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# Anchoring, memory and relaxation phenomena in the phase transition of poly(vinylidene fluoride–trifluoroethylene) copolymers

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**Abstract.** The ferroelectric-to-para-electric phase transition in poly(vinylidene fluoride–trifluoroethylene) copolymers, with concentrations ranging from 20 to 40 mol% trifluoroethylene, has been investigated by x-ray diffraction. Since the transition is history dependent, melt-quenched samples were used and measurements were taken for the first thermal runs. The volume fraction of the ferroelectric phase has been determined for each sample as a function of the temperature. A phase transition occurs over very large intervals of temperature, reflecting a distribution of transition temperatures for different crystallites. On annealing the samples in the region of phase coexistence, relaxation phenomena are observed. Anchoring of the transition and memory effects during the thermal cycle are also found. These effects were assumed to be related to mobile defects present in the copolymers.

## 1. Introduction

Poly(vinylidene fluoride–trifluoroethylene) (P(VDF-TRFE)) copolymers are semicrystalline materials presenting a ferroelectric phase at room temperature for TRFE contents ranging from 18 to 63 mol% (Yagi *et al* 1980, Furukawa *et al* 1980). These copolymers present a structural phase transition (PT) to a high-temperature para-electric phase (Furukawa *et al* 1980, Tajitsu *et al* 1980, Yamada *et al* 1981, Yamada and Kitayama 1981). The transition has a first-order character—at least for the copolymers with less than 48 mol% TRFE (Ikeda *et al* 1987)—being of an order–disorder type; the order parameter (OP) would be the polarisation. The low-temperature phase is the same as the PVDF  $\beta$ -phase (point group,  $m2m$ ), with trans-planar chains (TT). At higher temperatures the polymer chains assume a dynamically disordered conformation, with hexagonal structure (Davis *et al* 1982, Lovinger *et al* 1983a, b, Tashiro *et al* 1981, Tashiro and Kobayashi 1986). The point group of this phase is probably  $6/mmm$ .

Although much work has been done on the low- and high-temperature phases of these copolymers, the thermal history dependence of the transition sequence has been subjected to special attention only recently (Lovinger *et al* 1983a, b, Stack and Ting 1988). In previous work, we have used calorimetric and dielectric techniques to analyse

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the thermal history influence on the PT. It appeared that the different defects in the bulk of the material play a fundamental role in the transition (Moreira *et al* 1988).

The purpose of the present work is to obtain a better understanding of the role played by defects in the ferroelectric-to-para-electric PT in P(VDF-TRFE) copolymers with different compositions. The structural evolution of the sample during the course of the thermal history was followed by systematic measurements of the x-ray spectrum. In particular, it appears that, on annealing the melt-quenched samples in the region of phase coexistence, the system configuration becomes stabilised (anchored) over a range of some degrees Celsius (about 8 °C), during which it does not present any structural evolution. This effect, which is accompanied by memory and presents relaxational properties, can also be attributed to the presence of certain types of defect in the samples. These results are discussed in comparison with the ferroelectric phase stabilisation induced by electrical or mechanical stresses (Lovinger *et al* 1983b, c, Tashiro and Kobayashi 1986).

## 2. Experimental details

The P(VDF-TRFE) copolymers with 20, 25, 30 and 40 mol% TRFE were provided by Atochem (France) (references P 988, P 989, P 997 and P 990, respectively). The samples were melted between aluminium foils, pressed at 200 °C and then air quenched to room temperature. The films obtained were about 250  $\mu\text{m}$  thick.

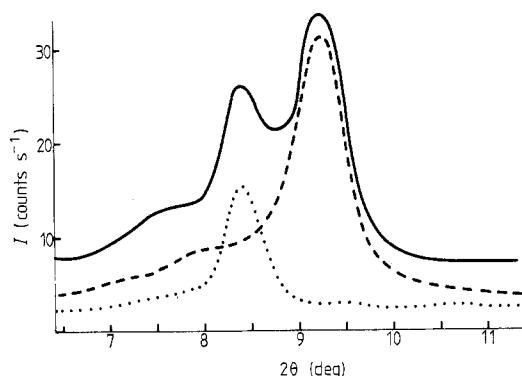
X-ray transmission scans ( $2\theta$ ) were realised with a computer-controlled apparatus, using monochromatic Mo K $\alpha$  radiation. Step-by-step counting was carried out with a Philips PW1390 photon counter. Sampling times were typically 40 s.

