

Influence of Processing on Structure of β -Nucleated Poly(propylene) Fibers

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ABSTRACT: Fibers colored with quinacridone pigment spun at low take-up velocities were obtained. The spun fibers, with a very high β -form content, were drawn at room temperature and at a temperature of 120°C at different draw ratios. They were then heat stabilized at different temperatures, ranging from 140 to 150°C for different time intervals. As a result of drawing, the transition from β to mesophase, as well as that from β to α , was observed. The β to mesophase transition results from cold drawing at room temperature, while the β to α transition results from drawing at 120°C. In both cases, the significant decrease of β -form content occurs at the low draw ratio of 2. At higher draw ratios, the β -form content gradually decreases, and at a draw ratio

of 7 the β -form disappears altogether. As a result of heat stabilization, the β to α transformation was observed. The first change of the β -form content was noticed at 140°C. For fibers stabilized at temperatures above 140°C, the decrease of the β -form content is more significant and increases with the increase of the stabilization temperature. At 150°C, a rapid drop of the β -form content occurs after only 3 min, and after a few more minutes the β -form disappears. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 91: 1413–1418, 2004

Key words: poly(propylene); fibers; structure; polymorphism; WAXS

INTRODUCTION

Poly(propylene) fibers are obtained by a melt spinning process followed by drawing and heat stabilization. The structure of the spun fibers, formed during solidification of the extruded stream, undergoes further modification by subsequent processes.

As a result of processing, a fiber structure containing three phases is formed. The content of all three phases, amorphous phase, mesophase and crystalline phase, varies over a broad range, depending on the poly(propylene) characteristics and the processing parameters.^{1–9}

The crystalline phase in poly(propylene) fibers usually consists of the monoclinic α -form, the most thermodynamically stable modification commonly encountered in poly(propylene) products. The trigonal β -form was observed in poly(propylene) fibers by Chen et al.¹⁰ Our recent investigations revealed that the β -form can be obtained in the spun poly(propylene) fibers colored with quinacridone pigment spun at low temperature and a very low take-up velocity.^{11–13}

The formation of the β -form in such fibers is a consequence of the nucleating effect of the quinacridone pigment.

The addition of special nucleating agents is a common method applied to obtain the β -form of poly(propylene).¹⁴ Many different substances possessing the ability to nucleate the β -form have been reported: aromatic compounds with coplanar phenyl rings,¹⁵ N',N' -dicyclohexyl-naphthalene-2,6-dicarboxamide,^{16,17} calcium salts of dicarboxylic acids,^{18,19} a mixture of pimelic acid and calcium stearate,^{20–22} quinacridone²³ and other organic pigments.^{24,25}

Of the abovementioned substances, quinacridone pigment is one of the most effective additives.^{26,27} Through the addition of quinacridone pigment, injection moldings^{28–30} and films^{31–33} with high β -form contents were obtained.

Quinacridone pigment crystallizes, forming several crystal modifications with very high thermal stability.^{34–36} The benzene rings of the γ modification form a structural periodicity on the surface of the quinacridone crystal, which insures nearly perfect matching with a helix distance of the poly(propylene) chain.^{37,38} In this way, the crystals of quinacridone enable the epitaxial growth of the β crystals of poly(propylene).

During fiber formation, the effect of nucleating additives is strongly restricted. The crystallization process occurring inside the cooled stream of the spun filament is strongly influenced by a high molecular orientation. Under the influence of orientation, certain poly(propylene) molecules straighten up and form very effective row nuclei. The crystallization process proceeds very quickly on such formed nuclei and

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leads to the formation of the α -form of poly(propylene).

The β -form can be obtained only by careful selection of the spinning parameters to avoid formation of the row nucleated α -form.

The β -form of poly(propylene) formed in the spun fibers is not stable. It is well known that the β -form of poly(propylene) transforms itself into more stable polymorphic forms. This transformation is caused by thermal treatment and mechanical deformation.

