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Morphology of the noncoloured and coloured polypropylene fibres

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Abstract

The scanning electron microscopy investigations of the morphology of the polypropylene fibes were carried out. The studies were performed for gravity spun fibres as well for fibres taken at different take-up velocities in the range from 100 to 1350 m/min. The noncoloured fibres and fibres coloured with quinacridone and phthalocyanine pigments were investigated.

The studies revealed that the morphology of fibres is strongly influenced by take-up velocity and the presence of pigments.

At low take-up velocity the spherulitic structure is observed. While in noncoloured fibres the big spherulites are formed in coloured fibres fine spherulites occur. In fibres coloured with quinacridone pigment spherulites possess a sheaf-like structure. The wide angle X-ray scattering measurements showed that spherulites occurred in noncoloured fibres consist of the α modification, whereas the sheaf-like spherulites in fibres coloured with quinacridone pigment of the β modification.

At higher velocities the spherulitic structure transforms into a fibrillar one. The fibrils possess a hierarchical structure and consist of microfibrils formed from a bundle of nanofibrils.

The change of the fibres morphology was interpreted by a change of the nucleation mechanism.

Keywords: polypropylene fibre; pigment; morphology

1. Introduction

In last years polypropylene fibres find wider and wider application. The great interest of polypropylene fibres has attracted a significant number of studies on a fibre structure.

Many investigations carried out so far concentrated on the crystallographic and lamellar levels of the fibres structure. As a result of those investigations it was stated that the structure changes depending on the formation parameters from the less ordered mesophase to the well ordered crystalline monoclinic structure [1].

The spherulitic level, so called morphology of the fibres, until now has not been studied extensively. The first studies on the morphology of polypropylene fibres were carried out analysing orientations factors for the crystallographic axes. On the basis of such analysis Spruiell and White [2] proposed a model of the fibre morphology consistent with the model proposed by Dees and Sprueill [3] for changes of morphology of the polyethylene fibres spun with different velocities. According to this model at very low velocities the fibre morphology is spherulitic. With increasing take-up velocity the spherulitic structure transforms into a row nucleated structure formed in a epitaxial growth of polypropylene crystals on the row nuclei generated by the elongational straining of the melt. The SAXS investigations of Nadella [4] confirmed a correctness of this model for polypropylene fibres.

Hautojärvi [5,6] reported morphological studies of as-spun polypropylene fibres formed at different draw ratios by atomic force microscopy (AFM). The investigations revealed that an increase in the draw ratio causes a gradual transformation from a spherulitic to a fibrillar morphology. The fibrillar structure shows a hierarchical structure including fibrils (width in the order of micrometers), microfibrils (width in the order of hundreds of nanometers) and nanofibrils (width in the order of tens of nanometers). De Rovere [7] used the AFM for the investigations of a gravity spun, melt spun and melt blown polypropylene fibres. The studies revealed many different types of morphologies such as spherulites, shish-kebab, lamellar and fibrillar structures, as well showed that the morphology of fibres depends on a manner of the formation and processing conditions.

The above mentioned investigations of the fibre morphology were carried out for noncoloured fibres.

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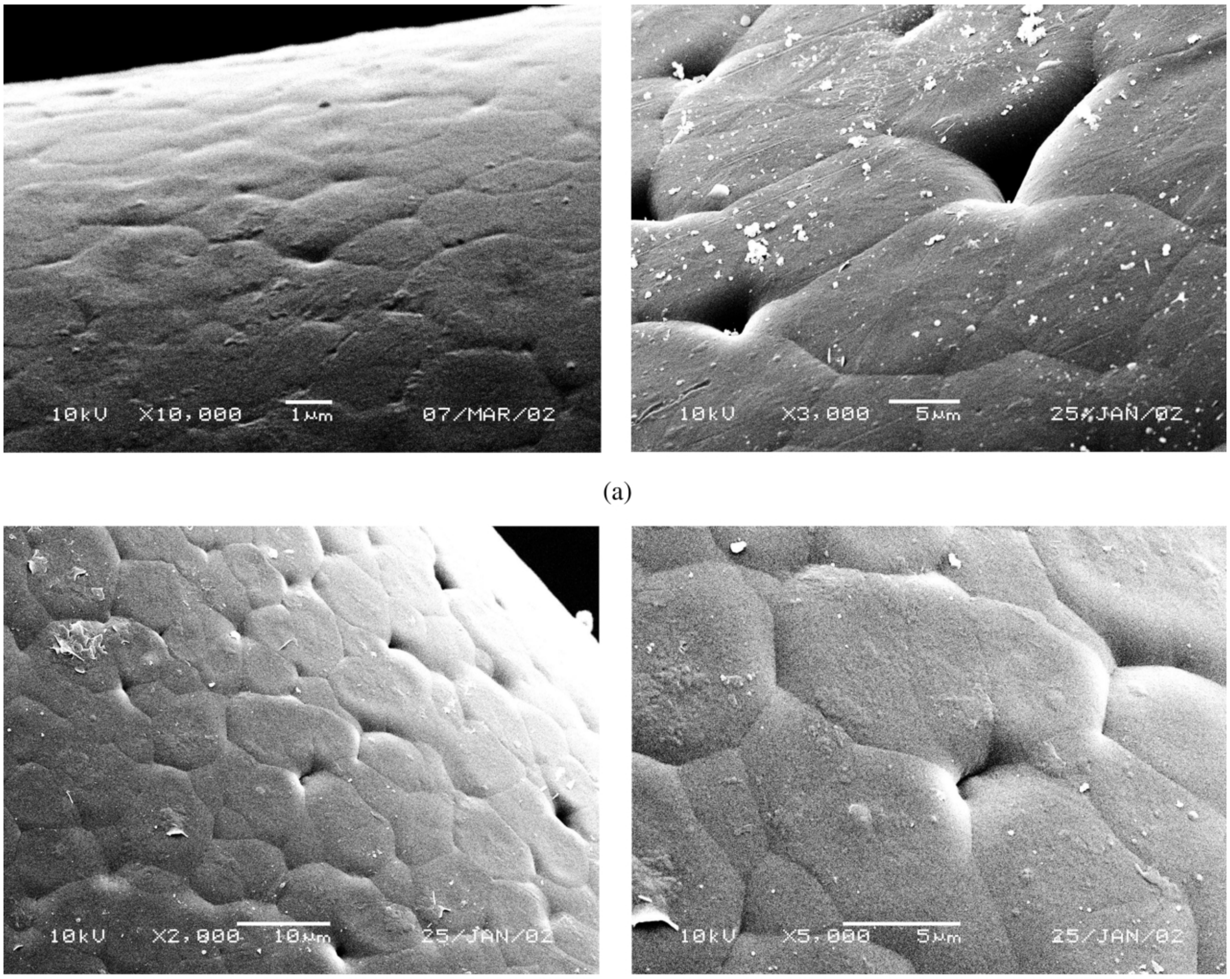


(a)

(b)

Fig. 1. The morphology of the noncoloured fibres: (a) gravity spun fibres; (b) fibres taken at 100 m/min.

