.5\,°C$, $t_p = 15$ min. $t_s = 1$ min, E_p (kV cm^{-1}): (a) 32, (b) 48, (c) 80. $t_s = 30$ min, E_p (kV cm^{-1}): (d) 32, (e) 48, (f) 80.

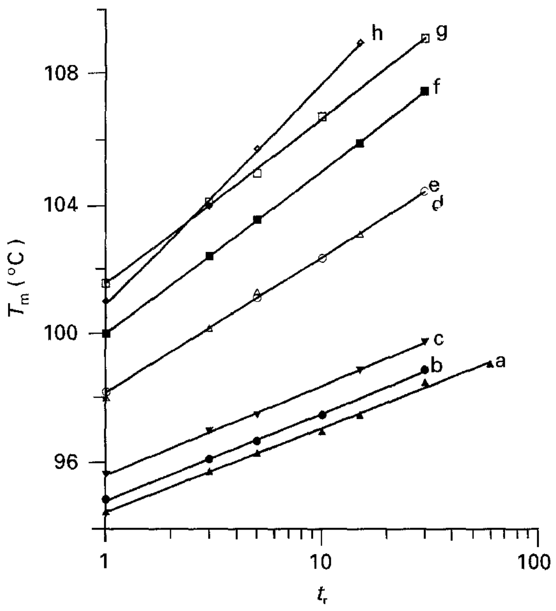

Figure 6 ρ relaxation maximum temperatures versus log (t_r) for several polarization temperatures and polarizing fields. $t_p = 15$ min. $T_p = 82.7\,°C$, E_p (kV cm^{-1}): (a) 80, (b) 24, (c) 12. $T_p = 88.5\,°C$, E_p (kV cm^{-1}): (d) 80, (e) 48. $T_p = 91.0\,°C$, E_p (kV cm^{-1}) : (f) 90, (g) 60. $T_p = 93.0\,°C$, E_p (kV cm^{-1}): (h) 80.

TABLE I T_m versus log (t_r) slope values, for the polarization temperatures studied

T_p(°C)	n(°C)
82.7	1.17
88.5	1.84
91.0	2.21
93.0	2.97

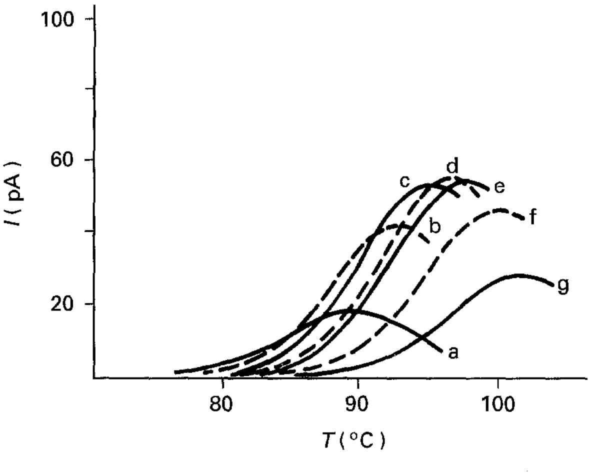

Figure 7 TSDC discharges of PET-a windowing polarized electrets. $E_p = 80$ kV cm^{-1}; $t_p = 15$ min; $t_s = 1$ min; T_p (°C): (a) 77.0; (b) 82.5; (c) 85.0; (d) 88.5; (e) 89.5; (f) 91.0; (g) 94.5.

The values of I_m versus T_p are plotted in Fig. 8 for several applied fields. The plotted values were obtained by decreasing the applied field in the successive assays corresponding to a fixed polarization temperature. The storage time was $t_s = 1$ min in all cases. Because of the divergent behaviour of the isotherms, which related the maximum intensity to the applied field at a fixed polarization temperature, the variations of I_m for high fields are important, which justifies the behaviour of the plotted lines: smooth for low-field values and with a sharp maximum for high-field values. It can be seen that the optimum polarization temperature, T_{po}, does not seem to depend on the polarizing field.

