

# Polymorphism in Polypropylene Fibers

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**ABSTRACT:** The structure of polypropylene fibers formed by different spinning conditions was studied. The investigations were carried out using wide-angle X-ray scattering (WAXS) and small-angle X-ray scattering (SAXS) methods. It was stated that in noncolored fibers the mesophase and the monoclinic  $\alpha$  forms were formed. The highest content of the mesophase was observed for fibers extruded at the higher temperature and taken at the medium take-up velocity. In fibers colored with quinacridone pigment the structure containing the monoclinic  $\alpha$  and the trigonal  $\beta$  forms was obtained. The highest content of the  $\beta$

form occurred in fibers taken at the lowest take-up velocity. The increase of the take-up velocity caused a rapid drop in  $\beta$  form content. In fibers taken at higher velocities only the  $\alpha$  form was formed. It was found that the content of different forms as well lamellar thickness depends on crystallization conditions, which were influenced by the formation parameters. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 89: 3364–3370, 2003

**Key words:** isotactic; poly(propylene) (PP); fibers; structure; polymorphism

## INTRODUCTION

In the last few decades the dynamic development of polypropylene fibers has been observed. The great interest in polypropylene fibers attracted a significant number of investigations into the fiber's structure.<sup>1–9</sup>

These investigations showed that the structure of as-spun polypropylene fibers is strongly influenced by processing conditions. A change in the formation conditions causes a change in the cooling rate of the extruded filament and a change in the molecular orientation inside the cooled stream, parameters influenced the crystallization process, leading to the formation of the fiber structure.

Depending on the processing conditions, the fiber structure can assume a less ordered mesophase or a highly ordered crystalline phase.<sup>10</sup> The mesophase is formed at high cooling rates and a low orientation. Low cooling rates and a high orientation lead to the formation of the crystalline structure.<sup>11</sup>

The crystalline phase of isotactic polypropylene can exist in three modified forms:  $\alpha$ ,  $\beta$ , and  $\gamma$  forms.<sup>12,13</sup> The monoclinic  $\alpha$  form is the most stable and the most common form to arise from the polypropylene melt. The trigonal  $\beta$  and orthorhombic  $\gamma$  forms rarely are

formed during crystallization and only under special conditions. The  $\beta$  form arises during crystallization in a temperature gradient,<sup>14</sup> during crystallization from a sheared melt,<sup>15</sup> or during crystallization in the presence of nucleating agents.<sup>16–18</sup> The  $\gamma$  form can be obtained in polypropylene copolymers,<sup>19</sup> by crystallizing under shear,<sup>20</sup> by slow-cooling of low-molecular-weight fractions of polypropylene,<sup>21</sup> or by crystallization under high pressure.<sup>22–23</sup>

For many years only the  $\alpha$  crystals were observed in fibers. Nucleating agents that cause a growth of  $\beta$  crystals in quiescent melts of polypropylene added to the extruded melt are not effective and do not lead to the formation of a significant amount of the  $\beta$  form in polypropylene fibers.<sup>24</sup>

Nevertheless, our previous investigations revealed that  $\beta$  crystals can be formed in fibers colored with quinacridone pigment.<sup>25</sup> Quinacridone is known as a very good nucleating agent of the  $\beta$  form of isotactic polypropylene.<sup>26</sup> During crystallization of the polypropylene melt with a small amount of this pigment, a structure containing  $\beta$  crystals is formed.<sup>27–28</sup> Consequently, by the addition of quinacridone, films<sup>29–30</sup> and injection moldings<sup>31–33</sup> characterized by a high content of the  $\beta$  form can be obtained.

Results of our previous investigations led to a more systematic study of the polymorphisms of polypropylene fibers. The investigation enabled us to determine the conditions for the formation of different forms of polypropylene fibers. The results of that investigation are presented in this article.

