Journal of Thermal Analysis, Vol. 40 (1993) 711-719

COOPERATIVE RELAXATIONS/TRANSITIONS IN FERROELECTRIC POLYMERS

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Dielectric relaxation and thermal transitions in β-PVDF have been investigated by Thermo-Stimulated Current spectroscopy and Differential Scanning Calorimetry respectively. A comparative study of spectra and thermograms has been performed.

The relaxation mode associated with the glass transition of the true amorphous phase is characterized by relaxation times obeying a compensation law due to cooperative molecular movements. A conformationally disordered structure is proposed for β-PVDF to explain thermal events occurring around 60°C. Ageing of ferroelectric properties of β-PVDF has been associated with cooperative molecular movements liberated largely below the melting point.

Keywords: dielectric relaxation, DSC, ferroelectric polymers, TSC spectroscopy

Introduction

The purpose of this work is to investigate relaxation phenomena occuring in ferroelectric polymers in order to improve the understanding of the structure/ferroelectric properties relationships. Polyvinylidene fluoride (PVDF) has been chosen for this work.

Differential Scanning Calorimetry (DSC), pyrocurrent measurements, and ThermoStimulated Current (TSC) spectroscopy, have been used for investigating relaxational behaviour associated with transitions in the polymer.

Materials and methods

Samples of poled, bioriented, 40 μm-thick PVDF films (Solef®) were supplied by Solvay. The effect of stretching is to transform the α-phase of PVDF into a

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β-ferroelectric phase. By poling under a high electric field, the material is rendered piezo- and pyro-electric.-

The DSC thermograms were recorded on a Perkin-Elmer DSC 7. Thermo-Stimulated Current experiments were performed on a Solomat TSC/RMA spectrometer.

The principle of the TSC technique is as follow: The sample is subjected to a DC electric field at a temperature T_p during a time t_p (2min). The temperature is then decreased till $T_o \ll T_p$ with the applied field in order to freeze the dipolar orientation. The polarization recovery is induced by increasing the temperature at a given heating rate (7 deg·min^{-1}) and the depolarization current flowing through the external circuit is measured by an electrometer.

Experimental

DSC spectra

Figure 1 shows the time derivative of the enthalpy, d*H*/d*t* *vs.* temperature reached at 20 deg·min^{-1}. The (a) and (b) curves have been recorded successively.

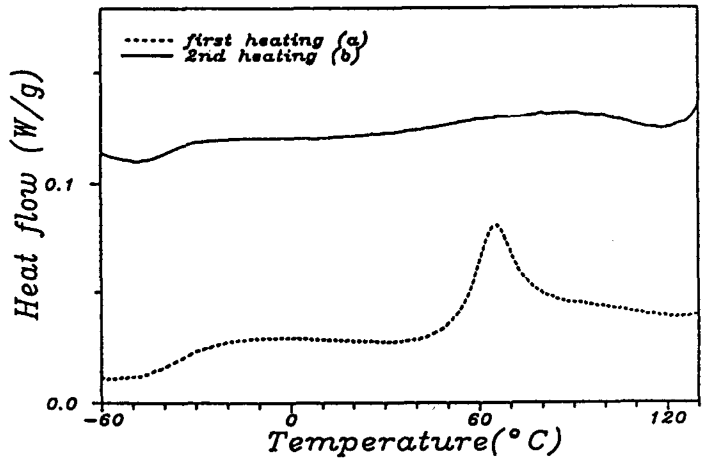

Fig. 1 DSC curves of β-PVDF. Heating rate: 20 degmin^{-1}

The classical step of the glass transition is observed for both spectra. The glass transition temperature was found at –38°C (midpoint of scan (b)). Moreover, an upper component of the glass transition is observed at 10°–15°C. It acts as a small variation in the slope of the spectrum. This thermal event has already been observed by Choy [1] in α-form PVDF.

The (a) scan displays an endothermic peak whose maximum is located at 65°C. A step in the heat flow occurs. This phenomenon is not observed on thermograms recorded immediately after the first one (Fig. 1b). An annealing of some hours at room temperature makes it to reappear. This transition will be now referred as α_c.

Pyroelectric spectra

By recording the current without previous polarization in the TSC technique, pyroelectric spectrum of the sample (Fig. 2) was obtained. Thermal cleaning with short-circuited electrodes was previously done to avoid residual charges.

