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Polymorphism of poly(vinylidene fluoride) induced by poling and annealing

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Résumé. — Dans les films étirés de fluorure de polyvinylidène, l’application d’un champ électrique de 1 MV/cm produit une transformation structurale α non polaire → αp polaire. La phase αp orientée, avec les mêmes paramètres cristallins que la phase α, est toujours accompagnée de taches de Bragg diffuses. Cette structure disparait par recuit à 170 °C pour donner une nouvelle phase orientée (α′) plus stable dans laquelle la chaîne a une conformation T3GT3G−.

Abstract. — In stretched poly(vinylidene fluoride) films, the transition from unpolar α-form to a polar form (αp) is produced by poling at 80 °C by an electric field of 1 MV/cm. This oriented form has the same lattice constants as α-form but is associated with extra diffuse reflections. This form and the diffuse reflections disappear by annealing above 170 °C and give an oriented and more stable form (α′) in which the chain has the T3GT3G− conformation.

Introduction. — It has been established for several years that poly(vinylidene fluoride), PVDF, exists in at least three crystalline forms designated as α, β, γ or respectively II, I, III and the transitions among them under various conditions (high pressure, heat treatment, drawing) have been extensively studied [1-8].

The chain in polar β-form has the all trans conformation (planar zigzag like in polyethylene) with a high dipole moment perpendicular to the c-axis. The films of β-form PVDF prepared by stretching and poling exhibit strong pyro- and piezoelectric effects.

In unpolar α-form the molecule have the TGTG− conformation and the unit cell consists of two anti-parallel dipoles, which leads to large interactions with an applied field.

Recently pyro- and piezoelectricity have been found [9] in poled α-form of PVDF. Experimental results obtained with isotropic and biaxially oriented samples have indicated a change in the crystal structure of α-form, after the poling process. It has been reported [9] that fields near 1 MV/cm cause a phase transition to a polar form (αp) with no significant change in chain conformation (TGTG−) and that higher fields near 5 MV/cm produce the β-form.

This note presents preliminary results of further investigations on the effect of poling. We report new structural changes in uniaxially oriented samples induced by poling and subsequent annealing.

Experimental. — The 100 μm thick PVDF films containing exclusively α-form with 5 % of defects of head-to-head and tail-to-tail type (HHTT) are supplied by Kureha chemical industry Co LTD of Japan.

They are extended to drawing ratios δ = 4 at 145 °C and δ = 5.5 at 155 °C. This treatment results in the orientation of the c-axes of the crystallites parallel to the drawing direction. Aluminium electrodes are evaporated on both surfaces and the films are subjected to a high d.c. field of 1 MV/cm at 80 °C for 10 min, and then cooled to room temperature with the field applied. Subsequently, the poled films are heated and annealed at high temperatures (T > 170 °C) below the melting point (178 °C). Differential thermal analysis measurements are performed with a Mettler 2000 equipment.

X-Ray fibre diagrams are taken with a cylindrical camera, with a radius of 58 mm and CuKα monochromatic radiation (λ = 1.54 Å) is used with point collimation.
Results and discussion. — 1. Poled samples exhibit a strong piezoelectric effect. The measurements of the piezoelectric coefficient $d_{33}$ have given 8.5 pC/N for $\delta = 4$ and 13 pC/N for $\delta = 5.5$. A structural analysis of these samples was carried out in order to explain the effect of poling. The X-Ray fibre diagrams were taken in the directions : a) perpendicular and b) parallel to the sample (Fig. 1), and then compared to those of unpoled films.

Furthermore the (100), (120) and (121) reflections tend to disappear in both orientations. They are pointed out by arrows in figure 2b.

Finally, annealing of these poled films for an hour at 100 °C results in a decreasing of about 50 % in piezoelectric activity, but no significant change is seen on the X-Ray diagram. Most of the trapped charges injected during the poling process have relaxed at 100 °C (10), therefore it is very likely that the residual permanent polarisation essentially arises from the oriented crystalline phase. These results confirm the previous observations in poled biaxially oriented samples and are consistent with a transition from $\alpha$-form to a polar form ($\alpha_p$) involving the rotation of TGTG$^-$ molecules [9]. The permanent polarisation in $\alpha_p$-form is due to the identical orientations of all TGTG$^-$ molecules.

Two types of additional diffuse reflections designated $D_1$ and $D_2$ have been observed out of the layer lines of the poled $\alpha$-form. No corresponding upper orders appear on the X-Ray spectrum. Both reflections are located in the reciprocal plane $(a^*, c^*)$.

