

Ultra-High Modulus Isotactic Polypropylene. I. The Influence of Orientation Drawing and Initial Morphology on the Structure and Properties of Oriented Samples

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SYNOPSIS

The influence of a number of factors (temperature–speed regime and the quantity of draw stages, molecular weight of a polymer, etc.) on the deformability of initial isotropic IPP and on mechanical characteristics of highly-oriented samples, obtained in the process of a two-stage isothermal orientation drawing, was studied. It was shown that the maximum achievable values of elastic modulus and draw ratio depended not only on the molecular weight of a polymer and the sizes of spherulites, constituting initial IPP, but on the structural organization of inner- and interspherulite regions. Upon physical aging of initial isotropic films, irreversible structural changes take place, which result in the formation of microvoids while being drawn and in the reduction of mechanical properties of obtained material. An extremal dependence of elastic modulus and draw ratio of maximum drawn IPP samples on draw speed was discovered. A structural model, which is supposed to possess tie molecules with various degrees of tautness in amorphous layers, was proposed. Higher effectiveness of two-stage drawing in comparison with one-stage drawing was established. The optimum temperature–speed regime of orientation drawing, which permits the reception of highly oriented, ultra-high modulus IPP with maximum high mechanical characteristics (elastic modulus $\sim 30\text{--}35$ GPa and tensile strength $\sim 1,1$ GPa), was determined.

INTRODUCTION

At present, the production of high modulus fibers and films from flexible-chain, semicrystalline polymers is intensively developed with the help of various methods of deformation. To achieve the greatest possible values of the elastic modulus and tensile strength, the methods of deformation have been widespread, and these include orientation change of the already-formed structure of a polymer. The main methods are: (1) uniaxial orientation drawing^{1–7}; (2) die drawing^{8,9}; (3) solid state extrusion^{10–13}; (4) rolling and roll-drawing^{14,15}; (5) zone drawing^{16,17}; (6) the combined methods, including several processes for treating a polymer, for example, solid state

extrusion with further drawing,^{18,19} the combination of zone drawing with zone annealing,²⁰ and melt or solution spinning with further orientation drawing.^{17,21,22–26}

Most high mechanical characteristics were obtained with the help of combined technologies. For instance, gel-forming from the dilute solution method, with further drawing of dry gels, provides films with the greatest values of Young's modulus (E) and tensile strength (σ_b) for polypropylene at the present time (respectively, 36 GPa and 1.03 GPa²⁶ and 40 GPa and 1.5 GPa²⁴). However, it is worth mentioning that these methods require specific values of molecular weight and molecular weight distribution of a polymer and the intensive extraction of a solvent in the course of production. The methods, under which a solvent is not used, usually provide materials with essentially worse mechanical

properties. Nevertheless, it was shown in the literature^{27,28} that highly oriented, ultra-high modulus polypropylene, the separate samples of which have elastic modulus higher than 36 GPa, can be obtained by the usual method of uniaxial orientation drawing. In connection with this, research into the possibility of creating ultra-high modulus material by this method, on the basis of melt-crystallized films from polypropylene of industrial production, with the medium value of molecular weight, is of obvious interest.

In this work, the results of systematical research on the process of receiving ultra-high modulus films from isotactic polypropylene (IPP), by the method of two-stage isothermal orientation drawing, is presented. The influence of a number of factors (temperature–speed regime of drawing, morphology and molecular weight of initial material, etc.) on deformation capability of IPP, and on final mechanical characteristics obtained in the process of drawing oriented samples, is discussed.

EXPERIMENTAL

The Obtaining of Initial Materials

The granules of commercial IPP, grade 21020-16 (Guriev Chemical Plant, USSR), with the following characteristics: $\bar{M}_w = 2.29 \times 10^5$, $\bar{M}_n = 7.76 \times 10^4$, with crystallinity measured by the method of differential scanning calorimetry (DSC): 60.5%, melting temperature (DSC): 163°C, melt flow index: 1.91

g/10 min, and isotacticity index measured by the method of IR-spectroscopy: 93%, were used as the initial material for obtaining isotropic, nonoriented films.

To study the influence of initial morphology on orientation parameters and on the properties of oriented samples the initial, nonoriented films were obtained from IPP granules by three different methods: (1) by extrusion forming (without blowing) of IPP granules at 190°C with further natural cooling in air until room temperature ("blown" film, designated as IPP-1); (2) by compression molding at 190°C with further crystallization during 2 h at 165°C and by slow (natural) cooling in the press at the speed of 0.1°C/min until room temperature (slow cooling, film IPP-2); (3) by compression molding at 180°C with further rapid cooling at the speed of 100°C/min in icy water (quenching, film IPP-3).

In addition, the rules for orientation drawing of ultra-high molecular weight polypropylene films ($\bar{M}_n \sim 18.9 \times 10^5$), synthesized under laboratory conditions,²⁹ were researched. These films were prepared by compression molding at 230°C with further quick cooling in icy water (quenching, film IPP-4). The films from low-molecular IPP ($\bar{M}_w \sim 1.5 \times 10^5$), produced by ICI, Ltd. (quenching, film IPP-5), were obtained by the same method. In all cases, the molding pressure constituted 100–150 bar. Some properties of the above enumerated initial, nonoriented IPP films are given in Table I.

The effect of physical aging on the orientation drawing process was studied on the samples of IPP-

Table I Morphological Characteristics and Physico–Mechanical Properties of Initial Isotropic IPP Films

Parameters	Materials				
	IPP-1	IPP-2	IPP-3	IPP-4	IPP-5
Molecular Weight $M \times 10^{-5}$	2.29	2.29	2.29	18.9	1.5
Crystallinity X_c , %	60.5	47.1	46.7	41.1	50.0
Melting Temperature T_m , °C	161–163	166	166	164	167
The Sizes of Spherulites d_{sp} ^a	40	220	35	49	32
Elastic Modulus E , GPa	1.36	1.50	1.28	1.37	—
Tensile Yield Point σ_y , MPa	34.1	36.8	32.9	31.8	—
Necking Tension σ_n , MPa	24.9	31.3	19.8	22.6	—
Tensile Strength at Break σ_b , MPa ^b	255	34.1	279	168	—
Extension Strain at Break ϵ_b , %	650	13.6	1006	576	—
The Conditions of Obtaining Films	Extrusion	Slow Cooling	Quenching	Quenching	Quenching

^a Determined by optical microscopy.

^b Calculated at final (actual) cross-sectional area of sample.

1 film, which were stored in air at room temperature ($20 \pm 1^\circ\text{C}$) and relative humidity about 60–70%. Samples were protected from exposure to sunlight.

The Obtaining of Oriented IPP Films by the Method of Orientation Drawing

In the present work, the orientation of IPP films was conducted by the method of two-stage, isothermal orientation drawing on tensile testing machine "Instron 1122" at temperatures of 145°C and 165°C

in a thermal chamber. The peculiarity of the drawing at draw temperature $T_d = 165^\circ\text{C}$ was that the first stage of drawing was performed at lower temperature ($163\text{--}164^\circ\text{C}$) in clamps, insulated from samples to prevent the melting of initial isotropic films in these clamps of a testing machine. Since, with the growth draw ratio (λ), the melting temperature of IPP increases,^{1,4,25,30} the following drawing of oriented films at the second stage can be already made at 165°C .

