DSC and TSC study of a VDF/TrFE copolymer [1]

G. Teyssedre, A. Bernes and C. Lacabanne *

Solid State Physics Lab., Paul Sabatier University, 31062 Toulouse Cedex (France)

(Received 11 November 1992; accepted 20 April 1993)

Abstract

The semi-crystalline 75/25 mol.% P(VDF/TrFE) copolymer has been studied by thermo-stimulated current (TSC) spectroscopy. The analysis of the fine structure of the complex TSC spectrum has revealed that the relaxation mode associated with the glass transition has two components: the lower temperature component is characterized by relaxation times obeying a compensation law with $T_c \approx T_g + 25°C$ and has been associated with the glass transition of the true amorphous phase of the copolymer; the upper temperature component has been attributed to the constrained amorphous phase.

The mode observed at highest temperature is characterized by a compensation phenomenon with a compensation temperature corresponding to the Curie transition temperature. Therefore, it has been associated with the ferro/paraelectric transition of the crystalline phase.

INTRODUCTION

Polyvinylidene fluoride (PVDF) and its copolymers with tri-fluoroethylene (TrFE) have been extensively studied because of their ferroelectric properties. Copolymers of $\approx$50–80 mol.% VDF are of great interest, firstly because they crystallize directly in the β-ferroelectric phase, and secondly because they exhibit a ferro/paraelectric, or Curie, transition below the melting point.

The purpose of this work is to investigate relaxation phenomena associated with transitions in a 75/25 mol.% P(VDF/TrFE) copolymer. Comparative studies of transitions, by differential scanning calorimetry (DSC), and of the dielectric relaxations, by thermostimulated current (TSC) spectroscopy, have been performed.

---

* Corresponding author.

MATERIALS AND METHODS

We have investigated samples of Al-metallized, 50-μm-thick P(VDF/TrFE) 75/25 mol.% films supplied by Solvay. These copolymers are composed of randomly located $-CH_2-CF_2-$ and $-CHF-CF_2-$ sequences.

The DSC analysis was performed on a Perkin-Elmer DSC 7.

TSC experiments were carried out on a Solomat TSC/RMA spectro-meter. In this technique [1], the sample is subjected to a static field at a temperature T_p for a time t_p (2 min), which allows for orientation of the mobile dipolar units. The temperature is then lowered to $T_o \ll T_p$ where the field is turned off. The polarization recovery is induced by increasing the temperature at a linear rate (7 K min^{-1}), and the depolarization current is recorded as a function of temperature.

EXPERIMENTAL RESULTS

DSC thermogram

Figures 1–3 show the DSC thermograms of the copolymer. Figure 1 was recorded at a heating rate of 20 K min^{-1}. In the region of the glass transition temperature, there is the expected jump in heat capacity associated with the glass transition of the copolymer, T_{g_1}. The glass transition temperature defined from the midpoint is $-36°C$. At higher temperatures (5–10°C), a change in the slope of the C_p curve is observed. This behavior will be discussed below.
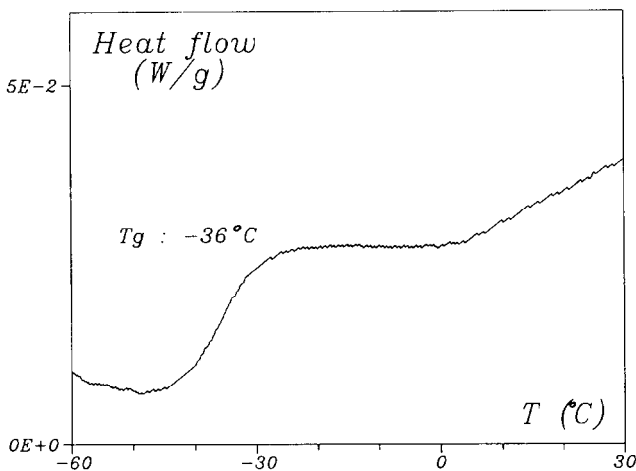

