Kinetics of crystallization of isotactic polypropylene and polypropylene fibres studied by infrared absorption spectroscopy
II. Fine structure of polypropylene fibres

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The use of continuous recording of the transmittance change at the wavelengths $\lambda_1 = 10.03$ μm and $\lambda_2 = 11.8$ μm in the infrared spectrum of isotactic polypropylene for investigation of the process of isothermal crystallization is described in this paper. On the basis of the results obtained, there are defined the structural parameters — conformational regularity and crystallinity which enable us to estimate intra- and intermolecular interactions of polymer chains in the polypropylene fibres prepared by polymer melt extrusion in the presence of additives.

В работе приводится использование непрерывной регистрации изменений пропускаемости при длинах волны $\lambda_1 = 10,03$ мкм и $\lambda_2 = 11,8$ мкм в инфракрасном спектре изотактического полипропилена для исследования процесса изотермической кристаллизации. На основании полученных данных определяются структурные параметры — конформационная регулярность и степень кристалличности. Последние позволяют обнаруживать внутримолекулярные и межмолекулярные взаимодействия полимерных цепей в полипропиленовых волокнах, приготовленных вытягиванием расплава полимера в присутствии добавок.

A rapid cooling of the polymer melt flow forming a polypropylene fibre gives rise to an imperfect crystalline structure from the view-point of regularity of the arrangement of polymer chains [1]. The crystallinity as a structural parameter of polypropylene fibres is the predominant factor which affects their final physical and mechanical properties.

In this study, we were concerned with the investigation of kinetics of the process of isothermal crystallization of isotactic polypropylene by using infrared absorption spectroscopy. We estimated the absorbance of two absorption bands at $\lambda_1 = 10.03$ μm and $\lambda_2 = 11.89$ μm.

Experimental

For investigating the progress of isothermal crystallization we used the foils of isotactic polypropylene of about 30 μm width prepared by melting and pressing the polymer between the KBr windows. Some organic pigments (Phthalocyanide Blue, Chinacrydon Red) in the amount of 1 wt % served as nucleation agents. The measurements were performed according to the procedure described in the preceding paper [2]. The temperature of melt was 473 K. The melt was kept at this temperature for 15 min and subsequently the determinate temperature of isothermal crystallization was reached in the course of about 3 min. As soon as the required temperature of isothermal crystallization had been attained, the transmittance at the above-mentioned wavelengths started to be continuously recorded with which the zero time coordinate was also determined.

The polypropylene fibres were prepared by melt extrusion at 548 K, the spinning rate being 450 m min^{-1}. The one-dimensional deformation was carried out at 403 K. The substances used as additives were: a pigment — Phthalocyanide Blue (0.5 wt %) with nucleation effect and a high-molecular modifier on the base of a copolymer of ethylene with alkyl-acryl ester (8 wt %) with retardation effect.

The infrared spectra as well as continuous recording of transmittance at the wavelengths $\lambda_1 = 10.03$ μm and $\lambda_2 = 11.89$ μm during isothermal crystallization were taken with an infrared spectrophotometer UR-20.

The polypropylene fibres were valuated by means of the KBr tablet experimental technique. Because of considerable scattering loss of radiation on particles of the fibres pressed in the KBr tablets, the statistically significant values of structural parameters (conformational regularity and crystallinity) were obtained as a mean of 20 values with the variation coefficient of 2—7%.

Results and discussion

Kinetics of isothermal crystallization of isotactic polypropylene

The kinetics of isothermal crystallization was evaluated by means of the Avrami equation

$$\alpha = 1 - e^{-k_0 t^n} \qquad (1)$$

where α is the amount of substance which underwent the phase transition in the time t, k_0 is the rate constant, and n is a constant which determines the character of the growth process. In order to eliminate the influence of varying width of sample as well as the influence of radiation intensity, the normalized crystallization isotherms, *i.e.* the relationships $\ln(-\ln(1 - \alpha)) = f(\ln t)$, were constructed for the comparison of results. These relationships were used for determining the parameters n and k_0.

The value of α was calculated from the following equation

$$\alpha = \frac{A_\infty - A_t}{A_\infty} \qquad (2)$$

where A_∞ is the absorbance of the measured absorption band after crystallization and A_t is the absorbance of this band in the time moment t.

The measured transmittance curve exhibiting the typical sigmoid form was used for calculating the values of A_∞ and A_t at the particular wavelength. The parameters describing the progress of isothermal crystallization of isotactic polypropylene at three temperatures are given in Table 1.

The induction period and half-time of isothermal crystallization of isotactic polypropylene increases with temperature while the rate constant decreases. Similar conclusions concerning isothermal crystallization of isotactic polypropylene which are based on calorimetric measurements or application of polarization microscopy are described in papers [3, 4] and [5], respectively.

