Studies on α to β Phase Transformations in Mechanically Deformed PVDF Films

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ABSTRACT: PVDF cast films were drawn at different temperatures to different draw ratios at constant draw rate to understand the mechanism of α to β phase transformation during mechanical deformation. WAXD and FTIR studies were carried out to determine the formation and content of β phase in the drawn films. Lower stretch temperatures gave higher fractions of β phase. The cast PVDF films were also drawn at suitable temperatures below the PVDF ambient melting point to the draw ratio of 6.4. The highest fraction of β phase obtained in these ultra drawn films was 0.98. SALS studies carried out for films at different stretch ratios show the change in spherulitic structure with the stretching parameters and give information for the understanding of phase transformation during stretching of PVDF films. © 2010 Wiley Periodicals, Inc. J Appl Polym Sci 117: 3491–3497, 2010

Key words: PVDF; uniaxial deformation; WAXD; FTIR; SALS

INTRODUCTION

Among the different crystal phases of Polyvinylidene fluoride (PVDF),[1] the β phase exhibits piezoelectricity due to its dipolar conformation.[2] β phase PVDF films are useful for piezo and pyroelectric applications like sensors, robotics, security elements, acoustic and optical devices, mechanical accessories, automotive and traffic devices, sports and leisure goods.[3] The α phase obtained by the crystallization of melt can be transformed to the β phase by mechanical deformation.[1] Drawing at lower temperatures to the natural draw ratio of ~ 4 and at higher temperatures to higher draw ratios (>4) favors the transformation from α to β phase.[4–7] Hsu and Geil[7] studied the morphological aspects of the α to β phase transformation on PVDF thick and thin films deformed at different temperatures. They reported that the α phase remains in thick films when drawn at higher temperatures, even after fibril formation.

Gregorio and Cestari[8] studied the crystallization behavior of PVDF from Dimethylacetamide (DMA) solution and reported that the crystallization rate of β phase is highest at 60°C or even slightly lower temperatures and the α phase crystallization rate is very high around 130°C. The crystals deformed during stretching are reorganized in the phase that is most stable at the processing temperature. Sajkiewicz et al.[9] showed the maximum orientation of crystallites occurs at the temperature of the α_c transition (around 65°C) and gives more β form on stretching above that temperature. Salimi and Yousefi[10] studied the β phase formation using FTIR in two grades of PVDF films and no significant difference was observed in the results of the two grades.

Sajkiewicz et al.[9] reported that the draw rate has no effect on the content of β form in particular grade of PVDF samples. A similar observation for the PVDF films drawn to lower draw ratios was reported by Mhalgi et al.[11] Matsushige et al.[4] reported that for the samples stretched at lower temperatures, the crystal transformation occurs in the region where necking is initiated and for the samples stretched at higher temperatures the necking point could not be defined as the tensile deformation at higher temperature proceeded uniformly without necking. The neck formation leads to local deformation of spherulites and lamellae in the semicrystalline sample. During mechanical deformation, spherulites are first destroyed and transformed into fibrillar morphology. Further deformation can occur by destruction of lamellar morphologies which requires more stress and lead to final up-turn in the stress–strain curve before terminal failure of the sample. This process leads to a disorganized lamellar structure.[12] In the small angle light scattering studies, Das Gupta et al.[13] observed eight-lobed patterns for the PVDF films stretched to lower draw ratios at 60°C. By X-ray diffraction studies, they found α to β phase transformation in those films. They reported that the formation of eight lobes at

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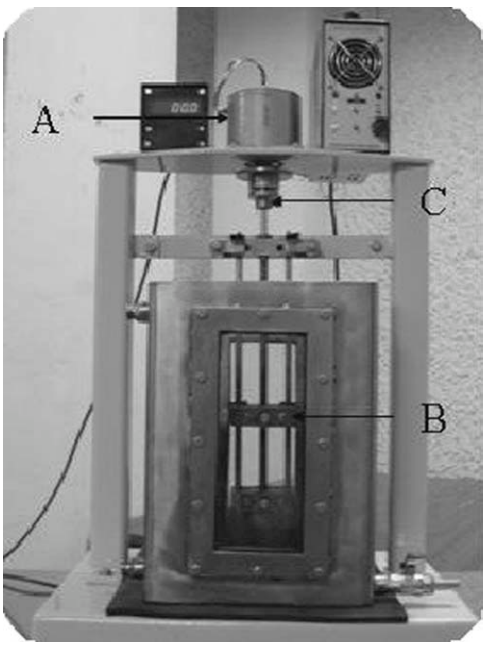