At the first stage, the dumbbell samples with a working part 35 mm long and 5 mm wide were

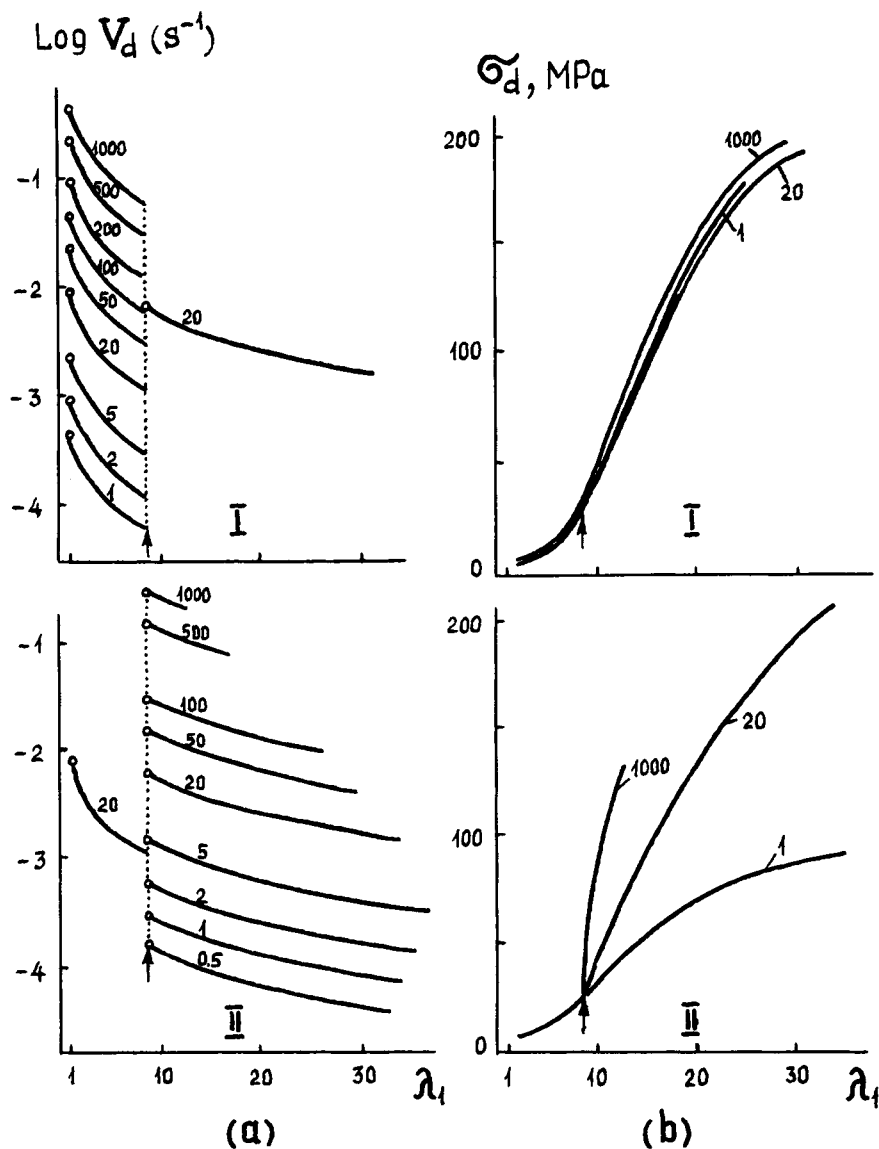


Figure 1 Draw speed V_d (a) and draw tension σ_d (b) changes at 145°C with the growth of draw ratio λ_1 during experiments I and II. The figures on the curves are the values of shifting speed of clamps V_c (mm/min). The moments of transition from the first to the second draw stage are marked by arrows.

stretched out until equal length (corresponding to the "natural" draw ratio, $\lambda \sim 8.5\text{--}9.0$), and at the second stage—strips, 50 mm long, cut out from the middle of the stretched dumbbell samples. The standard shifting speed of clamps (V_c) for the present work was constant, excluding the experiments with various draw speed, and constituted 20 mm/min, which corresponded to initial draw speed $9.5 \times 10^{-3} \text{ s}^{-1}$.

The draw ratio was determined by the linear displacement of transverse marks, preliminarily plotted on an initial isotropic sample (λ_1), and by the change of cross-sectional area of a sample while it was stretched out (λ_2), according to proportions $\lambda_1 = l/l_0$ and $\lambda_2 = S_0/S$, where l_0 and S_0 are length and cross-sectional areas of a sample before drawing, and l and S are the current values of length and cross-sectional area of a sample in the process of drawing. The volume change of a deformed sample was judged by a proportion: $\lambda_2/\lambda_1 = (S_0/S)/(l/l_0) = v_0/v$, where v_0 and v are the volumes of initial isotropic and drawn samples, respectively. On terminating the draw, the oriented samples were cooled in the air under free conditions. Furthermore, on choosing optimum conditions to perform orientation drawing, two kinds of experiments were conducted: in one case, draw speed was changed at the first stage, while at the second stage it remained the same one (experiment I), and in the other, draw speed was changed at the second stage but at the first stage it remained unchanged (experiment II). It is worth noting that these experiments were conducted under the conditions of constant shifting speed of clamps V_c , while in each case the real draw speed continuously decreased with the growth of draw ratio according to the proportion $V_d = V_c/(l'_0 + \Delta l) = V_c/(\lambda_1 \times l'_0)$, where l'_0 is the initial gage length and Δl is the lengthening in the process of drawing. The changes of draw speed V_d with the growth of draw ratio λ_1 for experiments I and II are shown in Figure 1. In the same figure, typical draw diagrams for samples IPP-1 at $T_d = 145^\circ\text{C}$ are given and they correspond to minimum, intermediate, and maximum draw speeds. Draw tension σ_d was calculated for final (real) cross-sections of stretched out samples and mechanical indexes of isotropic films (E , σ_y , σ_n) for the initial cross-sectional area.

The Measurement of Mechanical Characteristics

Mechanical properties of nonoriented and oriented IPP samples with various draw ratios were researched on a tensile testing machine "Instron 1122" at 20°C , with speed shifting of clamps equal to 20

mm/min and the initial test base equal to 35 mm. The measurement of the mechanical properties of oriented samples was made 2–3 days after drawing. The modulus of elasticity in tension (axial Young's modulus) E was determined according to "stress-strain" ($\sigma - \epsilon$) diagram by the initial slope of the curve at deformation $\epsilon \leq 0.45\%$. To prevent slipping in the clamps during the test, the oriented samples were glued up in special frames.³¹ All the values of mechanical characteristics and parameters of the drawing are the average ones, obtained by measuring at least 5 samples.

RESULTS AND DISCUSSION

The Interconnection of Morphology and Deformation Capability of Initial Isotropic IPP Films

To research the interconnection between spherulite structure and deformation properties of polymers, the way in which the mechanical properties of a polymer depend upon the size of spherulites should be first determined. The spherulites of various types in IPP, which differ not only in size and appearance, but in internal structure, can be obtained by changing the conditions of thermal treatment in the process of crystallization of a polymer from melt.^{32–35} It is, however, difficult to establish quantitative connections between the nature of supermolecular structure and mechanical properties of IPP, in particular, its ability for deformation. In order to choose any parameter (for example, the size of spherulites), and to study its influence on properties, it is necessary to observe an indispensable condition: all the rest of the parameters must remain constant. Upon the formation spherulite structure, this condition is observed with difficulty, since the process of IPP crystallization is rather complex and formed spherulites of equal size can have different internal structure.

To study the influence of initial IPP morphology on its deformability, three types of samples were used in the present work and they were obtained under different conditions of crystallization from melt: by extrusion forming (IPP-1), by compression molding with further slow cooling (IPP-2), and by compression molding with further quenching (IPP-3). These materials had the same molecular weight ($\sim 2.3 \times 10^5$) and practically the same crystallinity (50–60%), but they differed in the size of spherulites, respectively, 40, 220, and 35 μ . The mechanical properties of these initial (nonoriented) IPP sam-

ples, with various morphologies, are presented in Table I and Figure 2. It is seen that almost all mechanical characteristics of IPP, especially deformation properties, depend on the size of spherulites. Upon an increase in the size of spherulites, extension strain at break (ϵ_b) most intensively decreases and tensile strength σ_b , calculated for the final cross-section of a sample, also reduces. Characteristics such as initial modulus of elasticity E , tensile yield point σ_y , and recrystallization tension σ_n , calculated for the initial cross-section of an isotropic sample, comparatively weakly depend upon the size of spherulites. These values, however, tend to increase when the size of the spherulites grows. It is possible to conclude that the deformability of IPP at 20°C worsens upon transference from small size spherulite to large size spherulite structure; this transference is accompanied by the appearance of a great number of defects in the kinds of cracks mainly on the boundaries of spherulites due to the development of already existing cracks in initial films under mechanical tensions.