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## EXPERIMENTAL

### Samples

The investigations were carried out formed in laboratory conditions by means of a Brabender extruder. A five-hole spinneret with a diameter of  $\phi = 0.2$  mm was used. Fibers were extruded at a constant throughput rate of 3 g/min from the melt, whose temperatures were 210°C and 250°C, to the air, whose temperature was 20°C. Fibers were spun at take-up velocities of 100–1350 m/min.

Mosten 52.945, a commercial isotactic polypropylene, supplied by Chemopetrol (Litvinou, Czech Republic), was used. Mosten 52.945 is characterized by a narrow molecular weight distribution and a melt flow index of 25 g/10 min.

Noncolored and colored fibers were produced. For the coloring of fibers, quinacridone pigment (Echtrot E3B; Hoechst, Germany) was used. The pigment, in the amount of 0.5% to the polymer mass, was mixed with a polymer granulate immediately before forming fibers.

### Measuring methods

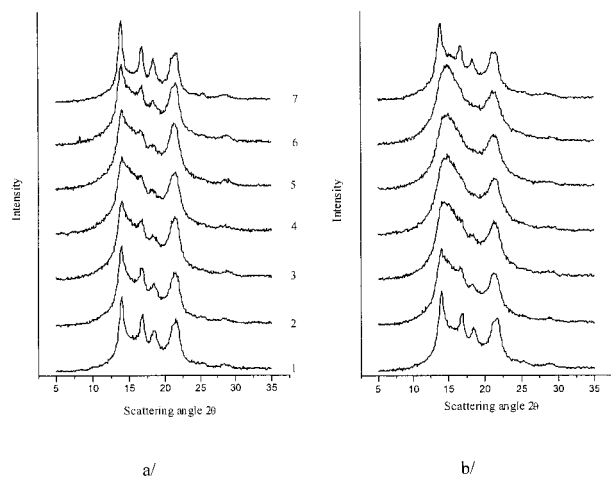
Investigation of the fiber structure was performed using the wide-angle X-ray scattering (WAXS) and small-angle X-ray scattering (SAXS) methods.

The WAXS measurements were carried out with an X-ray diffractometer (HZG-4). The diffraction patterns were registered for the powder samples in an angular range from 5° to 35°. The fibers were powdered on a Hardy microtome to segments of 10–15  $\mu\text{m}$ .

The diffraction pattern analysis was carried out according to the Hindeleh–Johnson method,<sup>34–35</sup> constructing a theoretical curve approximating the experimental curve. The theoretical curve was constructed as a sum of functions describing a background scattering, an amorphous halo, and crystalline or mesophase peaks. The parameters of the component functions were found by minimizing the sum of squared deviations of the theoretical curve from the experimental one. The minimization was carried out according to Rosenbrock's method using the OptiFit computer program.<sup>36</sup>

The crystallinity index and mesophase and  $\beta$  form-contents were calculated. The crystallinity index and the mesophase content were calculated as a ratio of the area under the crystalline or mesophase peaks to the total area. The content of the  $\beta$  form was characterized by the  $K$  value, determined as a ratio of the intensity of the  $(300)_{\beta}$  peak to the sum of intensities of the  $(110)_{\alpha}$ ,  $(040)_{\alpha}$ ,  $(130)_{\alpha}$ , and  $(300)_{\beta}$  peaks.<sup>37</sup>

SAXS analysis was performed with an MBraun SWAXS camera utilizing a conventional Kratky collimating system. The camera was mounted on top of the



**Figure 1** WAXS patterns of the noncolored polypropylene fibers extruded from the melt at temperatures (a) 210°C and (b) 250°C taken at: 1—100 m/min, 2—200 m/min, 3—300 m/min, 4—400 m/min, 5—880 m/min, 6—1050 m/min, 7—1350 m/min.

tube shield of a stabilized Philips PW 1830 X-ray generator.

The scattered radiation in the direction according to the fiber axis for a bundle of parallel fibers placed in a vacuum chamber was registered with a position-sensitive counter in the range of  $2\theta$  from 0° to 5°.

