Evaluation of the Morphological Structure of Polymers

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Received 15 July 1997

The method of small angle laser scattering is suggested for the evaluation of the morphological structure of polypropylene sheets and fibres as well as polyethylene terephthalate fibres. This method enables qualitative and quantitative evaluation of present morphological formations in polymeric materials. On the basis of known procedure of preparation of the evaluated sheets and fibres it is possible to find connections between their morphological structure and their properties.

The morphological structure of polymers on a certain quantitative and qualitative level expresses a development stage of the preparation of polymer material (fibres, sheets) with given physical properties. Polymer materials on a lower development technological stage of preparation (nonoriented fibres) contain structural configurations of crystallites in a polymer amorphous phase – spherulites. Spherulites are three-dimensional morphological configurations with a certain size and periodicity, attaining the dimensions comparable with the wavelength of visible light. They have various size and shape. A nondeformed spherulite is symmetric and it has properties of an isotropic configuration in an isotropic polymer. A deformed spherulite demonstrates itself as an isotropic configuration of crystalline grouping in an isotropic environment [1].

The presence of spherulites in polymer, their size and shape can be intentionally influenced by means of various manners [2, 3]. One of the intentional structural modifications is reached with various chemical agents. These agents form in the polymer heterogeneous centres and influence the crystalline size, or the presence of spherulites [4, 5]. Another way of intentional transition of the polymer morphological structure is the physical action, especially the polymer deformation at various temperature spinning conditions. During fibre forming the morphological structure is markedly changed. The growing mechanism of the morphological configuration passes over from three-dimensional growing of spherulites (for polyethylene terephthalate fibre $\Delta n \cdot 10^3 = 25$—30) through a two-dimensional lamellae growing (for polyethylene terephthalate fibre $\Delta n \cdot 10^3 = 40$—45) and at last to one-dimensional growing of fibrils, with a profound orientation in the longitudinal direction of the fibre axis (for polyethylene terephthalate fibre $\Delta n \cdot 10^3 = 50$ and more) [2, 3, 6]. The knowledge of the qualitative and quantitative level of the morphological structure of the polymer material is important from the viewpoint of the further processing, stability and in connection with its physical, mechanical, and optical properties.

With regard to the optical dimensions of the morphological configurations optical methods are used to evaluate the morphological structure (light polarization microscope, electron microscope, X-ray methods ...). The small angle scattering of the polarized laser beam (SALS) suitably supplements the former mentioned methods at the study of the morphological structure of polymers. The advantage of the laser light is the coherence and monochromatic character. The laser with incident light on spherulite in polymer material is scattered with a small angle and the diffusion is registered in the background. The scattered image renders more information on the morphological structure of the studied material (kind of the structural configuration, size, deformation degree) [7—9].

For the calculation of a radius R of a spherulite the following relation is used [1]

$$R = \frac{c \cdot \lambda}{n \ \pi \ \sin \Theta_{\max}}$$

where c is the constant characterizing the shape of the spherulite, λ laser light wavelength, n refraction in polymer, and $\Theta_{\max}$ maximum angle of scattering.

The constant c is different for a homogeneous anisotropic sphere, homogeneous anisotropic disc or fibrilar spherulite.

The aim of the presented work is evaluation of the morphological structure of polymer materials by the optical methods, especially by the SALS method. The morphological structure of polymers for foils was intentionally changed by means of nucleation agents and of fibres forming polymers by different spinning rates.

EXPERIMENTAL

Sheets of unmodified and modified polypropylene of the type Tatren FF 520 with 20—25 μm thickness were prepared. The size of spherulites was intentionally changed by means of synthetic nucleation agents

