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# WAXS investigations of mass-coloured polypropylene fibres

**Abstract**

*WAXS investigations into the structure of polypropylene fibres formed under different conditions were performed. The studies were carried out on noncoloured fibres and fibres coloured with two organic pigments: quinacridone and phtalocyanine. It was stated that, for fibres taken at low take-up velocity, the structure of coloured fibres differs from that of noncoloured fibres. In noncoloured fibres, a structure containing the mesophase and the crystalline α form is formed. The content of the mesophase changes with a change in the formation parameters. In coloured fibres, two polymorphic forms of polypropylene α and β were observed. The high content of the β form was obtained for fibres coloured with quinacridone pigment. With increase of the take-up velocity, the content of the β form rapidly decreases. For fibres taken at higher velocities, the structure of coloured fibres becomes similar to that of noncoloured fibres.*
*During heat stabilisation, the β form which occurred in fibres coloured with quinacridone pigment transforms into the α form. The transformation starts at temperatures above 140°C. At 150°C the transformation occurs rapidly, and after 10 min is finished.*

**Key words:** *isotactic polypropylene, fibres, pigment, structure, polymorphism*

## 1. Introduction

The first polypropylene fibres were obtained shortly after the synthesis of isotactic polypropylene in 1957. The low light stability and difficulties with dyeing meant that the application of polypropylene fibres was limited for many years. In the 1980s, the weaknesses of these fibres were overcame and dynamic development in their usage was observed.

It was already stated at the beginning of the investigations of the structure of polypropylene fibres that the structure of polypropylene fibres is strongly differentiated and changes from the less ordered mesophase to the well ordered crystalline monoclinic structure [1-6]. The changes in the fibres' structure were observed depending on the formation conditions. It was established that the mesophase is formed in fibres extruded at a high cooling rate and low orientation. Lower cooling rate and higher orientation lead to the formation of the crystalline structure [7].

Most such investigations have been carried out on noncoloured fibres. The structure of coloured fibres is quite different. The polypropylene fibres, due to their features, cannot be dyed with the methods commonly applied to other fibres. Dyeing of the polypropylene fibres is performed during spinning [8-10]. Pigments mixed with the polymer melt are extruded together with the melt through spinnerets to the cooling air. Pigments occur inside the cooled stream during the processes leading to the formation of the fibre structure.

Changes in the fibre structure resulting from the introduction of two organic pigments, phthalocyanine and quinacridone, are presented in this paper.

## 2. Non-coloured fibres

In fibres formed under different conditions, mesophase occurs together with the α monoclinic form. In this case three phases occur in the fibre: the crystalline phase, the mesophase and amorphous phase [9]. The content of these phases changes depending on the formation parameters.
The mesophase gives a WAXS pattern with two broad maxima, the first at 14.8° and the second at 21.2°. -(Fig. 1)

The crystalline α form gives a WAXS pattern with five strong peaks: (110) at 14.09°, (040) at 16.84°, (130) at 18.44°, (111) at 21.22° and (041) at 21.8°. -(Fig. 2)
For fibres containing three phases, the WAXS pattern is a result of the overlapping of two patterns. -(Fig. 3)
The analysis of this pattern was carried out by constructing a theoretical curve best fitted to the experimental curve. The theoretical curve was constructed

