Molecular mobility interpretation of the dielectric relaxor behavior in fluorinated copolymers and terpolymers

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ABSTRACT

Thermo Stimulated Current and Dynamic Dielectric Spectroscopy have been applied to investigate dielectric relaxation modes of poly(vinylidene-fluoride-trifluoroethylene) copolymer and poly(vinylidene-fluoride-trifluoroethylene-chlorofluoroethylene) terpolymer. The aim of this work is to check the molecular origin of the ferroelectric relaxor behavior of the terpolymer. The combination of data obtained by both dielectric methods allows us to describe the molecular mobility of the amorphous phase and the cooperativity of the order/disorder dipolar transition in the crystalline phase. The introduction of 1,1-chlorofluoroethylene units in the main chain induces an increase of the Cooperative Rearranging Region size associated with less ordered and smaller crystallites. This morphological evolution is responsible of a lack of cooperativity and it explains the dielectric relaxor behavior of the poly(vinylidene-fluoride-trifluoroethylene-chloroethylene) terpolymer.

1. Introduction

Since the discovery of the piezoelectric behavior of poly(vinylidene-fluoride) — PVDF by Kawai [1] and the understanding of the molecular origin of this electroactivity [2–5], organic ferroelectric materials have attracted the interest of researchers for their potential use in specific applications such as low weight and flexible sensors [6,7], electromechanical devices [8,9] and high-K capacitors [10,11]. Many classes of polymers such as odd-polyamides [12], even odd polyamide copolymers [13], have shown piezoelectric and pyroelectric activities. Nevertheless, the poly(vinylidene-fluoride-trifluoroethylene) — P(VDF-TrFE) copolymer [14,15] and the poly(vinylidene-fluoride-trifluoroethylene-chlorofluoroethylene) — P(VDF-TrFE-CFE) terpolymer [16,17]. For electroactive applications, P(VDF-TrFE) copolymer is the most useful polymer because of the low poling field required to give ferroelectric behavior and high dielectric permittivity, compared with other ferroelectric polymers. Another important point is that this copolymer does not require any mechanical stretching before the poling process. Recently, it has been demonstrated that an electron irradiation of the P(VDF-TrFE) and the random incorporation of the CFE unit in P(VDF-TrFE-CFE) can achieve an electrostrictive strain greater than 5% [18–20] (higher than the P(VDF-TrFE) copolymer). This large electrostrictive behavior has been attributed to the relaxor behavior induced by defects in the crystalline phase caused by the irradiation or introduction of CFE units which is responsible of a high dielectric permittivity at room temperature [21,22]. The introduction of random defects broadens the ferroelectric transition and reduces the ferroelectric–paraelectric transition

temperature. However, the molecular origin of the dielectric relaxor behavior of fluorinated terpolymer or electron irradiated copolymer remains obscure.

The main objective of this paper is to investigate the molecular mobility over a wide frequency range by means of thermal and dielectric analysis. Thermostimulated current analysis of the terpolymer and the copolymer was used for the first time and allows us to give a molecular interpretation of the cooperativity and of the ferroelectric/paraelectric transition, called Curie transition, in fluorinated polymers.

2. Experimental section

2.1. Samples elaboration

Two kinds of fluorinated polymers were used in this study: the poly(vinylidene-fluoride-trifluoroethylene) (P(VDF-TrFE) 70–30 mol.%) copolymer and the poly(vinylidene-fluoride-trifluoroethylene-chlorofluoroethylene) (P(VDF-TrFE-CFE) 55.8–35–9.2 mol.%) terpolymer. Both of them have been purchased from Piezotech (France). P(VDF-TrFE-CFE) was synthesized by a suspension method with an oxygen-activated initiator [23].

For dielectric experiments, both as-received polymer powders were hot pressed 20 °C above their melting temperature. Films of 100 μm in thickness and 20 mm in diameter were obtained.