Fig. 1. Low temperature DSC thermogram of P(VDF/TrFE) upon heating at 20 K min^{-1}.
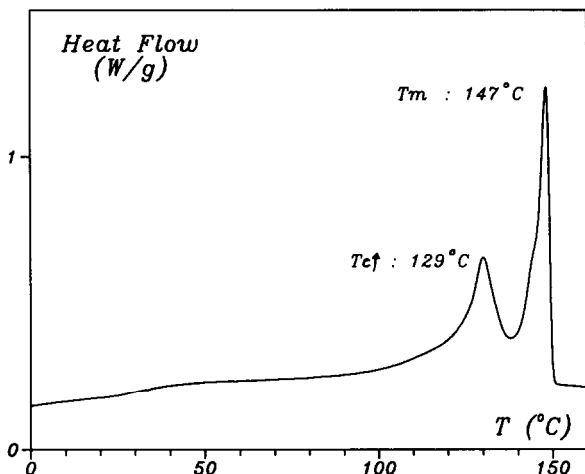
Fig. 2. High temperature DSC thermogram of P(VDF/TrFE) upon heating at 10 K min^{-1}.

Figures 2 and 3 were obtained on heating and cooling, respectively, at 10 K min^{-1}. The fusion of crystallites occurs at 147°C (Fig. 2). This temperature is lower than that for PVDF ($\approx$175°C) or TrFE (200°C) [2]. The endothermic peak at 129°C is associated with the ferro- to paraelectric transition in the copolymer. This transition temperature on heating is designated as $T_{c\uparrow}$. On cooling (Fig. 3), the exothermic peak at 76°C corresponds to the para- to ferroelectric transition ($T_{c\downarrow}$). The Curie transition refers to both phenomena. This transition is characterized by a large thermal hysteresis because $T_{c\uparrow} \approx T_{c\downarrow} + 50$°C. This thermal lag will be discussed below.
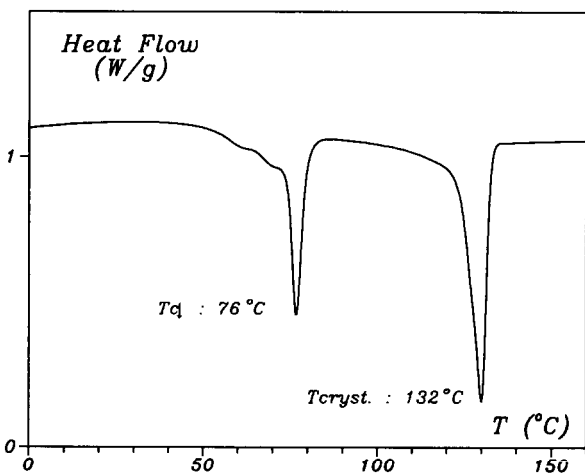

Fig. 3. High temperature DSC thermogram of P(VDF/TrFE) upon cooling at 10 K min^{-1}.
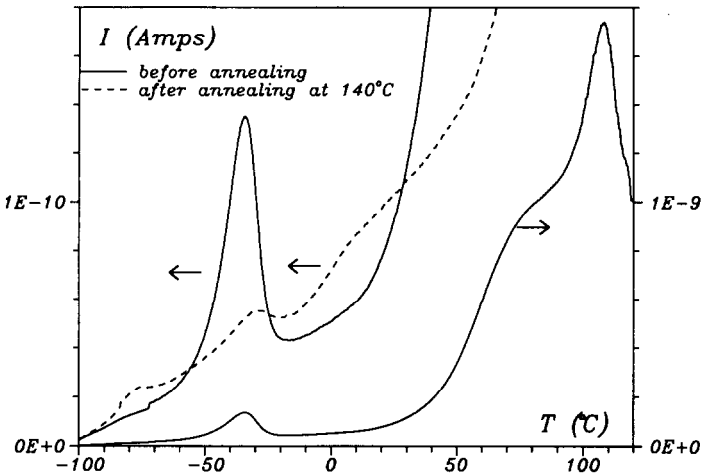
Fig. 4. TSC complex spectra of P(VDF/TrFE) 75/25 after polarization at 100°C.