Subsequently, we proceeded to test the sensitivity of the method applied to the determination of nucleation effect of two pigments — Phthalocyanide Blue and Chinacrydon Red — which are used in the technological process of spun-dyeing of polypropylene fibres.

The parameters of isothermal crystallization of isotactic polypropylene in the presence of the pigments having nucleation effect are given in Table 2. In general, the nucleation effect manifested itself by a shift in the isotherms to the left, *i.e.* smaller half-time of crystallization, greater rate constant, and shorter induction period. The pigment Chinacrydon Red exhibited a more intense nucleation effect than the pigment Phthalocyanide Blue.

The crystallization isotherms of isotactic polypropylene alone and in the presence of the pigment Chinacrydon Red are represented in Fig. 1 for two temperatures of crystallization.
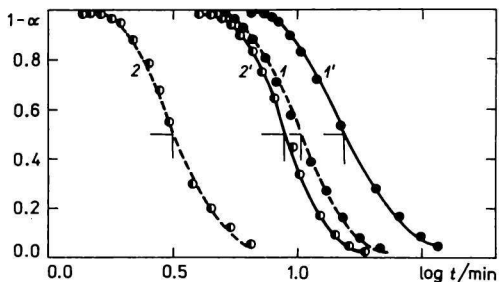

Fig. 1. Crystallization isotherms of isotactic polypropylene samples.

1, 1'. Isotactic polypropylene sample (temperature of crystallization 405 and 410 K); 2, 2'. isotactic polypropylene sample with 1% content of Chinacrydon Red (temperature of crystallization 405 and 410 K).

Table 1

Parameters of isothermal crystallization of isotactic polypropylene determined at $\lambda_1 = 10.03$ µm and $\lambda_2 = 11.89$ µm
($\tau_{1/2}$ — half-time of crystallization, IP — induction period, k_0 — rate constant, n — growth parameter)

T/K	$\log \tau_{1/2}$ min		IP min		$\log k_0$		n	
	$\lambda_1 = 10.03$ µm	$\lambda_2 = 11.89$ µm	$\lambda_1 = 10.03$ µm	$\lambda_2 = 11.89$ µm	$\lambda_1 = 10.03$ µm	$\lambda_2 = 11.89$ µm	$\lambda_1 = 10.03$ µm	$\lambda_2 = 11.89$ µm
403	0.99	0.98	0.4	0.5	−4.0	−4.0	2.60	2.50
408	1.05	1.01	4.0	3.5	−4.5	−4.01	2.47	2.32
410	1.19	1.19	22.2	21.3	−5.6	−5.5	2.80	2.40

Table 2

Parameters of isothermal crystallization of isotactic polypropylene (i-PP) determined in the presence of the pigments with nucleation effect at the wavelength $\lambda_1 = 11.89$ µm and 405 K
($\tau_{1/2}$ — half-time of crystallization, IP — induction period, k_0 — rate constant, n — growth parameter)

Sample	$\log \tau_{1/2}$ min	IP min	$\log k_0$	n
i-PP	1.01	3.5	−4.10	2.32
i-PP + Phthalocyanide Blue	0.77	2.6	−2.31	2.26
i-PP + Chinacrydon Red	0.49	1.8	−1.70	2.34

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In order to complete the information about the nucleation effect of pigments, we investigated the crystallized samples by polarization microscopy. We found that the mean diameter of the spherulites in the samples of isotactic polypropylene crystallized without additives varied about 100 μm while the diameter of spherulites in the samples containing nucleation agents was under border of microscopic resolution.

Fine structure of polypropylene fibres

The study of the experimental data concerning the progress of isothermal crystallization of isotactic polypropylene and analysis of the origin of bond vibrations in polymer chains at particular wavelengths enabled us to come to the following conclusions. The existence of the absorption band at $\lambda_2 = 11.89$ μm corresponds to the presence of the helix segments consisting of 11—13 monomer units in which the concerted skeletal C—C vibrations manifest themselves [6]. The vibrations of this type are localized in larger polymer segments and occur only in regular structures from the point of view of intramolecular order in the chain, which is confirmed by one of the papers by *Krimm* [7]. By evaluating the absorbance of such absorption bands, the information about the regularity of polymer chains may be obtained. The absorbance ratio of the absorption bands at $\lambda_2 = 11.89$ μm and $\lambda_3 = 3.66$ μm used as an internal standard may be called the conformational regularity of isotactic polypropylene ($A_{11.89}/A_{3.66}$).

The presence of regular conformational structures is a necessary but not sufficient condition of the ability to crystallize which is, to a great extent, affected by conditions of the treatment of polymer melt.