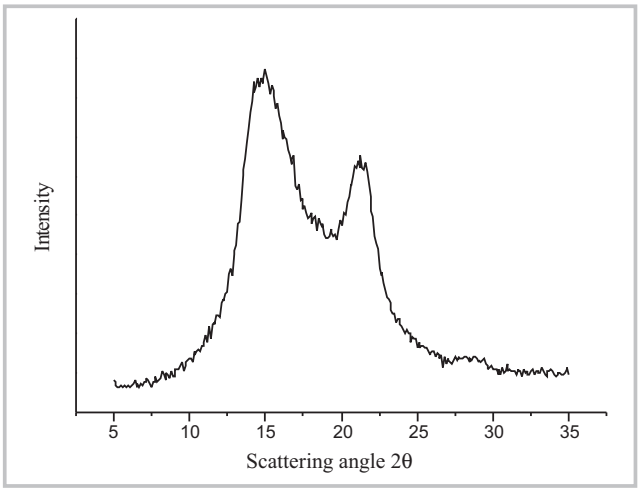


***Figure 1.*** *The WAXS pattern of the mesophase.*

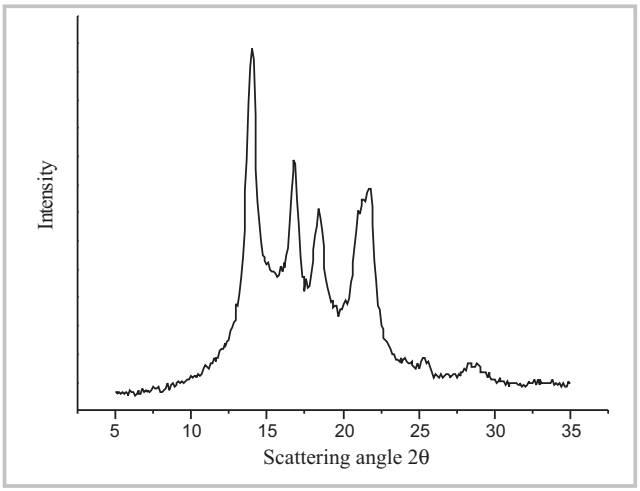


***Figure 2.*** *The WAXS pattern of the α form of polypropylene.*

as a sum of two mesophase peaks, seven crystalline peaks and one amorphous peak. -(Fig. 4)

The mesophase content increases in fibres spun from the melt at the temperature of 210°C at low take-up velocities with increase in the take-up velocity. -(Fig. 5) Then, at higher take-up velocity, the mesophase content decreases. At the same time the content of the crystalline phase increases, so the common content of the ordered phases does not change. At higher take-up velocity, above 1350 m/min, only the crystalline α form occurs.

The mesophase content is greater in the fibres spun from the melt at the higher temperature of 250°C. At higher melt temperature, the difference between melt temperature and the cooling air temperature increases. Consequently the cooling rate is greater, and as a result the mesophase content increases. As for the lower melt temperature, the mesophase content decreases with increase in the take-up velocity.

At the higher take-up velocity, the orientation of the cooled stream increases. The orientation of the crystallised melt strongly influences the polymer crystallisation. In this orientation, some extended chains form row nuclei. As a result of the formation of row nuclei, the crystallisation rate increases rapidly, leading to the formation of the crystalline structure.

## 3. Coloured fibres

### 3.1. Phtalocyanine pigment

In fibres coloured with the phthalocyanine pigment only the crystalline monoclinic structure is formed. For all fibres coloured with this pigment the WAXS pattern characteristic for the α form of polypropylene was obtained. -(Fig. 7)

The analysis of the pattern was carried out by constructing the theoretical curve as a sum of seven crystalline peaks and 1 amorphous peak -(Fig. 8).

In fibres coloured with phthalocyanine pigment, the crystalline structure occurs within a broad range of the formation parameters, at different take-up velocities and at different melt temperatures. The α form is also observed in such conditions in which the mesophase was observed for pure polypropylene.

The formation of the crystalline form is a result of the nucleating ability of the phthalocyanine pigment [11-12]. During the crystallisation of polypropylene, aggregates of the phthalocyanine pigment act as nucleating agents.

