

$\gamma \rightarrow \beta$ Phase Transformation Induced in Poly(vinylidene fluoride) by Stretching

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ABSTRACT: The purpose of this work was to show in a conclusive way the $\gamma \rightarrow \beta$ phase transformation induced by uniaxial stretching in poly(vinylidene fluoride). Poly(vinylidene fluoride) films were melted and crystallized at 163°C for 36 h. Under these conditions, a mixture of α and γ phases was formed, with a predominance of the latter. These films were uniaxially stretched at 130°C at a draw ratio of 4. Fourier transform infrared and differential scanning calorim-

etry analyses showed a $\gamma \rightarrow \beta$ phase transition in the solid state, whereas orientation of the α phase without any transition was observed. Optical microscopy analysis permitted the observation of the transformation of spherulitic structures into oriented lamellae during stretching. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 110: 3242–3246, 2008

Key words: drawing; FTIR; phase behavior; spherulites

INTRODUCTION

Because of its important pyroelectric and piezoelectric properties, poly(vinylidene fluoride) (PVDF) has been widely investigated for the last 3 decades. PVDF is a semicrystalline polymer that can crystallize into at least four forms, α , β , γ , and δ ,¹ the last three of which are polar. The β phase is the most used in pyroelectric and piezoelectric applications. However, the most readily obtained is the α phase, which is produced by crystallization from the melt or from dimethylformamide or dimethylacetamide solutions at temperatures above 120°C.² Many studies have been carried out on the phase transitions of this polymer, the most extensively reported of which is the $\alpha \rightarrow \beta$ transition induced by uniaxial or biaxial stretching at draw ratio (R) values of 4–6 and at temperatures of 70–100°C (R is the ratio of the initial and final lengths).^{3–11} This is the most commonly used technique to produce β -phase films for applications in sensors and actuators. At higher temperatures, the amount of the β phase decreases, and the amount of the oriented α phase increases. At temperatures exceeding 120°C, an $\alpha \rightarrow \beta$ transition occurs only with $R \geq 6$.

The γ phase is obtained only by the crystallization of PVDF at temperatures above 155°C or by the annealing of α -phase films for long periods at temperatures above 155°C.^{2,12,13} Only rarely are samples obtained exclusively in the γ phase, and certain amounts of the α phase will always be present. The melting temperatures of the α and β phases depend on the resin used. For Forafon (PVDF F4000 from Atochem, São Paulo, Brazil), they practically coincide at approximately 168°C.^{2,14} This value obviously increases with the crystallization temperature increasing, and it may reach 172°C.¹⁵ The γ phase of Forafon presents two melting temperatures, which depend on the origin. When it is crystallized directly from the melt, the melting temperature is approximately 179°C, and when it is formed from the $\alpha \rightarrow \gamma$ solid-state phase transition, the melting temperature is approximately 188°C.^{12,14} All melting temperatures refer to the melting peak endotherms obtained by differential scanning calorimetry (DSC).

To the best of our knowledge, until now there has been no conclusive study yet proving the possible γ -phase transitions induced by drawing. Doll and Lando,¹⁶ Prest and Luca,¹⁷ and Tashiro et al.¹⁸ reported that attempts to orient the γ phase appeared to cause a transition to the oriented β phase, but no experimental data were presented. Hasegawa et al.¹⁹ reported a $\gamma \rightarrow \beta$ transition caused by rolling, but the authors also did not present any experimental evidence. Servet et al.²⁰ stated that they obtained this transition by drawing γ -phase films at 150°C with $R = 4$. However, the technique that they used for preparing γ -phase films (casting from a dimethyl sulfoxide solution at 100°C) is

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controversial. Under those conditions, the β phase is predominantly formed, with some α -phase inclusions.¹⁴ The film obtained by those authors probably already predominantly presented the β phase before the drawing. At that time, much confusion was very common regarding the identification of the β and γ phases by infrared spectroscopy and X-ray diffraction. The purpose of this work was to demonstrate that the $\gamma \rightarrow \beta$ phase transition occurs when a sample containing a mixture of α and γ phases is uniaxially drawn at 130°C with $R = 4$.