The polypropylene fibres cannot be dyed with bath methods commonly applied to other fibres. Dying of the polypropylene fibres is performed with pigments during spinning [8–11]. 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 processes leading to the formation of the fibre structure.

According to our previous investigations pigments influence the fibre structure on the crystallographic and lamellar levels [12,13]. The significant effect of pigments is observed especially for fibres taken at low take-up velocities. In the presence of a quinacridone pigment the structure with a high content of β form is formed.

The effect of pigments on the fibre structure observed so far on the crystallographic and lamellar levels should be reflected on the morphological level. The evaluation of the morphology of the noncoloured and coloured polypropylene fibres formed in laboratory conditions by variable formation parameters is the aim of these studies.

2. Experimental

2.1. Samples

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

Additionally gravity spun fibres were obtained. The gravity spun fibres were collected without drawing directly under the die head.

The commercial isotactic polypropylene—Mosten 52.945 supplied by Chemipetrol (Czech Republic) was used. Mosten 52.945 is characterising by a narrow molecular weight distribution and the melt flow index 25 g/10 min.

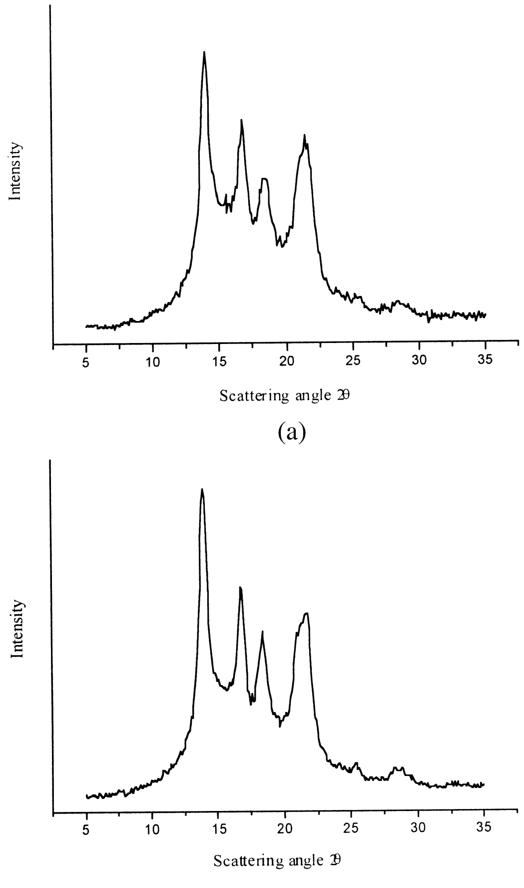


Fig. 2. The WAXS pattern of the noncoloured fibre taken at: (a) 100 m/min; (b) 1350 m/min.

The noncoloured and coloured fibres were produced. For colouring of fibres the quinacridone pigment—Pigment Violet 19, C.I.73900 (Echtrot E3B-Hoechst) and the phthalocyanine pigment—Pigment Blue 15, C.I. 74160 B (Wola Kszysztoporska-Poland) were used. Pigments were mixed with a polymer granulate immediately before forming fibres in the amount of 0.5% to the polymer mass.

2.2. Methods

The morphology of fibres was investigated by scanning electron microscopy (SEM) using the scanning electron microscope Jeol JSM 5500 LV. The investigations were carried out for polypropylene fibre without any pretreatment.

The surface morphology as well as the morphology of the fibre ends revealing the morphology of the inner parts of the fibre were investigated. The observations were performed at magnifications from 500 × to 50,000 × for samples sputtered with gold in Jeol JFC 1200 ionic sputter.

The polymorhic structure was determined by the wide angle X-ray scattering (WAXS) method. The WAXS measurements were performed 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 fibres were powdered on a Hardy microtome to segments of 10–15 μm. These were formed to tablets of constant mass and thickness in a holder for X-ray measurements.

3. Results

3.1. Noncoloured fibres

For gravity spun fibres and fibres taken at low take-up velocities big and round spherulites are observed. The spherulites have distinct boundaries and are randomly distributed over the surface of the fibre. In a space between spherulites deep craters occur.

The greatest spherulites with a diameter from 10 to 30 μm occur in gravity spun fibres (Fig. 1(a)). For fibres taken at the 100 m/min the diameter of spherulites decreases to 5–10 μm (Fig. 1(b)). Simultaneously the craters between spherulites become smaller. With the decrease in the sizes of spherulites the roughness of the fibre surface decreases.