The crystallization temperature is 132°C (Fig. 3).

TSC complex spectra

Figure 4 shows the complex TSC spectra obtained with a polarization temperature of 100°C. The field applied on a 1 cm² area sample was 5 MV m⁻¹. The spectrum for the as-received sample is represented by solid lines. The lower spectrum corresponds to the right-hand scale; the upper spectrum obtained after magnification corresponds to the left-hand scale. The spectrum represented as a broken line (left-hand scale) was recorded after annealing for 5 min at 140°C.

The peak centered at -34°C (solid line) is located in the vicinity of the glass transition temperature; it has been ascribed to the dielectric relaxation associated with the glass transition of the amorphous phase of the material and will be designated T_{g_1}-relaxation. Unreported data showed that when the polarization temperature was increased, a shoulder appeared above the T_{g_1} peak, as well as an increase in the TSC current below the glass transition region.

Upon annealing at 140°C, the magnitude of the T_{g_1}-relaxation is drastically reduced (see Fig. 4, broken line). Such an annealing above the ferro-/paraelectric transition (129°C) is known to enhance the crystallinity of the material [3]. Thus, our observations are consistent with this because the magnitude of this relaxation varies with the amount of amorphous phase. In addition, there are two shoulders at about -80°C, and 10–20°C; they are designated sub-T_g and T_{g_u} processes respectively.

In the high temperature range, above 50°C, a broad, intense peak is observed. Note that the field was applied at 100°C, so that molecular

movements having long relaxation times at this temperature were not affected by the field during the polarization time. Hence, this high-temperature mode is not fully represented on the spectrum.

Fine structure of TSC spectra

The above relaxation spectrum is obviously complex. The technique of fractional polarizations enables us to resolve it into elementary processes, and to calculate the relaxation time distribution spectrum by a subsequent analysis.

The principle is the following: the polarization is applied at a temperature T_p during a time t_p (2 min). Then, the temperature is decreased to $T_d = T_p - \Delta T$ where the electrodes are short-circuited during t_d. ΔT is the temperature window (5°C). Therefore, mobile dipolar units having long relaxation times at T_p are not oriented by the field; and those with short relaxation times at T_d are randomized by the short-circuit.

The temperature is then decreased to $T_o \ll T_p$ and the depolarization current is recorded in the same conditions as for the complex spectrum. The temperature window is shifted by 5°C along the temperature axis such that we obtain a set of elementary peaks whose envelope varies in the same way as the complex TSC spectrum (Fig. 5).

The relaxation time associated with each elementary peak is deduced from
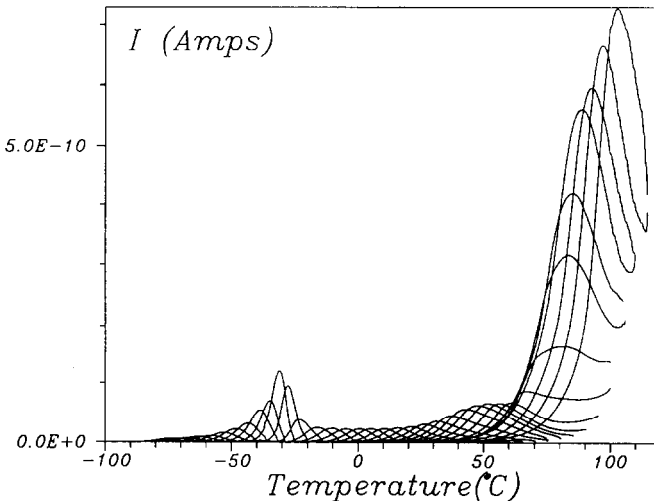
$$\tau(T) = \frac{P(T)}{j(T)} \tag{1}$$