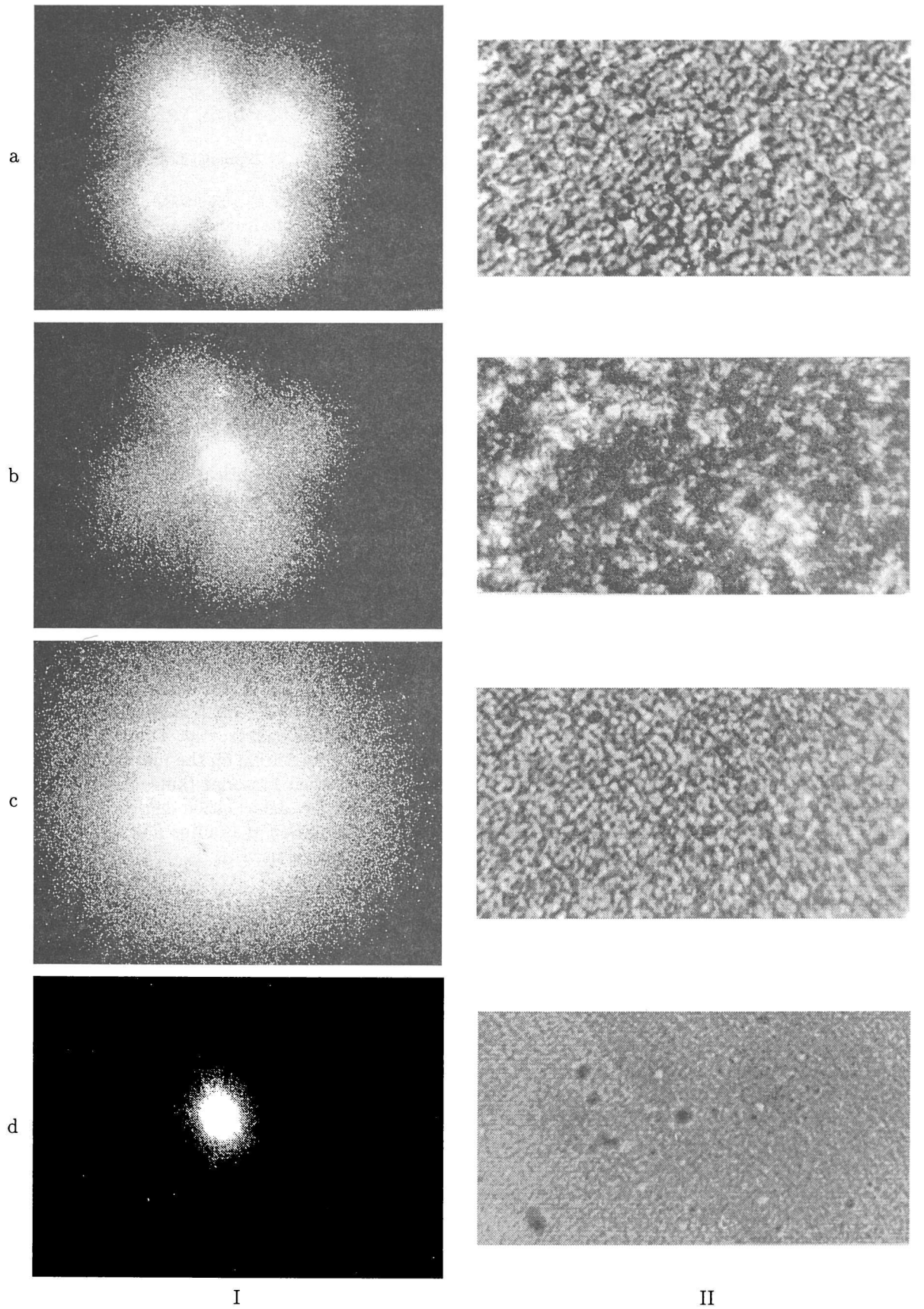

Fig. 1. Influence of additives on the morphological structure of polypropylene in sheets recognized by the SALS method (I) and by light polarization microscopy (II).

(sorbitol derivates) having melting temperature T_m = 110—230 °C. The content of the nucleation agents in the polypropylene was 0.5 mass %. The homogenization was secured by remelting. The isotropic morphological spherulites in isotropic material were evaluated.

Polypropylene fibres were prepared at the spinning rate of ν_n = 1800 m min^{-1}, 2700 m min^{-1}, and 4000 m min^{-1} in the operation conditions.

For polyethylene terephthalate fibres preparation a polymer from the current production was used. Fibres were prepared at the operation spinning equipments. There was used a spinning nozzle of circular diameter. The polymer melting point on the snake was 288 °C. Fibres with a titre T_{dt} = 84 dtex with a number of 24 and 48 elemental fibres in a yarn were prepared. Fast spinning was used at the rates 2500 m min^{-1}, 3000 m min^{-1}, and 3500 m min^{-1} Anisotropic morphological configurations in isotropic and anisotropic environments were evaluated.