Figure 1 Ministretching unit (A) stepper motor, (B) stretching mechanism, and (C) arrangement for detaching the stretching mechanism.

that draw temperature is due to the deformation of spherulites, which occurs due to the conformational changes at a discrete yield boundary within the spherulite or by the growth of new structure due to localized melting.

In most of the literature, the drawing studies in PVDF were carried by using compressed sheet or solution cast film samples. The main objective of this work is to understand the mechanism of α to β phase transformation in PVDF films during uniaxial stretching of extruded cast films. In the present investigation, the film samples were stretched at different temperatures to different draw ratios at constant draw rate. Roll drawing was carried out to draw the films to higher draw ratios at a temperature just below the PVDF melting point. XRD and FTIR studies were carried out to determine the formation and content of β phase in the stretched films. Spherulitic structure changes with increase in draw ratios at different draw temperatures was studied using small angle light scattering technique.

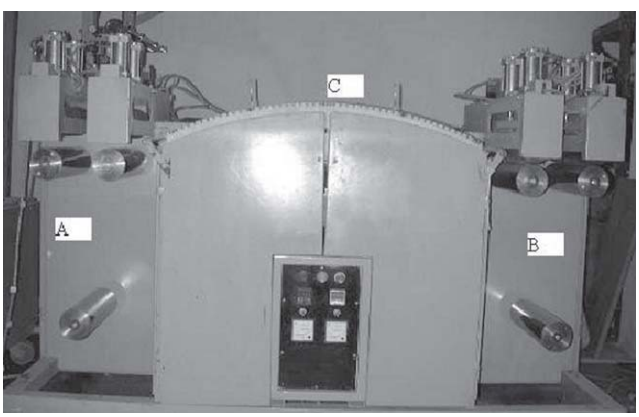

Figure 2 Continous stretching unit (A) Godet 1, (B) Godet 2, and (C) Hot plate.

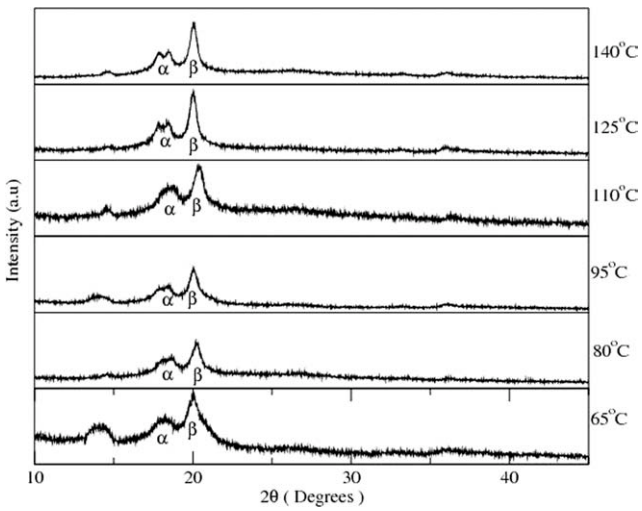

Figure 3 WAXD of the 30 μm films stretched at different temperatures to draw ratio of 1.5.

EXPERIMENTAL

Sample preparation

For experiments in the mini stretching unit, film strips of length 150 mm and a width of 15 mm were cut from the PVDF cast film produced in our laboratory. The thicknesses of the films were 30 μm and 100 μm. The film roll with 100 μm thickness was used for the experiments in the continuous