Fig. 5. Experimental resolution of complex TSC spectrum: the polarization window was shifted by 5°C steps; T_p varied from −85 to 90°C; for the −31°C peak, $T_p = 40$°C.
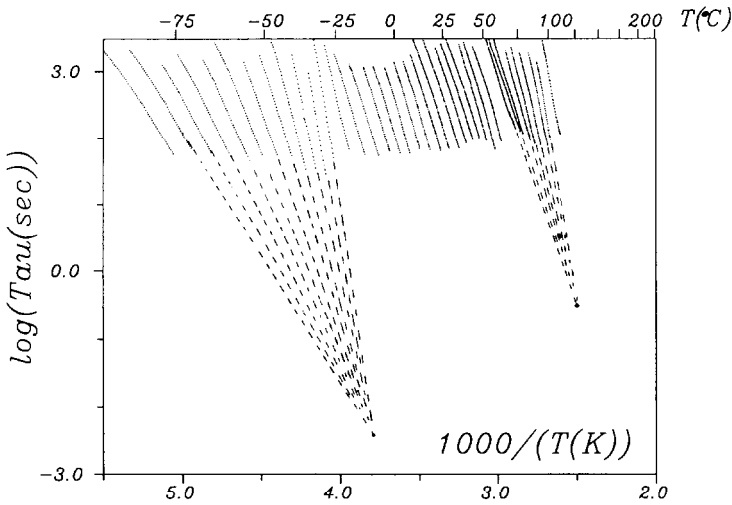
Fig. 6. Arrhenius diagram of dielectric relaxation times deduced from the analysis of the elementary peaks in Fig. 5. Intersections occur at compensation parameters.

where $P(T)$ is the polarization remaining in the sample at temperature T, and $j(T)$ is the current density recorded at this temperature.

Figure 6 shows the Arrhenius representation of the distribution of relaxation times deduced from fractional polarizations performed from $-90°C$ to $100°C$.

The experimental data obtained from one elementary peak follow a straight line, which means that the corresponding relaxation times obey an Arrhenius law

$$\tau_i(T) = \tau_{oi} \exp \frac{\Delta H_i}{kT} \tag{2}$$

where τ_{oi} is the pre-exponential factor, ΔH_i is the activation enthalpy, and k is the Boltzmann constant.

When a linear relationship exists between $\log(\tau_{oi})$ and ΔH_i for several processes, the relaxation times are described by only one parameter, ΔH_i; so that

$$\tau_i(T) = \tau_c \exp \frac{\Delta H_i}{k} \left(\frac{1}{T} - \frac{1}{T_c} \right) \tag{3}$$

where T_c and τ_c are the compensation temperature and time, respectively. Relaxation times of processes involved in a compensation phenomenon have the same value of τ_c at T_c. So, the straight lines on an Arrhenius diagram intersect at these coordinates. Two compensation phenomena appear in the relaxation time spectrum of the polymer, with parameters: $\tau_{c1} = 3 \times 10^{-3}$ s, $T_{c1} = -10°C$; and $\tau_{c2} = 0.25$ s, $T_{c2} = 130°C$. From eqns. (2)
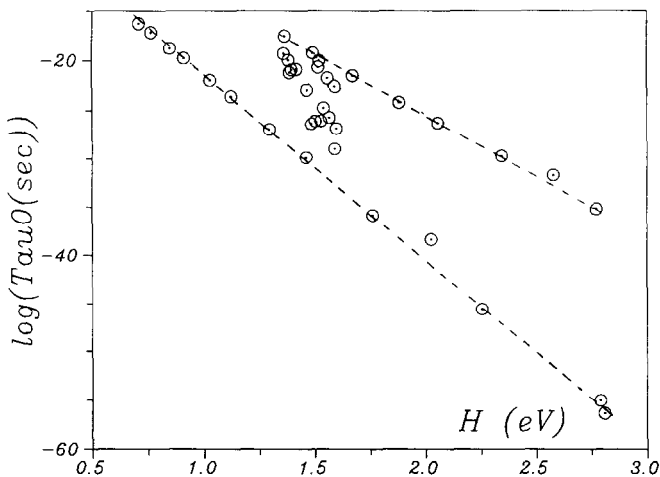
Fig. 7. Pre-exponential factors versus activation enthalpies: the broken lines show the two compensation phenomena.