Air-quenched samples were heated or cooled (with  $\pm 2\text{ }^\circ\text{C min}^{-1}$  rates) in a homemade programmable oven with very thin Mylar windows (6  $\mu\text{m}$ ). Each scan was performed isothermally for about 30 min at the measurement temperature (temperature steps were generally 5 or 10 °C). Measurements were taken only for the first thermal cycles. Anchoring effects were produced in the samples by holding them for more than 12 h at a given temperature, in the region of coexistence of the two phases.

## 3. Results and discussion

### 3.1. Data analysis

At room temperature, the polymers studied here present the ferroelectric PVDF  $\beta$ -phase, which belongs to the orthorhombic system (space group, Cm2m). This structure differs slightly (about 1%) from a quasi-hexagonal one. The polymer chains present a zigzag  $\pi\pi$  conformation, with a repetition along the chain axis (the  $c$  parameter) of 2.56 Å. For this structure, the x-ray  $2\theta$  scans obtained present three more important peaks, corresponding to the reflection planes (200) + (110), (001) and (201) + (111), located, respectively, at about  $2\theta = 9, 16.3$  and  $18.6^\circ$ . On heating the samples, these peaks are continuously replaced by two others, which appear at about  $2\theta = 8.5$  and  $17^\circ$ . The first corresponds to the inter-chain spacing, and the other to the repetition along the chains in the hexagonal high-temperature phase. The PT occurs over a large temperature range (30°C or more), which depends on the sample composition (Lovinger *et al* 1983c, Moreira *et al* 1988).



**Figure 1.** X-ray scans ( $2\theta$  between 6 and  $11^\circ$ ) showing peak deconvolution for a copolymer with 25 mol% TRFE: —, diffractogram for this sample at  $120^\circ\text{C}$  (on heating); ---, weighted and shifted diffractogram of its low-temperature phase; ····, the weighted and shifted diffractogram of its high-temperature phase.

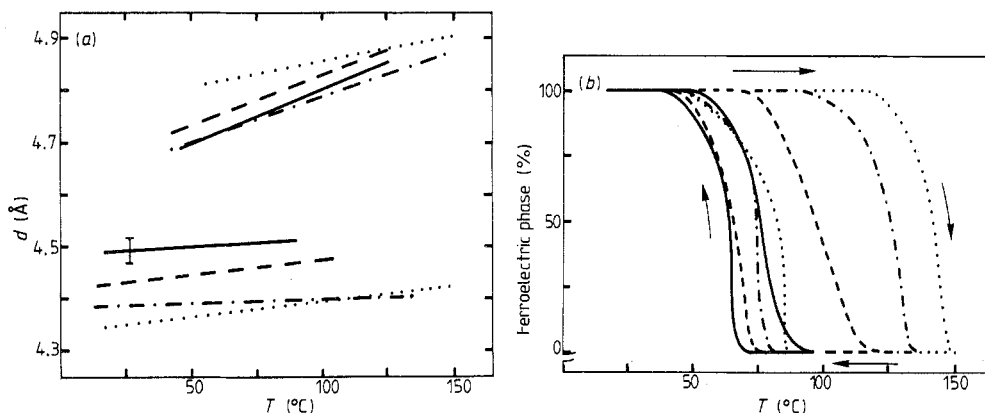
In the region of phase coexistence, each scan can be fitted by a sum of two scans (corresponding to the low- and high-temperature scans), correctly weighted and adjusted to the new peak positions. This procedure is presented in figure 1 ( $2\theta$  between 6 and  $11^\circ$ ), which shows the peak deconvolution of x-ray scans obtained at  $120^\circ\text{C}$  (first heating), for a sample with 25 mol% TRFE. The full curve represents the obtained scans; the broken and dotted curves, respectively, represent the weighted and shifted patterns corresponding to the ferroelectric and para-electric phases.