The WAXS pattern for noncoloured fibres taken at 100 m/min exhibits crystalline peaks characteristic for the monoclinic α form of polypropylene (Fig. 2(a)). The WAXS

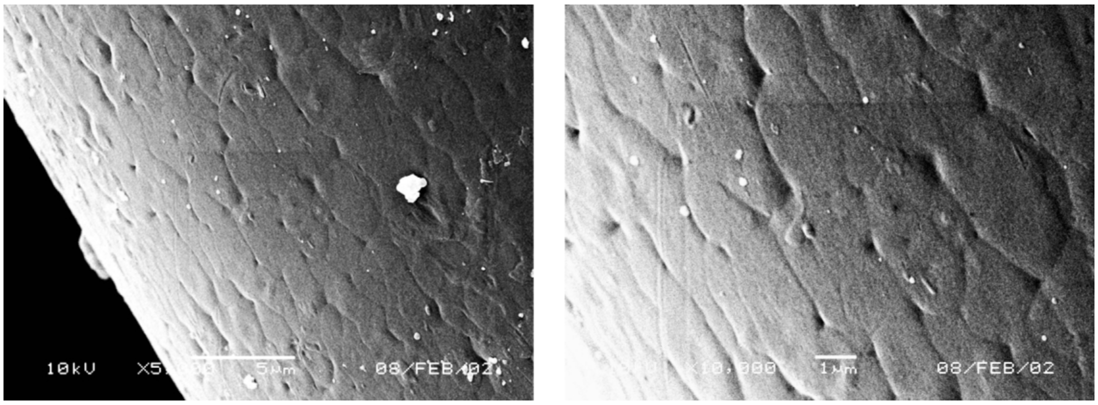
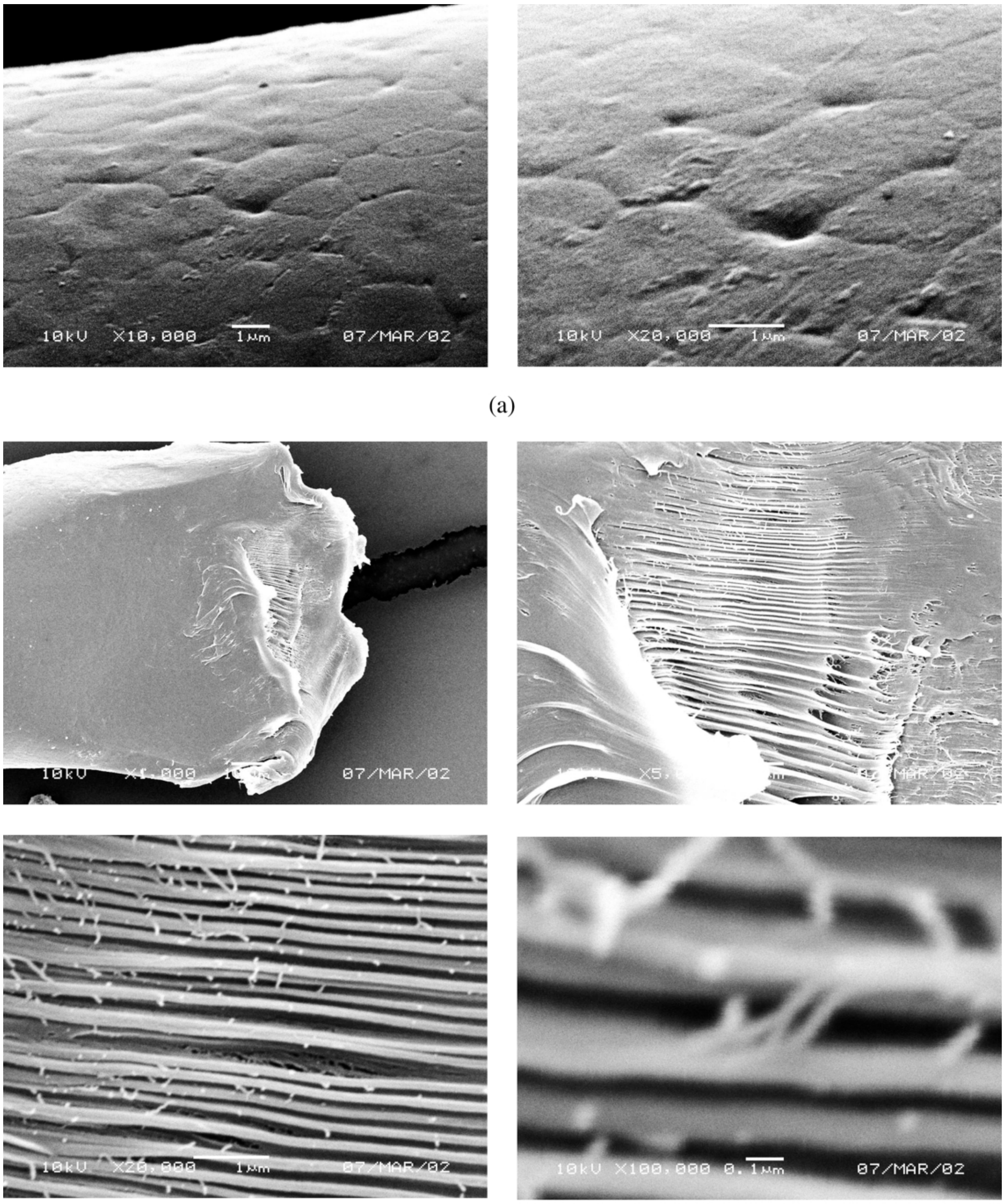


Fig. 3. The elongate spherulites in noncoloured fibres taken at 300 m/min.



(a)

(b)

Fig. 4. The morphology of noncoloured fibres taken at 880 m/min; (a) the spherulitic structure; (b) and (c) the fibrillar structure.