It is worth noting that in forming mechanical properties of IPP, not only the sizes of structural formations, constituting the material, but the nature and the degree of the organization of their internal structure (which change, to a considerable extent, depending upon the method of formation of the in-

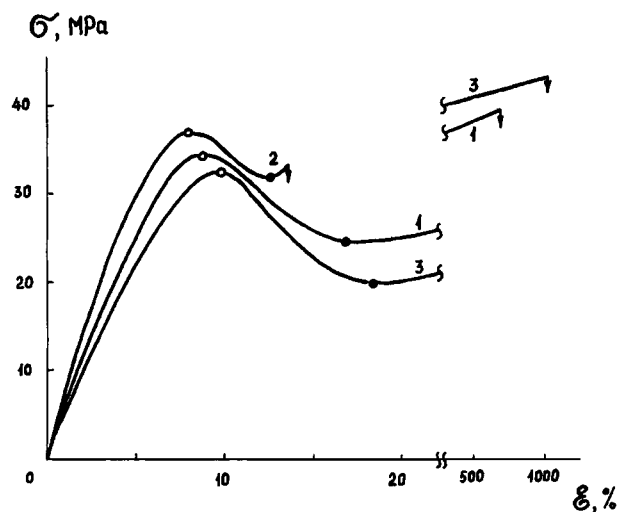


Figure 2 The diagrams of drawing isotropic IPP films of various supermolecular structure (calculated from initial cross-sectional area): 1 = "Blown" film, IPP-1 ($d_{sp} = 40 \mu$); 2 = Slowly cooled film, IPP-2 ($d_{sp} = 220 \mu$); 3 = Quenched film, IPP-3 ($d_{sp} = 35 \mu$). $T = 20^\circ\text{C}$, $V_c = 20$ mm/min. Break points are marked by arrows; tensile yield points σ_y are designated by light circles, the values of necking tension σ_n are designated by dark circles.

ternal structure) play an essential role.^{1,32,36} Therefore, the above described dependence of mechanical behavior of IPP on the size of supermolecular structures that form it, should be considered as the most extreme and vividly expressed case, permitting various deflections. For example, in spite of the fact that the sizes of spherulites of "blown" film IPP-1 and quenched film IPP-3 differ rather insignificantly (40 and 35 μ , respectively), causing practically equal values of σ_y (34.1 and 32.9 MPa), the deformability of these films, measured by value ϵ_b , is essentially different (see Figure 2, curves 1 and 3). The possible explanation of this effect will be given later.

As a rule, with increasing temperature, the deformability and ductility of IPP grows. Increasing test temperature (T) leads to the monotonous decrease of elastic modulus E and yield point σ_y and to the growth of extension strain at break ϵ_b (or maximum draw ratio λ_1^*)^{*} (Fig. 3). Upon creation of a different supermolecular structure in the initial polymer material, one can be convinced that the effect of test temperature on mechanical properties is different. The IPP samples of a homogeneous, small-spherulite structure at low T display greater deformability than the samples of a large-spherulite, heterogeneous structure, also including spherulite strips and other more rough formations. However, as is shown in Figure 3, at increased T this difference in deformation properties becomes smooth, and the differences in values E , σ_y and λ_1^* for small- and large-spherulite IPP samples do not exceed 25%. Nevertheless, at any temperatures, the differences in the morphology of initial, nonoriented IPP films exert a certain influence both on the deformability of IPP and on the mechanical characteristics of oriented samples, obtained in the process of orientation drawing. As an example, with the growth of draw ratio λ_1 , the change of elastic modulus E of oriented samples and draw tension σ_d , calculated for the final cross-section, is shown for IPP of various supermolecular structure in Figure 4. One can see that at the given draw temperature ($T_d = 145^\circ\text{C}$), small-spherulite samples possess better deformability than large-spherulite ones do, and IPP-1 samples occupy an intermediate position between them. However, at all values λ_1 , the dependence $E(\lambda_1)$ for "blown" film is higher than analogous dependencies for small- and large-spherulite samples, confirming the greater effectiveness of the orientation process on drawing IPP-1 samples. The obtained results can be ex-

* In the text, all the characteristics, relating to stretched out at most samples under the given draw conditions, are marked by an asterisk.

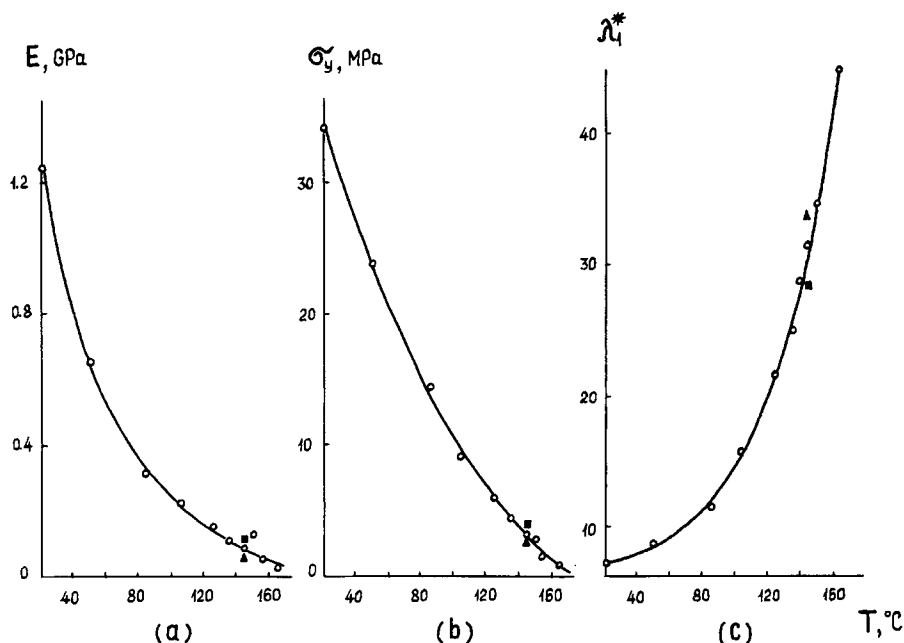


Figure 3 Temperature dependencies of elastic modulus E (a), tensile yield point σ_y (b), and maximum draw ratio λ_1^* (c) of isotropic IPP samples with different initial morphology: \circ = IPP-1; \blacksquare = IPP-2; \blacktriangle = IPP-3. $V_c = 20$ mm/min.

plained as follows. In Ref. 34, the supposition was made that the deformability of melt-crystallized PE and PP samples depended not only on the sizes of spherulites but also on the structure of inner- and interspherulite regions. Small-spherulite (quenched) samples have greater quantity of the first sort of violations in spherulite crystallites as compared with large-spherulite samples; they also have denser spherulite interlayers. Moreover, the quantity and sizes of these adjacent spherulite interlayers in small-spherulite samples are usually less than in large-spherulite samples and, therefore, the deformation of such structure occurs more easily and homogeneously than in large-spherulite samples and it leads to higher experimentally observed values λ_1^* (Figs. 3 and 4). At the same time, the drawing of samples with small-spherulite structure, to all appearances, is accompanied by the relaxation of the molecular chain orientation both in crystalline and in amorphous regions; this causes fewer values of the elastic modulus in samples to exist, which are obtained upon orientation of a small-spherulite structure. The higher values of E , received at the orientation drawing of "blown" IPP-1 film, are evidently conditioned by the regime of its formation (extrusion forming without blowing), which permits quasiisotropic films with optimum ratio of inner- and interspherulite structure to be obtained.³⁷ It should be noted that, according to the data of X-

ray diffraction studies,²⁸ initial isotropic IPP-1 films, having spherulite morphology, are characterized by the insignificant degree of molecular chain orientation. Thus, the obtained results lead to the conclusion that mechanical characteristics and IPP deformability depend not only on the sizes of constituting material of structural formations (spherulites) (see Fig. 4), but on the structural organization of inner- and interspherulite regions, determined by the regime of crystallization of an initial material. However, depending upon the conditions of crystallization, not only the sizes and the degree of the organization of structural elements, but crystallinity, and also other factors, are usually change, it is therefore complicated to establish strict quantitative dependencies.