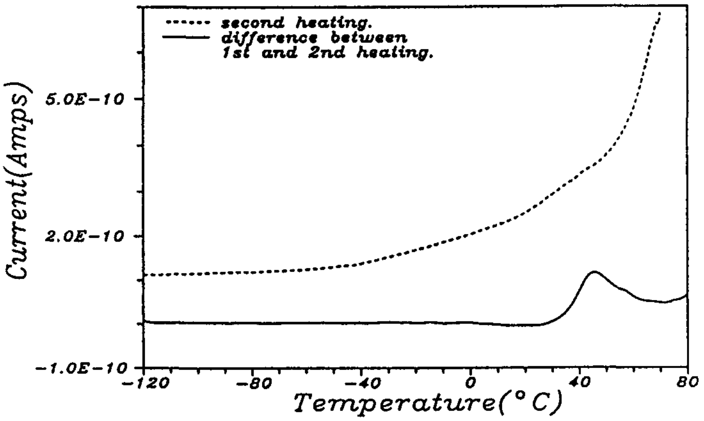

Fig. 2 Pyroelectric spectrum of β–PVDF

The pyroelectric coefficient at a temperature T is given by:

$$p_y(T) = \frac{dP}{dT} = \frac{I(T)}{\beta S},$$

where β is the heating rate, S is the sample area, and I is the current.

At 25°C, p_y (= p_3) = −28 μC/m/K. The negative value means that a temperature increase induced a polarization variation ΔP opposite to the remanent polarization P_o, i.e. a pyroelectric current opposite to the poling current. Three significant variations in the slope of the pyroelectric coefficient are observed at respectively ≈−40°C, 10°–15°C, and ≈45°C. These results are in good agreement with data previously published by Burkard and Pfister [2].

Successive pyrocurrent spectra display a large peak at 47°C, which disappears after the first run. After an annealing of some hours at room temperature, this peak reappears. It is observed whether the pyrocurrent is positive or negative, and its intensity is lowered when the pyroelectric activity of the sample is reduced. Because of close correlations with the pyroelectricity of the material, this phenomenon is ascribed to an effect of the local field on dipolar units imbedded in 'structural entities' relaxing at that temperature.

Complex TSC spectra

The complex TSC spectrum with a polarization temperature $T_p = 60°C$ is reported on Fig. 3 (circles). The field (5 MV/m) was applied during 2 min. The depolarization current was recorded at a heating rate of 7 deg·min^{-1} from −120° to 70°C. The pyroelectric signal constituted a base line. This signal was then subtracted from the recorded spectrum, for isolating the TSC component.

The peak at −38°C located in the vicinity of the glass transition temperature (T_g), has been ascribed to the dielectric relaxation associated with the glass transition.

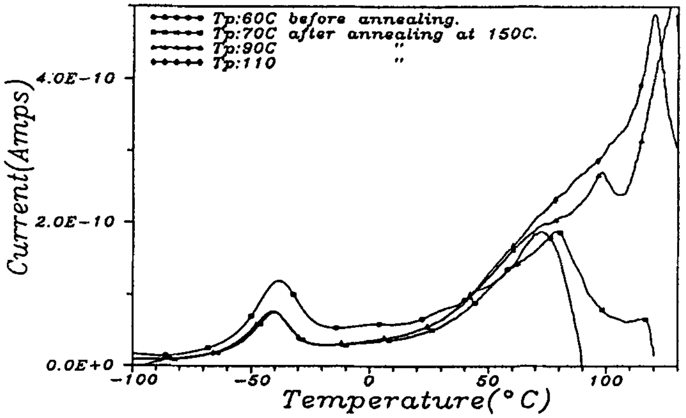

Fig. 3 TSC spectra before and after annealing at 150°C. Field: 5 MV/m

A strong increase of the TSC current is observed above room temperature. For reducing the pyroelectric component of the current, the sample was annealed at 150°C for 5 min. Thus, TSC investigations were made at higher temperatures, without being out of the range of the electrometer. Several TSC spectra with T_p varying from 70° to 120°C are reported in Fig. 3. These spectra display a relaxation mode located around 80°–90°C.

