

NMR STUDY OF MACROMOLECULAR ORIENTATION IN DRAWN POLYPROPYLENE FILMS

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The present paper deals with the problem of the study of macromolecular orientation in drawn polypropylene (PP) films. For the determination of the degree of macromolecular orientation in crystalline and in noncrystalline regions the NMR method and optical birefringence were used. Dependences of the orientation parameters f_{2c} and f_{2a} on the draw ratio λ gained by these methods enable to determine the characteristic properties of the deformation process. The study of orientation was realized on two kinds of PP foils denoted as Tatten EB 111 and Tatten PE 141. From each kind of PP there were made four foils with different draw ratios λ . The NMR measurements were performed at the temperature $T_m = 186$ K, from the temperature range within which the only free rotation of CH_3 groups takes place.

ИССЛЕДОВАНИЕ МАКРОМОЛЕКУЛЯРНОЙ ОРИЕНТАЦИИ В ТЯНУТЫХ ПОЛИПРОПИЛЕНОВЫХ ПЛЕНКАХ ПРИ ПОМОЩИ ЯМР

Работа посвящена проблеме изучения макромолекулярной ориентации в тянутых полипропиленовых пленках. Для определения степени макромолекулярной ориентации в кристаллических и некристаллических областях использовались метод ЯМР и двойное оптическое лучепреломление. Зависимости параметров ориентации f_{2c} и f_{2a} от коэффициента вытягивания λ , полученные при помощи этих методов, позволяют определить характеристические свойства процессов деформации. Исследование ориентации проводилось на двух типах полипропиленовых пленок с фирменным названием Таттен ЕВ 111 и Таттен РЕ 141; из каждого типа приготовлена изготовлены четыре пленки с различными коэффициентами вытягивания λ .

ЯМР-измерения проведены при температуре $T_m = 186$ К, находящейся в области температур, когда имеет место единственное свободное вращение групп CH_3 .

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I. INTRODUCTION

The deformation process, e.g. the uniaxial drawing, is one of the important technological processes with possibilities of influencing the physical properties of polymer fibres and foils. By those processes a preference orientation of macromolecular chains occurs in a certain direction, most frequently in the direction of the deformation force. The deformation process in polymers is a complex phenomenon, which depends on the molecular and morphological structure of the polymer, on the velocity of the deformation and on the temperature at which the deformation is realized.

According to the fact that the elongation makes essential changes in the physical properties of the polymer, the study of the deformation processes is important from the point of view of the basic and also of the application research.

The orientation of the macromolecules involved by the drawing of the polymer gives rise to an anisotropy of the mechanical, thermal, electrical, optical and other properties of the polymer. The study of anisotropy of those properties gives the possibility to describe the orientation of the macromolecular system on different levels of structure (microscopic and macroscopic ones).

For the study of orientation several methods were elaborated, namely: an X-ray method [1, 2], birefringence [3, 4], the sonic modulus method [5, 6], the method of fluorescence polarization [7, 8], the light scattering method [6, 9], the anisotropy of the heat conductivity [20, 21] and others.

To the above methods there belongs also the method of nuclear magnetic resonance (NMR), through which the study of orientation of the macromolecular chains is based on the analysis of the angular dependencies of the second and the fourth moments of the NMR spectra, respectively.

The papers published so far, which seriously influence the application of the NMR method to the study of oriented polymers, are referred to in our papers [12, 13].

In paper [13] the theory of the NMR second moment for oriented polymers is developed to gain information about the degree of macromolecular chain orientation both in the crystalline and the noncrystalline regions of the polymer. The theoretical results of paper [13] are applied in the present paper to the study of macromolecular chains orientation in drawn foils from isotactic polypropylene (made in Czechoslovakia) denoted as Taren PE 141 and Taren EB 111.

According to the available documentation, the problem of the study of orientation for PP foils or fibres by the NMR method has not been solved up to now. In paper [23] changes in the shape of the NMR lines and their parameters were observed in connection with the degree of elongation of the PP fibres.