and (3), the pre-exponential factors are related to the activation enthalpies by

$$\tau_{oi} = \tau_c \exp - \frac{\Delta H_i}{kT_c} \tag{4}$$

Then another representation of the compensation phenomenon is obtained by plotting in a semi-log scale the pre-exponential factors τ_{oi} versus the activation enthalpies ΔH_i (Fig. 7). The compensation temperature is then deduced from the slope of the straight line, and the compensation time corresponds to $\Delta H = 0$.

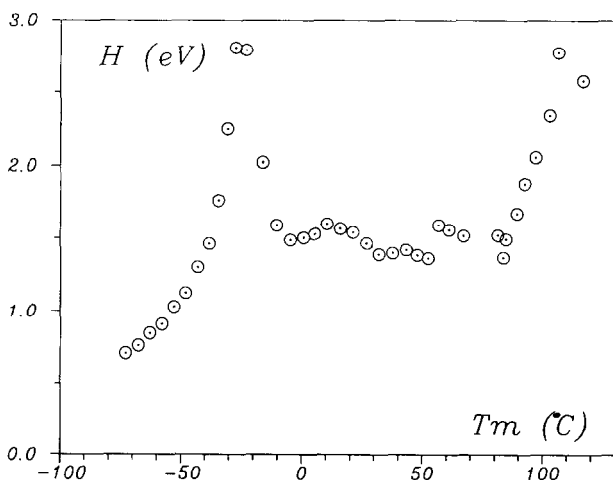Figure 8 shows the activation enthalpies versus the temperature of the

Fig. 8. Activation enthalpies of elementary processes vs. peak maximum temperatures of the elementary peaks.

maximum of the elementary peaks T_m. In the glass transition region, and at high temperatures, the enthalpies are increasing. It is within these domains that we observe the compensation phenomena. In the region of the T_{g_u} transition–relaxation, these enthalpies remain roughly constant.

DISCUSSION

Glass transition–relaxation

T_{g_1} transition–relaxation

The main relaxation phenomenon observed below room temperature is located at −34°C, i.e. very close to the lower component of the glass transition observed on the DSC thermogram. The study of the fine structure of this relaxation mode reveals that the relaxation times of the elementary processes obey a compensation law. This behavior has been observed in many others polymers, both amorphous (polymethylmethacrylate [4], polycarbonate [5]) and semi-crystaline (polyvinylidene fluoride [6], polyethylene terephthalate [7]), and is a characteristic of the amorphous phase of polymers around their glass transition temperature; it indicates the cooperativity of the molecular movements involved in the transition. Moreover, its magnitude decreases upon enhancement of the crystallinity rate due to annealing at 140°C. Koga and Ohigashi [3] correlated this substantial increase in crystallinity to the Curie transition rather than to the crystallization temperature. For this copolymer, these temperatures are close, both being below the annealing temperature. However, for different VDF/TrFE ratios, they are not close. Crystallinity is also enhanced by polarizing at this temperature.

Finally, this relaxation mode has been attributed to the dielectric manifestation of the glass transition of the "true" amorphous phase of the copolymer.

A comparison of compensation and glass transition temperatures reveals that the $T_c - T_g$ lag is about 25°C. Similar relationships have been observed in many semi-crystalline polymers, and more generally in polymers characterized by local order [1, 4]. Therefore, this lag might be predicted from the high crystallinity rate (≈60%) of the studied copolymer.

T_{g_u} transition–relaxation

The T_{g_u} mode is observed about 40°C above the lower component of the glass transition, i.e. in the vicinity of the upper component of T_g. We have shown that its magnitude is enhanced upon annealing.

Double glass transitions have also been observed for α-PVDF by Enns and Simha [8] by dilatometry and by Choi [9] by DSC. These authors have ascribed the upper component to the amorphous phase constrained by crystallites (T_{g_u}).