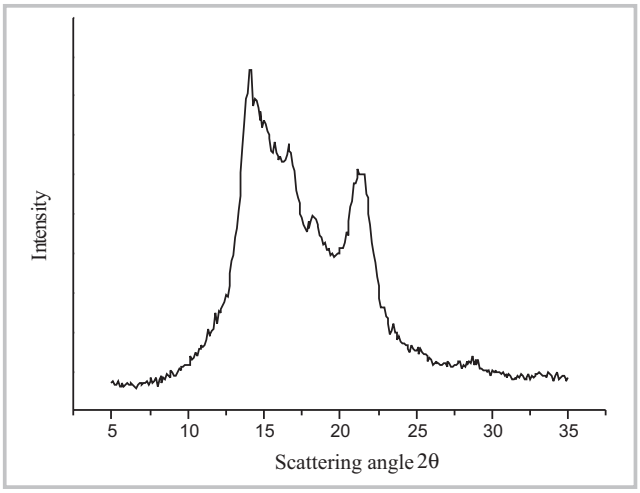


***Figure 3.*** *The WAXS pattern of the structure containing the mesophase and the crystalline α form.*

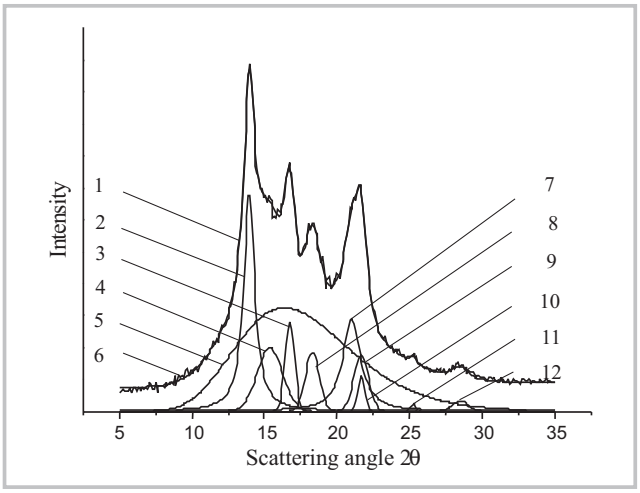


***Figure 4.*** *Analysis of the WAXS pattern for fibres containing the mesophase and the crystalline α phase; 1/ theoretical curve, 2/ crystalline peak (110), 3/ crystalline peak (040), 4/ mesophase peak, 5/ amorphous peak, 6/ experimental curve, 7/ crystalline peak (111), 8/ crystalline peak (130), 9/ mesophase peak, 10/ crystalline peak (041), 11/ crystalline peak (060), 12/ crystalline peak (220)*

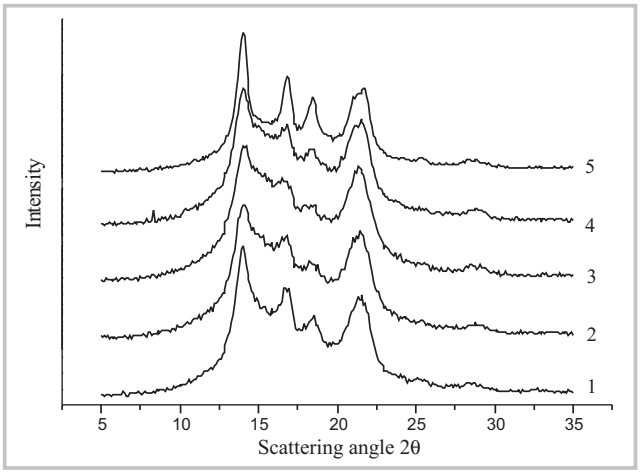


***Figure 5.*** *The WAXS pattern of non-coloured fibres spun from the melt at temperature of 210°C taken at: 1/ 200 m/min; 2/ 300 m/min; 3/ 880 m/min; 4/ 1050 m/min; 5/1350 m/min*