However, the orientation of the PP films and fibres was studied by other methods than the NMR one [5, 6, 14, 15, 24]. In paper [6] using the X-ray method, birefringence and the sonic modulus the orientation parameters f_{2c} and f_{2n}

characterizing the degree of macromolecular orientation in crystalline (subscript *c*) and in noncrystalline (subscript *n*) regions were estimated. The authors of the paper found that the degree and the character of the macromolecular orientation in crystalline and in noncrystalline regions were different.

Polypropylene has been studied by several authors by the NMR method, but with the intention to get information about the motion of molecules [16—19]. It has been found that the motion of CH₃ groups takes place already at temperatures below 77 K and that in the range of approximately 150 K up to 250 K a free rotation of those groups occurs both in the crystalline and the noncrystalline regions of PP in the same way. At temperatures above 250 K a segmental motion of the main chains occurs predominantly in the noncrystalline regions.

II. THEORETICAL PART

The NMR study of macromolecular chain orientation is the most convenient under conditions where the molecular motion, active from the point of view of NMR, has the same character in all the regions. Such conditions for isotactic PP are realized at temperatures from about 150 K to 250 K [16—19]. Only a free rotation of CH₃ groups is the NMR active motion in this temperature range. In such cases as shown in our paper [13] the parameters f_{2c} and f_{2n} characterizing the orientation of macromolecules in crystalline and noncrystalline regions cannot be determined only by means of a second moment analysis. This problem can be solved by the use of another method, e.g. birefringence. According to paper [13] the angular dependence of the second moment M_2 of the NMR spectrum for a film drawn in one direction (or a fibre) can be expressed in the form:

$$M_2 = A \cos^4 \Theta + B \cos^2 \Theta + C, \quad (1)$$

where Θ is the angle between the direction of the drawing and the direction of the external magnetic field induction B_0 . The coefficients A , B , C depend on the configuration and the motion of resonating nuclei and on the parameters \bar{f}_2 and f_4 , which characterize an average degree of macromolecular orientation.

The configuration and the motion of resonating nuclei within a polymer can be described by the quantities G_1 , G_2 and G_3 which are explicitly expressed in paper [13] and which can be calculated on the basis of our knowledge of the structure and the kind of the molecular motion. However, numerical values of the quantities A , B and C can be determined by eq. (1) on the basis of experimental angular dependences. By means of these quantities the parameters f_4 and \bar{f}_2 can be expressed in the form:

$$\begin{aligned} \bar{f}_4 &= A/G_1, \\ \bar{f}_2 &= (6A + 7B)/(6G_1 + 7G_2), \end{aligned} \quad (2)$$

but it is possible to express \bar{f}_1 and \bar{f}_2 as

$$\begin{aligned}\bar{f}_1 &= K_p f_{1c} + (1 - K_p) f_{1n} \\ \bar{f}_2 &= K_p f_{2c} + (1 - K_p) f_{2n}\end{aligned}\quad (3)$$

where K_p is the crystallinity of the polymer, f_{1c} , f_{1n} , and f_{2c} , f_{2n} are the orientation parameters of the 4-th and the 2-nd order for crystalline and noncrystalline regions.

In accordance with [4, 20] a total birefringence can be expressed by the relation:

$$\Delta = \Delta_{0c} K_p f_{2c} + \Delta_{0n} (1 - K_p) f_{2n}, \quad (4)$$

where Δ_{0c} and Δ_{0n} are intrinsic birefringences for crystalline and noncrystalline regions, respectively.

The parameters of orientation f_{2c} and f_{2n} can be determined from eqs. (3) and (4) by the relations

$$\begin{aligned}f_{2c} &= (\bar{f}_2 \Delta_{0n} - \Delta) / K_p \Delta_{0c} \\ f_{2n} &= (\Delta - \bar{f}_2 \Delta_{0c}) / (1 - K_p) \Delta_{0c},\end{aligned}\quad (5)$$

where $\Delta_0 = \Delta_{0n} - \Delta_{0c}$.