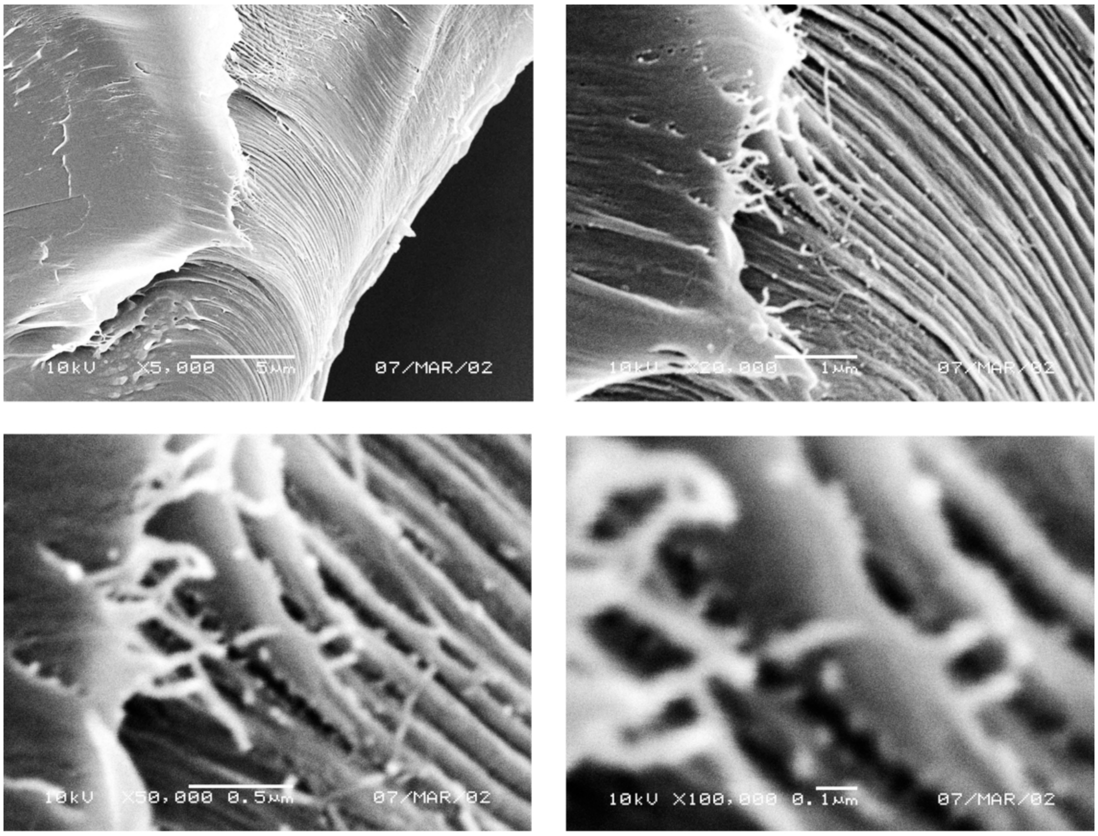
pattern clearly indicates that the spherulites consist of the α modification.

With increase in the take-up velocity to 300 m/min the spherulites elongate in the direction of the fibre (Fig. 3). At the same time with a change of the shape of spherulites the further decrease in their sizes is observed. In a consequence the craters between spherulites become smaller and the roughness of the surface decreases.

For fibres formed at 880 m/min the spherulitic structure coexists with the fibrillar structure. On the fibre surface the elongate spherulites are observed (Fig. 4(a)). Simultaneously the observations of the parts near the fibre ends reveal the fibrillar structure (Fig. 4(b) and (c)).

Fibrils, so called microfibrils, lay parallel to the fibre axis. The microfibrils are well separated from one another and their diameter equals to 150 nm.

The fibrils are the common entities encountered in drawn films and synthetic fibres. The microfibrils with an axis aligned in the direction of orientation and an average diameter 100–150 nm were observed for uniaxial drawn



(c)

Fig. 4 (*continued*)

polypropylene films [14,15]. The similar microfibrils were obtained for polypropylene fibres spun at higher draw ratios [5,6].

At the bigger enlargements between microfibrils one can see thinner fibrils with the diameter from 40 to 50 nm (Fig. 4(b) and (c)). Such fibrils correspond to nanofibrils observed by Hautojärvi by AFM [5,6].

The structure of nanofibrils is not seen on photographs. One can suppose that nanofibrils are formed from alternating lamellar crystals and amorphous layers and according to Crämer [16] and Hautojärvi [5,6] reveal the shish-kebab morphology consisting of transverse lamellae growing from a central linear thread [17].

For fibres extruded at the highest velocities 1050 and 1350 m/min the spherulitic structure disappears. In fibres, only fibrillar structure is observed.

According to WAXS investigations the fibrillar structure contains crystals of the α form of polypropylene (Fig. 2(b)).

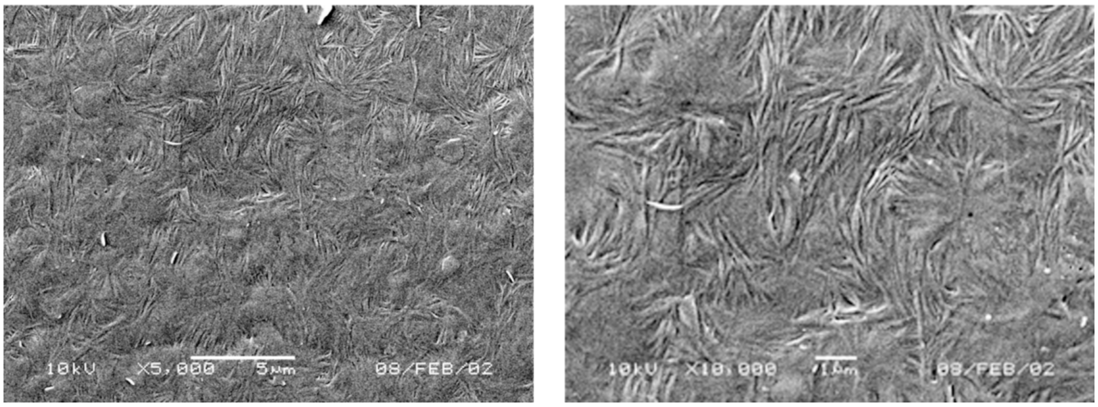
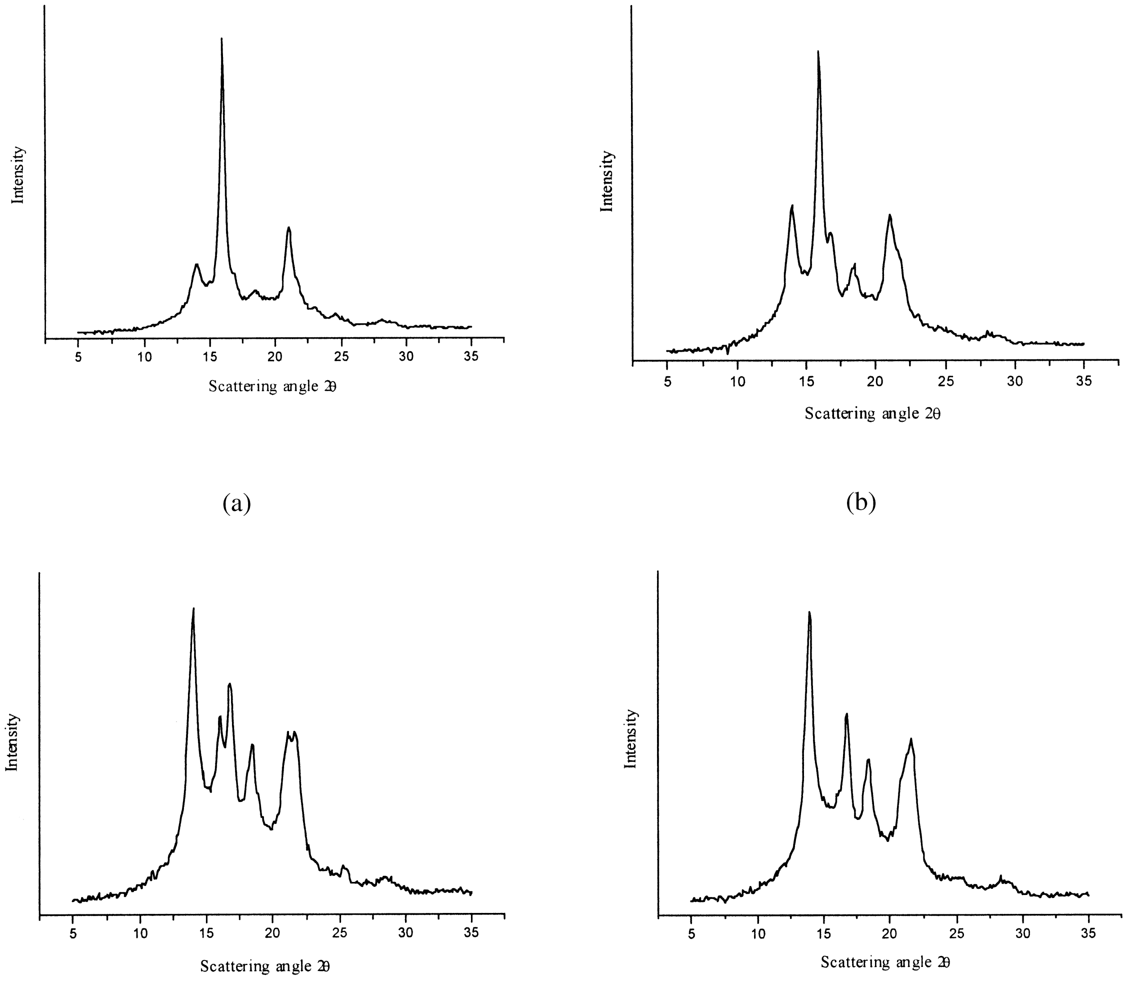