All the obtained scans could be well fitted in this way. Since no broadening of individual peaks was observed, this procedure shows indirectly that each crystallite presents either a ferroelectric or a para-electric phase. Thus, at each temperature, some crystallites have changed to the para-electric phase, and others, presenting a PT at higher temperatures, are still in the ferroelectric phase. The large temperature range of the PT that has been observed reflects a distribution of the Curie temperatures over different crystallites. In other words, for some crystallites the ferroelectric phase is more stable than for others.

Using the method described above, we could calculate, for each temperature, the volume fraction of the two phases and the corresponding peak positions (for the reflections corresponding to the inter-chain spacing). Since the samples were heated to relatively high temperatures and then subsequently cooled to room temperature, some recrystallisation was always depicted. Therefore, in order to obtain correct estimations of the volume fractions of each phase, it was necessary to take into account the sample crystallinity change. It could be realised by renormalising peak surfaces to values obtained for constant crystallinity.

### 3.2. Transitional behaviour of different copolymers

In figures 2(a) and 2(b), we present the temperature dependences of the inter-chain spacings and volume fractions of the ferroelectric phase, respectively, for the copolymers (for the first thermal cycles). We can observe that, with an increasing amount of TRFE, the transition temperatures (for heating or cooling runs), the thermal hysteresis and the jump in the lattice spacing decrease. Moreover, the slopes of the curves corresponding to the coexistence region (figure 2(b)) decrease when the amount of TRFE is increased from 20 to 30 mol% but increase thereafter (the converse is true of the width of the interval of phase coexistence). It should be noted that the curves for the 20 mol% TRFE sample are not exactly comparable with the others, since melting occurs before complete



**Figure 2.** Temperature dependence of (a) the interchain spacings and of (b) the volume fractions of the ferroelectric phase, for the P(VDF-TRFE) copolymers: —, 40 mol% TRFE; ---, 30 mol% TRFE; — · —, 25 mol% TRFE; ····, 20 mol% TRFE. In (a) the estimated error bar is indicated.

solid state transformation (Moreira *et al* 1988); the heating curve of this copolymer drops more quickly, and the cooling curve corresponds rather to a slowly (re)crystallised sample.

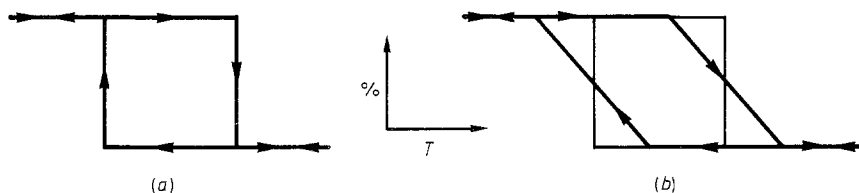
For the observed variations with copolymerisation, we could try to explain the behaviour in terms of the influence of defects contained in the material, as we have already done previously (Moreira *et al* 1988). In that work, we discussed how some TRFE-dependent defects would participate in the PT. In fact, the different defects present in the copolymers could be classified into two main categories (table 1): those that are directly dependent on the amount of TRFE, and the others which are independent of the amount of TRFE. The first group consists of head-to-head (Yagi and Tatemoto 1979), tacticity and conformational defects (Moreira 1988), and probably inhomogeneous strain fields and TRFE distributions in the different crystallites (Legrand *et al* 1988). The second group contains the amorphous phase, the semicrystalline (or anchored amorphous) phase (sometimes called the 'strained amorphous phase') and impurities.

On increase in the amount of TRFE, the system (macroscopic sample) will generally contain more defects of the first type (except for the random TRFE distribution), reducing the stability of the ferroelectric phase. Then TRFE-dependent defects are responsible for transition temperature lowering. Moreover, they reduce the crystallinity polarisation (the OP), allowing possibly a reduction in the jump of the OP to zero at the PT, and then a decrease in the first-order character of the transition. This could probably explain the narrowing of the thermal hysteresis and the reduction in the lattice spacing jump at the PT.