Methods used for evaluation of the morphological structure were SALS and light polarization microscopy. The source of laser light was a semiconductive diode LDD 3.3 with an optical output of 25 mW. The optical diffractograph was arranged according to the following diagram: the source of laser light → the polarizer → the tested sample → the analyzer → the photographic device. There was used a light polarization microscope (Olympus Comp., Japan). The optical light permeability was measured through a polypropylene sheet with a Spekol device (Zeiss, Jena).

RESULTS AND DISCUSSION

Figs. 1I*a*—I*d* gradually show the morphological configurations in polypropylene sheets by the SALS method at the crossed position (Hv) of the analyzer and polarizer. A quatrefoil with sharp contours corresponds to developed spherulites in polypropylene A without nucleation agents (Fig. 1I*a*) while that with blunt contours is a result of a less compact spherulite structure B (Fig. 1I*b*). The configuration with unspecified structure C results in scattering without a quatrefoil (Fig. 1I*c*). Finally no scattering corresponds to a fine morphological structure of polypropylene D containing an additive with a profound nucleation effect (Fig. 1I*d*). In Figs. 1II*a*—II*b*, the corresponding records of these sheets *a*—*d* in polarized light microscope are shown. The presence of large spherulites in the sheets decreases the light permeability (Table 1).

In Fig. 2 are recorded the Hv scatterings of laser light on morphological configurations in polypropylene preoriented fibres at spinning 1800 m min^{-1}, 2700 m min^{-1}, and 4000 m min^{-1}

In Figs. 3I*a*—I*c* are recorded the Hv scatterings of laser light on morphological configurations in polyethylene terephthalates preoriented fibres at spinning rates 2500 m min^{-1}, 3000 m min^{-1}, and 3500 m min^{-1} with a titre T_{dtj} = 3.50 dtex and in Figs. 3II*a*—II*c* to them corresponding microscopic records of fibres in the dark visual field of the polarization microscope are shown. A two-foil with expressive contours (Fig. 1II*a*) corresponds to the presence of developed spherulites in polyethylene terephthalate fibres obtained at the spinning rate of ν_n = 2500 m min^{-1} A two-foil with less expressive contours (Fig. 1II*b*) is a result of the presence of less compact spherulites in polyethylene terephthalate fibres (spinning rate of ν_n = 3000 m min^{-1}). A lamellar structure obtained by a spinning rate of ν_n = 3500 m min^{-1} is characterized by centric scattering (Fig. 1II*c*).

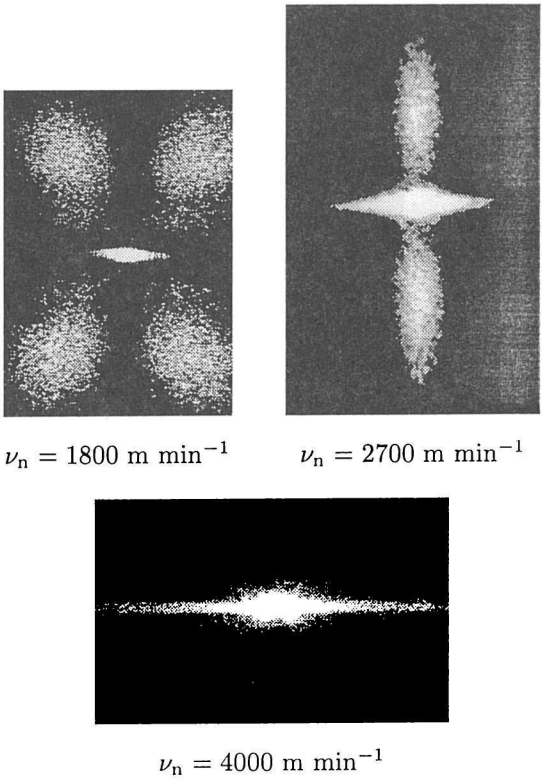

Fig. 2. Influence of spinning rate on the morphological structure of polypropylene fibres recorded by laser scattering.