Fig. 5. The sheaf-like spherulites on the surface of the fibres coloured with quinacridone pigment.



(a) (b)

(c) (d)

Fig. 6. The WAXS pattern for fibres coloured with quinacridone pigment taken at: (a) 100 m/min; (b) 200 m/min; (c) 300 m/min; (d) 1350 m/min.

3.2. *Fibres coloured with quinacridone pigment*

In the case of fibres coloured with quinacridone pigment for the gravity spun fibres as well as for fibres taken at 100 m/min fine spherulites are observed. The sizes of spherulites do not exceed the 3 μm (Fig. 5).

The WAXS pattern measured for those fibres exhibits peaks of two polymorphic forms of polypropylene: the

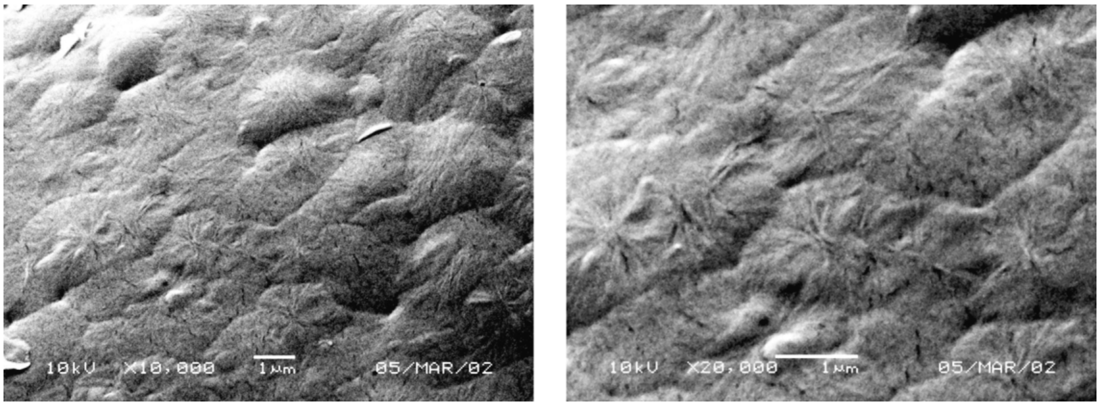


Fig. 7. The morphology of fibres coloured with quinacridone pigment taken at 200 m/min.

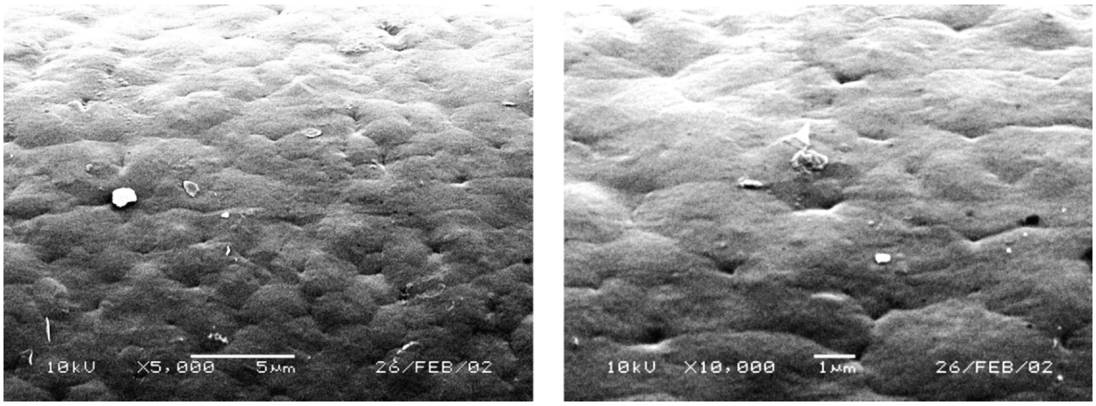


Fig. 8. The spherulitic morphology of fibres coloured with quinacridone pigment taken at 300 m/min.

monoclinic α form and the hexagonal β form (Fig. 6(a)). The peaks of the α form are weak, while the peaks of the β form are very strong. The high intensity of the β form peaks resulting from a high content of the β form points that the spherulites observed on the fibres surface consist of the β modification.