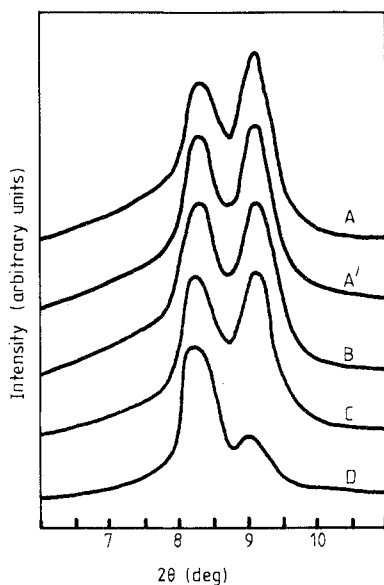
The large interval of phase coexistence could also be attributed to the presence of defects. In fact, as we represent schematically in figure 3, a perfect crystal (without defects) which presents a first-order PT would show a quasi-rectangular phase-temperature cycle (curve A), while an imperfect crystal (with defects) would behave like curve B, showing a defect-anticipated and a defect-delayed PT. The observed broadening of the coexistence region for TRFE amounts up to 30 mol% could be explained by the increase in the TRFE-dependent defects. Nevertheless, since defects act on PT via interaction with the OP, and this effect is less on increase in the amount of TRFE, there

Table 1. List of defects and their conjectured role in the observed phenomena.

Defect	TRFE dependence	Mobility	Relaxation time $\tau$	Ferroelectric phase stabilisation by poling or stretching	Anchoring and memory
Head-to-head (intra-chain)	$\nearrow$	Fixed			
Tacticity (intra-chain)	$\nearrow$	Fixed			
Conformational (intra-chain)	$\nearrow$	Fast		*	*
Strain fields (inter-chain)	$\nearrow$	Fast		*	*
TRFE distribution	$\searrow$	Fixed			
Amorphous phase	Independent		$\tau = \infty$		
Anchored amorphous	Independent	Slow	hours		*
Impurities	Independent	Slow	hours		*



**Figure 3.** Schematic drawing showing PT behaviour for systems (a) without and (b) with defects.

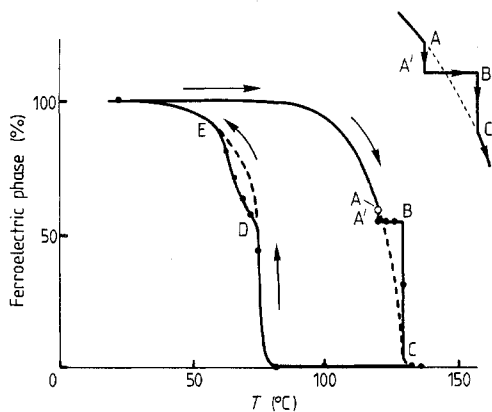


**Figure 4.** X-ray scans ( $2\theta$  between 6 and  $11^\circ$ ) for the 25 mol% TRFE copolymer curve A, before annealing; curve A', after annealing for 19 h at  $120^\circ\text{C}$ ; curve B on subsequent reheating to  $123^\circ\text{C}$ ; curve C on subsequent reheating to  $126^\circ\text{C}$ ; curve D, on subsequent reheating to  $129^\circ\text{C}$ .

would be a compensation between defects increasing and OP decreasing. The latter would become predominant for the 40 mol% TRFE copolymer, which shows a narrowing of the PT interval.