Table 1. Effect of the Spherulite Size in Modified Polypropylene on the Light Permeability

Polypropylene sample	R	ϑ	T_m
	μm	%	°C
A	2.7	71	
B, nucl. agent I	1.9	78	215
C, nucl. agent II	Unspecific scattering	79	110
D, nucl. agent III		87	230

Nucl. agents I, II, III are various nucleation agents in polypropylene used, R is spherulite radius, ϑ is permeability, and T_m is the melting temperature of the nucleation agent.

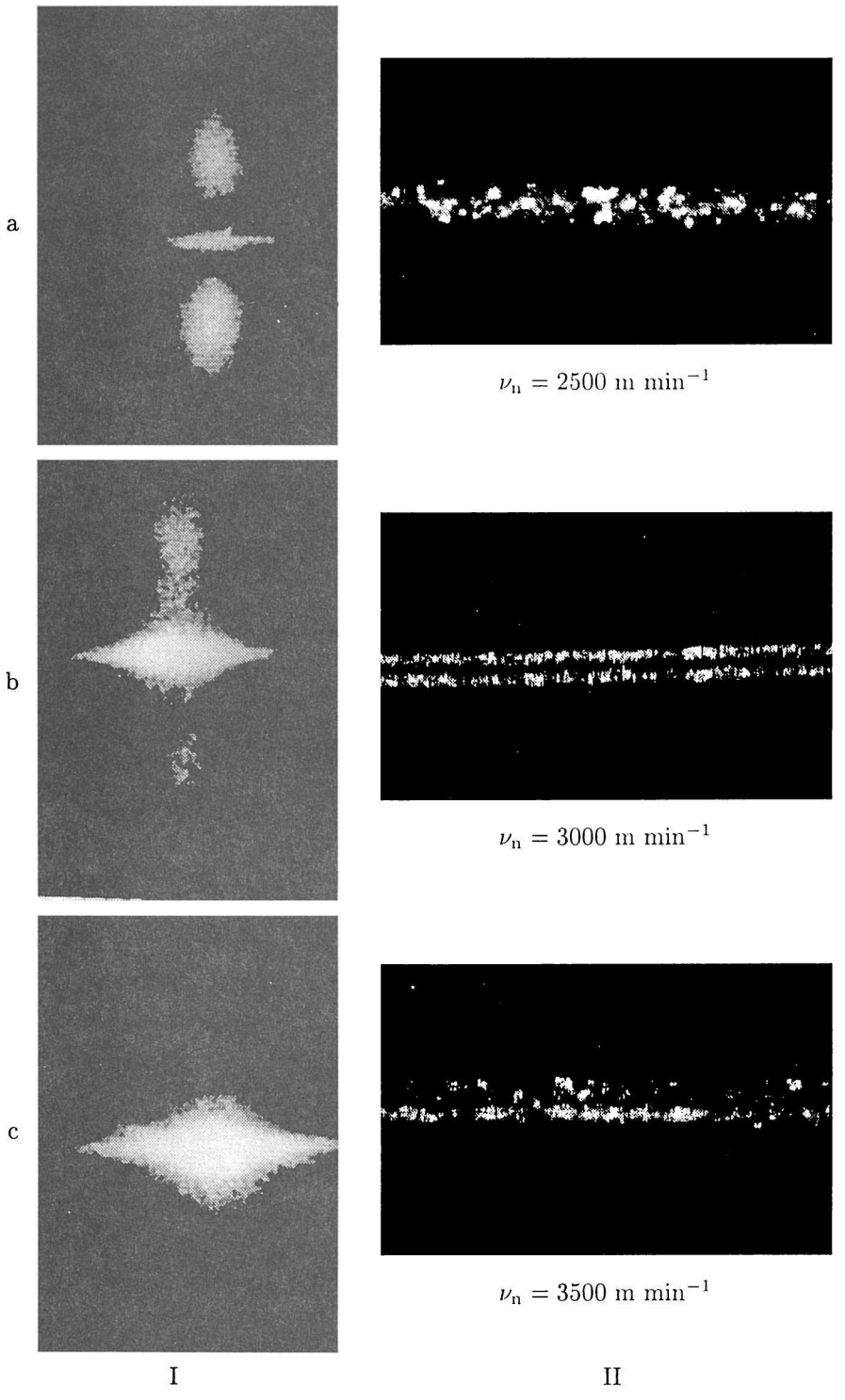

Fig. 3. Influence of spinning rate on the morphological structure of polyethylene terephthalate fibres with a titre $T_{dtj} = 3.50$ dtex recognized by the SALS method (I) and by light polarization microscopy (II).