The spherulites exhibit a sheaf-like structure formed from bundles of crystallites being separated from one another by the amorphous phase. The boundaries between the spherulites are hardly distinguishable. Bundles of lamellae of neighbouring spherulites tend to cross each other.

The sheaf-like spherulites can be considered as a intermediate structure between single lamellar crystals and mature spherulites. The sheaf-like β spherulites are formed from the lamellar crystals which develop initially as rod-like structures, and then by branching of the lamellae evolve into sheaves [18–20]. The further growth of such spherulites through continuous branching leads to the formation of the spherulites with a spherical shape.

For fibres taken at 200 m/min the sheaf-like β spherulites possess a spherical shape and the boundaries between them become more distinct (Fig. 7). Besides the sheaf-like β spherulites on the fibre surface a few round spherulites appear. According to WAXS results (Fig. 6(b)) in fibres taken at 200 m/min the content of the α modification slightly increases, indicating that the few round spherulites appearing on the fibres surface consist of the α modification.

With increase in the take-up velocity to 300 m/min a rapidly drop in the β form content is observed (Fig. 6(c)). The sheaf-like β spherulites observed earlier for fibres taken at lower velocities disappear. On the fibre surface occur only round spherulites of the α modification (Fig. 8).

For higher take-up velocities above 1050 m/min the spherulitic structure transforms into the fibrillar structure. The microphotographs for fibres coloured with quinacridone pigment and taken at 1350 m/min exhibit microfibrils with the diameter 100–150 nm, similarly as in noncoloured fibres (Fig. 9).

On the basis of the WAXS investigations one can state that the fibrillar structure in fibres coloured with quinacridone pigment is built from crystals of the α modification (Fig. 6(d)).

3.3. Fibres coloured with phthalocyanine pigment

For fibres coloured with phthalocyanine pigment taken at the lowest velocities the spherulitic structure is formed. The

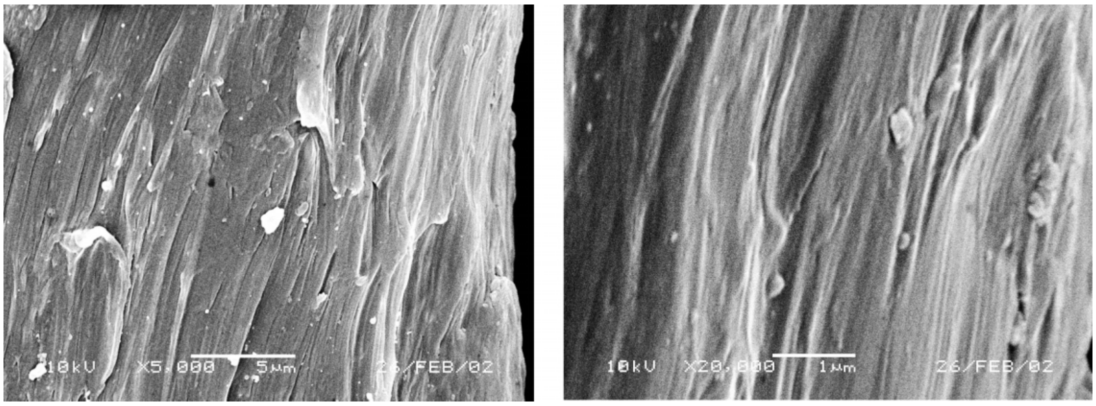


Fig. 9. The fibrillar structure in fibres coloured with quinacridone pigment taken at 1350 m/min.

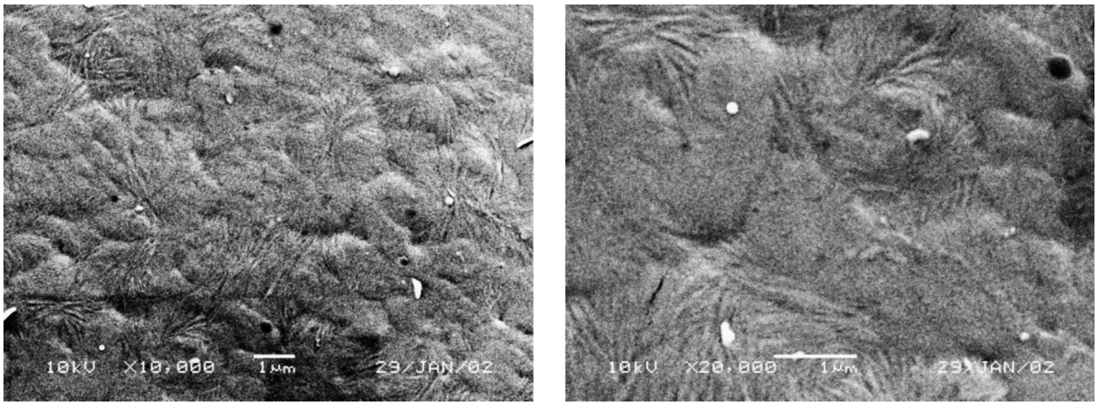


Fig. 10. The surface morphology for fibres coloured with phthalocyanine pigment taken at 100 m/min.

fine and round spherulites with the diameter from a range 1–3 μm are distributed randomly together with a sheaf-like spherulites (Fig. 10).

The WAXS pattern shows that in the fibres two polymorphic forms α and β occur (Fig. 11(a)). On the basis of the WAXS investigations one can conclude that in fibres coloured with the phthalocyanine pigment the round spherulites consist of the α modification, while the sheaf-like spherulites of the β modification.