As a result of thermal treatment, the β -form transforms into the α -form. The transformation is not reversible and occurs in the temperature range of 130 to 150°C.^{41,42}

Several mechanisms of the transformation have been proposed. Garbarczyk^{43,44} suggested that the transition proceeds in a solid state in three intermediate stages based on rotations and translations of poly(propylene) chains. Samuels⁴⁵ concluded that, because of considerable differences in unit cells of both modifications, the β to α transition must take via the liquid phase. The investigations of Vleeshouwers⁴⁶ confirmed that the transition is connected to the melting of the β -form. Zhou⁴⁷ stated that the melting of β crystals occurs partially, starting from the less perfect β crystals possessing the lowest melting temperature. Rybnikar⁴⁸ suggested that new α crystals form on the lateral faces of the remaining, thickened β lamellae by regular, probably epitaxial, overgrowth. Varga⁴⁹ and Lotz⁵⁰ stated that the transformation process can be attributed to the formation of α nuclei within the β spherulites during secondary crystallization at temperatures below 100°C. During heating, such nuclei act as very effective promoters of the α phase, and during partial melting of the β -form they initiate the growth of the α -form crystals.

As a result of mechanical deformation, the β -form can transform into the α -form or into the mesophase. The β crystals transform into the mesophase when drawing occurs at low temperatures. With drawing at higher temperatures, the β to α transformation is observed.⁵¹⁻⁵³

The abovementioned transitions occur during drawing and heat stabilization of the spun fibers containing the β -form of poly(propylene). This article aims to evaluate these transitions by studying drawing and heat stabilization under different conditions.

EXPERIMENTAL

Samples

Investigations were carried out for poly(propylene) fibers formed under laboratory conditions by means of a laboratory Brabender extruder with a five-hole spinneret with a diameter (ϕ) of 0.2 mm. The fibers were spun at a temperature of 210°C and a low take-

up velocity, in the range from 100 m/min to 300 m/min. The spun fibers were quenched in air at 20°C.

Commercial isotactic poly(propylene) (Mosten 52.945), supplied by Chemopetrol (Czech Republic), with a narrow molecular weight distribution, a density of 910 kg/m³ and a melt flow index of 25 g/10 min, was used.

As a nucleating agent, a quinacridone pigment (Pigment Violet 19, C.I.73900, Echtrot E3B, Hoechst, Germany) was applied. The polymer granulate was blended with the powdered pigment at a concentrations between 0.1 and 1 wt %.

The selected spun fibers, with maximum β -form content, were drawn and heat stabilized. Segments of fibers were drawn in an Instron tensile machine at draw ratios of 2, 3, 5 and 7. The drawing was conducted both at room temperature (20°C) and at 120°C.

Heat stabilization was performed on fibers of the same length in a Werner Mathis LTF stabilizer by putting the fibers into the preheated oven. The fibers were kept in hot air at 130, 140, 142, 144, 146, 148 and 150°C for 3, 5, 10 and 30 min.

Measurement Methods

Fiber structure was studied by wide-angle X-ray scattering (WAXS). The investigations were carried out with an X-ray diffractometer HZG-4. Diffraction patterns were registered for the powdered samples in the angular range of 5–35°. Analysis of the diffraction pattern was performed by constructing a theoretical curve, consisting of background scattering, an amorphous peak and seven crystalline peaks from the α form and two from the β form. All peaks were fitted by linear combination of the Gaussian and Cauchy functions. The parameters of the component peaks were found by minimizing the sum of the squared deviations of the theoretical curve from experimental one. The calculations were carried out with Rosenbrock's method using the computer program OptiFit.⁵⁴

The crystallinity index and K -value characterizing the content of β -form were determined. The crystallinity index was calculated as a ratio of the area under crystalline peaks to the total area. The K -value was determined according to the proposed method of Turner-Jones⁵⁵ as a ratio of the intensity of the (300) _{β} peak to the sum of intensities of the (110) _{α} , (040) _{α} , (130) _{α} and (300) _{β} peaks.

RESULTS AND DISCUSSION

Spinning

Figure 1 shows WAXS patterns of the spun fibers taken at three take-up velocities: 100 m/min, 200 m/min and 300 m/min.