According to paper [6] $\Delta_{0c} = 29.1 \times 10^{-3}$ and $\Delta_{0n} = 60.0 \times 10^{-3}$ and values of the G parameters for a temperature interval 150–250 K by [12, 13] are: $G_1 = 24.46 \times 10^{-8} \text{ T}^2$, $G_2 = -24.78 \times 10^{-8} \text{ T}^2$ and $G_3 = 18.23 \times 10^{-8} \text{ T}^2$.

III. EXPERIMENTAL PART

A study of orientation was realized on films of two kinds of isotactic PP, Taiten PE 141 and Taiten EB 111 (produced in Slovnaft, Bratislava). These two kinds of the polymer were drawn in the Research Institute of Chemical Fibres in Svlt to obtain films with different degrees of drawing. The polymer melted in an extruder was extruded on a set of rotated cylinders of the drawing machine by which the drawing was realized at the temperature +110°C. The films obtained in this way were analysed in Svlt, the results of the analysis are in Table 1.

The samples prepared from these films for NMR measurements consisted of stripes with dimensions 2×0.6 cm. The stripes formed parallelepipeds connected with a goniometer by means of a teflon holder in such a way that it was possible to turn the sample about the axis parallel to the longer side of the stripes. By this procedure two types of samples were prepared from each kind of the film. They are denoted A and B. For the A type of the sample the direction of drawing (extruding) of the film is identical with the axis of the sample turning in a magnetic field. By turning the A type sample it was possible to change the angle ϕ between the direction of the magnetic field induction and the plane of the film. The angle Θ between the direction of drawing and the B_0 did not change during turning and was

Table 1

Characteristics of the studied PP foils

Polymer	λ	d [μm]	Δ $\times 10^3$	$\psi_{1/2}$ [110]	$\psi_{1/2}$ [040]	T_m [K]	H_m [kJ kg ⁻¹]	K_p [%]
TATREN	1.0	66.1	0	—	—	430.0	67.1	47.3
PE 141	2.0	42.1	11.57	31.8	32.5	431.0	66.3	46.7
LVN=86.4 ml g ⁻¹	4.0	30.1	21.40	9.5	8.7	433.0	80.4	56.6
	6.65	23.6	23.00	5.6	4.8	436.5	83.6	58.9
TATREN	1.0	59.8	3.69	—	—	427.0	72.2	50.9
EB 111	2.0	48.0	12.61	31.4	27.3	431.0	66.8	47.1
LVN=269.1 ml g ⁻¹	6.0	26.3	26.32	4.8	4.9	437.5	77.2	54.4
	6.8	24.6	29.55	5.0	5.1	440.0	81.9	57.7

$\lambda = l/l_0$ is the draw ratio, d is the thickness, Δ is the total birefringence, $\psi_{1/2}$ is the half angle of the blacking of the X-ray diffraction spots from the denoted crystallographic planes $\{h k l\}$, T_m is the softening temperature, H_m is the latent heat of fusion and K_p is crystallinity.

equal to $\pi/2$. For the B kind sample the direction of the film drawing is perpendicular to the axis of turning of the sample in the magnetic field. Hence it was possible to change the angle Θ between the direction of the film drawing and the direction of the magnetic field induction B_0 . The values of the angle ϕ (for A kind sample) and of the angle Θ (for the B kind sample) were changed within the interval 0° – 90° with an increment of 15° .

The NMR measurements were performed by a commercial RJa-2301 spectrometer at a constant frequency $f = 13.02$ MHz. Proton NMR spectra were recorded in a differential form and the second moments of these spectra were calculated numerically by means of a MINSK computer (Department of Computer Science UPJŠ, Košice).

For a choice of a temperature at which the measurements of the angle dependences of the second moments M_2 were carried out, the temperature dependence of the spectra of one sample studied (PE 141, $\lambda = 1$, A) was measured in the temperature range from 120 K to 250 K.