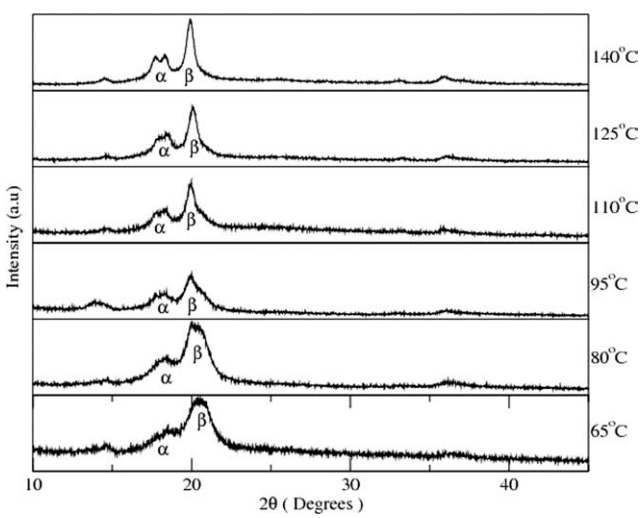

Figure 4 WAXD of the 30 μm films stretched at different temperatures to draw ratio of 2.

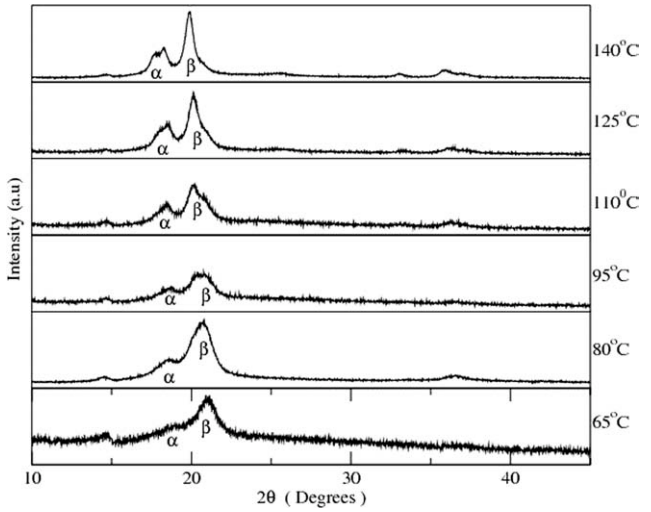

Figure 5 WAXD of the 30 μm films stretched at different temperatures to draw ratio of 3.

stretching unit. The extrusion conditions and the properties of raw material, Kynar 720 (Atofina, France), used for the film production are reported elsewhere.[11]

Stretching unit and drawing

A mini stretching unit, which operates on the principle similar to that of a Universal Testing Machine (UTM), was used for stretching studies (Fig. 1). The stretching mechanism has two grips, the bottom one is fixed and the top one is movable. The sample of desired dimension is fixed between the two grips and the stretching mechanism is connected to the assembly which is connected to the stepper motor. The rate of movement of top grip toward upward direction can be controlled by the speed of stepper motor.

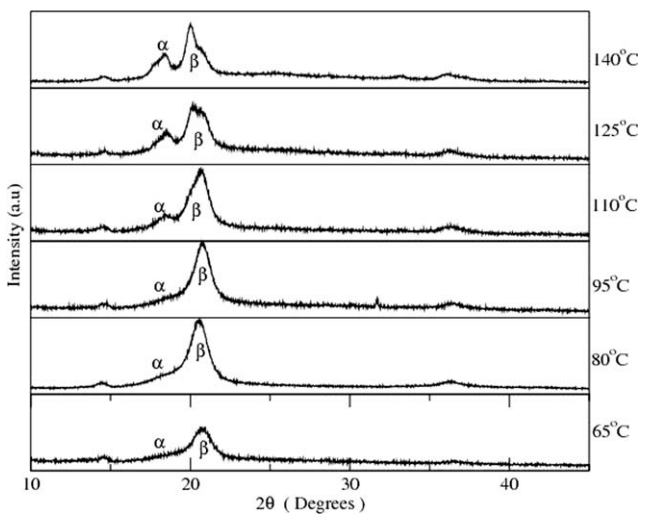

Figure 6 WAXD of the 30 μm films stretched at different temperatures to draw ratio of 4.

