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Ferroelectric transitions and relaxation processes of vinylidene fluoride/trifluoroethylene copolymers

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Résumé. — Des mesures de dépolarisation thermostimulées associées à un bruit piézoélectrique ont permis d’identifier la transition ferroélectrique-paraélectrique de copolymères fluorure de vinylidène/trifluoroéthylène, de diverses concentrations molaires. D’autre part, la présence d’un deuxième pic indiquerait une nouvelle transition, laquelle ne modifie pas le comportement ferroélectrique du matériau. Des processus de relaxations lents accompagnent toujours ces transitions. Les énergies d’activations associées à ces transitions ont été calculées par la méthode de la pente initiale. Les valeurs de 0,73 et 0,33 eV ont été trouvées respectivement pour la transition ferro/para et pour l’autre transition. Deux transitions ont également été observées pour le copolymère VDF/TrFE 90/10 mol %, considéré comme ayant une conformation non ferroélectrique. Une grande quantité de charge observée par des mesures de TSC, relaxent aux températures de transitions.

Abstract. — Thermally Stimulated Depolarization (TSD) measurements with a superimposed piezoelectric noise allowed us to identify the ferroelectric-to-paraelectric phase transition in vinylidene fluoride/trifluoroethylene (VDF/TrFE) copolymers, with different molar ratios. A second peak was also detected in TSD measurements which maintain the ferroelectric features of the material. Long relaxation processes always accompanied both peaks. Using the initial rise method we calculated the activation energies for these relaxations. We found 0.73 eV for the ferroelectric-to-paraelectric peak transition and 0.33 eV for the other. Two peaks were also observed in the 90/10 mol % VDF/TrFE copolymer. However it is considered, hitherto as having a non ferroelectric conformation. A great amount of charge was recorded in TSC measurements, around the transition temperatures.

1. Introduction

The discovery of ferroelectric polymers in the last decade a great impulse on the investigation of these materials. In particular, the polyvinylidene fluoride (PVDF) was the most studied, seeing that in its β conformation it presents considerable piezoelectric and pyroelectric effects [1-4]. These properties provide several technological applications [5]. Meanwhile, its low melting point makes difficult a complete study of its ferroelectric properties.

The vinylidene fluoride/trifluoroethylene (VDF/TrFE) copolymers have piezoelectric and pyroelectric properties similar to those presented by the β-PVDF [6, 7]. Besides, they have the advantage to present, in appropriate molar ratios of VDF and TrFE, the Curie temperature [8, 9]. This ferroelectric-to-paraelectric (F-P) transition has a first-order behaviour for copolymers with a VDF molar concentration bigger than 60 % [10, 11]. Structural studies carried out in the 52/48 mol % copolymer VDF/TrFE by Lovinger et al. [12] showed that before the transition it exhibits two crystalline phases. One of them was identified to have a hexagonal packing of 3/1 helical chains (non polar), and the other a similar packed trans-planar chains (polar). Above the Curie temperature, only the disordered 3/1 helical conformation was detected. Horiuchi et al. [13] detected three peaks by X-ray diffractometric measurements at 66 °C, on samples of 54/46 mol % VDF/TrFE copolymer. To explain
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their results, they assumed the presence of an intermediate phase, which would take place between 66 and 90 °C.

In the present work we study phase transitions on 90/10, 80/20, 70/30, and 60/40 mol % VDF/TrFE copolymers by Thermally Stimulated Processes. Relaxation processes and space charge joined to these transitions are also studied.

2. Experimental procedures.

Vinilidene fluoride/trifluoroethylene copolymers with compositions 90/10, 80/20, 70/30, and 60/40 mol % of VDF/TrFE, as well as pure PVDF, were provided by Atochem (France). Resins were melted and pressed at a temperature above the melting point, then quenched to room temperature. Samples were circular with a diameter of 4 cm and a thickness of 50 µm. Rectangular aluminium electrodes (1.0 by 2.5 cm) were high vacuum deposited on both sides.

Thermally Stimulated depolarization (TSD) and Thermally Stimulated Current (TSC) were carried out following the conventional procedure. A linear heating rate of 1.9 °C/min was used for all measurements. During the TSC measurements a weak electric field of 50 kV/cm was applied to the samples, and glow peaks were observed superimposed to the conductivity curves. For the TSD measurements, samples were first polarized by an electric field of 500 kV/cm at 65° C during 20 min. Afterwards they were cooled to room temperature under the applied field. The samples were short-circuited and several minutes were waited before starting the measurements, to ensure a negligible value of the dielectric absorption discharge current.