### 3.3. Anchoring and memory effects

The curves shown in figure 2(b) represent the typical hysteresis cycles obtained for samples that have been heated or cooled at  $\pm 2^\circ\text{C min}^{-1}$ , and 'annealed' for 30 min at each measurement temperature. The x-ray scans for the corresponding measurements showed continuous evolution with temperature (for peak intensities and positions). Nevertheless, a very interesting anchoring effect has been observed when a given sample has been held for more than 12 h at a fixed temperature in the phase coexistence interval. Figure 4 shows the x-ray  $2\theta$  scans for a 25 mol% TRFE sample before (curve A) and after (curve A') an annealing for 19 h at  $120^\circ\text{C}$  (on heating). After this anneal, the sample is reheated, and we can observe that the diffractogram intensities do not present any evolution up to  $126^\circ\text{C}$  (curve C) (curve B for  $123^\circ\text{C}$  is the same as curve C). Thus the system evolution has been anchored by the thermal treatment described. Nevertheless, the  $129^\circ\text{C}$  diffractogram (curve D) shows a dramatic change when compared with the others, indicating that anchoring no longer occurs. We have observed this anchoring of



**Figure 5.** Anchoring of the phase transition in a 25 mol% TRFE copolymer held at 120 °C (on heating) for 19 h. Segment AA' shows a little relaxation of the system configuration. The PT is anchored until point B, where it is suddenly unlocked (point C). Point D corresponds to a memory effect linked to the annealing at point A. The drawing in the upper right of the figure is intended to indicate, schematically, the anchoring effect.

the transition for different temperatures in the coexistence region (both for heating and for cooling runs), for the 25 and 30 mol% TRFE samples.

In order to analyse quantitatively this phenomenon, we have calculated the ferroelectric phase content for each diffractogram, and plotted them in figure 5, over a 'normal' curve (only data of interest are given). First, we can observe a relaxation of the system configuration during annealing at 120 °C (segment AA'). After the sample has been reheated, the system does not evolve for a few degrees Celsius (segment A'B), until a sudden unlocking, joining the normal curve at point C. In the upper right of this figure, we have drawn schematically the path AA'BC followed by the system. When the sample is subsequently cooled, an anomaly DE appears at point D, which corresponds to the configuration that the system had when it was locked. This represents a memory effect of the system (the measurement corresponding to point D was taken 5 h after restarting the heating from point A').

Anchoring and memory effects have been observed in incommensurate crystals and have been explained in terms of interaction between mobile defects and discommensuration walls (Saint-Gregoire 1984, Lederer *et al* 1986). In the present case, before the observed phenomena are discussed, we consider the results of Lovinger *et al* (1983b, c) and Tashiro and Kobayashi (1986), who have shown that the ferroelectric phase can be stabilised by electrical poling or mechanical stretching. In their measurements, it appeared that the effects of these stresses were to shift transition temperatures to higher values and to increase the slope of the transition curves (a reduction in the interval of phase coexistence). Nevertheless, cooling curves do not present important differences, irrespective of sample polarisation or stretching. This indicates that the stabilisation produced by classical electrical or mechanical treatments disappears at high temperatures, giving no 'memory' on cooling.

We can try to explain these effects (i.e. stabilisation of the ferroelectric phase) in terms of defects. First, with reference to the classification proposed in table 1, head-to-head, tacticity and inhomogeneous TRFE distributions can be considered as fixed defects, which do not change with electrical or mechanical stresses. Thus, they can be neglected in the present case. Next, since all the polymers studied here have glass transition temperatures below room temperature (Yagi *et al* 1980), the amorphous phase can relax quasi-instantaneously (annealed defect) and easily follow the system in all its configurations. It is clear that the amorphous phase cannot be responsible for the ferroelectric phase stabilisation. Finally, the system presents some 'mobile' defects:



TRFE-dependent conformation, inhomogeneous strain fields and independent anchored amorphous phase and impurities. These defects could be the origin of the observed stabilisation of the ferroelectric phase.

It is well known that thermal annealing (as well as electrical or mechanical stress) reduces the conformational defects present in PVDF homopolymer. The same behaviour holds for the present copolymers as long as recrystallisation does not occur (Moreira *et al* 1988, Tashiro and Kobayashi 1986). If a sample that has undergone one of these treatments is heated to its high-temperature phase, the order (reduction in these defects) that has been previously attained is lost. On subsequent cooling of the sample to room temperature, conformational defects would reappear—as soon as cooling rates are not very low (Moreira *et al* 1988). Thus, we think that conformational defects (and related inhomogeneous strain fields) are essentially responsible for the effects shown by electrical polarisation or mechanical stretching. This hypothesis is still supported by the results of Lovinger (1983b, c) which show that the shift in Curie temperature to higher temperatures with poling is more important for higher TRFE contents. This indicates that the poling process acts on TRFE-dependent defects.

