

Behaviour of the Ferroelectric Phase Transition of P(VDF/TrFE) (75/25) with Increasing Deformation

V. SENCADAS

Departamento de Física
University of Minho
4710-057 Braga, Portugal and
Department of Polymer Engineering
University of Minho
4800-058 Guimarães, Portugal

S. LANCEROS-MÉNDEZ

Departamento de Física
University of Minho
4710-057 Braga, Portugal

J. F. MANO

Department of Polymer Engineering
University of Minho
4800-058 Guimarães, Portugal and
3B's Research Group
University of Minho
4710-057 Braga, Portugal

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Samples of P(VDF-TrFE) 75/25 with several permanent deformations along the two main directions of the material were investigated by means infrared spectroscopy and calorimetric methods. The evolution of the phase transition temperature and the ferroelectric anomaly with increasing deformation was monitored and correlated with the structural changes occurring in the material.

Keywords Ferroelectrics; polymers; FTIR; DSC

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Introduction

Semi-crystalline vinylidene fluoride-trifluoroethylene (VDF-TrFe) copolymers exhibit for certain concentrations ferroelectric (FE) properties below the Curie transition temperature T_c . Upon heating the orthorhombic FE crystals transform to a paraelectric (PE) hexagonal

Address correspondence to S. Lanceros-Méndez, Departamento de Física, University of Minho, 4710-057 Braga, Portugal. E-mail: vsencadas@fisica.uminho.pt

phase before reaching the melting temperature T_m . The disappearance of the FE phase involves drastic conformational changes from the trans to gauche states [1–4]. The character of the FE transition changes from the first order to a diffuse transition with a change in the ratio of intermolecular and intramolecular interactions, which depends on parameters such as VDF content, poling, and the application of tensile stress [1].

Experimental

Films with 100 μm thickness of P(VDF/TrFE) 75/25 weight% were obtained from PIEZOTECH S.A. [4]. Different permanent stretching levels were induced along the direction of the extrusion (L) and perpendicular to it (T) with an Instron 4505 apparatus. Differential scanning calorimetry (DSC) experiments were performed with a Perkin-Elmer DSC7 apparatus at $10^\circ\text{C} \cdot \text{min}^{-1}$. Fourier Transformed Infrared (FTIR) spectra were obtained in transmission at room temperature from 400 to 6000 cm^{-1} using polarised light parallel to both L and T directions on a BRUKER 66 V spectrometer, with a resolution of 1 cm^{-1} .

Results and Discussion

DSC scans of the P(VDF-TrFE) (75/25) films after different levels of irreversible stretching showed two peaks corresponding to the FE-PE transition ($T_c = 140^\circ\text{C}$), and to the melting ($T_m = 147^\circ\text{C}$) (Fig. 1). Whereas for stretching along the L direction no significant changes were observed in both transitions, the stretching along the T direction induces destruction and destabilization of the ferroelectric phase [4].

Several cycles of DSC runs were also performed (Fig. 1). In the first cycle, the samples were heated 1°C above the FE-PE peak; the samples were melted only after the second cycle. Deformed and non-deformed samples show a similar behavior: after the first cycle in which T_c occurs at $\sim 140^\circ\text{C}$, T_c decreased $\sim 10^\circ\text{C}$ for the second heating and the transition latent heat was reduced. The same pattern is reproduced for the third run, but in a more reduced way. This means that irreversible destruction and loss of the FE phase occurs after

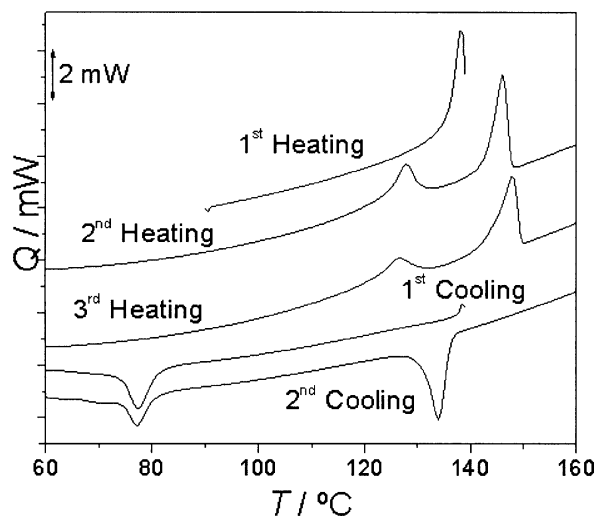


FIGURE 1 DSC curves for the copolymer before deformation. The various thermal runs are indicated in the figure.

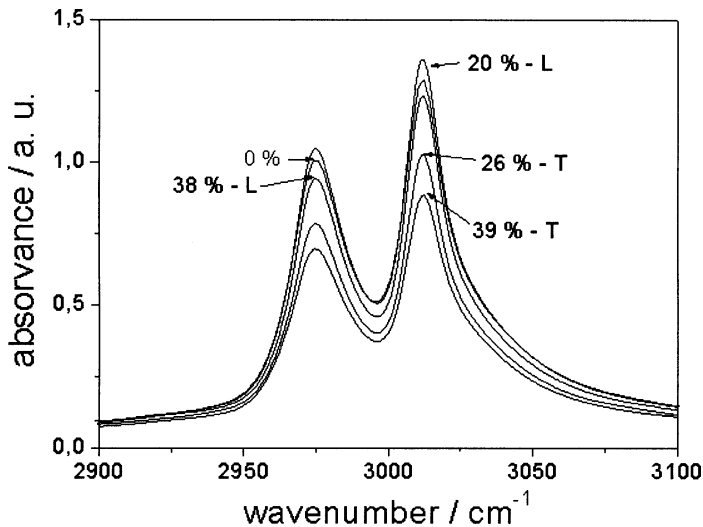


FIGURE 2 FTIR spectra of different samples of P(VDF-TrFE) in the C-H mode region. Comparison of two different deformations (T and L) and the virgin sample. The electric vector of the light is parallel to T.

the FE-PE transition. The quality of the FE phase was optimised during extrusion and the FE-PE transition was sufficient to erase the processing history, which in turn points to the importance of the poling process and the interphase for the ferroelectricity in this materials. The thermal anomalies do not show the presence of induced bond defects and show that the deformation-induced defects [4] disappear at T_c . The loss of stability of the FE crystalline phase is higher for the melted re-crystallized sample than for the deformed ones [4]. The crystallinity of the sample is slightly reduced by successive recrystallizations but it is not affected by the deformation [4].

The CH_2 symmetric (2987 cm^{-1}) and asymmetric (3012 cm^{-1}) stretching vibrations can be employed for dipolar orientation analysis [3]. Whereas only minor changes for stretching along the L direction are detected, both the CH_2 symmetric and asymmetric stretching vibrations change significantly in the presence of a deformation along T (Fig. 2), indicating a progressive dipole reorientation. Similar reorientation processes have been already observed in PVDF [5].

Infrared spectroscopy in another frequency regions, e.g. 1290 cm^{-1} , 848 cm^{-1} or 602 cm^{-1} do not show significant changes. It cannot be conclude that the deformation process changes the amount of *trans* or *gauche* conformers, as these bands are highly dependent on the degree of dipole orientation as well as on the amount of *trans* isomers and *gauche* isomers.

Conclusions

The destabilization of the FE phase with T-stretching is mainly due to a dipole reorientation. The FE-PE phase transition erases-the effects of stretching.

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