2.2. Standard differential scanning calorimetry

Standard differential scanning calorimetry (DSC) measurements were performed using a DSC/TMDSC 2920 setup. The sample temperature was calibrated using the onset of melting of tin ($T_m = 231.88$ °C),

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indium ($T_m = 156.6$ °C) and cyclohexane ($T_m = 6$ °C) with a heating rate of $q_h = +5$ °C min^{-1}. The heat-flow was calibrated with the heat of fusion of indium ($\Delta H = 28.45$ J g^{-1}) and the baseline was corrected using sapphire. DSC experiments were systematically carried out over a temperature range from the equilibrium state (in order to remove the effect of previous thermal history) $T_{eq} = T_m + 20$ °C down to the glassy state $T_0 = T_g - 70$ °C with a constant cooling rate $q_c = +10$ °C min^{-1}, and followed by a linear heating rate $q_h = 10$ °C min^{-1}. The crystallinity ratios of the copolymer and the terpolymer have been determined. Thanks to the heat of fusion value of the 100% crystalline homopolymer.

2.3. Thermostimulated currents

Complex Thermo Stimulated Currents [24] (TSC) thermograms were carried out using a TSC/RMA Analyser. For complex experiments, the sample was polarized by an electrostatic field $E = 3$ kV mm^{-1} over a temperature range from the polarization temperature ($T_p = 40$ °C for the terpolymer and $T_p = 110$ °C for the copolymer) down to the freezing temperature T_0 (LNT temperature) with a constant cooling rate. Then, the field was turned off and the depolarization current was recorded with a controlled heating rate ($q_h = +7$ °C min^{-1}); the equivalent frequency of the TSC thermogram was $f_{eq} \sim 10^{-2}$–10^{-3} Hz. Elementary TSC thermograms were obtained with a polarization window of 5 °C. The field was removed and the sample cooled to a temperature $T_{cc} = T_p - 30$ °C. The depolarization current was recorded with a constant heating rate q_h. The series of elementary thermograms was generated by shifting the polarization window by 5 °C toward higher temperature. ΔH and ΔS uncertainties, extracted by this method, have been estimated near 10 and 20% respectively.

2.4. Dynamic dielectric spectroscopy

Dynamic Dielectric Spectroscopy (DDS) experiments were performed using a BDS400 set up covering a frequency range of 10^{-2} Hz–3.10^6 Hz, with 10 points per decade. Experiments were carried out in a temperature range from -100 °C to 130 °C. Dielectric isothermal spectra were measured every 2 °C. During each frequency scan, the temperature was kept constant to ± 0.2 °C. The real ε'_T and imaginary ε''_T parts of the relative complex permittivity ε^*_T were measured as a function of frequency F at a given temperature T.

3. Results and discussion

3.1. Physical structure

Differential scanning calorimetry thermograms of the terpolymer and the copolymer are shown in Fig. 1. This experimental technique allows us to perform a quantitative and comparative study of the thermal transitions in semi-crystalline polymers. The heat capacity steps associated with the glass transition are weak. The glass transition temperatures have been approximately determined near -29 °C and -23 °C for the copolymer and the terpolymer respectively. For both polymers, two endothermic peaks are pointed out; according to the literature [25–27], they have been attributed respectively to the Curie transition (T_c) and to the melting (T_m), in the order of increasing temperature. Both are dealing with the crystalline regions of polymers.