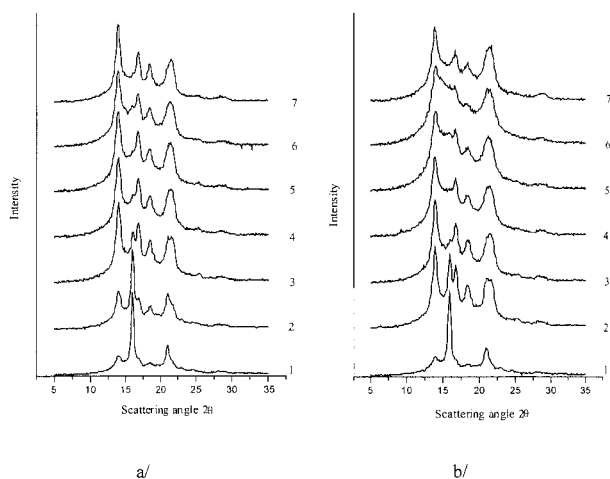
The experimental SAXS curves were corrected for sample absorption and desmeared using the direct method of desmearing, which was implemented on MBraun software (3DV).<sup>38</sup>

On the basis of the SAXS measurements, the long period and lamellar thickness were calculated. The long period was estimated from the position of the peak using Bragg's law. The lamellar thickness was calculated by multiplying the value for the long period by the volume fraction of the ordered phases estimated from the crystallinity index.

## RESULTS

### Wide-angle X-ray scattering

Figure 1 presents the WAXS patterns for the noncolored fibers spun in different conditions. For fibers taken at the lowest take-up velocity, 100 m/min, the characteristic WAXS pattern for the  $\alpha$  form of polypropylene was observed. At higher take-up velocities mesophase peaks that overlapped the crystalline peaks appeared. With an increase in the take-up velocity to 880 m/min, the intensity of the mesophase peaks increased. A great increase of the mesophase peaks was observed especially for fibers extruded at the higher temperature, 250°C. Above 880 m/min the intensity of the mesophase peaks decreased, and at the highest take-up velocity, 1350 m/min, only crystalline peaks were observed.



**Figure 2** WAXS patterns of the polypropylene fibers colored with quinacridone pigment extruded from the melt at temperatures (a) 210°C and (b) 250°C taken at: 1—100 m/min, 2—200 m/min, 3—300 m/min, 4—400 m/min, 5—880 m/min, 6—1050 m/min, 7—1350 m/min.

The series of WAXS patterns for fibers colored with quinacridone pigment are presented in Figure 2. On patterns obtained for colored fibers taken at lower velocities, crystalline peaks characteristic for the  $\alpha$  and  $\beta$  forms were observed. The highest intensity of the  $(300)_\beta$  peak occurred for fibers taken at the lowest take-up velocity, 100 m/min. With an increase in the take-up velocity, the intensity of the  $(300)_\beta$  peak decreased. An especially rapid drop in the intensity of the  $(300)_\beta$  peak could be observed for fibers extruded at the higher temperature, 250°C. At higher take-up velocities the  $(300)_\beta$  peak disappeared, and only the  $\alpha$  peaks were observed.

In fibers extruded at the higher temperature, 250°C, taken at higher velocities, from 400 m/min to 1050 m/min, weak mesophase peaks were observed.

The WAXS patterns revealed that in polypropylene fibers a structure containing crystalline, mesophase, and amorphous phases was formed. The content of those phases changed across a broad range depending on the formation parameters. The values of the crystallinity index and the mesophase content are presented in Table I.

### Small-angle X-ray scattering

For all fibers independent of the formation parameters, SAXS patterns exhibited a distinct maximum. For noncolored fibers at velocities from 100 to 400 m/min the maximum moved to a higher value. Increasing the take-up velocity at higher velocities caused a shift in the peak position back toward lower values (Fig. 3).