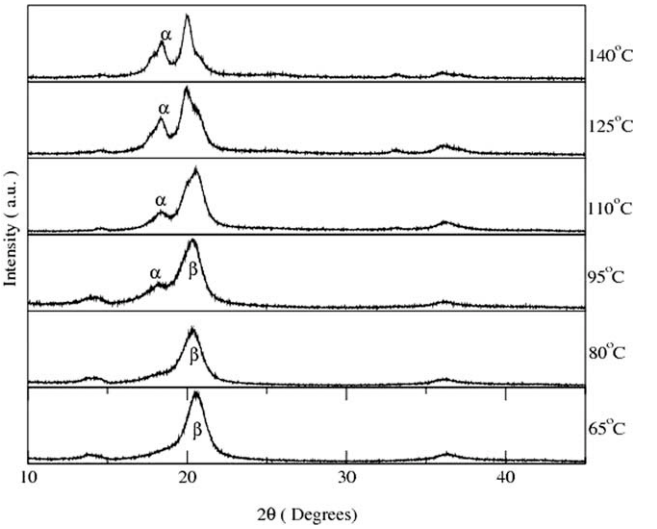

Figure 7 WAXD of the 100 μm films stretched at different temperatures to draw ratio of 4.

The stretching mechanism is kept inside an oil bath which can be heated up to 145°C.

Drawing of the film strips was performed by heating the oil to the desired temperature (65, 80, 95, 110, 125, and 140°C). The draw ratio was calculated by the relative length extension of inked lines, 5 mm apart, imprinted laterally on the film before stretching. The samples from 30-μm thick films were drawn to draw ratio of 1.5, 2, 3, and 4 and the samples from 100-μm thick film were drawn to draw ratio of 3 and 4. At the draw ratios of 1.5 and 2, the 100-μm film samples showed nonuniform stretching in the inked line region. All the experiments were carried out at a constant deformation rate of 55.5 mm/min.

A schematic of the continuous stretching unit is shown in the Figure 2. In this unit, the hot plate was heated by the electrical heaters. The temperature on the plate can be controlled. The film from the unwinder is passed into the Godet 1 in which rollers are rotating at a constant speed. From these rollers, the film is passed over the hot plate and then to the rollers in the Godet 2. Rollers in Godet 2 are rotated at higher speed compared with the rollers in the Godet 1. By controlling the speed of the Godets, the draw ratio is controlled. The film roll having 100 μm thickness was drawn to draw ratio of 6.4 at 145°C. Beyond the draw ratio of 6.4, the film formed fibrils and tore. At this temperature, the 30-μm thick film

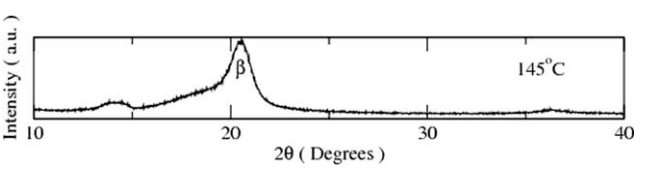

Figure 8 WAXD of the 100 μm films stretched to draw ratio of 6.4 at 145°C.

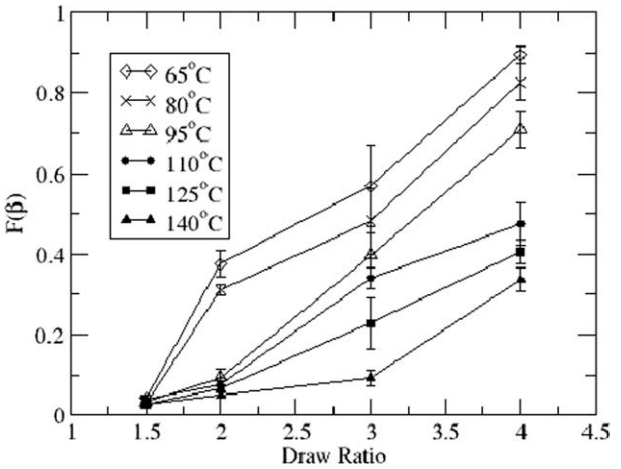

Figure 9 Fraction of β-phase for the 30 μm films stretched to draw ratio of 1.5, 2, 3, and 4 at different temperatures.