The connection between IPP structure and its mechanical characteristics is not simple, since the change of one structural characteristic (especially primary characteristics such as molecular weight, molecular weight distribution, the degree of chain branching, etc.) causes essential change of the rest of the parameters of a material. Therefore, the choice of one variable characteristic under similar studies is frequently impossible. Nevertheless, the comparison of separate results permits one to retrace the way in which the change of one parameter affects the rest of the structural parameters and, in consequence, the mechanical characteristics and the

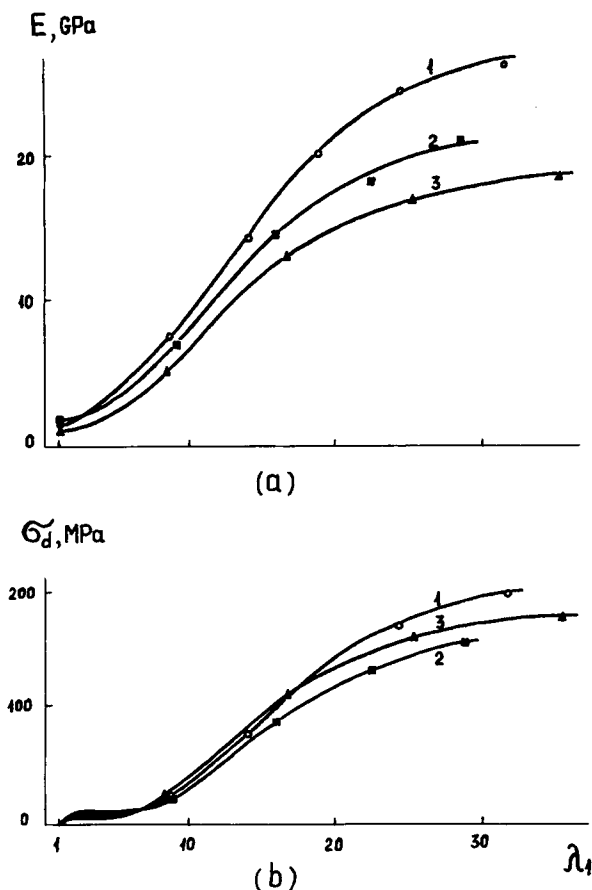


Figure 4 The dependences of elastic modulus E (a) and draw tension σ_d (b) of samples oriented at $T_d = 145^\circ\text{C}$ on draw ratio λ_1 for IPP of various supermolecular structure (designation, see Fig. 3).

deformability of a sample. In connection with this fact, the quenched IPP samples were chosen that had the close values of crystallinity (40–50%), spherulite sizes (35–50 μ), and they differed only in the values of molecular weight, IPP-3, IPP-4, IPP-5 (see Table I). The influence of molecular weight on the deformability of isotropic films and on the mechanical properties of oriented samples, obtained from these films, was studied.

The current knowledge of polymer deformation and destruction mechanisms^{1,3,11,38} testifies to the fact that the direct influence of molecular weight and MWD on the properties of polymers is relatively weakly expressed. This is because, in a crystalline polymer, the molecular nature of a polymer is unrelated to the properties of sufficiently large segments of macromolecules, for example, the ability for crystallization, etc. However, the distinct influence of IPP molecular weight, both on its deformability and on the mechanical properties of the sam-

ples, was revealed in the process of orientation drawing. So, in Figure 5, the dependences of the elastic modulus E of films oriented at $T_d = 145^\circ\text{C}$ on draw ratio λ_1 for quenched IPP samples with various molecular weights are presented. It is seen that in the case of ultra-high molecular IPP-4, the greater values of E are achieved at considerably lower draw ratios λ_1 , which are indicative of the more intensive strengthening of a material in the process of orientation drawing compared with lower molecular weight samples. It was also revealed that with the growth of molecular weight, the maximum value of elastic modulus (E^*) of highly oriented IPP samples essentially increases (from 15 to 30 GPa), while the deformability of isotropic IPP, which is characterized by maximum limit of draw ratio λ_1^* , achievable under the given deformation conditions, noticeably decreases ($\times 2$) (Fig. 6). The similar influence of molecular weight on the achievable maximum limit of draw ratio was also revealed upon study of the orientation drawing of linear PE.^{1,39}

It should be noted once more that the draw conditions of all quenched IPP samples, having different molecular weights (IPP-3, IPP-4, and IPP-5) were the same in this work: two-stage isothermal orientation drawing at $T_d = 145^\circ\text{C}$ and $V_c = 20$ mm/min. Moreover, the geometry and sizes of the unoriented samples were identical. To all appearances, our results may be considered as an additional contribution to the study of molecular weight effects on the IPP deformability and on the elastic properties of oriented samples. Undoubtedly, more detailed investigations of the molecular weight effects are necessary, conducted in other temperature and speed conditions of drawing.

As a result of the study, it was revealed that molecular weight was of great importance in determining the highest possible draw ratio; it can be explained by the decrease in the degree of macromolecular entanglement in an unstretched out material with diminishing molecular weight. The above described observations permit a more strict approach to the interpretation of the character of the proceeding of deformation process. It follows from this that upon consideration of the IPP behavior during orientation drawing, molecular topology and the deformation of polymer macromolecular network should be taken into account. The main structural elements of the deformed polymer body are the gearings (physical crosslinks) of molecular chains in amorphous regions and crystalline regions, which together form the semistable network with contact points. Evidently, macromolecular entanglements plays a predominant role for highly molecular weight

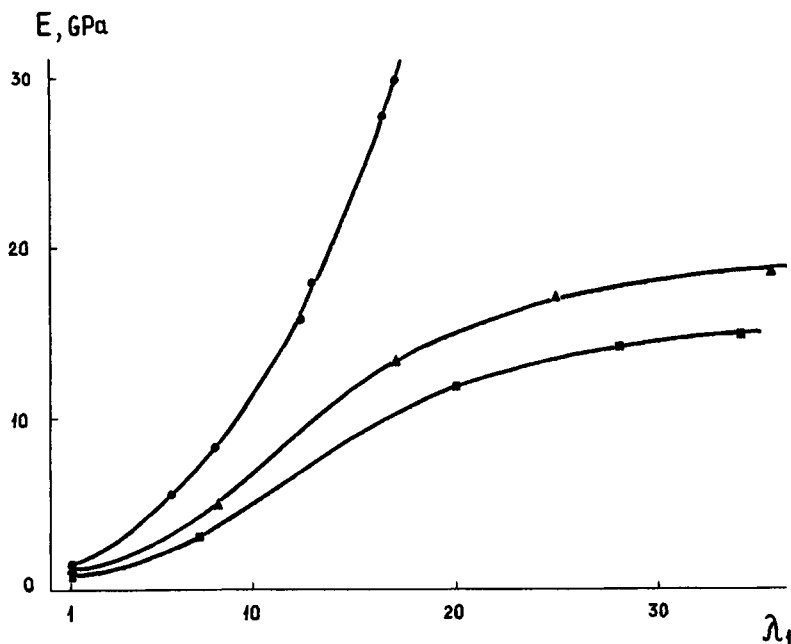


Figure 5 The dependencies of elastic modulus E on draw ratio λ_1 for quenched IPP with different molecular weight: ● = IPP-4; ▲ = IPP-3; ■ = IPP-5. $T_d = 145^\circ\text{C}$.

IPP while the morphology of a sample is of comparatively little importance. However, the morphology of a low molecular weight sample, with little entanglement of chains and somewhat higher crystallinity, becomes a decisive factor.