The dependences M_2 and δB (δB is a linewidth of the spectrum measured between the maximum and the minimum of the derivative spectrum) vs. temperature T for this sample are shown in Fig. 1. For the measurement of the angular dependence of the spectra the temperature $T_m = 186$ K was chosen from the temperature interval in which the M_2 and the δB practically do not depend on temperature. In this temperature range a free relation of CH_3 groups is realized within the isotactic polypropylene and it is possible from the NMR point of view to consider the CH and CH_2 groups as rigid [16–18].

The NMR spectra of PP films do not present a fine structure (see Fig. 2). This is caused by a "smoothing" of a proton dipole-dipole interaction of individual CH_2 and CH groups which are close to one another. It is possible to observe some changes in the form of the spectrum at different positions of the B kind samples. These changes are most pronounced in films with the maximum ratio of the drawing.

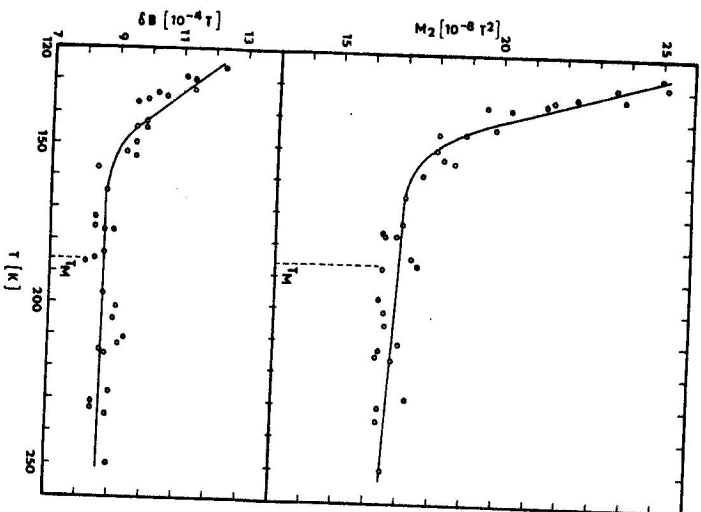


Fig. 1. Temperature dependence of the second moment M_2 and width δB of the NMR spectrum for the PP foil EB 111 ($\lambda = 1$, A type).

The halves of the derivative spectra for the sample EB 111 with $\lambda = 6.8$ (type B) for three different positions of this sample in the magnetic field with $\Theta = 0^\circ, 45^\circ$ and 90° are shown in Fig. 2.

For the samples of the A-type the spectrum does not change with the angle Φ (Φ is the angle between B_0 and the surface plane of the sample).

The angular dependencies of the second moment M_2 are shown in Fig. 3 for some samples of the A-type. For the samples of the A-type we can state that their NMR spectra and the second moments do not change with the angle Φ .