It is, therefore, very convenient to valuate simultaneously the absorbance of the band at the wavelength $\lambda_1 = 10.03$ μm in which the vibrations of the CH_3 groups localized in the segments consisting of 11—13 monomer units manifest themselves. The vibrations at this wavelength are significantly affected by intermolecular forces and thus exhibit intermolecular character. The absorbance ratio of the bands at $\lambda_1 = 10.03$ μm and $\lambda_3 = 3.66$ μm (internal standard) is proportional to the real crystallinity of the sample, *i.e.* to the degree of the intermolecular interactions of polymer chains giving rise to monoclinic structural arrangement of isotactic polypropylene. The evaluation of the structural parameters — conformational regularity and crystallinity — of the polypropylene fibres prepared by polymer melt extrusion may give information about the character of fine structure on the level defined by the size of the assumed polymer segments.

For this reason, we valuated the polypropylene fibres prepared without any addition, with an addition (0.5 wt %) of the pigment Phthalocyanide Blue having nucleation effect, and with an addition (8 wt %) of a high-molecular modifier with retardation effect.

All the above absorption bands in the infrared spectra of polypropylene fibres were evaluated by the method of the fundamental line plotted along the lowest transmittance points of the absorption bands.

The relations $A_{11.89}/A_{3.66} = f$ and $A_{10.03}/A_{3.66} = f$ (draw ratio) for the samples of polypropylene fibres prepared without additives show that the curve proportional to crystallinity is above the curve of conformational regularity, *i.e.* their comparison may serve as a relative measure for the content of monoclinic structural arrangement (Fig. 2).

The measured values of conformational regularity and crystallinity of polypropylene fibres are influenced by spinning conditions. It results from our present experience that the character of these relationships for valuating the polypropylene fibres without additives prepared under different technological conditions is always equal, *i.e.* the curve proportional to crystallinity is always above the curve of conformational regularity. The relations $A_{11.89}/A_{3.66} = f$ and $A_{10.03}/A_{3.66} = f$ (draw ratio) are represented in Fig. 3 for the polypropylene fibres prepared with additives.
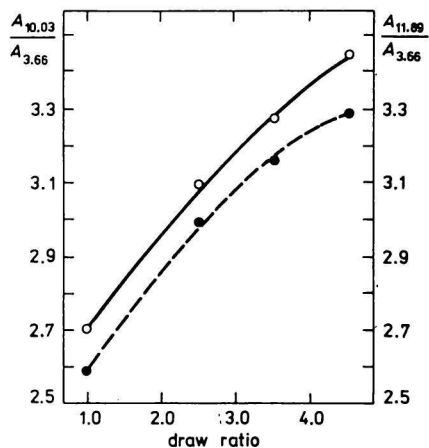

Fig. 2. Dependence of conformational regularity $A_{11.89}/A_{3.66}$ (----) and crystallinity $A_{10.03}/A_{3.66}$ (——) on the draw ratio for polypropylene fibres without additives.
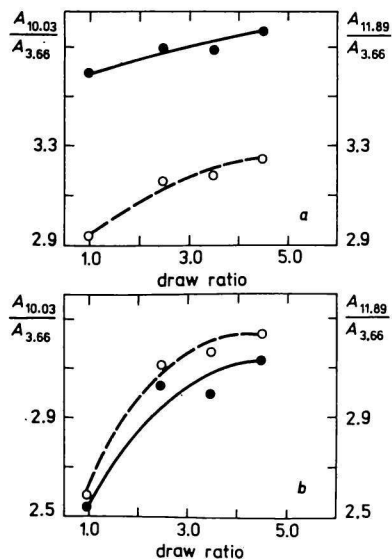
Fig. 3. Dependence of conformational regularity $A_{11.89}/A_{3.66}$ (----) and crystallinity $A_{10.03}/A_{3.66}$ (——) on the draw ratio.
a) Polypropylene fibres containing 0.5 wt % of Phthalocyanide Blue.
b) Polypropylene fibres containing 8 wt % of high-molecular modifier.

The experimental results given in Fig. 3 show that the nucleation effect of the pigment present in the concentration of 0.5 wt % manifested itself by an increase in overall amount of crystalline regions with respect to the progress of conformational regularity. This piece of knowledge is very important for the selection of technological conditions of one-dimensional deformation because the fibres containing a higher content of crystalline regions are less deformable.

On the other hand, the presence of high-molecular modifier showed itself by a decrease in the amount of crystalline regions in comparison with conformational regularity. As the high-molecular modifier used is also applied to the preparation of surface-dyed polypropylene fibres, the evaluation of the above structural parameters enables us to clear up its role in the studied physical modification. According to our results, we may state that the high-molecular modifier prevents intermolecular interactions of polymer chains and thus favours the formation of a structure favourable to diffusion of low-molecular substances such as dyestuffs.

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