The Phenomenon of Physical Aging and Orientation Drawing of IPP

It is known^{32,40,41} that when keeping quenched isotropic IPP films and some other polymers (PE,

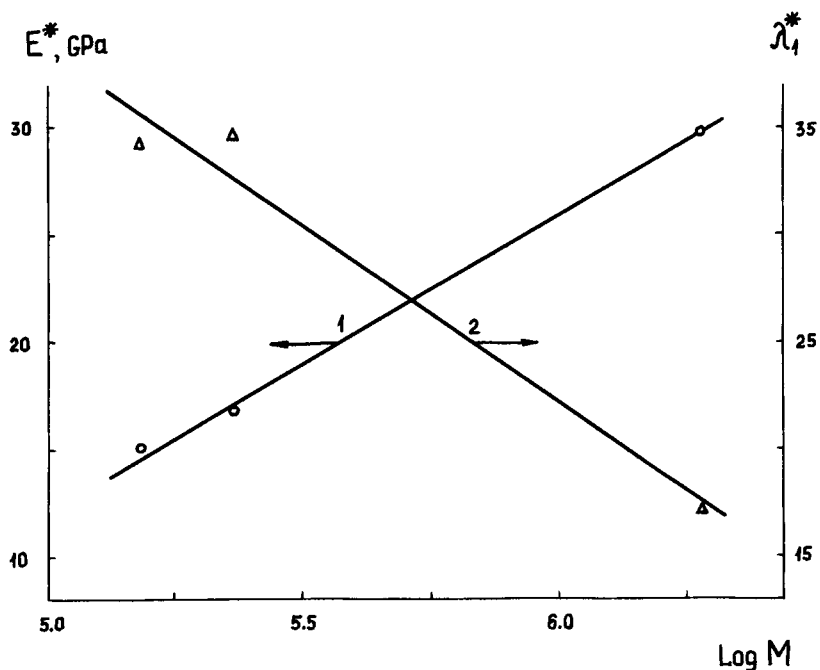


Figure 6 The dependencies of the maximum values of elastic modulus E^* (1) and draw ratio λ_1^* (2) on molecular weight M for quenched IPP samples. $T_d = 145^\circ\text{C}$.

PETP) at room temperature, the change of their structure, and consequently some physico-mechanical properties (elastic modulus, durability, density, gas-permeability, and others), occurs in due course. As was shown above, the structural organization of inner- and interspherulite regions plays an essential role in the deformation behavior of IPP. It may be assumed that the results of the study of physical aging can provide additional information about the internal structure of these regions. In the course of the research of the orientation drawing of IPP-1 films, carried on during a long period of time (more than 2.5 years), we found⁴² that the phenomenon of physical aging exerted essential influence not only on the mechanical properties and the ability of initial isotropic IPP films for deformation, but on stress-strain characteristics of the oriented at most samples, obtained from these films.

So, in Figure 7 it is shown that the change of the mechanical properties of isotropic IPP-1 films, measured at various temperatures in the interval of $20 \div 165^\circ\text{C}$, depend upon the time of keeping, τ_k . Time of keeping is from the moment of the extrusion forming of initial "blown" film until the moment of obtaining an oriented sample from it. It can be seen that with the growth in time of keeping, a noticeable increase of elastic modulus and yield point of isotropic films occurs at all test temperatures; this increase is more intense during the initial period, up

to 5–6 months. The analogous behavior is observed in Ref. 40, despite the fact that the experiments were conducted with other time intervals, from 1 to 100 h. The authors in Ref. 40 marked the growth of their crystallinity, calculated according to the measurement of density, as one of the reasons for the increasing mechanical properties of IPP samples with the passing time. However, in the present work on measuring crystallinity with DSC, its change with the growth of τ_k was not revealed. Obviously, the increase of rigidity and strength of isotropic IPP samples in the course of aging is determined by other factors and not by the change of general crystallinity. In the course of keeping isotropic IPP samples, the secondary crystallization can occur in these samples, and it leads to the formation of a crystalline bridge bonds and to the reduction of segmental mobility of molecular chains in the innerspherulite amorphous regions of a polymer.^{32,34,40} In addition, the reduction of chain connectivity and the loosening of molecular chains in interspherulite regions probably takes place less intensively and, therefore, the total effect of these factors results in increasing mechanical indices (E and σ_y) of isotropic films upon keeping.

Evidently, the higher the heterogeneity of the spherulite structure is (i.e., the stronger inner- and interspherulite regions differ in their ability to transfer loading), the more intensive microcracks (microvoids) must be formed in the process of ori-

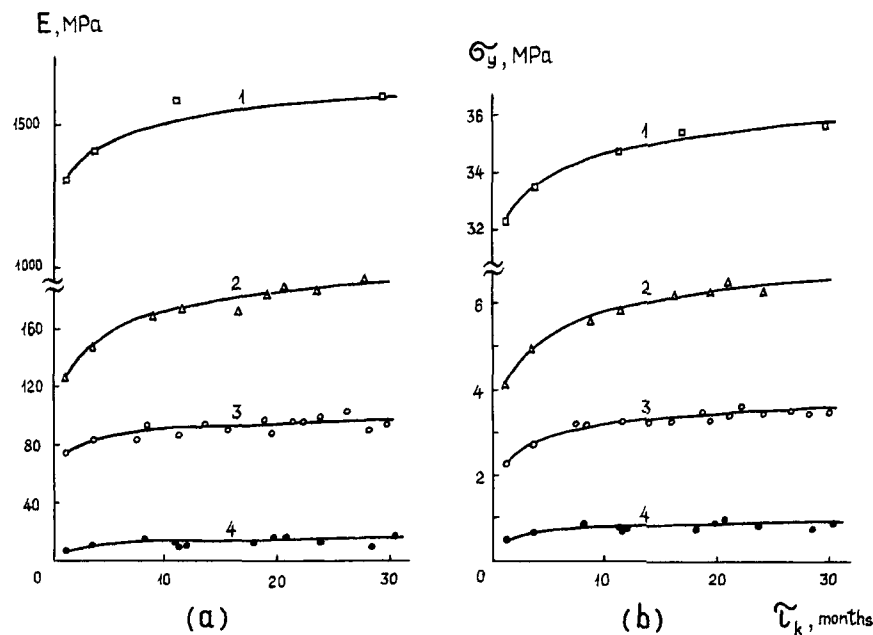


Figure 7 The dependencies of elastic modulus E (a) and tensile yield point σ_y (b) of isotropic IPP-1 films, measured at different temperatures (1 = 20, 2 = 125, 3 = 145, 4 = 165°C) on the time of keeping τ_k .

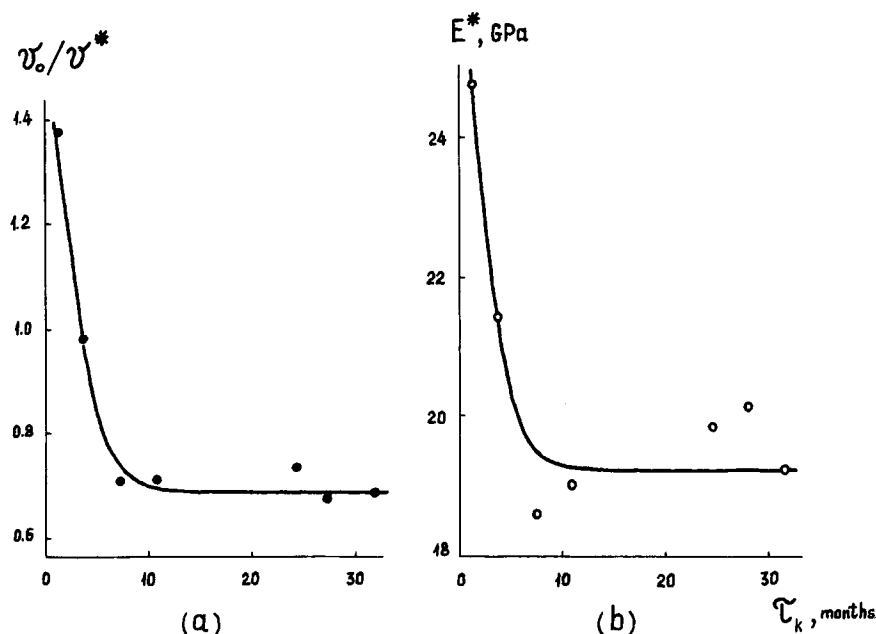


Figure 8 The influence of the time of keeping τ_k of isotropic IPP-1 films on ratio v_0/v^* ($= \lambda_2^*/\lambda_1^*$) (a) and on elastic modulus E^* (b) of stretched at most samples, obtained from these films at $T_d = 145^\circ\text{C}$.