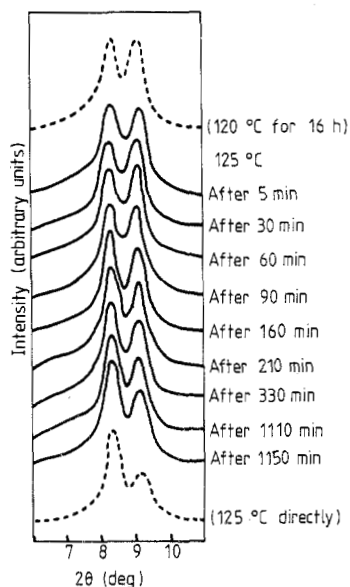
Conversely, the anchoring of the phase transition, with subsequent memory, shown in this work cannot be explained by the action on conformational defects (or inhomogeneous strain fields). Indeed, even if these defects could be reduced when 'writing up' the process, this 'information' would be erased as soon as the sample is heated to its high-temperature phase. The defects that could be at the origin of these phenomena should be mobile and would have the configuration that they took during annealing. The anchored amorphous phase (a semicrystalline region on the surfaces of the crystallites, which contains many defects) and the various types of impurity present in the sample could play this role. Mobile defects have relaxational properties. As we have already seen from segment AA' in figure 5, the system configuration evolves when the sample is held at constant temperature for some hours. Let us now present a more thorough investigation of the relaxational behaviour of the system configuration.

### 3.4. Relaxation

In order to investigate the system configuration relaxation we show, in figure 6, the time evolution of the x-ray  $2\theta$  scans at 125 °C, for a 25 mol% TRFE sample that has been previously held at 120 °C for 16 h. We can see that the system does not evolve significantly in the first hour but that, after a sufficient time, it slowly relaxes to normal behaviour. The full stabilisation is not achieved even after 12 h, a time that was necessary to write information (the relaxation time depends, of course, on the temperature).

The data in figure 6 did not allow us to obtain accurately the relaxation law followed by the system (i.e. whether it was exponential, logarithmic or of another type). If we take corrected times (each measurement takes 30 min), these data seem to follow a logarithmic decay rather than an exponential one, but this point needs more precise analysis.

In any case, the role of mobile defects in the observed mechanisms seems to be clear. During the annealing (writing the process), these defects would have sufficient time to adopt a configuration that minimises the free energy of the whole system. Subsequently, after the thermal run has been restarted, this configuration would remain until the energy difference between the low- and high-temperature phases becomes higher than the energy gain due to defect relaxation. At this point, the system changes to normal behaviour. Thus, if a cycle is realised during a relatively short time compared with the



**Figure 6.** X-ray scans (between 6 and 11°) at 125 °C, showing the relaxations of the anchored phase transition, for a sample with 25 mol% TRFE, which has been previously annealed for 16 h at 120 °C. The times indicated in the figure are the time delays between the start of a run and the moment that the sample was heated from 120 °C.

defect relaxation time, locking of the transition appears while the system configuration recovers to the state it was in when the process commenced. In these terms, the memory effect can be easily understood.

#### 4. Conclusions

Defects have been shown to play a very important role in the transitional behaviour of P(VDF-TRFE) copolymers. On increase in the TRFE content, a reduction in transition temperature, changes in thermal hysteresis and inter-chain spacing at the PT, as well as changes in the interval of phase coexistence, have been observed. These effects could be attributed to some TRFE-dependent defects.

The PT can be anchored for some degrees Celsius (about 8 °C) by long-time (12 h) annealing in the PT region. This anchoring is accompanied by the appearance of memory and relaxational processes. Mobile defects (TRFE-independent ones) such as those in the surface of the crystallites (the anchored amorphous phase) or impurities are the origin of these phenomena.

#### Acknowledgment

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