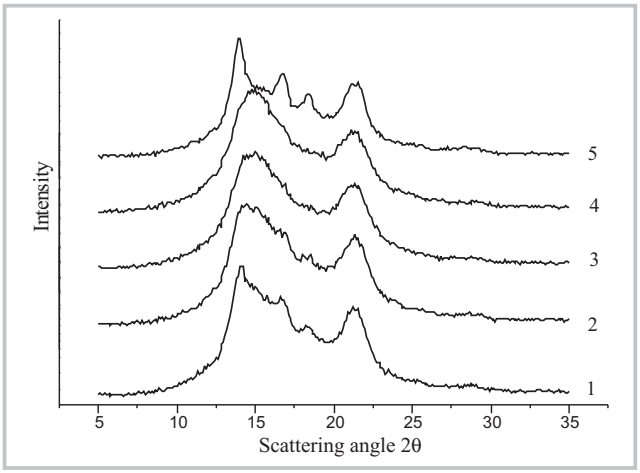


***Figure 6.*** *The WAXS pattern of non-coloured fibres spun from the melt at temperature of 250°C taken at: 1/ 200 m/min; 2/ 300 m/min; 3/ 880 m/min; 4/ 1050 m/min; 5/ 1350 m/min*

The nucleating agents accelerate the nucleation process resulting in the increase of the overall crystallisation rate. As a result the crystalline monoclinic structure is formed.

### 3.2. Quinacridone pigment

The crystalline structure is formed in fibres coloured with quinacridone pigment. The β crystallites are observed additionally to the α crystallites in fibres spun at very low take-up velocity.

On the WAXS pattern of the β form, two strong peaks occur, the first peak (300) at 15.9° and the second peak (301) at 21.2°. -(Fig. 9)

In fibres the β form occurs usually together with the α form. In this case, the peak (300) from the β form and three peaks (110), (040) and (130) are visible on the WAXS pattern. The peaks (301) from the β form and two peaks (111) and (041) from the α form occur very close one to another. As a result of the overlapping of all these peaks at 21°, one broad peak is observed. -(Fig. 10)

The analysis of the pattern obtained for fibres containing both crystalline forms was carried out by constructing the theoretical curve as a sum of seven crystalline peaks from the α form, two crystalline peaks from the β form and one amorphous peak.

The high content of the β form was observed in fibres spun at low melt temperature and at very low take-up velocity. With increase in the take-up velocity, the content of the β form rapidly decreases. For fibres taken at 200 m / min, the β form content evendrops by half. At 400 m / min the β form is only just visible. At higher take-up velocities, higher than 880 m / min, the β form is absent and the crystalline α form is observed. -(Fig. 12)

The formation of the crystalline structure in fibres coloured with quinacridone pigment is a result of the nucleating ability of this pigment. Quinacridone is known as a very good nucleating agent of the β form of polypropylene [13-14]. Thanks to their surface structure, the quinacridone crystals cause epitaxial growth of the β form crystallites [15]. The epitaxial growth of the β form crystallites occurs at low take-up velocity under low orientation. At low orientation, chains of polypropylene diffuse from isotropic melt, and match the surface of the quinacridone crystals. At higher orientation, some polypropylene chains orient parallel to the fibre axis, and the free matching of

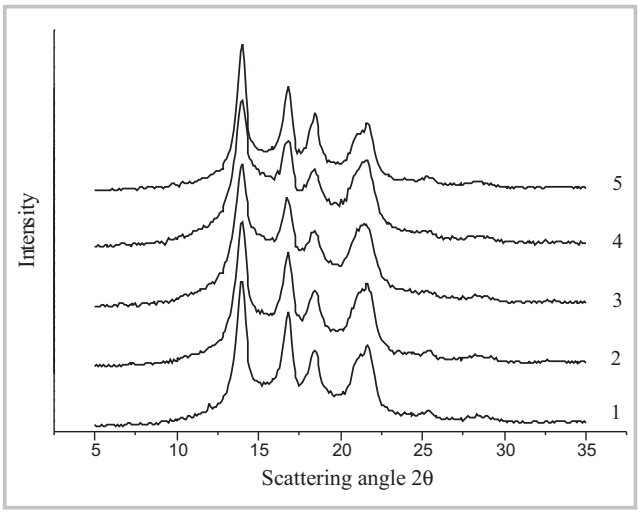


***Figure 7.*** *The WAXS pattern of fibres coloured with phtalocyanine pigment spun from the melt at temperature of 210°C taken at: 1/ 300 m/min; 2/ 400 m/min; 3/ 880 m/min; 4/ 1050 m/min; 5/ 1350 m/min.*