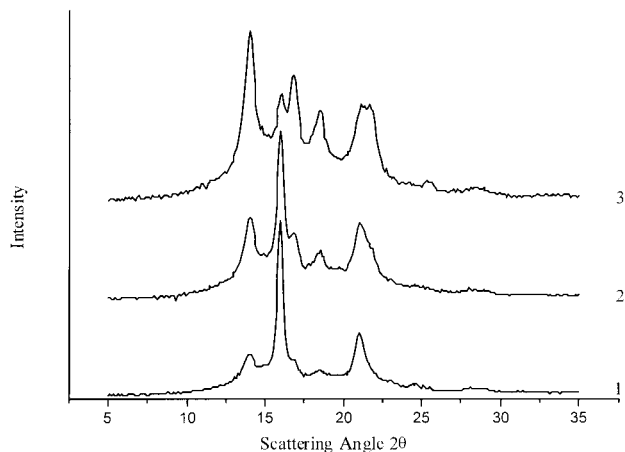


Figure 1 WAXS pattern of spun poly(propylene) fibers colored with quinacridone pigment (0.5%) taken at 1/100 m/min, 2/200 m/min and 300 m/min.

On the pattern obtained for fibers taken at 100 m/min at $2\theta = 15.95^\circ$, the strong crystalline peak (300) characteristic of the β -form of poly(propylene) is visible. Besides this peak, several weak peaks from the α -form of poly(propylene) can be observed. For higher take-up velocities, the intensity of the peak (300) decreases. Simultaneously, the intensities of crystalline peaks from the α -form of poly(propylene) increase.

The decrease of the peak intensity for fibers taken at higher velocities suggests lower β -form content. The calculated K -value characterizing the β -form content decreases from 0.81 for fibers taken at 100 m/min, to 0.58 for fibers taken at 200 m/min and to 0.18 for fibers taken at 300 m/min.

The β -form content in spun fibers depends on the pigment concentration. At lower amount of added pigment, an increase of the pigment concentration causes an increase of the β -form content. At concentrations of 0.5 and 0.7%, the β -form content achieves the highest level, and over a broad range of pigment concentration shows no change. At higher concentrations, the amount of β -form decreases, as shown in Figure 2.

These results are in accord with those of Duswalt⁵⁶ and Sterzynski.⁵⁷

The investigations of the spun fibers revealed that the highest β -form content can be obtained in fibers spun at the lowest take-up velocity of 100 m/min with a pigment concentration of 0.5%. The fibers with the maximum β -form content were chosen for further investigations.

Drawing

Figure 3 shows a series of the WAXS patterns obtained for fibers drawn at room temperature (20°C).

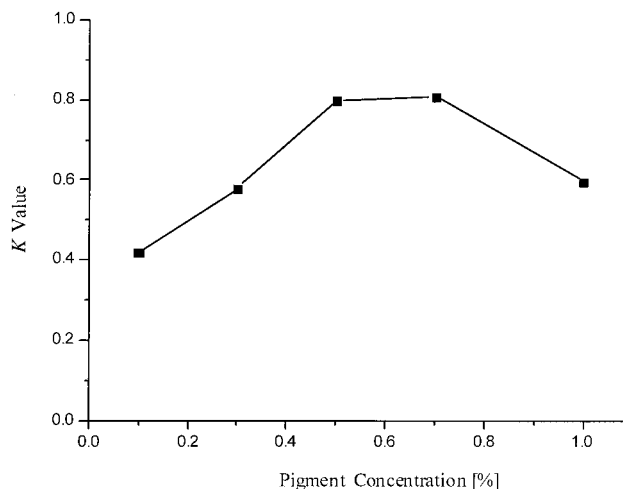


Figure 2 β -form content in poly(propylene) fibers taken at 100 m/min and colored with quinacridone pigment versus pigment concentration.

For fibers drawn at room temperature, the crystalline peaks overlap two broad mesophase peaks at $2\theta = 14.8^\circ$ and 21.2° . With the change of draw ratio, the intensity of the crystalline peak (300) of the β -form gradually decreases. The peak (300) becomes weaker and weaker, and for fibers drawn at a draw ratio of 7, it disappears. Simultaneously, the intensity of the mesophase peaks systematically increases. At a draw ratio of 7, only the mesophase peaks are visible on the pattern.