A slight mechanical vibration (around 1 Hz) was imposed to the sample, in order to superimpose a piezoelectric noise on the TSD recording measurements. It did not appear for non piezoelectric samples, so it helped us to identify unambiguously the F-P transition.

3. Results.

3.1 TSD MEASUREMENTS. — Figure 1 shows the Thermally Stimulated Depolarization curves of the VDF/TrFE copolymers, and the α-PVDF homopolymer. We classify by A and B the peaks according respectively to the permanence or the disappearing of the piezoelectric noise. To present a clear picture, the noise was removed of all the curves drawn in figure 1. The figure 2 presents the measurements of the 70/30 and the 90/10 copolymers with the noise. As we can see it increased with the temperature, in accordance with the piezoelectric effect presented by the VDF/TrFE copolymers [6]. Meanwhile it began to decrease as soon as the B peak started, and vanished completely when its maximum was reached.

The 60/40 copolymer presented only the B peak at 80° C. While it exhibited a long relaxation process for temperatures below its maximum, after it the current quickly fell down. The activation energy of this relaxation process was calculated by the initial rise method, and the found value was 0.73 eV (Fig. 3a). The charge density of this peak was obtained from the integration versus time, being Q = 5.6 µC/cm². The pyroelectric current for this copolymer was estimated, in the present experimental conditions, to be approximately 0.1 nA. This estimation was based on a linear relation of the pyroelectric constant with the remanent polarization obtained by Furukawa et al. [7]. The A peak of the 70/30 copolymer appeared at 102 °C, while its B peak at 108 °C. This B peak had a similar behavior as that exhibited by the 60/40 copolymer, since showed a similar abrupt current decay. The charge associated with this TSD curve was 6.0 µC/cm²,
almost the same value as that obtained from the 60/40 copolymer. The TSD measurement of the 80/20 copolymer presented only the A peak at 87 °C, but a new one started around 110 °C.

Figure 3b shows the monolog curve derived of the beginning of the A peaks of the 70/30 and 80/20 copolymers. The calculated activation energies of these relaxation processes presented the same value: $E = 0.33 \text{ eV}$. This indicates that they have the same origin. The charge density variations (corresponding to the remanent polarization) with temperature for the 60/40 and 70/30 copolymers, were obtained from their TSD curves, and are presented in figure 4. From this result were verified that the ferro-to-paraelectric transition would not be detected by a direct measurement of the remanent polarization, in spite of its evidence in the TSD measurements. For the other copolymers it was not possible to outline this curve, since the TSD peaks remained unfinished.

The 90/10 copolymer presented two weak and broad peaks in TSD measurements (Fig. 1). The A peak appeared at 63 °C, and the B at 120 °C. For this copolymer the B peak exhibited a slow down decay, showing a different characteristic from that presented by the 60/40 and 70/30 copolymers. In this measurement it was not possible to calculate the activation energy of the A peak, seeing that a superimposed leakage current of about 0.1 nA (subtracted from the curve presented in Fig. 1) was detected before the heating process. The overlapping between the peaks also hindered the calculation for the 8 peak. Finally, figure 1 shows a TSD measurement with a $\alpha$-phase PVDF homopolymer sample. It exhibited only a broad and very weak peak around 65 °C.

3.2 TSC MEASUREMENTS. — Thermally Stimulated Current measurements were carried out with the same copolymer samples used in the TSD experiments reported above. The applied field was weak enough (50 kV/cm) to avoid either switching phenomenon [14, 15], or transformation of the crystalline phase of the material [12]. Figures 5(a), (b), and (c) show the results of the TSC measurements. As it can be seen, each TSC recording curve presented a similarity with the corresponding TSD curve, since the peaks appeared at approximately the same temperatures. In spite of this, the charge associated with the TSC peaks were about two order of magnitude higher. We can also observe that the storage charge increased for the copolymers with higher quantity of TrFE component. All the TSC thermograms had a good reproducibility, even if the measurements were carried out one after the other.

We present a complete TSC cycle (heating and cooling) with the 70/30 copolymer (Fig. 5b). During the cooling it was also recorded two peaks, with maxima around 72 and 67 °C. So it presented a hysteresis in the measurements. The charge associated with these peaks was of the same order of magnitude of that obtained from the TSD measurement.