This behaviour can be explained by supposing that for $T_p < T_{po}$, charge trapping exceeds detrapping, and for $T_p > T_{po}$ charge detrapping exceeds trapping. It can also be noted that the energy required to charge detrapping increases with T_p, which is reflected by the fact that T_m shifts to higher values with T_p. When the material is polarized, $T_p < T_{po}$, increasingly deeper traps are filled with T_p. At $T_p = T_{po}$, all traps can be filled, which explains that at this temperature the peak area reaches its maximum. Finally, for $T_p > T_{po}$, although all traps can be filled during the polarization process, carriers trapped in shallow traps can be released from them, because of thermal energy. For increasing values of T_p, the carriers are released from increasingly deeper traps, and charge trapping is less

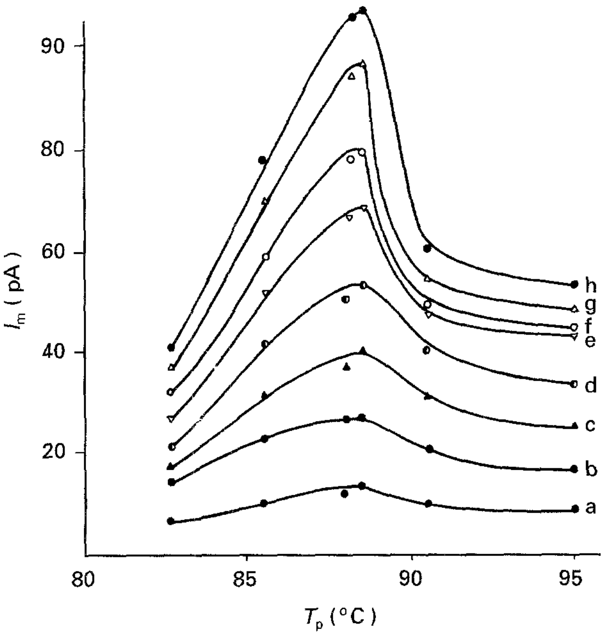

Figure 8 ρ relaxation maximum intensities versus the polarization temperature, for several polarizing fields. $t_p = 15$ min, $t_s = 1$ min, E_p (kV cm^{-1}) : (a) 10; (b) 20; (c) 30; (d) 40; (e) 52; (f) 60; (g) 72; (h) 80.

efficient during polarization, so that although there is less trapped charge it is localized at deeper levels. In this case, higher energy is required to detrap this charge and T_m shifts to higher values.

References

1. B. HILCZER, and J. MALECKI. "Electrets. Studies in electrical and electronic engineering", Vol. 14 (Elsevier, PWN-Polish Scientific, Watszawa, 1986).
2. G. M. SESSLER, "Electrets. Topics in applied physics", Vol. 33, Edited by G. M. Sessler. (Springer, Berlin, 1980) pp. 81–215.
3. J. VANDERSCHUEREN and J. GASSIOT, "Thermally stimulated relaxation in solids. Topics in applied physics", Vol. 37, edited by P. Braünlich (Springer, Berlin, 1979) pp. 135–223.
4. J. VAN TURNHOUT, "Thermally stimulated discharge of polymer electrets", (Elsevier Scientific Amsterdam, 1975).
5. J. MARSHALL and A. TODD, *Trans. Faraday Soc.* **49** (1953) 67.
6. T. HINO, *J. Appl. Phys.* **46** (1973) 1956.
7. M. ZIELINSKI and M. KRYSZEWSKI, *Phys. Status Solidi* **A42** (1977) 305.
8. I. DUACONU and S. V. DUMITRESCU, *Europ. Polym. J.* **14** (1978) 971.
9. C. LACABANNE, P. GOYAUD and R. F. BOYER, *J. Polym. Sci. Polym. Phys. Ed.* **18** (1980) 277.
10. S. K. SHRIVASTAVA, J. D. RANADE and A. P. SHRIVASTAVA, *Thin Solid Films* **67** (1980) 201.
11. A. GOURARI, M. BENDAOUD, C. LACABANNE and R. F. BOYER, *J. Polym. Sci. Polym. Phys. Ed.* **23** (1985) 889.
12. J. BELANA, M. MUDARRA, J. CALAF, J. C. CAÑADAS and E. MENÉNDEZ, *IEEE Trans. Elec.* **28**(2) (1993) 287.

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