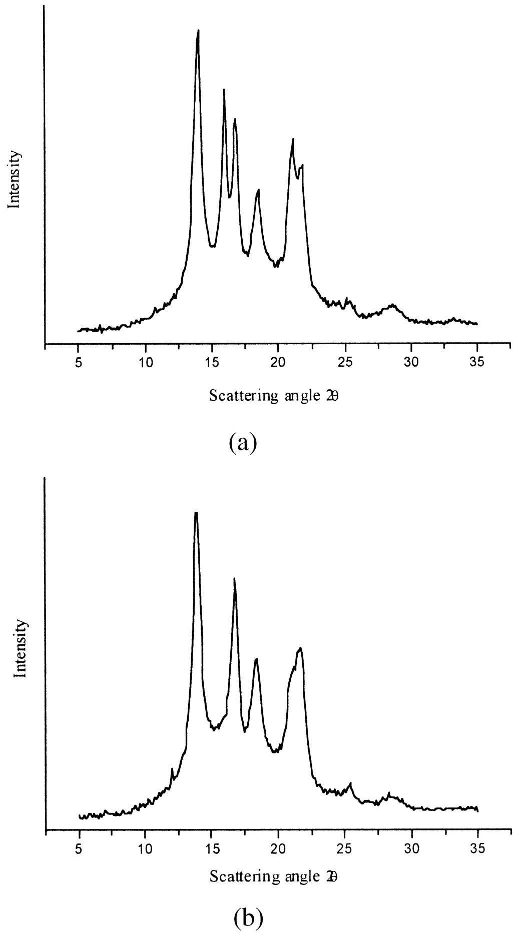


Fig. 11. The WAXS pattern for fibres coloured with phthalocyanine pigment taken at: (a) 100 m/min; (b) 300 m/min.

For fibres taken at velocities from 200 to 400 m/min the sheaf-like spherulites become invisible. On the surface only fine and round spherulites are observed (Fig. 12).

The WAXS pattern of those fibres exhibits only α form peaks showing that observed structure consists of α spherulites.

Fig. 12 shows the α spherulites in fibres coloured with phthalocyanine pigment taken at 300 m/min.

For fibres taken at highest velocities similarly as in noncoloured fibres and fibres coloured with quinacridone pigment the fibrillar structure is formed. The microfibrils have the same diameter equal to 100–150 nm (Fig. 13).

4. Discussion

In fibres spun at the very low velocity the spherulitic morphology is formed. In this case the growth of spherulites occurs similarly as in a quiescent melt.

In the early stages of growth a single lamella breeds more lamellae and develops into an embryo of the spherulite. The embryo grows along the length of the lamella at both ends. During the growth process the stacked lamellae splay apart and branch. As a result of continuous splaying and branching the lamellae gradually develop into a lamellae sheaf. The further growing, splaying and branching lead to the formation of the spherulite skeleton [21–23].

The spherulites formed in noncoloured fibres achieve big sizes. The greatest spherulites are formed in gravity spun fibres. For those fibres the crystallisation process proceeds by the lowest cooling rate and the lowest orientation. In such conditions the nucleation density is low and the space available for spherulites growth is greater. The growth of spherulites proceeding till an encounter with neighbouring spherulite lasts longer and leads to the coarse-grained structure.

The increase in the take-up velocity causes an increase in

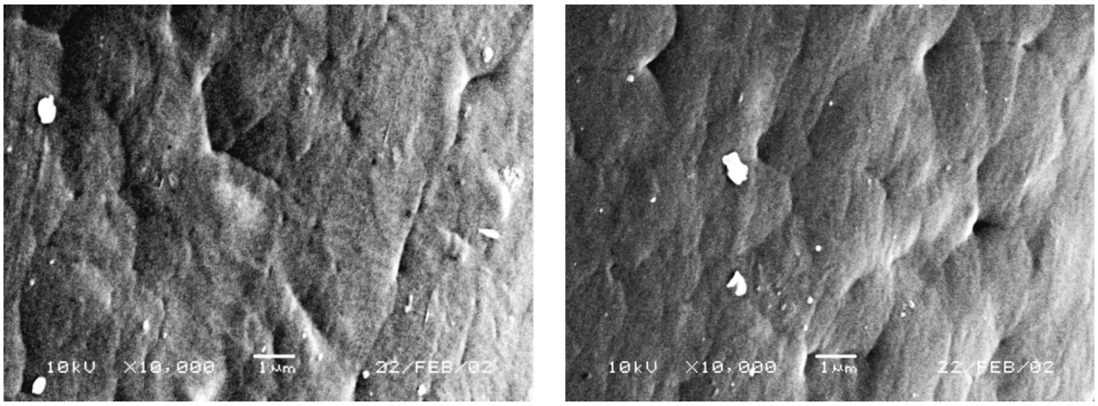


Fig. 12. The α spherulites in fibres coloured with phthalocyanine pigment taken at 300 m/min.

the cooling rate. As a result the nucleation density increases and as a consequence the sizes of spherulites decrease.

In coloured fibres pigments act as typical nucleating agents and cause the increase in the crystallisation temperature and the nucleation density. Consequently the sizes of spherulites in coloured fibres become multiple smaller in comparison to the noncoloured fibres.

The quinacridone pigment possess a very good nucleating ability for the polypropylene crystallisation [24]. In the presence of this pigment the crystallisation of polypropylene melts produces the polymorphic β form.

According to Varga [25] the formation of the β form has an upper and a lower critical temperature limit (T_c^* and T_c^{**}, respectively). During the isothermal crystallisation of the quiescent polypropylene melt in the temperature between T_c^* and T_c^{**} the pure β form is formed. In the temperature somewhat below T_c^{**} the crystallisation produces mixed polymorphic structure.