Fine structure of TSC spectra

The TSC spectrum of PVDF is obviously complex. It has been resolved by the technique of fractional polarizations [3] which has the great advantage to izolate elementary relaxation processes involved in the complex spectrum. The polarization was applied in a temperature window of 5°C which was shifted by 5° from −90° to 90°C. The obtained elementary TSC peaks are reported in Fig. 4. The relaxation time associated with each elementary process is deduced from:

$$\tau(T)=\frac{P(T)}{j(T)},\ \text{with}\, P(T)=\int_{T}^{\infty} j(T)\,\mathrm{d}T,$$

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

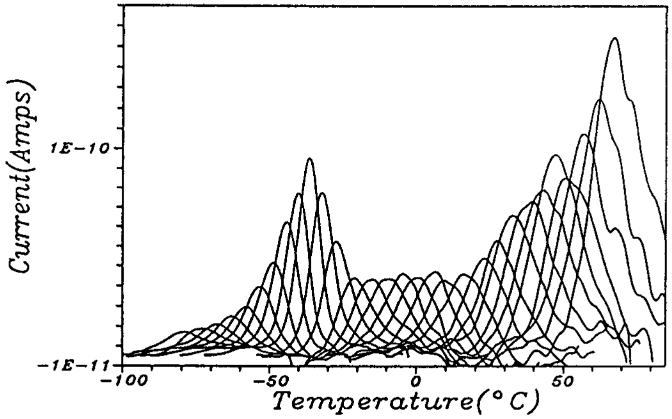

Fig. 4 Elementary peaks isolated by the technique of fractional polarizations

Arrhenian behaviour

The isolated relaxation times obey to an Arrhenius law:

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

where τ_{oi} is the pre-exponential factor, ΔH_i is the activation enthalpy, associated with a given process. The experimental data are reported on an Arrhenius diagram (Fig. 5).

Compensation law

Two groups of straight-lines clearly intersect at two points with coordinates designated by compensation temperatures (T_{c1} and T_{c2}) and compensation times (τ_{c1} and τ_{c2}).

Relaxation times obeying a compensation law are expressed by:

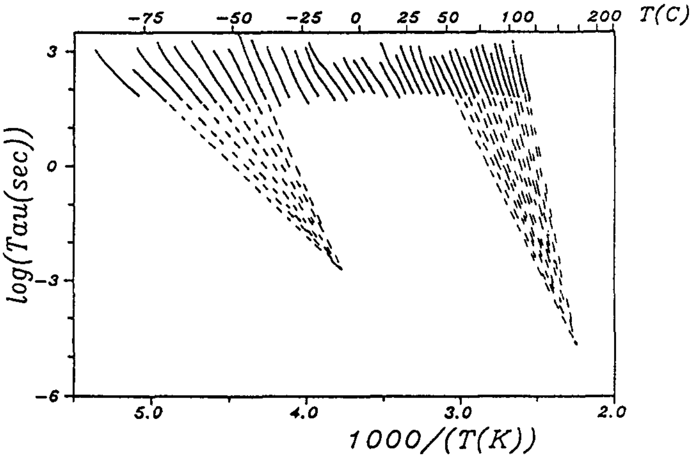

Fig. 5 Arrhenius diagram of dielectric relaxation times

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

Then, these relaxation times have the same value τ_c at T_c.

These compensation phenomena and associated parameters are characteristics of the structure of the material. The experimental values of the compensation parameters are:

$$\tau_{c1} = 2.5 \cdot 10^{-3}\ \text{sec} \qquad T_{c1} = -10°\text{C};$$

$$\tau_{c2} = 2.5 \cdot 10^{-5}\ \text{sec} \qquad T_{c2} = 170°\text{C};$$

for the lower and upper temperature component respectively.

Discussion

Glass transition/relaxation

The glass transition of β-PVDF deduced from DSC analysis and located at −38°C coincides with the TSC relaxation peak. Moreover, the study of the fine structure of this relaxation mode revealed that it is constituted of relaxation times obeying a compensation law. This behaviour has already been observed in many others polymers i.e. amorphous (polycarbonate [5]) or semicrystalline (polyamide 12 [4]). It is characteristic of the cooperative movements liberated at the glass transition in the amorphous phase. Then, this mode has been ascribed to the relaxation associated with the glass transition of the true amorphous phase of PVDF.

Effect of annealing

Upon annealing at 150°C, the pyroelectric coefficient was lowered at about 20% of its initial value. This treatment had also an effect on both the glass transition temperature and TSC peak which is lowered by 3°C in Fig. 3. Moreover, the TSC peak intensity decreases.

Yamada *et al.* [6] reported an influence of streaching on TSC in PVDF through structural changes in amorphous regions: the maximum temperature of the TSC peak is increased by higher relative amounts of β-form crystal.

The decreasing in magnitude of the thermally stimulated current in the glass transition temperature region may be ascribed to an enhancement of the crystalline rate of the material. A partial crystallisation into the α-form has probably occured upon annealing. This is consistent with the fact that PVDF streached at high temperature retains the α form [7].