Similarly, for fibers colored with quinacridone pigment, increasing the take-up velocity shifted the maximum toward higher values and at higher velocities toward lower values (Fig. 4).

The maximum of the SAXS curve was connected with the lamellar structure forming in the polypropylene fibers. The calculated values of the long period,  $L$ , and the lamellar thickness,  $l$ , are presented in Table II.

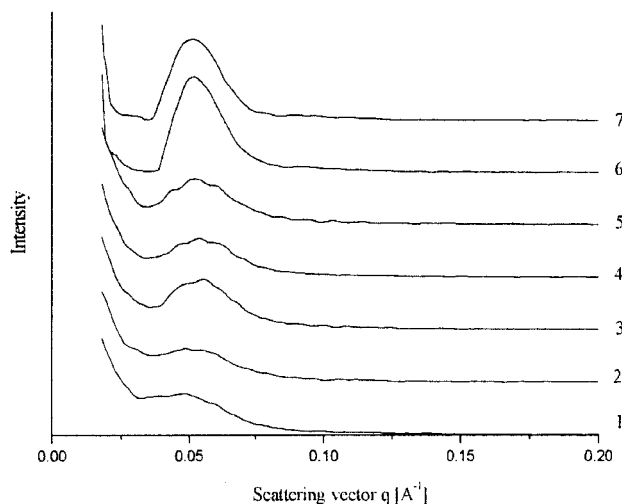
## DISCUSSION

The fiber structure was formed during the crystallization process occurring inside the cooled stream. Crystallization occurred in a complex nonisothermal way under varying stress conditions. In such conditions the crystallization process was governed by the cooling rate and the stress, which influenced the molecular orientation.

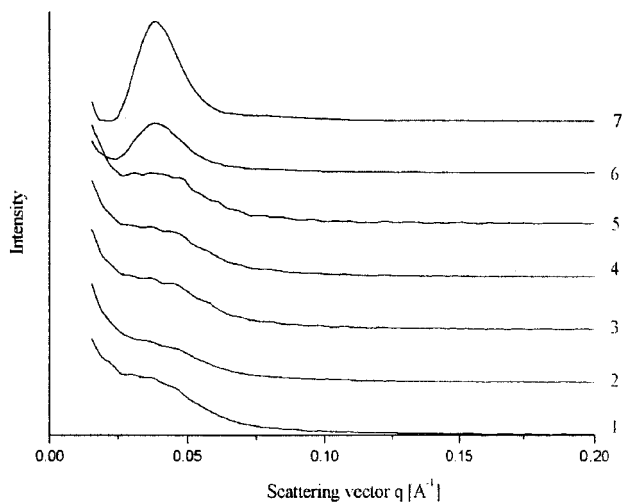
At a low take-up velocity the cooling rate dominated the crystallization process. In fibers taken at the

**TABLE I**  
Crystallinity Index and Mesophase Content in Polypropylene Fibers Formed in Different Conditions

Fibers	Take-up velocity [m/min]	Fibers extruded at 210°C		Fibers extruded at 250°C	
		Crystallinity index	Mesophase content	Crystallinity index	Mesophase content
Noncolored	100	0.52	—	0.41	0.09
	200	0.40	0.10	0.32	0.19
	300	0.34	0.16	0.18	0.33
	400	0.32	0.19	0.10	0.35
	880	0.33	0.17	0.10	0.35
	1050	0.35	0.16	0.12	0.33
	1350	0.53	—	0.41	0.10
Colored with quinacridone pigment	100	0.55	—	0.51	—
	200	0.52	—	0.51	—
	300	0.51	—	0.50	—
	400	0.51	—	0.40	0.11
	880	0.51	—	0.34	0.17
	1050	0.52	—	0.32	0.18
	1350	0.52	—	0.42	0.09