EXPERIMENTAL

Films 15–20 μm thick were obtained through the spreading of a PVDF (Forafilon F4000, Atochem) solution in dimethylformamide (Merck, São Paulo, Brazil; 99.5%) on a glass substrate. The initial PVDF concentration of the solution was 20 wt %. Solvent evaporation and subsequent crystallization of PVDF occurred on a heating plate at 130°C for 120 min, resulting in predominantly α -phase films. Next, these films, still adhering to the glass substrate, were melted at 220°C for 10 min and quickly cooled (20°C/min) to 163°C, at which they remained for 36 h to crystallize isothermally. After this period, the films were quenched by immersion in ice water and removed from the substrate. Subsequently, they were placed in an oven at 130°C and uniaxially drawn at a rate of 10 mm/min and at $R = 4$ by means of a device described in a previous work.¹¹ The thermocouple was maintained in the center of the stretched area of the films, with a maximum temperature variation of 2°C at the borders. The low ductility of the films did not allow drawing at lower temperatures. The films, before and after drawing, were characterized with Fourier transform infrared (FTIR) spectroscopy (Spectrum 100, PerkinElmer, São Paulo, Brazil; range = 400–1000 cm^{-1} , resolution = 2 cm^{-1} , and diaphragm diameter = 2 mm), DSC (Q100, TA Instruments; at a heating rate of 10°C/min under an argon atmosphere), and polarized light optical microscopy (model DMRXP, Leica).

RESULTS AND DISCUSSION

FTIR

Figure 1 shows FTIR spectra of one of the films before (a) and after (b) drawing. Before being drawn, the film presented a mixture of α and γ phases, as can be seen by the characteristic α -phase absorption bands at 408, 532, 614, 764, 796, 855, and 976 cm^{-1} and by the characteristic γ -phase absorption bands at 431, 512, 776, 812, 833, and 840 cm^{-1} (this last one appears as a shoulder at 833 cm^{-1}).^{12,14} This was as expected because crystallization from the melt of

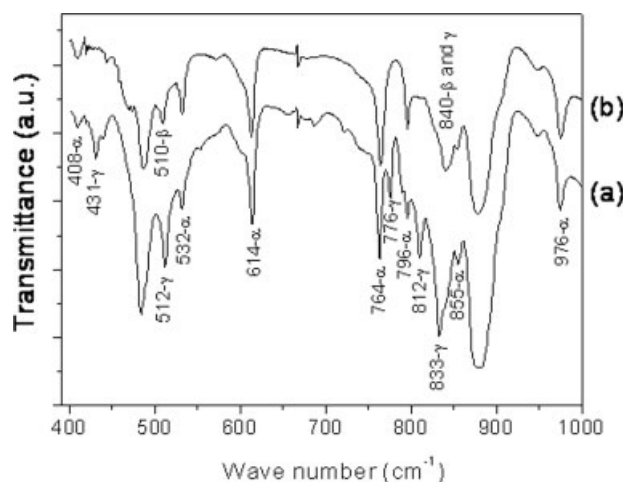


Figure 1 FTIR spectra of a film crystallized from the melt at 163°C for 36 h (a) before and (b) after uniaxial drawing at 130°C with $R = 4$. The characteristic absorption bands of the α , β , and γ phases are presented.

PVDF at temperatures above 155°C and for a long time results in these two phases.^{2,12,14} At higher temperatures and with longer crystallization times, larger amounts of the γ -phase result. The 840- cm^{-1} band is common to the β and γ phases,¹⁴ and the 493- and 879- cm^{-1} bands correspond to the amorphous phase of the polymer.²¹ After drawing, all characteristic γ -phase bands disappeared, whereas the characteristic α -phase bands remained, as well as the 510- cm^{-1} band, which is characteristic of the β phase, and the 840- cm^{-1} band, which is common to the β and γ phases. It is known that the drawing of originally α -phase films at temperatures exceeding 120°C and at $R = 4$ results in an oriented α phase,^{5,6,8,11} with a minor transition to the β phase. It can therefore be assumed that in this experiment, the α phase was oriented but remained during drawing. However, the disappearance of the bands exclusively belonging to the γ phase, the appearance of the 510- cm^{-1} band, and the permanence of the 840- cm^{-1} band demonstrated the occurrence of the $\gamma \rightarrow \beta$ solid-state phase transition.