The mentioned records of scattering of laser light on morphological structural configurations in polyethylene terephthalate fibres give information on preoriented fibres. Drawn fibres with fibril structure do not present scattering of the laser light.

The influence of the spinning rate of finer fibres with $T_{dtj} = 1.75$ dtex on the growing of morphological configurations is demonstrated at lower rates with a more oriented lamellar structure, as in Fig. 4, in comparison with more thick fibres, as in Fig. 3. The orientation of morphological structure configurations is a kinetic process and it depends on a number of technological conditions of preparation of polymer materials.

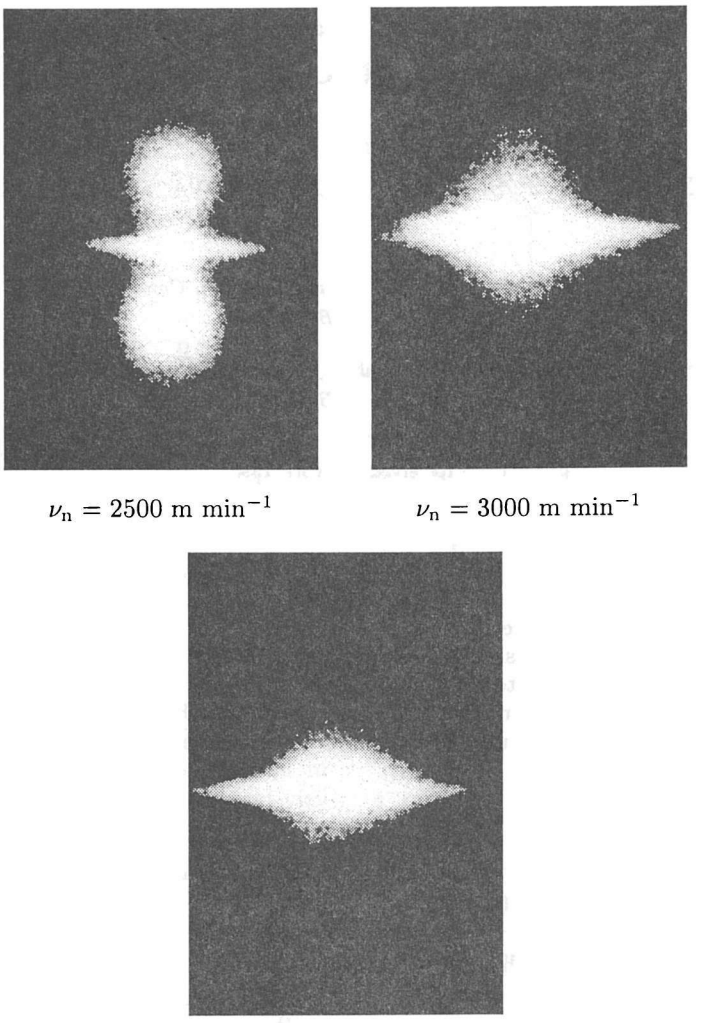

Fig. 4. Morphological structure of fine polyethylene terephthalate fibres with a titre $T_{dtj} = 1.75$ dtex at various spinning rates recorded by laser scattering.

CONCLUSION

The information on the development of morphological configurations during the forming of polymer material (fibres and sheets) is important from the viewpoint of the further processing to a final product. The applied optical methods are suitable for evaluation of the morphological structure of polymer materials, sheets and fibres.

The SALS method quickly and responsively determines the presence of large structural configurations in polymer material. The polypropylene sheets with developed spherulites have a lower permeability of light. The nucleation agents cause a clarification effect in polypropylene sheets. The spherulites in polypropylene and polyethylene terephthalate fibres have a typical growing mechanism in dependence on the spinning rate.

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