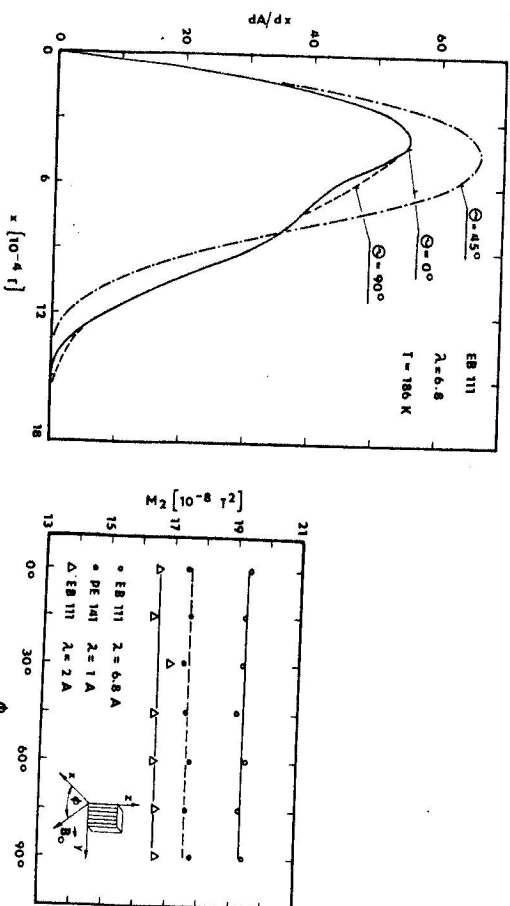


Fig. 2. Halves of the derivative records of the NMR spectra at different values of the angle Θ for the EB 111 foil ($\lambda = 6.8$, B type); $x = B - B_0$, where B_0 is the value of the induction of the external magnetic field corresponding to the resonance of protons.

Fig. 3. Angular dependencies $M_2(\Phi)$ for some PP foils (the samples of A type) at temperature $T_m = 186$ K.

M_2 and by Eq. (1) by means of the leastsquare method. The values of A , B and C are listed in Tab. 2. Besides this values in Tab. 2 there are introduced the parameters \bar{f}_2 and \bar{f}_4 evaluated according to Eq. (2) and the parameters f_{2c} and f_{2n} calculated by means of Eq. (5).

IV. DISCUSSION

The results presented in the previous part of this paper show that all the quantities measured change with the degree of drawing of the individual foils. From the quantities introduced in Tab. 1 and 2 the greatest importance have

For samples of the B-type the second moment M_2 depends on the angle Θ (the angle between the draw direction and B_0), i.e., the greater the draw ratio λ is the more significant is this dependence. This is evidenced by Figs. 4 and 5. Through the experimental points representing those dependencies we may draw curves which are defined by Eq. (1). The values of the parameters A , B and C , which characterize these dependencies, were estimated from the experimental values of

birefringence Δ , crystallinity K_p and the quantities derived from the NMR experiments. By means of those quantities it is possible to obtain the quantitative characteristics for the orientation of macromolecular chains in connection with the degree of elongation λ of the foils.

Other quantities introduced in Tab. 1 do not directly characterize the degree of orientation, they serve only for the characterization of the individual films. For this reason we shall not deal with these quantities.

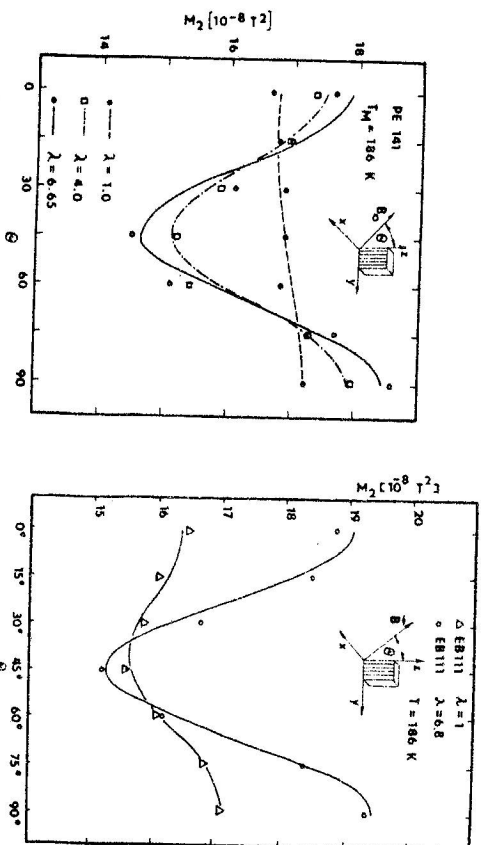


Fig. 4. Angular dependencies $M_2(\Theta)$ for PE 141 foils with different draw ratios λ (the samples B type).

Fig. 5. Angular dependencies $M_2(\Theta)$ for EB 111 foils ($\lambda = 1.0$ and 6.8 , B type).