DSC

Figure 2 shows DSC curves of a sample before and after drawing. The sample was cut into small pieces, and a mass of 5 mg was sealed in aluminum pans. Before drawing, three endotherms could be seen with peaks at 162, 181, and 190°C.

The first endotherm corresponds to the melting of α crystals formed during the quenching of the sample after crystallization at 163°C for 36 h. This time was sufficient for complete crystallization of the sample, but at 163°C (very close to the melting temperature of the α phase), in addition to the

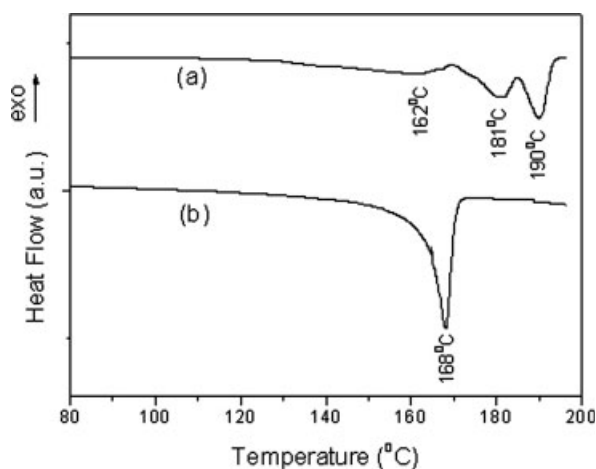


Figure 2 DSC curves of a sample (a) before and (b) after drawing. The sample mass and heating rate were 5 mg and 10°C/min, respectively.

crystallization, melting and recrystallization of the sample also occurred, and the remaining amount of molten material crystallized in the α phase during immersion in ice water. This produced crystals with very low lamellar thickness that melted at a lower temperature. The second endotherm corresponds to the melting of γ crystals formed during crystallization at 163°C, which predominated in the nonringed spherulites. The endotherm at 190°C corresponds to the melting of γ crystals formed by the $\alpha \rightarrow \gamma$ solid-state phase transformation, which occurred in the ringed spherulites. The small shoulder at the onset of the endotherm at 181°C corresponds to the melting of α crystals that crystallized at 163°C but did not yet suffer a transition to the γ phase.

After drawing, only one endotherm with a peak at 168°C could be seen, corresponding to the melting of α and β crystals^{2,14} that remained in the sample. No peak corresponding to the melting of the γ phase remained. This result corroborates those obtained by FTIR; that is, the drawing of films containing a mixture of α and γ phases causes a $\gamma \rightarrow \beta$ transition, whereas the α crystals are maintained.

Polarized light optical microscopy

Figure 3 shows a micrograph obtained by polarized light optical microscopy of a sample crystallized from the melt at 163°C for 36 h before drawing.

Two types of spherulites can be observed, ringed and nonringed. The ringed spherulites, formed during crystallization from the melt, contained predominantly the α phase.¹² During the period in which the sample remained at 163°C, an $\alpha \rightarrow \gamma$ solid-state conversion took place, increasing the amount of γ phase in these structures. The nonringed spherulites consisted predominantly of the γ phase, which crystal-

lized directly from the melt, with some α -phase inclusions.¹² Therefore, the characteristic FTIR γ -phase bands observed for the sample before drawing were due to these two types of phase formation.