entation drawing. This phenomenon was experimentally observed with the help of optical microscopy.²⁷ As the decrease of ratio λ_2^*/λ_1^* , equal to ratio of volume v_0 of initial unstretched sample to volume v^* of stretched at most sample, v_0/v^* , the time of keeping τ_k (Fig. 8a) grows. As is seen, at the initial period (up to 3–4 months), the drawing occurs with the decrease of volume ($v_0/v^* > 1$), while the orientation of samples, kept for a longer time, is accompanied by the increase of volume ($v_0/v^* < 1$).

It was revealed the essential influence of the duration of storage of initial IPP-1 films at room temperature on the deformation–strength properties of

highly oriented samples, obtained from these films by the method of two-stage isothermal ($T_d = 145^\circ\text{C}$) orientation drawing. Figure 8 and Table II show that at the initial period, the sharp fall of elastic modulus E^* of stretched at most samples, and also their breaking strength σ_b^* and extension strain at break ϵ_b^* , takes place. At the same time, the maximum achievable draw ratio λ_2^* essentially decreases, while the maximum draw ratio λ_1^* changes only insignificantly. The comparison of dependencies in Figure 8 shows that the higher the ratio v_0/v^* ($= \lambda_2^*/\lambda_1^*$) (i.e., the fewer holes (microvoids) that are formed at orientation drawing), the higher the value E^*

Table II The Influence of the Time of Keeping τ_k on Maximum Draw Ratios λ_1^* and λ_2^* and on Mechanical Properties of Stretched at Most IPP-1 Samples ($T_d = 145^\circ\text{C}$)

No.	n^a	τ_k , Month	λ_1^*	λ_2^*	Mechanical Properties		
					E^* , GPa	σ_b^* , GPa	ϵ_b^* , %
1	13	1.0	25.7	35.5	24.7 ± 2.8	1.04	6.5
2	10	3.5	30.6	30.0	21.5 ± 4.5	0.84	6.3
3	11	7.2	32.0	22.2	18.5 ± 1.6	0.62	6.1
4	10	10.6	32.9	23.5	18.9 ± 3.6	0.54	5.5
5	6	23.5	25.3	19.7	20.1 ± 4.3	—	—
6	12	27.4	30.0	20.5	20.8 ± 3.8	—	—
7	15	32.0	31.6	21.5	19.3 ± 1.2	0.58	5.6

^a n = the number of samples in each series.

that is acquired by a sample with the maximum limit of orientation, which was obtained under the given draw conditions.

Thus, the conclusion can be drawn that for reception of the highest possible mechanical properties of IPP, it is necessary to perform the orientation drawing right after obtaining the initial isotropic films, since during their keeping, irreversible structural changes take place. These changes lead to the intensive formation of microvoids in the process of drawing and, as a consequence, to the reduction of the mechanical indexes of an obtained oriented material. However, the physical aging of isotropic films is only one of the factors that affects the process of the orientation drawing of IPP. As was shown above, the ability of nonoriented IPP to deform and the mechanical characteristics of oriented samples are considerably influenced by the parameters of initial morphology (the sizes of spherulites, the nature of structural organization of inner- and interspherulite regions, etc.). These characteristics are also influenced by the molecular weight of the polymer. It should be noted that the data presented above were obtained at the strictly fixed values of temperature and draw speed ($T_d = 145^\circ\text{C}$; $V_d = 9.5 \times 10^{-3} \text{ s}^{-1}$), since, as will be shown below, the mechanism of IPP deformation considerably depends upon the speed and temperature of mechanical influence.

The Influence of the Regime of Orientation Drawing on the IPP Deformability and on Mechanical Properties of Oriented Samples

In the present work, the study of the influence of draw regime (draw temperature T_d , draw speed V_d and the number of draw stages) on the deformability of initial isotropic IPP films and on the stress-strain properties of highly oriented samples, obtained from these films, was carried out on the samples of IPP-1 "blown" films.⁴³ As was described in the Experimental section, to discover the influence of speed on the process of two-stage isothermal orientation drawing, two types of experiments were carried out: experiment I changed draw speed V_d at the first stage with the same V_d at the second stage; experiment II changed V_d at the second stage with the same V_d at the first stage of drawing. During experiment I, the influence of V_d at initial stages of the deformation of an initial isotropic structure was researched, and during experiment II, this influence was studied by further deforming the already-formed fibrillar structure at the first stage of drawing. The schemes of experiments I and II are shown in Figure 1 (a).

First, let us consider the influence of draw tem-

perature and speed on the IPP deformability, which is characterized by the maximum achievable draw ratio. It is well known that at a given temperature, the maximum limit of draw ratio exists and it is impossible to exceed it, since the material breaks. A question remains as to the reasons for the stop of the orientation drawing. Some authors explain the fracture of a sample, when achieving very great orientation extensions, by mechanical glass transition of a polymer under orienting loads.⁴⁴ Other authors propose an increase in the dispersity of the lengths of amorphous layers and, as a consequence, the growth of the number of "dangerous sectors."^{17,45,46} Still other authors describe a sharp decrease in the lifetime of a material affected by orienting loads at the last stages of drawing.⁴⁷

It is shown in Figure 9 that the value of maximum draw ratio (λ_1^* and λ_2^*) is essentially affected not only by temperature but also by draw speed. By increasing draw temperature, the IPP deformability

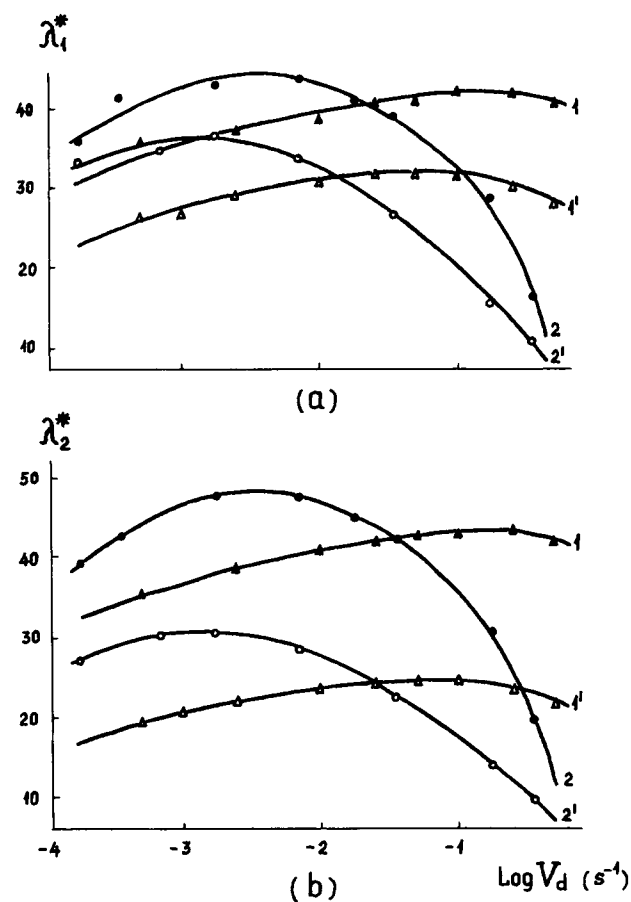


Figure 9 The dependencies of maximum draw ratios λ_1^* (a) and λ_2^* (b) of IPP-1 films on draw speed V_d at $T_d = 145^\circ\text{C}$ (1', 2') and 165°C (1, 2) for experiments I (1, 1') and II (2, 2').