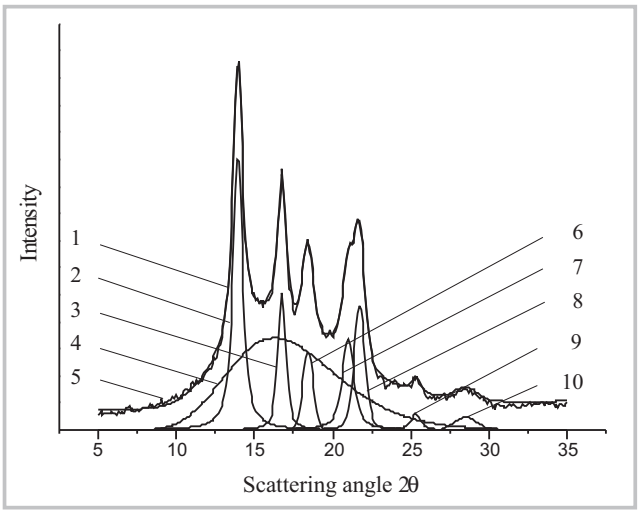


***Figure 8.*** *Analysis of the WAXS pattern for fibres containing the crystalline a form. 1/ theoretical curve, 2/ crystalline peak (110), 3/ crystalline peak (040), 4/ amorphous peak, 5/ experimental curve, 6/ crystalline peak (130), 7/ crystalline peak (111), 8/ crystalline peak (041), 9/ crystalline peak (060), 10/ crystalline peak (220)*

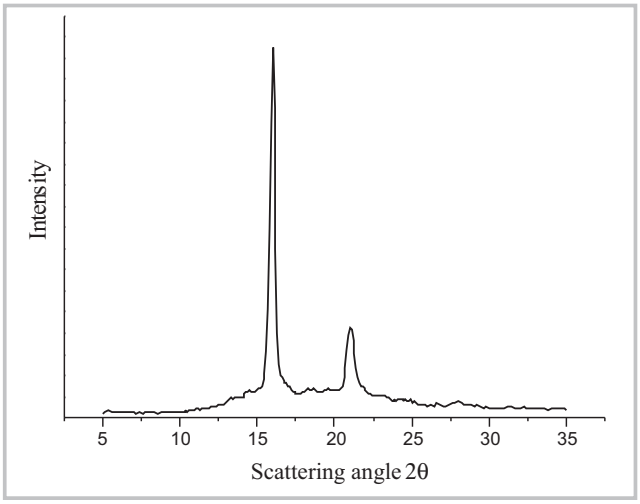


***Figure 9.*** *The WAXS pattern of the β form of polypropylene.*

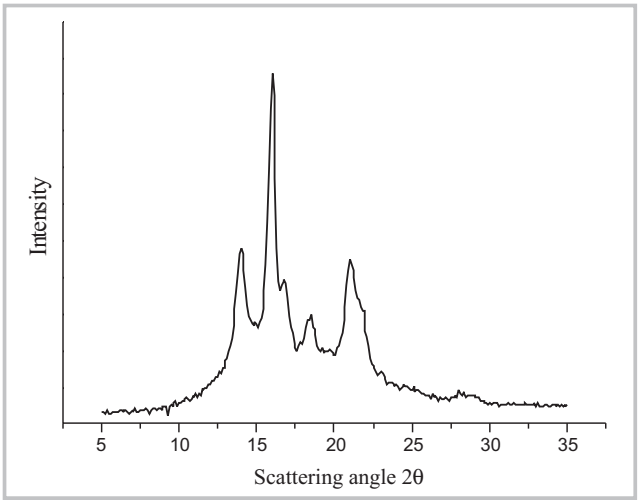


***Figure 10.*** *The WAXS pattern of the structure containing the crystalline α and β forms.*

polypropylene with the surface of the quinacridone crystals is much more difficult. At higher orientation, crystals of quinacridone pigment act as a nucleating agents in the nonepitaxial nucleation. They accelerate the nucleation process, which results in the increase of the overall crystallisation rate. As a result, the crystalline α form is formed in the fibres.