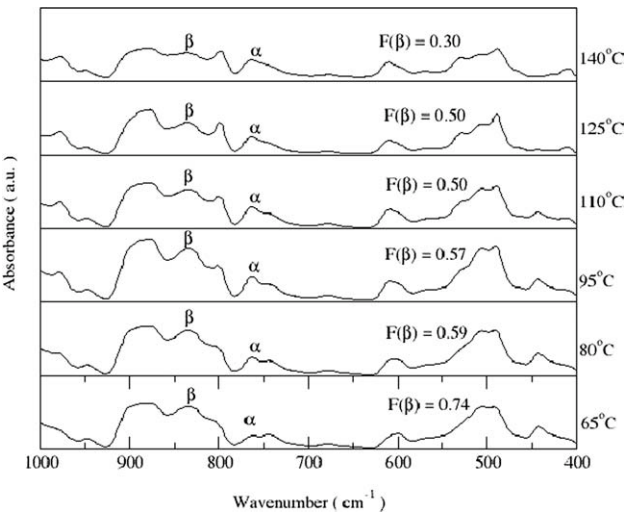

Figure 10 FTIR spectra of the 100 μm films stretched to draw ratio of 4 at different temperatures.

stick to the hot plate and hence are not used in the continuous stretching unit.

Characterization

Wide angle X-ray diffraction

X-ray scattering experiments were performed using Cu Kα radiation (1.54 Å) from X-ray diffractometer (Philips Analytical, Holland). The samples were scanned in the range of 10° to 45°. The peaks corresponding to the 2θ values of 17.7°, 18.4°, and 19.9° are ascribed to the diffraction in (100), (020), and (201) planes, belong to α phase. The peak at 20.4° refers to the sum of the diffraction in (110) and (200) planes, which is the characteristic of the β phase.[14]

Fourier transform infrared spectroscopy

FTIR spectra for the drawn films were obtained using a spectrophotometer (Nicolet, USA). All spectra were recorded with the resolution of 2 cm^{-1} in the range of 400 cm^{-1} to 4000 cm^{-1} and with the plane of polarization both in parallel and perpendicular to the drawn direction. Peak heights corresponding to 766 cm^{-1} and 840 cm^{-1} related to α and β phases, respectively, were measured by using the "peak height tool" of the software (omnic).

The quantitative analysis of the fraction of β phase present in the stretched films was obtained using the Beer–Lambert law, the procedure similar to that of Gregorio and Cestari.[8] The spectra obtained in parallel and perpendicular direction of elongation were used to calculate the structural absorbance (A) of the specified absorbtion band as follows:

$$A = \left(\frac{A_{\parallel} + 2A_{\perp}}{3}\right) \quad (1)$$

where $A_{\parallel}$ and $A_{\perp}$ are the absorbances in parallel and perpendicular directions for a particular wavelength. The fraction of β phase, $F(\beta)$, can be calculated using eq. (2) as follows:

$$F(\beta) = \frac{A_{\beta}}{(1.3A_{\alpha} + A_{\beta})} \quad (2)$$

where A_{α} and A_{β} are the absorbances for the α and β phases, respectively.

Small angle light scattering

The spherulitic structure of the stretched films was studied using small angle light scattering. A He-Ne laser source with wavelength of 632.7 Å was used. The scattered patterns were recorded using a digital camera (Nikon, Coolpix, Japan).

RESULTS AND DISCUSSION

X-ray diffraction patterns for the 30 μm films stretched at different temperatures to draw ratios of 1.5, 2, 3, and 4 are shown in the Figures 3–6. The peaks corresponding to 2θ = 20.4° and 2θ = 19.9° are marked β and α, respectively. The figures show an increase in the intensity of α phase peaks with increase in the stretch temperature at all draw ratios.

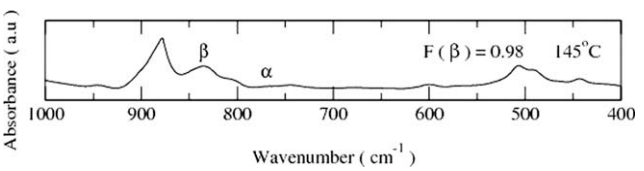

Figure 11 FTIR spectra of the 100 μm films stretched to draw ratio of 6.4 at 145°C.