A film with initial dimensions of 20 × 40 mm² was kept fixed in the stretching apparatus so that there would be a drawing region of only 10 mm. During drawing, orientation started in the necking region in the center of the sample. With R increasing, orientation proceeded toward the sample borders. After drawing, with $R = 4$, the sample, now measuring 70 mm, presented three different regions (Fig. 4). A central region of approximately 25 mm (region 1) was completely oriented. A second one was composed of two unoriented semiregions of 15 mm each at the edges of the film held between the clamps (region 3), and a third region was composed by two partially oriented semiregions, between the oriented and unoriented regions, of approximately 7.5 mm each (region 2).

In partially oriented region 2, the spherulites were destroyed by chain orientation, as can be seen in Figure 5. This destruction started in the interspherulitic regions and proceeded to the lamellae that made up the spherulites and that were more perpendicular to the draw direction, dividing these structures into two. The majority of ringed spherulites were destroyed before the nonringed ones. With an increase in R , all lamellae became oriented in the draw direction, and the spherulitic structures were completely destroyed.

Figure 6 shows a micrograph of the oriented region of the sample (region 1). The FTIR spectrum of the sample after drawing in Figure 1 was obtained from this region. The micrograph of the unoriented region (region 3) is similar to that presented in Figure 3.

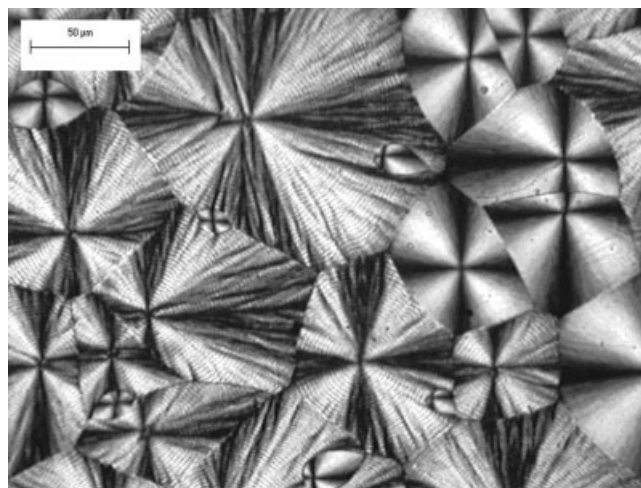


Figure 3 Morphology presented by a sample crystallized from the melt at 163°C for 36 h. The micrograph was taken at room temperature.

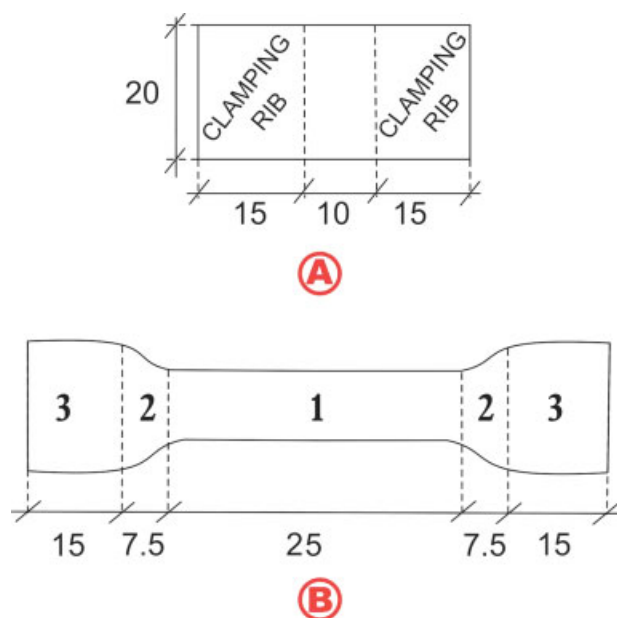


Figure 4 Scheme showing the dimensions (mm) of a film (A) before and (B) after drawing at 130°C with $R = 4$: (1) oriented region, (2) partially oriented region, and (3) unoriented region. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