## 4. Polymorphic transitions during processing

The as-spun polypropylene fibres are subjected to further processing, namely drawing and heat stabilisation. During those processes the fibre structure undergoes further modification. As a result of the recrystallisation, different polymorphic transformations are observed.

On drawing, the direction and the ratio of the transformation depend mainly on drawing ratio and drawing temperature. During cold drawing at room temperature and at a higher draw ratio, the α form transforms into the mesophase. During drawing at higher temperature, the transition in opposite direction, from mesophase to α form, is observed. In the case of fibres containing the β form, on cold drawing the transformation β → mesophase occurs. At higher temperatures, the β form transforms into the more stable α form.

On heat stabilisation, the transformations mesophase → α and β → α were observed. The β form transforms into the α form during stabilisation at temperatures above 140°C. For fibres stabilised at 140°C over 3 min, the β-form content decreases minimally. Over a longer time, the decrease of the β-form content is more significant, although even after a very long time of stabilisation the high content of the β-form remains in fibres. -(Fig. 13) At 140°C, the β → α transformation starts, but is not completed.

For fibres stabilised at the temperatures above 140°C in the range of 140-150°C, the decrease of the β form content is more significant and increases with the growth of the stabilisation temperature. With the increase of temperature, the decrease of the β form content occurs faster over a shorter stabilisation time. At every temperature within this range, after a long time of stabilisation, part of the β crystals still remain in the fibres. The definite β form content at each temperature from this range is related to the partial melting of the β crystals. Because of the broad melting range of polymer crystals, we can state that heating to a temperature which lies within the melting temperature range causes a partial melting of crystals with a melting temperature just below the

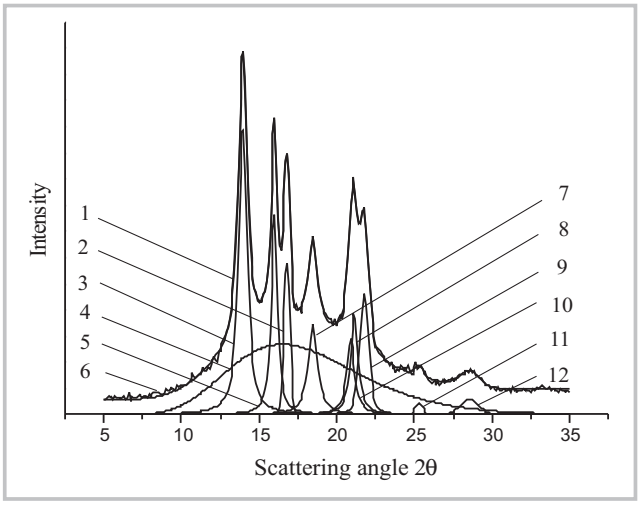


***Figure 11.*** *Analysis of the WAXS pattern for fibres containing α and β forms. 1/ theoretical curve, 2/ crystalline peak (040)a, 3/ crystalline peak (110)a, 4/ amorphous peak, 5/ crystalline peak (300)b, 6/ experimental curve, 7/ crystalline peak (130)a, 8/ crystalline peak (301)b, 9/ crystalline peak (041)a, 10/ crystalline peak (111)a, 11/ crystalline peak (060)a, 12/ crystalline peak (220)a*