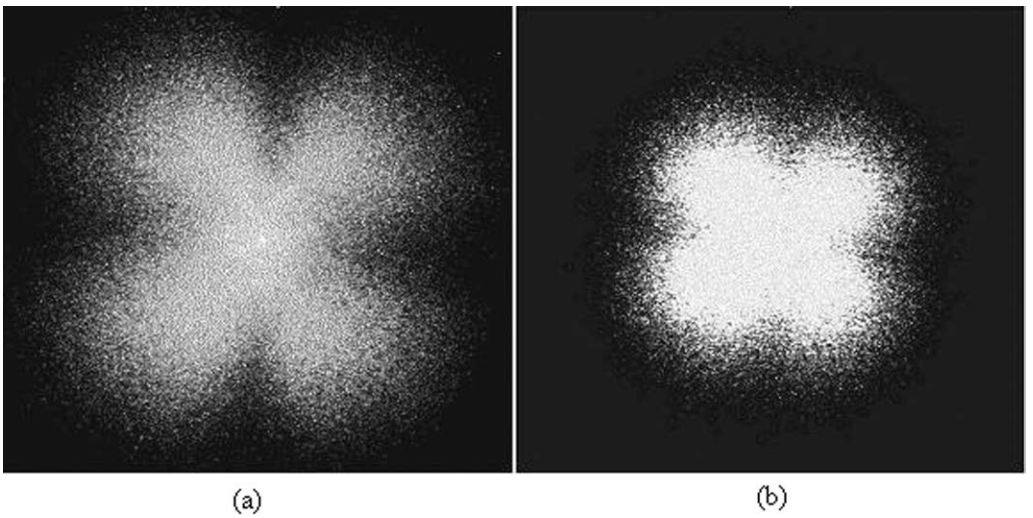

Figure 12 SALS photographs of unstretched PVDF cast films (a) 30 μm film and (b) 100 μm film.