Drawing at 130°C of exclusively α -phase films causes a minor transition to the β phase, likely because at this temperature chain mobility is sufficient to cause orientation of the crystals without considerable deformation. At this temperature, orientation of the α -phase crystallites is more likely to occur than the $\alpha \rightarrow \beta$ transition. When the temperature is reduced, the polymer viscosity increases, chain mobility drops, and the crystalline order is destroyed during the process. Recrystallization occurs then in the β phase, which is more likely to form at low temperatures.² Drawing between 70 and

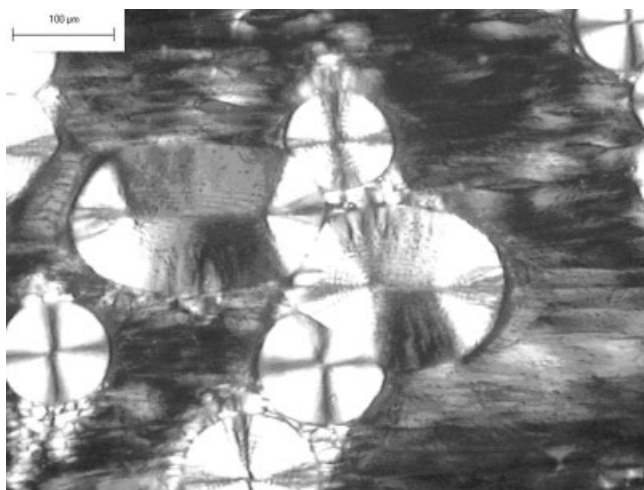


Figure 5 Micrograph of region 2 (intermediate between the oriented and unoriented regions).

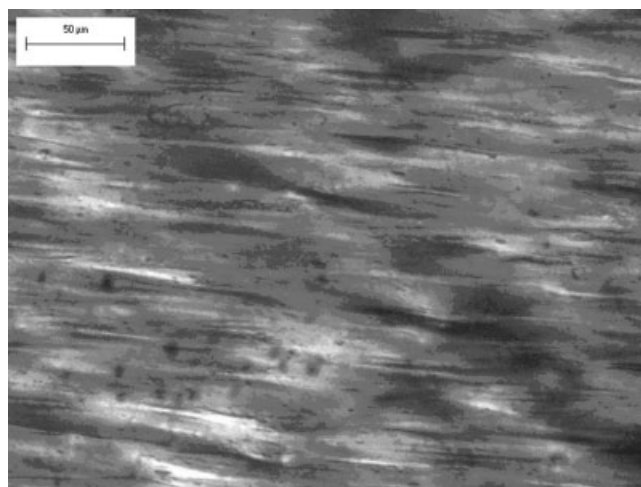


Figure 6 Micrograph of the oriented region of a sample (region 1).

80°C maximizes this transition. However, the $\gamma \rightarrow \beta$ phase transition observed here may occur even at 130°C, at which chain mobility is high. This likely occurs because the $T_3G^+T_3G^-$ conformation of the γ phase²² is more easily converted to the TTT conformation of the β phase²³ than to the TG^+TG^- conformation of the α phase.²⁴ It is unlikely that the crystallites in the γ phase will be destroyed and recrystallized during drawing because if that happens, the α phase will form, and it is the most likely to crystallize at 130°C.² The crystallites likely experience a $\gamma \rightarrow \beta$ solid-state transformation similar to the $\alpha \rightarrow \gamma$ transition observed during high-temperature annealing ($\geq 155^\circ\text{C}$) of α -phase films.^{12,17} Films in the β phase obtained in this way are likely better oriented than those obtained by the drawing of originally α -phase films between 70 and 80°C, as an increase in the draw temperature facilitates orientation and also allows higher R values.

CONCLUSIONS

PVDF films crystallized from the melt at 163°C for 36 h contain a mixture of α and γ phases. They present low ductility and break with $R \geq 2$ during drawing at low temperatures. When they are uniaxially drawn at 130°C with $R = 4$, the α phase becomes oriented, and the γ phase undergoes a $\gamma \rightarrow \beta$ solid-state phase transition. The resulting films present a mixture of α and β phases in the oriented region, with lamellae preferentially oriented parallel to the draw direction.

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