a/



b/

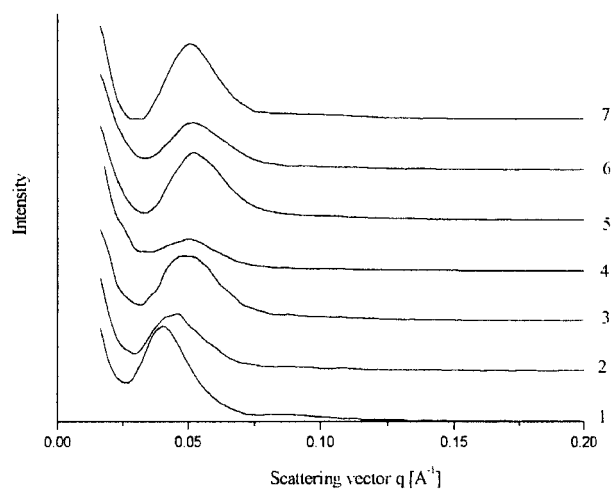
**Figure 3** SAXS patterns of the noncolored polypropylene fibers extruded from the melt at the temperatures (a) 210°C and (b) 250°C taken at: 1—100 m/min, 2—200 m/min, 3—300 m/min, 4—400 m/min, 5—880 m/min, 6—1050 m/min, 7—1350 m/min.

lowest take-up velocity, 100 m/min, while the cooling rate was the lowest, crystallization occurred at a relatively high temperature. In fibers the crystalline structure was formed, and lamellar thickness, depending, according to the Gibbs-Thomson equation, on the crystallization temperature,<sup>39</sup> achieved its highest value.

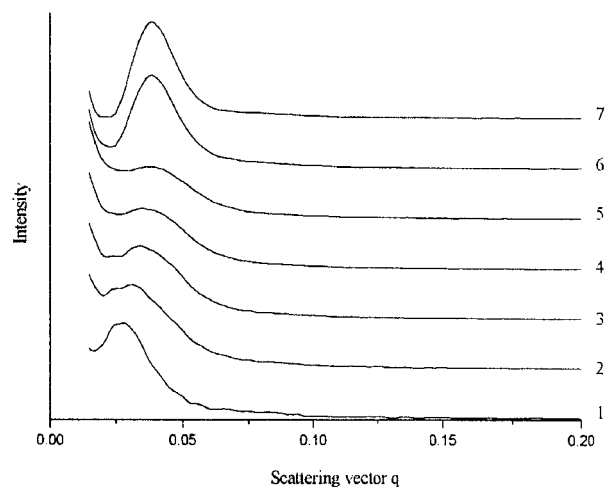
In noncolored fibers the crystalline structure consisted of the most stable  $\alpha$  crystals. In fibers colored with quinacridone pigment, crystals occurred in two forms,  $\alpha$  and  $\beta$ .

In colored fibers, as a result of the nucleating effect of the quinacridone pigment, the crystallization temperature was higher than in the noncolored fibers. The increase in the crystallization temperature produced an increase in lamellar thickness. The crystallization temperature exceeded the lower critical temperature,  $T_c^{**}$ , of the formation of the  $\beta$  form of polypropylene.<sup>41</sup> During crystallization at this temperature the polypropylene chains were matched to the  $bc$  surface of the quinacridone, initiating epitaxial growth of  $\beta$ -form crystals.<sup>42</sup>

The content of  $\beta$  crystals in fibers colored with quinacridone pigment taken at 100 m/min was very



a/



b/

**Figure 4** SAXS patterns of the polypropylene fibers colored with quinacridone pigment extruded from the melt at temperatures (a) 210°C and (b) 250°C taken at: 1—100 m/min, 2—200 m/min, 3—300 m/min, 4—400 m/min, 5—880 m/min, 6—1050 m/min, 7—1350 m/min.