The melting temperature of the P(VDF-TrFE) copolymer is located at $T_m = 152$ °C ($\Delta H_m = 26.3$ J g^{-1}); it decreases to $T_m = 122$ °C ($\Delta H_m = 23$ J g^{-1}) for the P(VDF-TrFE-CFE) terpolymer. The evolution of T_m is accompanied by a weak decrease of the melting enthalpies upon introduction of CFE units in the main chain. The width at half height of the terpolymer melting peak is twice the one of the copolymer. In the same way, the peak temperature and the enthalpies of the Curie transition decrease from $T_c = 102$ °C (higher temperature of the bimodal [28] Curie transition) and $\Delta H_{Curie} = 20.8$ J g^{-1} for P(VDF-TrFE), to $T_c = 19$ °C and $\Delta H_{Curie} = 3.3$ J g^{-1} in the case of P(VDF-TrFE-CFE).
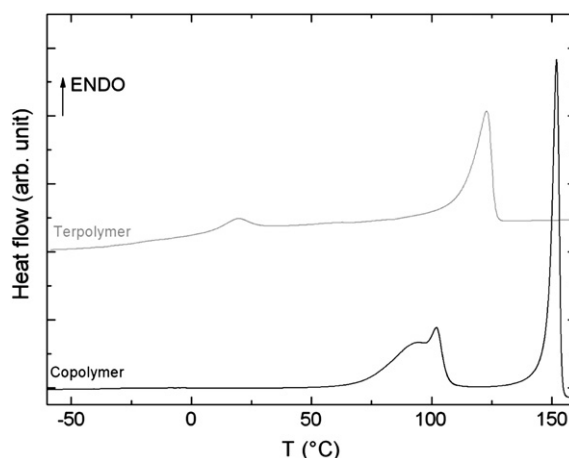

Fig. 1. DSC thermograms of the P(VDF-TrFE-CFE) terpolymer (gray line) and the P(VDF-TrFE) copolymer (black line) during the heating scan.

The degree of crystallinity has been estimated near 44% for P(VDF-TrFE) and 25% for P(VDF-TrFE-CFE). DSC experiments show that the introduction of CFE units highly influences the crystalline structure by creating less ordered crystallites. CFE units tend to reduce the crystallite sizes (T_m and T_c decrease) and increase the morphological heterogeneity of crystallites (full-width at half-maximum of the melting peaks increase). These results are consistent with the decrease of crystallinity ratio with CFE content previously reported by Klein et al. [19] and they confirm conclusions of Bao et al. [25] study about size and quality of the crystallites.

3.2. Dynamic dielectric relaxations

In order to understand the dielectric relaxor behavior of P(VDF-TrFE-CFE), dynamic dielectric spectroscopy and thermally stimulated currents have been used to characterize the molecular mobility over a wide frequency range. In Fig. 2-a/b the evolution of the imaginary (ε'') and real (ε') parts of the dielectric permittivity of P(VDF-TrFE-CFE) are reported as function of temperature for various frequencies ranging from 10 Hz to 1 MHz. Two relaxations are pointed out. The low temperature relaxation called α is localized near $T_\alpha = -15$ °C at 10 Hz. This relaxation has a Vogel–Tammann–Fulcher (VTF) behavior which has been associated with the dielectric manifestation of the glass transition. It is in agreement with previously published results [25]. The high temperature relaxation located near $T_{\alpha c} = 15$ °C at 10 Hz has been attributed to the dielectric manifestation of the Curie transition according to DSC results. The thermal evolution of the dielectric manifestation of the Curie process is more complex than the one of the α relaxation. For frequencies ranging from 10 Hz to 15 kHz, this relaxation is a quasi-isothermal process; it is consistent with a first order Curie transition. At $f_m = 15$ kHz, a merging between the α and Curie relaxations takes place. Above f_m, this merging gives rise to a unique relaxation mode with a thermal evolution similar to the α mode. The relaxor behavior of the terpolymer seems to be governed by the α process.

The real and imaginary parts of P(VDF-TrFE) are shown on Fig. 3-a/b. In both cases, two relaxations are found similar to the terpolymer. The VTF α process is located near $T_\alpha = -25$ °C at $f = 10$ Hz and the Curie peak is located at 110 °C according to DSC measurements: P(VDF-TrFE) is a ferroelectric polymer with an isothermal first order Curie transition. The dielectric strength $\Delta \varepsilon$ and the dielectric energy losses of the α relaxation in the terpolymer are higher than those of the copolymer. The high values of ε' and ε'' of the terpolymer above f_m are attributed to the superposition of the α and Curie processes.