An enhancement of crystallinity is expected to induce a stronger T_{g_u}

mode. Indeed, the crystalline phase induces limited molecular mobility in amorphous regions surrounding crystallites. Therefore, high crystallinity is expected to decrease the free amorphous phase fraction (T_{g_l}) and to increase the constrained amorphous fraction. These criteria are verified in our TSC results.

Moreover, the activation enthalpies deduced from the analysis of the fine structure are concentrated in a narrow window (≈ 1.4–1.6 eV). Such relaxation phenomena have already been observed by TSC slightly above the glass transition temperature in other semi-crystalline polymers such as polyethylene terephthalate [7] and polyamide [10], for example.

Thus, the T_{g_u} transition–relaxation has been ascribed to the amorphous regions constrained by crystallites.

Sub-T_g relaxation

This is located some 40°C below the glass transition temperature. Upon annealing at 140°C, its magnitude increases. The growth of crystallites induces stresses on the surrounding amorphous phase. Then some heterogeneity, such as inhomogeneous densities, is expected within this phase. Thus, this relaxation mode has been ascribed to density fluctuation due to local order in the amorphous phase. The appearance of local order and the segregation of rigid domains enhance this sub-T_g mode. This has been observed in the same copolymer by Koizumi et al. [11] by dielectric relaxation. It is also found in other semi-crystalline polymers such as polyethylene terephthalate [7] and polyphenylene sulfide [12]. It is also important to note that it can be observed in amorphous polymers like polycarbonate [5].

Curie transition–relaxation

The Curie transition is characterized by a large thermal hysteresis: by DSC, it is observed at 76°C ($T_{c\downarrow}$) upon cooling, and near 130°C ($T_{c\uparrow}$) upon heating. This behaviour does not seem to be a kinetic effect associated with cooling/heating rate considerations. Indeed, isothermal X-ray measurements at temperatures T_r between $T_{c\downarrow}$ and $T_{c\uparrow}$ have shown that the crystalline structure is that of the crystalline phase when T_r is reached from the low temperature side. Conversely, when T_r is reached from the high temperature side, the structure obtained is paraelectric [13]. According to the phenomenological theory of ferroelectricity, this thermal hysteresis is indicative of a first-order transition [14]: between $T_{c\downarrow}$ and $T_{c\uparrow}$, the free energy G exhibits a minimum at a polarization $P = 0$, allowing the paraelectric phase to remain till $T \geq T_{c\downarrow}$, and a double minimum at $P = \pm P_s$, allowing the ferroelectric phase to remain till $T \leq T_{c\uparrow}$. It is believed that the Curie transition is first order, at least for copolymers with VDF content ≥ 60 mol.% [15, 16].

Relaxation times isolated in the high temperature range of the complex TSC spectrum (Fig. 4) obey a compensation law (Fig. 6), with a compensation temperature $T_c = 130°C$ very close to the ferro-/paraelectric transition, i.e. 129°C, deduced from the DSC thermogram (Fig. 2). This feature suggests that the mode observed at about 80–100°C in the complex TSC spectrum is associated with the Curie transition of the polymer. It must be noted that thermal sampling analyses were performed in the ferroelectric phase. Therefore, most suitable parameter for comparison with the compensation temperature is T_{cf}.

We have shown that annealing above 80°C reduces the pyroelectric activity of polarized samples, which means that part of the remant polarization of the material is affected by this treatment.

These results strongly support the hypothesis that cooperative molecular motions of precursors of the ferro-/paraelectric transition are the origin of the high temperature relaxation mode of the complex TSC spectrum of the copolymer. Furukawa [14] has pointed out the cooperative nature of the Curie transition.

Characteristic transition–relaxation temperatures

A comparison of the results obtain by TSC (compensation temperature) and DSC (transition temperature) is presented Table 1. Relaxation phenomena associated with the Curie transition are characterized by a compensation temperature that practically corresponds to the transition temperature.