The observed changes of the WAXS pattern result from the transition of the β -form into the mesophase. The significant changes of the structure occur at a draw ratio of only 2. At this draw ratio, the β -form content drops to half of the value for undrawn fibers. Then, with the increase of the draw ratio, the trans-

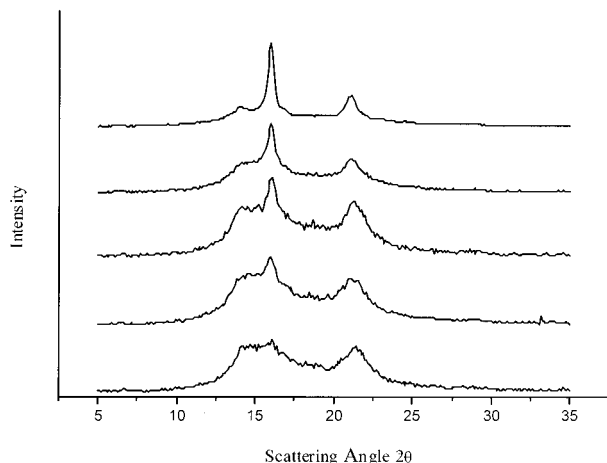


Figure 3 WAXS patterns of cold drawn fibers: (1) as-spun fibers, (2) draw ratio 2, (3) draw ratio 3, (4) draw ratio 5, (5) draw ratio 7.

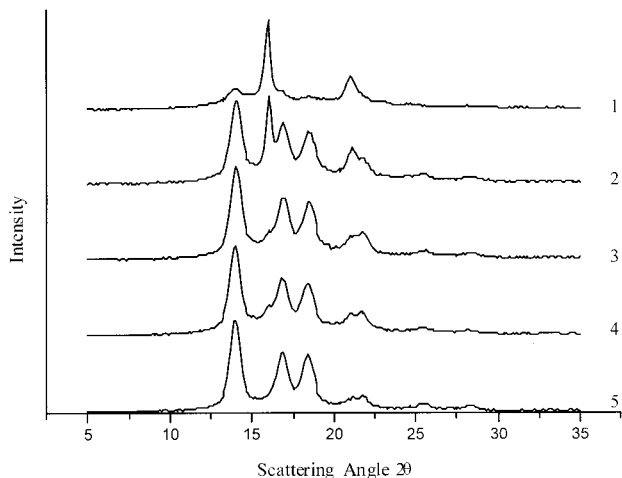


Figure 4 WAXS patterns of fibers drawn at 120°C: (1) as-spun fibers, (2) draw ratio 2, (3) draw ratio 3, (4) draw ratio 5, (5) draw ratio 7.

formation from β -form to mesophase proceeds further. The β -form content gradually decreases until the all crystals of the β -form transform into mesophase.

During drawing at 120°C, the gradual transition from β to α is observed. The series of WAXS patterns for fibers drawn at this temperature are presented in Figure 4.

For drawn fibers, the crystalline peaks of the β -form overlap the crystalline peaks of the α -form. At a draw ratio of 2, the intensity of the peak (300) of the β -form drops rapidly. At higher draw ratios of 3 and 5, the peak (300) is nearly visible, and at a draw ratio of 7 the peak (300) disappears. Simultaneous with the increase of draw ratio, the crystalline peaks of the α -form become stronger.

The observed changes of the peak intensities are caused by the β to α transition. As a consequence of this transition, the β -form content in fibers gradually decreases. At a draw ratio of 2, the K -value drops from 0.81 to 0.45, and at draw ratios of 3 and 5 it drops to 0.07.

Heat Stabilization

During heat stabilization, the first changes of the WAXS pattern occur at 140°C. For fibers stabilized at this temperature, the intensity of the characteristic (300) peak slightly decreases, shown in Figure 5. At the same time, the intensities of the crystalline peaks of the α -form increase.