grows at the whole interval of draw speeds, both in the deformation of initial spherulite structure (experiment I) and in the deformation of the fibrillar structure already formed at the first stage of drawing (experiment II); the dependencies of maximum draw ratio on draw speed have an extreme character, more distinctly displayed in the results of experiment II. Moreover, with the increase in temperature, upper limits become more pronounced (at least on deforming fibrillar structure) and there is little shift to the side of higher draw speeds. The results presented in Figure 9 allow estimation of the change in IPP volume, which occurs in the process of its orientation drawing. The average of all researched draw speed values of ratio $v_0/v^* = \lambda_2^*/\lambda_1^*$ are given below; they are determined from Figure 9:

$T_d, ^\circ\text{C}$	Type of Experiment	v_0/v^*
145	I	0.76 ± 0.01
145	II	0.83 ± 0.04
165	I	1.04 ± 0.02
165	II	1.10 ± 0.08

It is seen from these data that the change in the volume of stretched at most IPP samples virtually does not depend on draw speed, little depends on the type of experiment, and the change of volume is determined only by draw temperature; drawing at

145°C leads to increasing volume ($v_0/v^* < 1$) and drawing at 165°C leads to diminishing it ($v_0/v^* > 1$). The influence of temperature was also seen in the orientational formation of fibers^{32,48} and the solid state extrusion of IPP.^{10,49,50} As was shown earlier,^{28,30} the value of crystallinity, determined according to melting heat with DSC method, is almost identical to the value of IPP-1 samples, stretched at most at 145 and 165°C. Therefore, the decrease of volume in the process of drawing at 165°C is indicative of fewer microvoids in the samples and less structure defectiveness than in samples drawn at 145°C. It seems that the recrystallization processes in the course of drawing proceed more intensively if temperature T_d is higher.

Thus, temperature-speed conditions of drawing exert an essential influence on IPP deformability. These conditions exert analogous influence both on draw tension σ_d^* (Figs. 1b and 10) and on mechanical properties of stretched at most samples, in particular, on the value of their modulus elasticity in tension E^* (Fig. 11). It is worth noting that the change of draw speed exerts a much stronger influence on the values σ_d^* and E^* at the final draw stages (experiment II), that is, in deforming fibrillar structure. This is also confirmed by the character of tension diagrams (see Fig. 1b); in experiment I these diagrams weakly depend on draw speed and in experiment II the essential change of tension diagrams at speed change is observed. It should be noted that

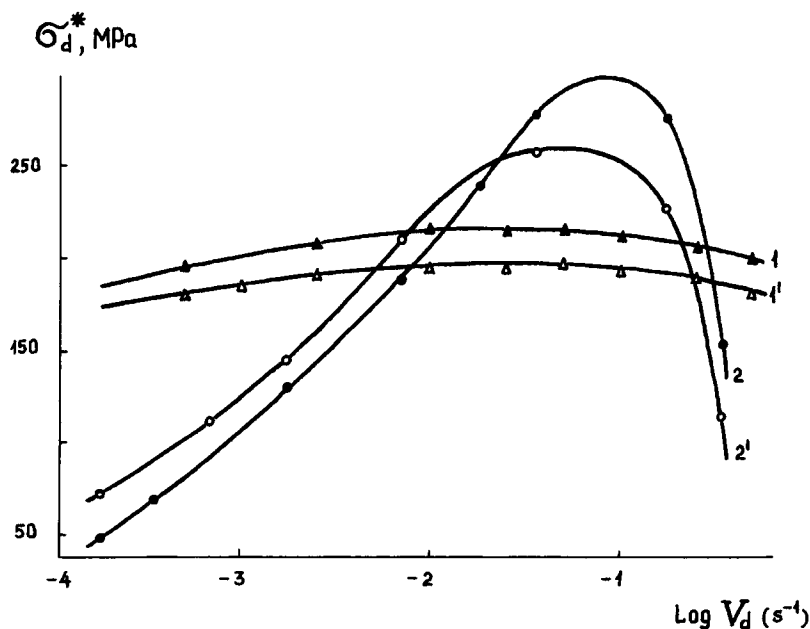


Figure 10 The dependencies of draw tension σ_d^* of stretched at most IPP-1 samples on draw speed V_d (designation, see Fig. 9).

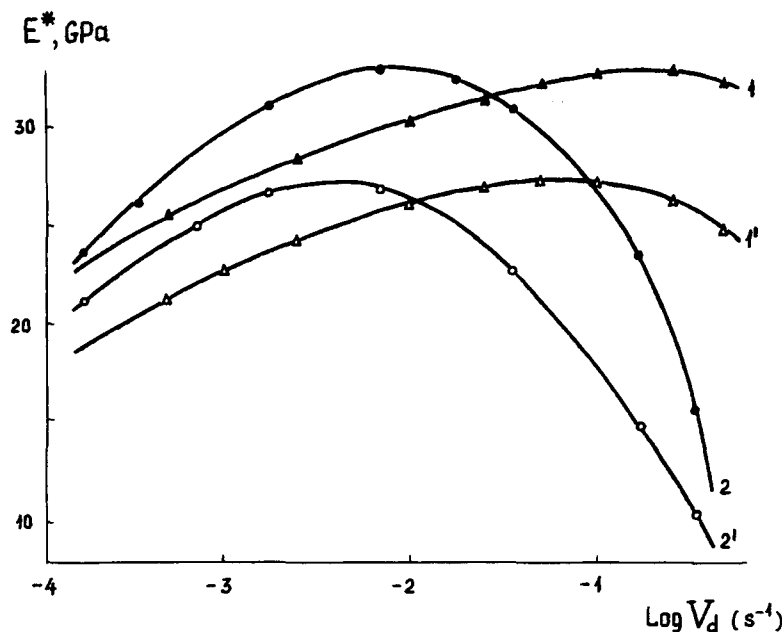


Figure 11 The dependencies of elastic modulus E^* of stretched at most IPP-1 samples on draw speed V_d (designation, see Fig. 9).

in relation to the maximum limit of draw ratio, the value of E^* is higher in the case of drawing at 165°C than at 145°C for any regime of drawing (experiment I or II) in the studied interval of draw speeds. Moreover, the values of V_d , at which the higher value of E^* is achieved, was close to those at which the maximum values of draw ratio λ_1^* and λ_2^* are observed. A conclusion can be made that the obtaining of the highest possible draw ratios, which in turn is determined by temperature-speed conditions of the process of drawing, plays a major role in achieving the greatest mechanical characteristics of material.

The results permit an explanation of the influence of draw speed and draw temperature on the ability of nonoriented IPP to deform and on elastic modulus of stretched at most samples. The X-ray diffraction and IR-spectroscopic studies of the structure of drawn IPP-1 films^{28,51} showed that the orientation of crystallites was perfect at the early stages of drawing and the orientation of macromolecular chains in amorphous regions grew noticeably as drawing was performed; the amorphous orientation achieved high values at maximum draw ratios. The amorphous regions of oriented IPP contain both bent, unstretched tie molecules (TM) and straightened taut tie molecules (TTM), connecting adjacent crystallites along the draw axis, as well as the loops and free ends of macromolecules. Evidently, the orientation of such a system can take place under the influence of an outer force in different ways, de-

pending on the draw speed. At low draw speeds, the increase of λ will lead to straightening bent at the beginning of TM and to slippage of TTM through crystallites, in which intermolecular interaction is considerably weakened under the influence of high temperature. This must result in a growing the number of chains, sustaining loads at the expense of diminishing the difference in TM lengths on the amorphous areas of a structure. However, due to the extremely great duration of drawing when the time of the relaxation of a system is much less than the draw time, the process of viscous flow and thermal destruction of macromolecular chains can develop and reduce the effectiveness of orientation drawing. As a consequence, in the given range of changing draw speeds under conditions of raised temperatures, the effect of increasing thermal destruction due to the growth (approximately 25 times) of the period of the sample's staying under orienting load exceeds the effect of increasing molecular mobility at the expense of reducing draw tension (see Fig. 10). This leads to the observed decrease in the values of λ_1^* and λ_2^* (Fig. 9) and E^* (Fig. 11) in the interval of the least values V_d . With the increase of draw speed, the intensity of the formation of TTM, carrying a load, in the amorphous regions grows, but at the same time tensions cannot be redistributed because of the insufficient duration of relaxation processes. This, along with the slippage of some TTM through crystallites, causes more and more TTMs to begin