TABLE II  
The Long Period and Lamellar Thickness for Fibers Formed in Different Conditions

Fibers	Take-up velocity [m/min]	Fibers extruded at 210°C		Fibers extruded at 250°C	
		Long period (L[A])	Lamellar thickness (l[A])	Long period (L [A])	Lamellar thickness (l[A])
Noncolored	100	107	52	127	61
	200	105	49	125	61
	300	102	48	123	60
	400	97	47	122	52
	880	98	47	120	52
	1050	106	51	125	53
	1350	106	53	135	65
Colored with quinacridone pigment	100	126	66	172	84
	200	122	61	136	66
	300	106	52	127	61
	400	104	51	124	60
	880	100	48	122	59
	1350	106	52	128	61

high. The  $K$  value, which characterizes  $\beta$  form content, was 0.8, which is comparable to the value obtained in quiescent conditions in the presence of very effective nucleating agents.<sup>17,43</sup>

With increasing take-up velocity the cooling rate increased, and the crystallization temperature moved to lower values. Simultaneously with the decrease in crystallization temperature, the mobility of the polypropylene chains decreased.

As a result of the shift in the crystallization temperature to lower values, lamellar thickness in noncolored as well as in colored fibers decreased.

The increase in the cooling rate and the decrease in chain mobility in noncolored fibers cause the mesophase to appear. The content of the mesophase increased with an increase in the take-up velocity (Fig. 5).

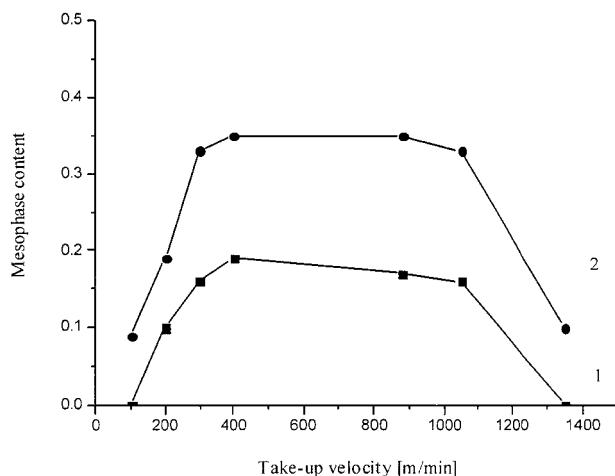


Figure 5 Mesophase content in noncolored polypropylene fibers; fibers were extruded from the melt at: 1—210°C, 2—250°C.

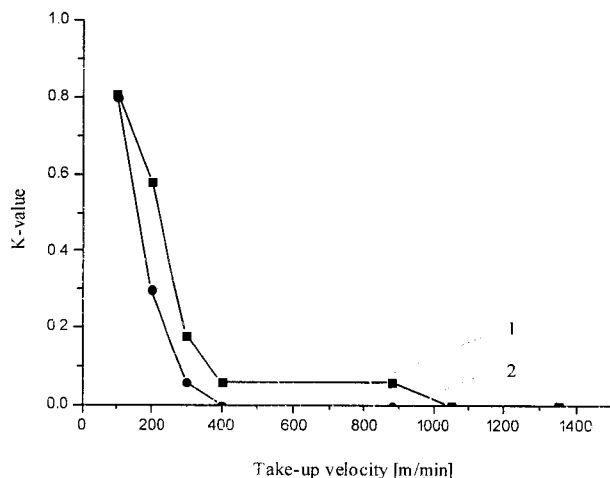
Fibers spun at the higher temperature of 250°C showed a greater difference between the temperatures of the extruded melt and the cooled air. At a given take-up velocity a higher extrusion temperature caused a decrease in viscosity in the upper part of the thread line. Lower viscosity resulted in lower molecular orientation that, together with a greater difference in temperatures between the melt and the cooling air, caused an increase in the crystallization rate. Because of the higher cooling rate in fibers extruded from the melt at the higher temperature of 250°C, a higher mesophase content was observed.

In colored fibers the increase in take-up velocity and consequent increase in the cooling rate lowered the crystallization temperature closer to the lower critical temperature,  $T_c^{**}$ . In such conditions crystallization started at a temperature above  $T_c^{**}$ . At the beginning of the crystallization process  $\beta$  crystals were formed. During crystallization the temperature decreased into the range below the  $T_c^{**}$ , and the remaining crystallizable material crystallized at a lower temperature, forming  $\alpha$  crystals.