$D_1$ reflections are seen in figure 1a when the incident beam is perpendicular to the film, but are not located on the $c^*$-axis. In orientation $b$, the maximum intensity is obtained by tilting the fibre axis by $15^\circ$ on the incident beam.

$D_2$ reflections are seen in figure 1b near the equator. Their shape suggests a decorrelation along the $c$-axis and their angular extension is about of $30^\circ$ with respect to the direction of the poling field. This extension does not vary significantly with the drawing ratio for $\delta = 4$ and 5.5. Its high value prevents us from determining the exact type of the disorder giving rise to the diffusion (planar or linear).

No similar reflections have been observed with the poled $\beta$-form of PVDF; therefore these diffuse reflections are presumed to arise from a particular arrangement within the $\alpha$-crystallites : packing and/or distortions of TGTG$^-$ chains.

2. In this second part, our interest is focused on the behaviour of the poled $\alpha$-form at high temperatures. The samples are fixed at both ends and then annealed above room temperature. Annealing at 100 °C for several hours does not cause any modification to the X-Ray spectrum of the poled $\alpha$-form. After annealing at 170 °C the diffuse reflections tend to decrease whereas new layer lines appear on the X-Ray fibre diagrams (Fig. 2).

Changes in intensities of the Bragg reflections are also observed in both orientations. The (100) reflection reappears in case b. The new period along the $c$-axis is found to be twice the period in $\alpha$-form. The doubling of the $c$ period can be interpreted as a change in chain conformation arising from a cooperative motion of molecules in the poled $\alpha$-form.
We suggest a T₃GT₃G⁻ conformation. Figure 3 shows the molecular conformations of TGTG⁻ type and T₃GT₃G⁻ type. In these exact models the values of the identity period are 4.4 Å for TGTG⁻ type and 8.8 Å for T₃GT₃G⁻ type. The proposed chain conformation of α'-form is similar to that of Rubber hydrochloride found by Bunn and Garner [11].

The transitions at high temperatures in poled α-form have been studied by DTA technique. The application of Differential Thermal Analysis in the case of PVDF is made difficult by:

a) the presence of numerous phases (α, β, α, α') in our samples,

b) the effect of annealing which results in thickening of lamellae and therefore increases the temperatures of the transitions [12],

c) and a possible surface phase transition which involves a change of folding plane [13].

The unannealed samples (with drawing ratio δ = 4) are heated from 140 °C to 200 °C. Figure 4 shows the melting behaviour of the unpoled and poled α-form at various heating rates. Two endotherm peaks at 177-178 °C and 180-181 °C are observed for poled films whereas only one exists in unpoled films. The first peak is common to both types of samples and coincides with the melting point of α-form. The second peak increases with decreasing heating rate, which indicates a conversion from the low temperature
Fig. 5. — X-Ray diffraction pattern of the poled α-form heated at 0.2 °C/min to 179 °C and quenched to room temperature. The rings of diffraction are due to unoriented α-form recrystallised from the melt.

(form to the high temperature form, following an activated process. The small shift of both peaks to the higher temperatures is explained by the well known phenomenon of lamellae thickening [12]. In order to identify the second peak, a sample has been heated at 0.2 °C/min to 170 °C (just between both melting peaks) and then quenched to room temperature. The X-Ray spectrum is consistent with the presence of oriented α’-form and unoriented α-form (i.e. rings of diffraction) obtained by recrystallisation from the melt (Fig. 5). This result confirms the existence in PVDF of a new form (α’) more stable than α-form (i.e. higher melting). This form must be compared to the γ-form [5-9] which is also more stable than α-form but has only been obtained in unoriented specimen.

Conclusion. — Changes in the reciprocal space have been examined for the poled α-form of PVDF. The results are consistent with a phase transition from α-form to an oriented polar form (αp) involving the rotation of the TGTG- chains, as reported in reference [9]. The additional diffuse reflections are presumed to arise from a particular packing and/or distortions of the TGTG- chains.

DTA and X-Ray diffraction analysis have revealed the existence of a new more stable form (α’) obtained by annealing the poled α-form at high temperature. The proposed chain conformation (T₃GT₃G-) is similar to that of Rubber hydrochloride. Further investigations are necessary to determine the origin of the diffuse reflections and the mechanisms of molecular deformation during poling and annealing. Present works are in progress to determine the crystal structure of this new form.

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