In crystalline materials such as hydroxyapatites, Hitmi et al. [17] found a compensation temperature corresponding to the hexagonal/monoclinic phase transition temperature.

In the case of the glass transition, we found a significant lag between transition and compensation temperatures. This lag, characteristic of the glass transition/relaxation has now been observed for a great number of polymers, both amorphous and semi-crystalline. Its amplitude, which varies with different polymers, has been correlated to physical structure, such as chain rigidity, orientation, local order, crystallinity, or to chemical parameters, such as crosslink density in polymeric networks.

TABLE 1

Comparison of compensation and transition temperatures

	TSC Compensation temperature	DSC Transition temperature
Glass transition	−10°C	−36°C
Curie transition	130°C	129°C

Thus, the glass transition is sensitive to the relaxational behavior of the polymer. Indeed, it has a kinetic character and is not considered as a true thermodynamic phase transition.

The lag we have observed between the transition temperature, and the parameter characteristic of the relaxational behaviour, the compensation temperature, may be correlated to the kinetic character of this transition, because in a true thermodynamic phase transition this lag is not observed.

CONCLUSIONS

Thermostimulated current spectroscopy has been applied to the investigation of molecular movements in a P(VDF/TrFE) copolymer.

The cooperative movements involved in the Curie transition have been characterized by a compensation temperature corresponding to the transition temperature. However, the cooperative movements involved in the low temperature component of the glass transition have a compensation temperature $T_c \approx T_g + 25°C$. This lag has been attributed to the kinetic character of the glass transition.

The molecular mobility liberated at the upper glass transition is characterized by a quasi-constant activation enthalpy. It has been located in amorphous domains constrained by crystallites.

REFERENCES

1 A. Bernes, R.F. Boyer, D. Chatain and C. Lacabanne, in S.E. Keinath, R.L. Miller and J.K. Ricke (Eds.), Order in the Amorphous State of Polymers, Plenum, New York, 1986.
2 Y. Higashihata, J. Sako and T. Yagi, Ferroelectrics, 32 (1981) 85.
3 K. Koga and H. Ohigashi, J. Appl. Phys., 59(6) (1986) 2142.
4 A. Chafai, D. Chatain, J. Dugas, C. Lacabanne and E. Vayssié, J. Macromol. Sci. Phys., 22(5, 6) (1983) 633.
5 A. Bernes, D. Chatain and C. Lacabanne, Polymer, 33(22) (1992) 4682.
6 G. Teyssedre, A. Bernes and C. Lacabanne, J. Therm. Anal., 40 (1993) 711.
7 A. Bernes, D. Chatain, C. Lacabanne and D. Lorentz, Thermochim. Acta, 192 (1991) 155; A. Bernes, D. Chatain and C. Lacabanne, IEEE Trans. Elec. Insul., 27(3) (1992) 464.
8 J.B. Enns and R. Simha, J. Macromol. Sci. Phys., 13(1) (1977) 633.
9 C.H. Choi, Thèse, Université de Lyon, 1989.
10 D. Chatain, P. Gautier and C. Lacabanne, J. Pol. Sci. Phys. Ed., 11 (1973) 1631.
11 N. Koizumi, N. Haikawa and H. Habuka, Ferroelectrics, 57 (1984) 99.
12 M. Mourgues-Martin, A. Bernes, C. Lacabanne, O. Nouvel and G. Seytre, IEEE Trans. Elec. Insul., 27(4) (1992) 795.
13 A.J. Lovinger, D.D. Davis, R.E. Cais and J.M. Kometani, Polymer, 28 (1987) 617.
14 T. Furukawa, Phase Transition, 18 (1989) 143.
15 S. Ikeda, H. Kominami, K. Koyama and Y. Wada, J. Appl. Phys., 62(8) (1987) 3339.
16 K. Tashiro, K. Takano, M. Kobayashi, Y. Chatani and H. Tadokoro, Ferroelectrics, 57 (1984) 297.
17 N. Hitmi, C. Lacabanne and R.A. Young, J. Phys. Chem., 47(6) (1987) 533.