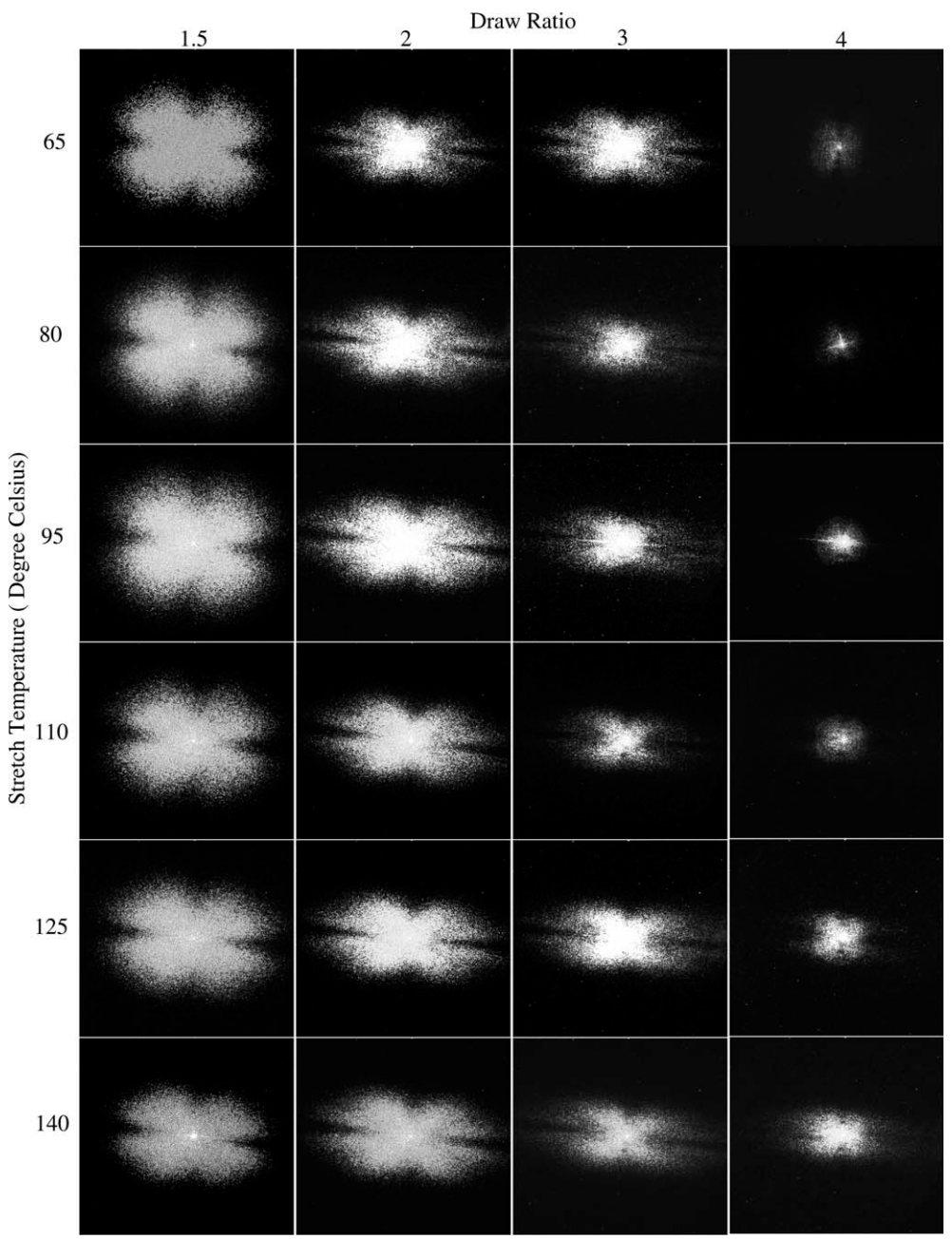

Figure 13 SALS photographs of 30 μm film stretched to different draw ratios at different temperatures.

At the draw ratio of 4, the α phase peaks completely disappear at the lower draw temperatures. The XRD patterns for the films stretched to the draw ratio of 3 and 4 clearly show the shifting of β phase peaks with increase in the stretch temperature. Thus lower stretching temperatures and stretching to a draw ratio of 4 gives a greater transformation of α to β phase. These results are consistent with earlier works on PVDF films.[4,6,7]

The XRD patterns for the 100 μm films stretched to draw ratio of 4 in the mini stretching unit and to draw ratio of 6.4 in the continuous stretching unit are shown in Figures 7 and 8. The intensity of the β phase peak for the films stretched to draw ratio of 6.4 at 145°C is higher than the intensity of β peak for the films stretched at higher temperatures to the draw ratio of 4. This sudden increase in the β form at higher draw ratio may be due to stress-induced phase transitions which occur by very high drawing stresses at high draw ratios.[5]

Quantification of the β phase fraction in the stretched films was done using FTIR spectroscopy. The fraction of beta phase ($F(\beta)$) for the 30 μm films stretched at different temperatures to the draw ratio of 1.5, 2, 3, and 4 are shown in the Figure 9. The $F(\beta)$ values increase with draw ratio at all temperatures but for a given draw ratio, the $F(\beta)$ decreases with increase in the stretch temperature. Thus $F(\beta)$ values confirm that lower stretch temperatures yield higher β phase content in PVDF films as reported previously.[9] The spectra for the 100 μm films drawn to a draw ratio of 4 in the mini stretching unit and to a draw ratio of 6.4 in continuous stretching unit are shown in the Figures 10 and 11. The peaks corresponding to 766 cm^{-1} and 840 cm^{-1} are marked as α and β, respectively. The fraction of β phase decreases with increase in the stretch temperature at the draw ratio of 4 and at higher temperature increases when stretched to higher draw ratio. Thus, the FTIR results corelate with the observations from XRD that the high stress at higher draw ratio, when the films stretched at higher temperature enhances the phase transformation in PVDF films.

SALS images of the unstretched films and for the stretched samples of 30 μm film are shown in the Figures 12 and 13. The films stretched at lower temperatures to draw ratios of 2 and 3 show eight-lobed structures. At the same draw ratios, but at higher stretch temperatures, the films show the typical four-lobed structures. As the 100 μm film samples show nonuniform stretching when drawn to draw ratio of 1.5 and 2, only the SALS images for the draw ratio of 3 and 4 are shown in Figure 14.