4. Discussion.

4.1 FERROELECTRIC TRANSITIONS. — Recent measurements of Differential Scanning Calorimetry [16] showed that two proeminent peaks take place in non polarized samples of 70/30 mol % of VDF/TrFE copolymer. Their temperatures were very close to those of the TSD peaks showed in figures 1 and 2. We interpret the B peak as due to the ferroelectric-to-paraelectric transition, since the piezoelectric noise disappeared just after its maximum. Due to the
Fig. 5. — Thermally stimulated current measurements with an electric applied field of kV/cm. (a) 60/40 copolymer. (b) 70/30 copolymer (- - -) during heating and cooling: 80/20 copolymer (---). (c) 90/10 copolymer.

Based on the TSD measurements presented here, and also in the recent DSC results [16] we suppose that the A peaks of the 70/30 and 80/20 copolymers could be connected to a ferro-to-ferroelectric phase transition. Figure 2 shows that the piezoelectric activity of the samples remains always present during this transition, and as it is well accepted, we assume here that the piezoelectric activity of VDF/TrFE copolymers comes from their ferroelectric phase. This supposed F-F phase transition takes place at higher temperatures for copolymers with small quantity of VDF, while in the F-P transition as the VDF/TrFE molar ratio decreases the Curie temperature becomes lower. The combination of the two temperatures dependence on the molar ratios explains the absence of the A peak in the TSD and TSC measurements of 60/40 copolymer, and that of the B peak in the 80/20 copolymer.

4.2 RELAXATION PROCESSES. — The long relaxation process connected with the F-P transition had already been studied by dielectric relaxation [18]. It has been explained to be due to molecular motions associated with the crystalline regions, and it was described in terms of a single relaxation process. Its activation energy was calculated to be equal to 16 kcal/mol [18]. Using the initial rise method for the TSD peak of 60/40 copolymer we obtained the value of 0.73 eV (equivalent to 16.6 kcal/mol.). A complete study of the ferroelectric relaxation requires a correct relation of the relaxation time $\tau$ with the temperature, seeing that near the transition temperature it does not obey the Arrhenius law.

The other peak (A) of the 70/30 copolymer was also joined with a structural transition of the material (corroborated by the results presented in reference [16]). The 80/20 copolymer also presented the same transition, since the activation energy calculated for both A peaks, gave the same value: 0.33 eV (Fig. 3b).

We suppose that the A peak of the 90/10 copolymer and of the $\alpha$-homopolymer should have the same origin, seeing that only a small fraction of TrFE would not cause an evident change on these properties. The likeness between these peaks confirm this supposition. Several papers studied a relaxation in $\alpha$-PVDF which takes place in the 50 to 100 °C temperature range [19], and it had been associated with molecular motions. These motions are believed to be executed both by molecules in the chain folds and in the crystalline regions.

4.3 SPACE CHARGE. — The present paper showed that beside the dipolar orientation, the ferroelectric transitions are also accompanied by a large amount of released charge (Figs. 5). Thermally Stimulated Current measurements of $\alpha$-PVDF owing to storage charge had been recorded in several papers [20-22],
and it is well accepted that molecular motions of this material is accompanied by charge liberation [23]. However, in the present study the charge appeared only if the samples remained under an applied field, since the TSD measurements (carried out in short-circuit) recorded only the dipolar depolarization. The reproducibility of the TSC measurements is a strong result against the storage space charge hypothesis. On the other hand, a recent study with the purpose to investigate the origin of storage charges in PVDF, concluded that bulk dissociated ions of absorbed water by the material give a transient electrical current, under an external applied field [25]. The charge associated with this transient current had the same value as that reported here.

5. Summary and conclusions.

In this paper we show that Thermally Stimulated Depolarization method became a good tool to explore ferroelectrical phase transitions in polymers, if a mechanical vibration is imposed to the electrodes. The Curie point of the ferroelectric-to-paraelectric phase transition of VDF/TrFE copolymers, were well determined. At the same time this technique provided us the recording of the phase transition relaxation process, and the temperature evolution of the remanent polarization.

We also detected an unknown TSD peak in the 70/30 and 80/20 mol % VDF/TrFE samples. We supposed that it is probably due to a ferroelectric-to-ferroelectric phase transition since a very proeminent peak was also recorded in DSC thermogram [16]. The activation energies calculated from the initial rise method were respectively 0.33 and 0.73 eV for the A and the B peaks.

Thermally Stimulated Conductivity measurements showed that there is a large space charge released during each phase transition. During the heating and cooling TSC cycle of the 70/30 copolymer, we observed a hysteresis phenomenon in the phase transitions indicating their first-order characteristics.

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References