In fibres coloured with quinacridone pigment the crystallisation starts in the temperature above T_c^{**}. The crystallisation in this temperature produces the sheaf-like β spherulites. During crystallisation as a result of a continuous

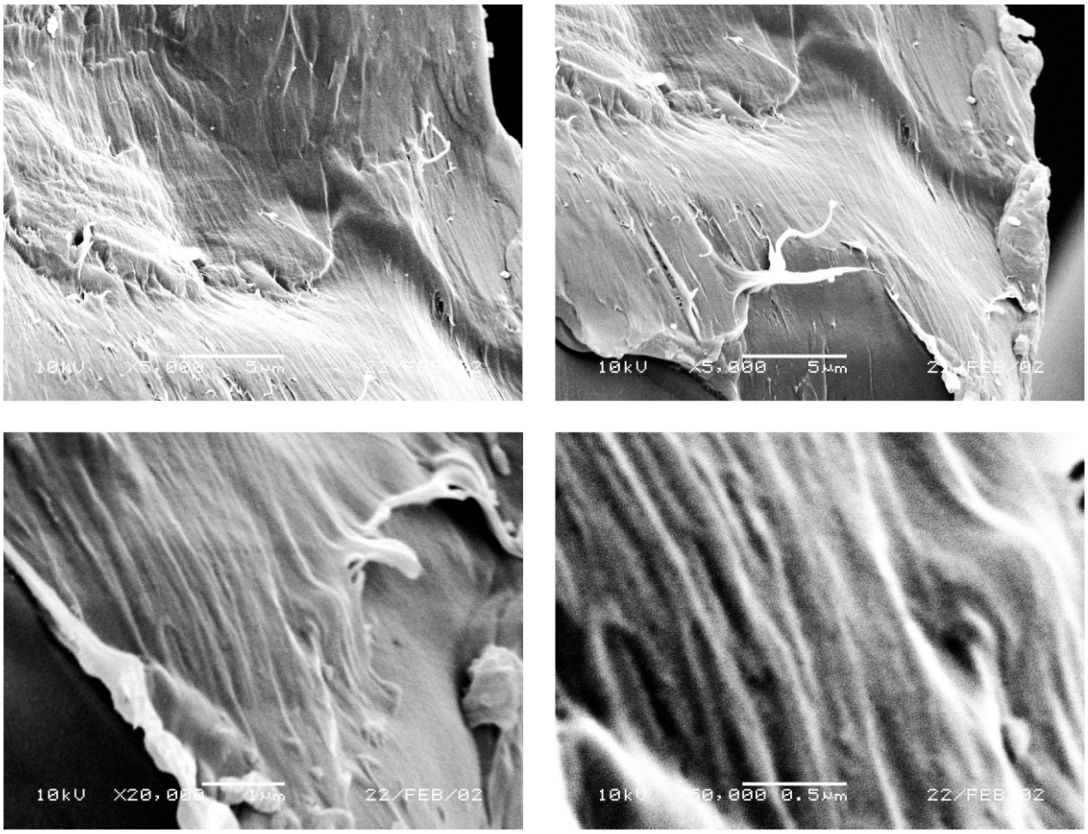


Fig. 13. The fibrillar structure in fibres coloured with phthalocyanine pigment taken at 1350 m/min.

cooling of the filament the temperature decreases below T_{c}^{**}, than uncrystallised material existing in the fibre crystallises in lower temperature forming small amount of the α phase. The resulting α crystals are highly dispersed in the existing β spherulite and are not visible on the fibre surface [26].

In fibres taken at higher velocity as a consequence of the higher cooling rate the crystallisation starts at lower temperature and the temperature of crystallising melt moves faster below the T_{c}^{**}. In such conditions at the beginning of the crystallisation the part of material form the β spherulites, than the rest of crystallisable material crystallises at lower temperature forming the α spherulites randomly distributed on the fibre surface.

At higher velocities the crystallisation temperature do not exceed the lower critical temperature T_{c}^{**} and only α spherulites are formed.

In a case of fibres coloured with the phthalocyanine pigment as a result of the nucleating effect of pigment the crystallisation temperature achieves value lower than in fibres coloured with quinacridone pigment, nevertheless above the T_{c}^{**}. A certain part of the polymer crystallises in this temperature producing a certain number of the sheaf-like β spherulites. At higher take-up velocity the crystallisation occurs below T_{c}^{**} and only α spherulites are observed.

In fibres taken at velocities above 300 m/min the aligned segments of polypropylene chains form row nuclei.

The formation of the row nuclei for a given chain length depends on a shearing rate and a shearing time [27,28]. During the formation of the polypropylene fibres the number of the row nuclei is affected by the molecular orientation depending on formation parameters.

At medium velocities, when the number of such nuclei is not very high, the lamellar crystals grow at the beginning perpendicularly to the nucleus and then splay apart and branch. As a result the so-called cylindites with cylindrical symmetry are formed. The cylindites are visible on the fibre surface as elongated spherulites.

With the increase in the take-up velocity the orientation of the polypropylene chains increases and as the consequence the number of the row nuclei laying parallel to the fibres axis increases. When the number of nuclei is high lamellar crystals growing in the perpendicular direction quickly meet crystals growing on the adjacent nuclei. The growth of the crystals is stopped very quickly before branching and splaying.

In such a condition the structure consisting of oriented and not branched lamellar crystals is formed. Under the influence of tensile forces the crystals can move along the fibre axis forming the fibrillar structure.

At higher velocities a great number of the row nuclei is formed very fast. Pigments do not participate in their formation and do not influence on this process. In the presence of the great number of the row nuclei the heterogeneous nucleation on pigments becomes insignificant. The crystallisation in coloured fibres occurs according to the same mechanism and at the conditions as in noncoloured fibres and produces a similar fibrillar structure consisting of the α modification.

5. Conclusions

The morphology of the polypropylene fibres strongly depends on spinning conditions. In fibres spun at very low velocity the spherulitic morphology is formed. With an increase in the take-up velocity the gradual transformation from a spherulitic to a fibrillar morphology is observed. In fibres taken at the highest velocity only fibrillar morphology is formed.

The change of the fibre morphology results from a change of the mechanism of the nucleation process. In fibres taken at the lowest take-up velocity the growth of crystals starts on point nuclei formed under thermal fluctuations of the polymer melt. At higher velocities the crystallisation occurs on the row nuclei formed under the orientation from the aligned polypropylene chains.

Pigments added to the polymer melt effect the fibre morphology by low take-up velocity. In the presence of pigments the large number of the heterogeneous nuclei is formed. The increase in the nucleation density causes the formation of the structure consisting of the fine spherulites. In fibres coloured with quinacridone pigment the sheaf-like β spherulites are formed. With increase in the take-up velocity the influence of pigments becomes weaker and at the highest velocities becomes invisible. The crystallisation proceeds on the row nuclei formed under the orientation without pigments.

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