The change of the β -form peak intensity is caused by the β to α transition. As a result of such transition, the β -form content minimally decreases for fibers stabilized for 3 min at 140°C. For longer times of stabilization, the decrease of the β -form content is slightly more pronounced; however, even after a very long

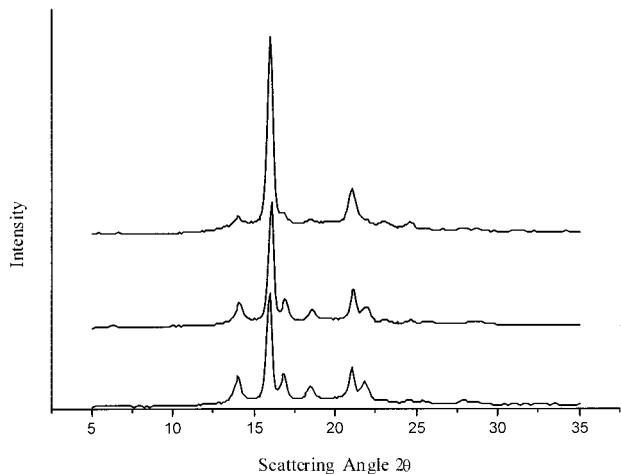


Figure 5 Effect of time of stabilization on WAXS patterns of fibers stabilized at 140°C: (1) not stabilized, (2) after 3 min, (3) after 30 min.

time, the high amount of β crystals remains unchanged.

For fibers stabilized at higher temperatures, in the range 140–148°C, the β -form content gradually decreases with the increment of the stabilization temperature, shown in Figure 6.

The greatest changes of the β -form content occur during the first 3 min of stabilization. For longer times (up to 10 min), the β -form content decreases slowly. Then the transition stops. Despite the long time of stabilization, the β -form content does not change.

Figure 7 presents WAXS patterns of fibers stabilized at 150°C. During stabilization at this temperature, a rapid drop of the intensity of the β -form peak occurs after only 3 min. After 5 min, the (300) peak of the β -form is nearly visible, but after 10 min it disappears (Fig. 7).

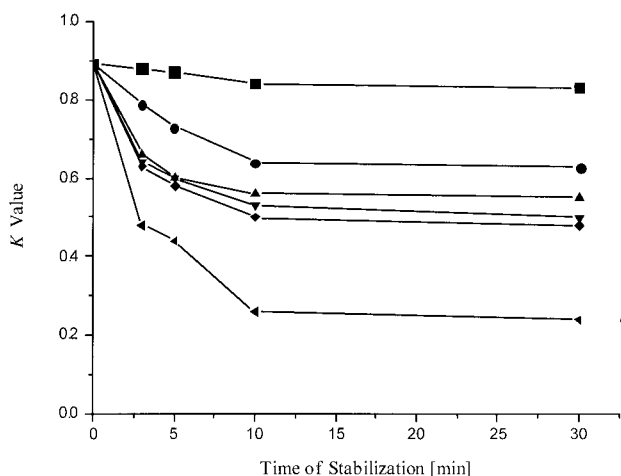


Figure 6 β -form content of the poly(propylene) fibers stabilized at: (1) 130°C, (2) 140°C, (3) 142°C, (4) 144°C, (5) 146°C, (6) 148°C.

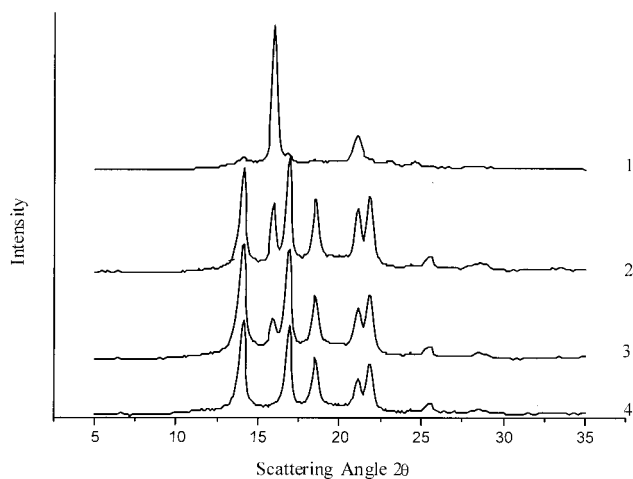


Figure 7 Effect of time on WAXS patterns of fibers stabilized at 150°C: (1) not stabilized, (2) after 3 min, (3) after 5 min, (4) after 10 min.