With an increase in the take-up velocity, the temperature went lower and lower, and less and less material could crystallize at a temperature above the  $T_c^{**}$ . With an increasing take-up velocity more and more material crystallized at lower temperatures, and the  $\beta$  form content decreased (Fig. 6).

For fibers extruded from the melt at the higher temperature of 250°C, when the cooling rate was higher, the crystallization temperature moved faster below the  $T_c^{**}$ . The decrease in  $\beta$  form content occurred more rapidly so that in fibers taken at 400 m/min the  $\beta$  form already had disappeared.

In fibers taken at the take-up velocity of 400–880 m/min, the more rapid cooling rate was balanced by



**Figure 6** The  $\beta$  form content in fibers colored with quinacridone pigment; fibers extruded from the melt at: 1—210°C, 2—250°C.

the higher orientation. As a consequence, the crystallization temperature achieved its lowest value, resulting in the lowest lamellar thickness.

The noncolored fibers taken in these conditions contained the highest mesophase content (Fig. 5). The colored fibers extruded at the lower temperature of 210°C exhibited a crystalline structure formed almost exclusively from  $\alpha$  crystals. The colored fibers spun at the higher temperature of 250°C because of the higher cooling rate had a small mesophase content.

At higher take-up velocities, above 880 m/min, the molecular orientation determined the crystallization process. Under the orientation a small amount of highly elongated segments of chains formed row nuclei that acted as very active nuclei for the polypropylene crystallization. The row nuclei caused a rapid increase in the nucleation process, resulting in an increase in the overall crystallization rate and the crystallization temperature.

As a result, in noncolored fibers mesophase content decreased, and at the highest take-up velocity, 1350 m/min, only the crystalline  $\alpha$  form was observed.

Pigments did not take part in the formation of the row nuclei. The crystallization process in colored fibers occurred at the same rate and at the same temperature as in noncolored fibers. The lamellar thickness for colored and noncolored fibers was the same, and for both fibers a crystalline structure containing only  $\alpha$  crystals was formed.

## CONCLUSIONS

In noncolored fibers the structure containing the crystalline  $\alpha$  form and the mesophase was formed. For fibers taken at the lowest take-up velocity only the  $\alpha$  form was observed. For higher take-up velocities the crystalline structure occurred together with the me-

sophase. The content of the mesophase increased with an increase in the take-up velocity and was highest for fibers extruded at higher temperatures and taken at the medium take-up velocity. At the highest take-up velocities the mesophase content decreased, and again only the crystalline  $\alpha$  form was observed. The observed changes of the structure resulted from the change in the cooling rate and the orientation occurring with the change of the formation parameters.

In fibers colored with quinacridone pigment taken at the low take-up velocity, the crystalline phase exhibited two forms of polypropylene: the monoclinic  $\alpha$  form and the hexagonal  $\beta$  form. The highest  $\beta$  form content was observed in fibers taken at the lowest take-up velocity. The increase of the take-up velocity caused a rapid drop in the  $\beta$  form content. In fibers taken at higher velocities only the  $\alpha$  form was formed. In fibers extruded at a higher melt temperature and taken at medium velocity, a small mesophase content was observed.

The appearance of the  $\beta$  form in colored fibers was a result of the nucleating ability of quinacridone pigment. The addition of quinacridone pigment moved the crystallization temperature to the region, making possible the formation of  $\beta$  crystals. The nucleating effect of the pigment was restricted to the fibers taken at the low take-up velocity, when the crystallization process was determined by the cooling rate. At higher take-up velocities crystallization was governed by the orientation, and the nucleating effect of the pigment was only marginal. The crystallization process occurred without pigment, leading to the formation of a structure containing only  $\alpha$  form, as in the noncolored fibers.

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