Table III Draw Parameters and Mechanical Properties of Stretched at Most IPP-1 Samples, Obtained under Optimum Draw Conditions

$T_d, ^\circ\text{C}$	Draw Conditions		The Number of Samples	λ_1^*	λ_2^*	σ_d^* , MPa	E^* , GPa
	V_d, s^{-1}						
	Stage I	Stage II					
145	4.8×10^{-2} (100)	1.7×10^{-3} (5)	10	34.5 ± 1.6	27.2 ± 1.3	128 ± 6	28.6 ± 3.2
165	9.5×10^{-2} (200)	3.3×10^{-3} (10)	13	44.4 ± 2.4	47.1 ± 2.5	176 ± 12	34.9 ± 3.0

Note: The respective values of shifting clamp speed V_c (mm/min) are indicated in parentheses.

to break. Tension continues to grow and at certain draw speed the processes of TTM fracture becomes so intense that draw tension falls and the deformability of IPP simultaneously decreases. Evidently, this is connected to the transition from isothermal to adiabatic conditions of deformation, that is, to thermal plastic character of fracture.^{36,52} In consequence, the sharp fall of the elastic modulus occurs at the greatest draw speeds for the given study (see Fig. 11).

From Figures 9 and 11 it is seen that the values of draw speed, corresponding to maximum values λ^* and E^* [to the maximum values in dependencies $\lambda^*(\log V_d)$ and $E^*(\log V_d)$], considerably differ in respect to the first and second draw stages, that is, in respect to the processes of the deformation of initial spherulite IPP structure (experiment I) and the deformation of formed fibrillar structure (experiment II). It appears that at the given draw temperature, the first draw stage should be conducted at high speeds to achieve maximum mechanical characteristics of IPP, and the second one should be conducted at considerably lower speeds. This conclusion conforms to the assumption made in Ref. 5. To confirm this, additional experiments were

conducted on two-stage drawing under close to optimum conditions, that is, at such draw speeds in the first and the second stages, during which maximum values of λ^* and E^* (see Table III) are achieved. The values obtained under optimum draw conditions were noticeably higher than the maximum ones achieved during experiments I and II.

The question of whether one-stage or two-stage methods of orientation drawing are more effective for achieving the high deformation-strength properties of a material remains unclear. Some authors^{5,19,27,53} prefer the two-stage draw process; others^{1,6,25} prefer a one-stage process, but they indicate the negative effect of annealing, which occurs during temperature increase before the second stage. Therefore, in the present work, the experiments on the one-stage and two-stage drawing of IPP-1 films at 145°C and at two speeds of deforming (4.8×10^{-2} and $9.5 \times 10^{-3} \text{ s}^{-1}$) were carried out; the true draw speeds for one-stage and two-stage processes were chosen so that they practically coincided during the whole draw process. The results of these experiments are given in Table IV. Table IV shows that despite the identical change of draw speed with the growth of λ at one-stage and two-stage drawing, in the latter

Table IV The Comparison of Draw Parameters and Mechanical Properties of Stretched at Most IPP-1 Samples at One- and Two-Stage Orientation Drawing ($T_d = 145^\circ\text{C}$)

No. Stages	Draw Conditions		The Number of Samples	λ_1^*	λ_2^*	σ_d^* , MPa	E^* , GPa
	V_d, s^{-1}						
	Stage I	Stage II					
1	4.8×10^{-2}	(6.7×10^{-3})	24	26.1 ± 2.0	22.2 ± 2.4	206 ± 25	20.6 ± 1.7
2	4.8×10^{-2}	6.7×10^{-3}	18	32.0 ± 1.3	24.4 ± 1.4	193 ± 12	26.9 ± 1.4
1	9.5×10^{-3}	(1.7×10^{-3})	6	25.9 ± 3.2	20.0 ± 1.3	149 ± 20	19.3 ± 1.8
2	9.5×10^{-3}	1.7×10^{-3}	5	36.1 ± 2.9	30.3 ± 1.5	142 ± 7	26.3 ± 2.4

Note: The values of draw speeds in brackets are calculated at the moment of transition from the first to the second stage during two-stage drawing.

case the essentially higher values of E^* were obtained at respectively higher draw ratios. It can be assumed that the relaxation processes, proceeding during the period between two draw stages and during the annealing with raising temperature before the second draw stage, favorably affect fibrillar IPP structure, increasing its deformability. The geometry of a second time drawn sample secures greater homogeneity of deformation than in the case of one-stage drawing. The high values of elastic modulus and strength of the samples (respectively 33 and 1.5 GPa), obtained in Refs. 18 and 19 by the method of solid state coextrusion of ultra-high molecular weight PP up to $\lambda \sim 6$ at 130°C, with further orientation drawing until a total of $\lambda \sim 66$ at 150°C, are an additional confirmation of the greater effectiveness of the two-stage orientation draw method.

CONCLUSIONS

1. As a result of the study of the process of two-stage isothermal orientation drawing of IPP, the essential influence of morphological characteristics of an initial material (the sizes of spherulites and molecular weight) on its deformability, and on mechanical properties of the highly oriented samples obtained, was established. The maximum values of elastic modulus and draw ratio of highly oriented samples depend not only on the molecular weight of a polymer and the sizes of the structural formations, constituting initial IPP (spherulites), but also on the structural organization of inner- and interspherulite regions, determined by the regime of the crystallization of an initial material.
2. The influence of the duration of physical aging of IPP on its deformability and on mechanical characteristics of oriented samples was discovered. The results confirm that the nature of the structural organization of inner- and interspherulite regions of a polymer plays a significant role in the deformation behavior of IPP and can serve as a base for a more detailed study of the structure of these regions. For the realization of the maximum deformation-strength properties of IPP, the orientation drawing should be performed right after the initial isotropic films are obtained, because irreversible structural changes occur while the initial isotropic films are kept; the intensive formation of microvoids occurs in the process of drawing and,

in consequence, the reduction of mechanical indices of an obtained oriented material.

3. The study of the influence of temperature-speed conditions of drawing on the ability of isotropic IPP films to deform, and on elastic properties of stretched at most samples, shows that on increasing draw temperature, the IPP deformability grows in the whole studied interval of draw speeds, both on deforming initial spherulite structure and on deforming the fibrillar structure already formed at the first draw stage; the dependencies of the maximum values of draw ratio and elastic modulus on draw speed have an extreme character; with the growth of draw temperature these maxima become more pronounced and they shift to higher draw speeds.
4. The higher effectiveness of two-stage drawing, in comparison with one-stage drawing, was experimentally determined. The samples, stretched at most during two stages, had an elastic modulus that was 30–35% greater than that of the one-stage stretched samples. It was also shown that at the given draw temperature, the first stage of drawing should be carried out at relatively high draw speeds to achieve the maximum mechanical characteristics of IPP, and the second stage should be carried out at considerably lower speeds.

Based on all presented studies, the optimum temperature-speed regime of orientation drawing was determined to obtain the samples of highly oriented IPP with maximum mechanical characteristics; as a result, a real possibility of receiving highly oriented, ultra-high modulus IPP with the method of two-stage isothermal orientation drawing was shown, which possessed great strength (~ 1.1 GPa) and the value of modulus of elasticity (30–35 GPa) close to theoretical modulus of ideal PP crystal along the chain axis (42 GPa^{54,55}). At present, studies of establishing quantitative relationships between structural parameters and physico-mechanical properties of such highly oriented samples of IPP are carried out.

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