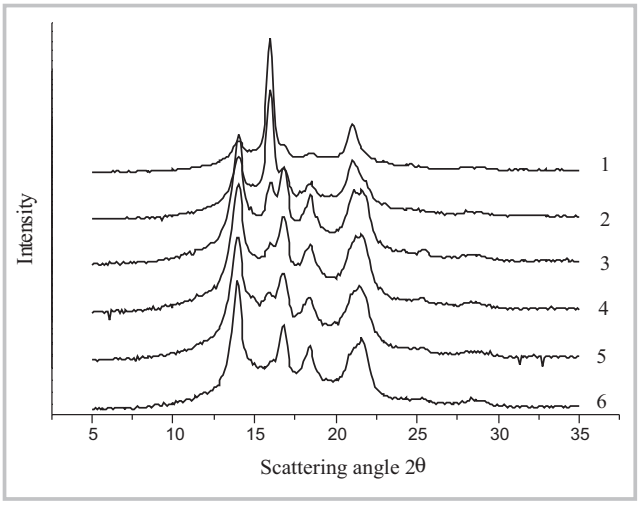


***Figure 12.*** *The WAXS pattern of fibres coloured with quinacridone pigment spun from the melt at temperature of 210°C taken at: 1/ 100 m/min; 2/ 200 m/min; 3/ 300 m/min; 4/ 400 m/min; 5/ 880 m/min; 6/ 1350 m/min.*

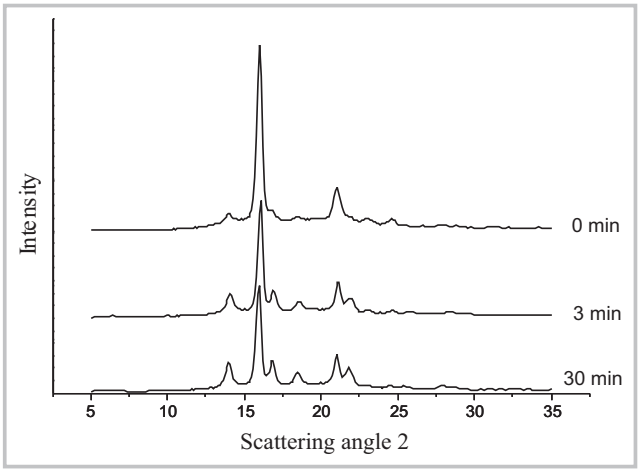


***Figure 13.*** *Effect of time of the stabilisation on WAXS patterns of fibres stabilised at 140°C.*

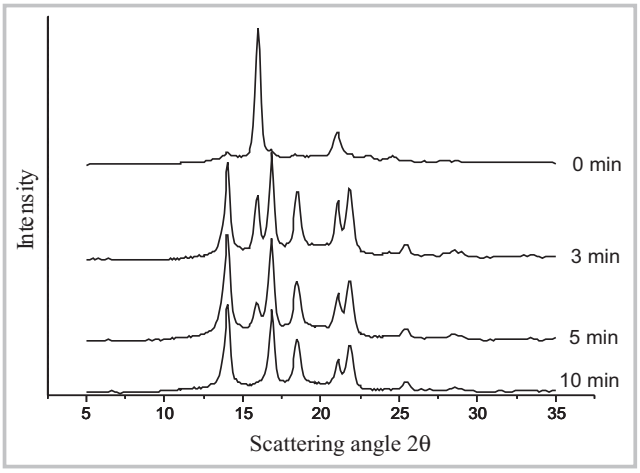


***Figure 14.*** *Effect of time of the stabilisation on WAXS patterns of the fibres stabilised at 150°.*

temperature of heat stabilisation. As a result, the β form content drops to a limiting value depending on the temperature of heat stabilisation.

During the stabilisation at 150°C, a rapid drop in the β-form content occurs after only 3 min. After 5 min, the β-form is barely visible, and after 10 min disappears. At this temperature the $\beta \rightarrow \alpha$ transformation occurs rapidly, and after 10 min is completed. -(Fig. 14)

## 5. Conclusions

- For non-coloured fibres, a structure containing the mesophase and the crystalline phase is formed; the content of the mesophase changes with the change in formation parameters.
- For coloured fibres, only the crystalline phase occurs; for phthalocyanine pigment, the crystalline phase is formed from α crystallites; for quinacridone pigment, in certain conditions, β crystallites are observed additionally.
- During processing the structure of fibres changes; as a result, different polymorphic transitions are observed.

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