α_c *transition/relaxation*

Between 40° and 80°C, an endothermic phenomenon is observed in DSC experiments. By pyroelectric measurements, we have also detected an anomalous behaviour in this temperature range. These observations disappear upon thermal cleaning and occur when the sample is annealed at room temperature for several hours. Both phenomena have probably the same molecular origin.

Moreover, relaxation processes isolated by the technique of fractional polarizations in this temperature range are characterized by decreasing activation enthalpies and by relaxation times of the order of the hour at room temperature (cf. Table 1).

Table 1 Activation parameters deduced from the technique of fractional polarizations

T_{pol}/°C	T_{pic}/°C	ΔH/eV	τ_o/sec.	τ(25°C)/h
30	42.7	1.86	$5.5\cdot10^{-29}$	0.41
35	47.4	1.90	$3.5\cdot10^{-29}$	1.30
40	52.0	2.01	$1.9\cdot10^{-30}$	6.00
45	57.1	1.57	$4.8\cdot10^{-23}$	4.60
50	62.7	1.66	$5.9\cdot10^{-24}$	19.00

Similar behaviour was observed in DSC by Loufakis & Wunderlich in α-PVDF [8]. Their interpretation was based on the existence of conformational disorder involving local $TGT\bar{G}$ to $GT\bar{G}T$ reorientations in the crystalline phase. The step in C_p may be due to a glass transition of conformationally disordered regions. The endothermic peak had been interpreted in terms of an irreversible condis crystal reorganization.

By analogy with results in α-PVDF, data obtained on β-PVDF might have a similar origin despite the TT packing of the β-phase. Moreover, Schultz *et al.* [9] found by X-ray measurements reversible changes in crystallinity between 25° and 72°C in β-PVDF. This result confirmed the role of paracrystalline regions. Further investigations are in progress for a better understanding of these phenomena.

Curie relaxation

The analysis of the fine structure of the TSC complex spectrum in the high temperature range reveales that a compensation phenomenon occured, at 170°C.

Such a behaviour had been previously observed in VDF/TrFE 75/25% mol% copolymer [10]. Copolymers of VDF and TrFE, with TrFE content ≥20% mol, are known to exhibit ferro- to paraelectric transition below the melting point. The compensation temperature corresponded to the Curie transition of the copolymer deduced from DSC thermogram (128°C).

By analogy with this result, we infered that the Curie temperature of β-PVDF is about 170°C. It confirmes the assumption proposed in the literature, that the Curie transition of PVDF is around its melting point (176°C).

The compensation phenomenon beginning at 60°C displays the cooperative character of molecular movements involved in this transition and shows that molecular mobility occurrs in crystalline regions largely below the melting point. In this way, partial reorganization of crystalline phase may be responsible for the ageing of pyroelectric properties observed upon annealing at – and above – 100°C. Such ageing of piezoelectric properties was also observed by Kolbeck [11].

Conclusion

Differential Scanning Calorimetry associated with Thermostimulated Current Spectroscopy have been applied to the investigation of transitions and relaxations of poled βPVDF.

The glass transition has two components. The lower component is found at –38°C from DSC curve. The corresponding relaxation mode was characterized by a compensation law due to cooperative movements in the true amophous phase. The upper component is located at ≈15°C. It has been associated with the glass transition of the constrained amorphous phase.

An endothermic peak (α_c), sensitive to thermal history of the material appears at ≈60°C and has been correlated to an anomalous peak on the pyrocurrent spectrum. Conformational disorder seems to be involved in these phenomena.

The Curie transition of βPVDF, 170°C, has been deduced from compensation law observed in the high temperature range of relaxation map.

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Zusammenfassung — Mittels TSC und DSC wurden die Dipolrelaxation und thermische Umwandlungen von ß-PVDF untersucht und dann eine vergleichende Analyse der Spektren und Thermogramme durchgeführt.

Die Realaxationsart bei der Glasumwandlung der echten amorphen Phase wird wegen zusammenhängender Molekülbewegungen durch Relaxationszeiten gekennzeichnet, die dem Kompensationsgesetz folgen. Zur Deutung der thermischen Vorgänge bei 60°C wird für ß-PVDF eine konformativ ungeordnete Struktur vorgeschlagen. Die Alterung der ferroelektrischen Eigenschaften von ß-PVDF wird mit den zusammenhängenden Molekülbewegungen in Zusammenhang gebracht, die unterhalb des Schmelzpunktes ausgeführt werden.