The eight-lobed structure formed for the 30 μm film samples stretched at lower temperatures (65°C, 80°C, and 95°C) to draw ratio of 2 and 3 is due to the initiation of spherulitic deformation due to high stress at lower temperatures.[3,11,12] The FTIR results also show higher β phase fraction for these samples (Fig. 9). At the draw ratio of 4, the spherulites may be completely deformed and transformed into fibrillar morphology, as no image is obtained by SALS. For the samples drawn at higher temperatures, the four-lobed structures of spherulites are seen at the draw ratios of 2 and 3. This indicates that the spherulites are not deformed at higher stretch temperatures and hence lower α to β phase transformation was observed from XRD and FTIR. Figure 14 shows that the 100 μm film samples stretched at higher temperatures have a spherulitic structure even at the

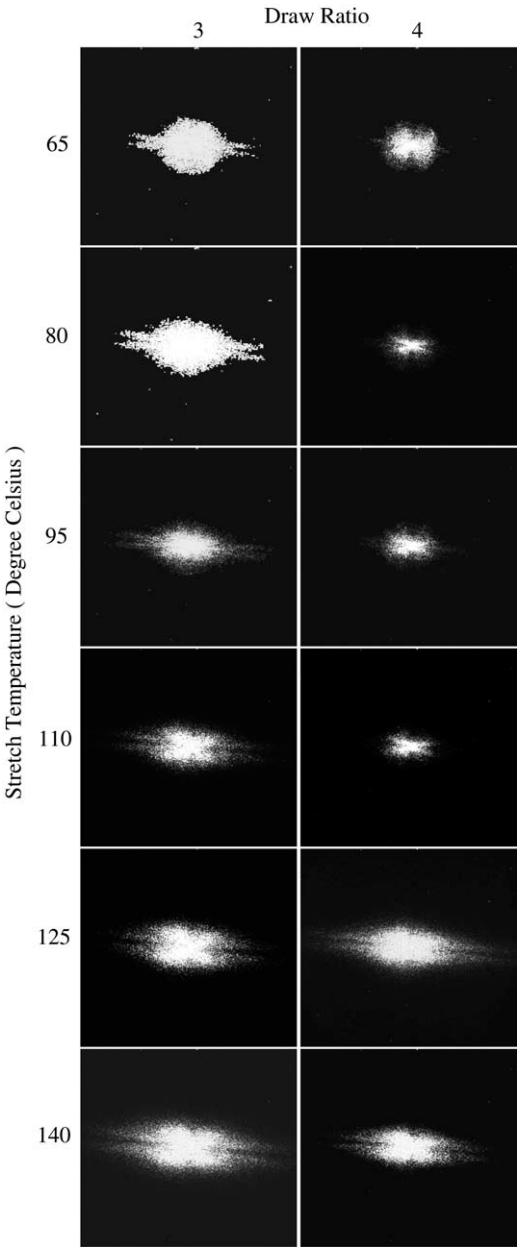

Figure 14 SALS photographs of 100 μm film stretched to draw ratio of 3 and 4 at different temperatures.

draw ratio of 4, whereas it was not seen for the samples stretched at lower temperatures. Figure 10 shows a decrease in β phase fraction for these samples with increase in the stretch temperature. This observation confirms that deformation of spherulites occurs slowly when the samples are drawn at higher temperature and results in lower β phase content compared with the samples drawn at lower temperatures. At lower temperatures the spherulitic structure is deformed during earlier stages of mechanical deformation as necking starts at lower strains in these samples.[4] At a higher temperature, the deformation of the spherulitic structure occurs only when stretched to higher draw ratios and results in high α to β phase transformation as observed for the 100 μm film samples stretched to draw ratio of 6.4 at 145°C.

CONCLUSIONS

From WAXD and FTIR studies, it is clear that there is a phase transformation during stretching and stretching at lower temperature to draw ratio of 4 or to higher draw ratios at higher temperature results in higher β phase contents. Light scattering studies on the stretched samples shown the change of spherulitic structures with increase in draw ratios for different stretch temperatures. This gives information that the maximum α to β phase transformation occurs for the films stretched at lower temperatures are due to the deformation of spherulites.

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