Discussion

During formation of the poly(propylene) fibers colored with quinacridone pigment, fibers containing the β -form can be obtained. Through appropriate selection of the spinning parameters, the content of the β -form in the spun fibers can achieve a high value, comparable to the value characterizing the β -form content in samples crystallized under quiescent conditions.^{26,58}

The structure with the highest β -form content occurs in fibers spun at a very low take-up velocity. In this case, the fiber formation proceeds under low stress and consequently under low molecular orientation. The effect of the molecular orientation on the crystallization process is minimal. The formation of row nuclei is completely avoided or strongly limited. Under such conditions, crystals of pigment act as effective nucleating agents, leading to the formation of β -form crystals.

The structures of the spun fibers undergo further transformation during the subsequent processes of drawing and heat stabilization. Heat treatment and mechanical forces cause the unstable β -form to transform into more stable polymorphic forms.

During drawing, the β form transforms into the mesophase or the α -form, depending on the drawing temperature. The β to mesophase transition, generated by drawing at room temperature, proceeds according to the mechanism proposed for the α to mesophase transition observed for cold drawn fibers containing the α -form of poly(propylene).⁵⁹ According to this mechanism, during drawing the poly(propylene) chains built in the lamellar β crystals are pulled out. As a result, partial destruction of the β crystals is observed. Due to limited molecular mobility at room temperature, the helical chains pulled from the crys-

tals aggregate into bundles with no specific arrangement of helical hands. Such bundles, representing a collection of helical segments with a random assembly of helical hands, form the mesophase, along with partially oriented chains from the amorphous regions.

At low draw ratios, only a few poly(propylene) chains are pulled out of the β crystals. At higher draw ratios, the number of pulled chains increases. Consequently, the β -form content in drawn fibers gradually decreases, while the mesophase content increases. At higher draw ratios, the regular lamellar structure of the β -form is completely destroyed, and the β -form disappears in drawn fibers.

During drawing at 120°C, the poly(propylene) chains pulled out of the β crystals possess much higher mobility. The pulled chains may form assemblies ready to crystallize into the well ordered α -form crystals.

During heat stabilization, the observed transition from β to α results from the melting of β crystals and their recrystallization into the α -form. Owing to the broad melting range of polymer crystals, one can conclude that heating to a temperature within the melting range will only cause partial melting of β crystals, those with melting temperatures just below the temperature of heat stabilization.⁴³ At temperatures near 140°C, only a small fraction of the less perfect β crystals with the lowest melting temperatures is melted. After the melting of such crystallites, the transformation stops in spite of the long time of stabilization. At higher temperatures closer to the melting temperature of β crystals, the greater part of the β lamellae is melted, and the transition proceeds further. At 150°C, the temperature above the melting temperature of β crystals, all β lamellae melt and recrystallize, forming α -form crystals. At this temperature, the β to α transition is completed, occurring rapidly (within 10 min).

CONCLUSIONS

Fiber processing causes significant changes in β nucleated fiber structure. By drawing and heat stabilization, the β form observed in spun fibers transforms into more stable forms, such as mesophase or α -form. As a result of the transition, the β -form content decreases. The range of the transition depends on processing parameters.

During drawing, the β to mesophase and the β to α transitions are observed. The transformations start at a draw ratio of only 2. At higher draw ratios, the β -form content gradually decreases with the increment of the draw ratio, until it completely disappears at a draw ratio of 7.

The transition of the β -form by drawing is connected to the pulling of the poly(propylene) chains from the lamellar crystals. At low temperatures, because of low molecular mobility, the pulled chains

may aggregate only into bundles without specific arrangement of helical hands. The rearrangement of the pulled chains into the correct helical hand registration, characteristic of the α -form of poly(propylene), can occur only with higher molecular mobility, during drawing at higher temperatures.

During heat stabilization, the β to α transformation occurs. The transformation starts above 140°C. Within the range 140–148°C, as a result of partial melting of β crystals, the β -form content drops to the limiting value, depending on the temperature of stabilization. At 150°C, all β crystals melt and the β -form disappears.

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