The angular dependencies M_2 for the foils studied are in agreement with the theoretical results of our paper [13].

According to these theoretical results the second moment of the NMR spectrum for the uniaxial orientation of the amacromolecular chains does not depend on the azimuthal angle Φ , but depends on the polar angle Θ according to Eq. (1). The angular dependences $M_2(\Phi)$ and $M_2(\Theta)$ shown in Figs. 3, 4 and 5 confirm these theoretical results.

It can be seen from Figs. 4 and 5 and from Tab. 2 that for all the foils studied (drawn and undrawn) by us the second moment M_2 depends on the angle Θ . The greater the draw ratio λ is, the more expressive is the dependence M_2 on Θ . The degree of the anisotropy of these dependences is given by the coefficients A and B according to Eq. (1). The quantity C gives the value of M_2 at $\Theta = 90^\circ$.

As it can be seen from Tab. 2 the quantities increase with an increasing draw

Table 2
Parameters characterizing angular dependences of the second moment and macromolecular chain orientation for PP foils

Polymer	λ	A [$10^{-8} T^2$]	B [$10^{-8} T^2$]	C [$10^{-8} T^2$]	f_{2c}	f_{2n}	\bar{f}_2	\bar{f}_1
PE 141	1.0	0.52	0.98	17.2	0.58	-0.25	0.14	0.02
	2.0	3.22	3.75	16.1	0.27	0.24	0.26	0.13
	4.0	10.40	10.79	17.9	0.65	0.28	0.49	0.42
	6.65	14.11	14.65	18.4	0.88	0.36	0.67	0.58
EB 111	1.0	3.93	4.67	17.1	(1.06)	-0.41	0.34	0.16
	2.0	4.29	4.99	16.6	0.55	0.16	0.34	0.17
	6.0	14.52	14.98	18.8	0.81	0.49	0.66	0.59
	6.8	16.10	16.50	19.4	0.72	0.69	0.71	0.66

ratio λ . The course of the quantity C with respect to λ is more complex; first it shows a decrease and then an increase, similarly as it is in the crystallinity K_p and the heat capacity H_m (see Tab. 1).

Other quantities f_2 and \bar{f}_2 derived from the NMR measurements characterize the effective degree of the orientation of the whole macromolecular system. As it is seen in Tab. 2 the values of these parameters increase with λ , which shows that with an increasing deformation the degree of macromolecular orientation also increases. However, variations of the quantities f_2 and \bar{f}_2 do not enable to understand changes in the orientation of macromolecular chains which are realized in the crystalline and the noncrystalline regions, respectively.

Such variations may be described by means of the orientation parameters f_{2c} and f_{2n} , which are derived from the NMR experiments and birefringence according to Eq. (5).

We may conclude on the basis of the values of f_{2c} and f_{2n} that for undrawn foils ($\lambda = 1$) the macromolecular chains in the crystalline regions are predominantly oriented in the extrusion direction ($f_{2c} > 0$), whereas the macromolecular chains in the noncrystalline regions are predominantly oriented perpendicularly to this direction ($f_{2n} < 0$).

Both quantities f_{2c} and f_{2n} are positive for the drawn foils ($\lambda > 1$), which shows that the macromolecular chains are predominantly oriented in the draw direction in the crystalline and noncrystalline regions. The degree of orientation in the crystalline regions is greater than that in the noncrystalline regions ($f_{2c} > f_{2n}$). The parameter f_{2n} gradually increases with the draw ratio λ , whereas the dependence of f_{2c} on λ is more complex. A decrease of the parameters f_{2c} for the foils with $\lambda = 2$ can be seen in comparison with the undrawn foils. Besides a decreasing f_{2c} we may

observe a simultaneous decrease of the crystallinity K_c , the heat capacity H_m and the quantity C characterizing the value of M_z at $\Theta = 90^\circ$. For the foils with greater extensions ($2 < \lambda < 6$) f_{2c} monotonically increases with the tendency to reach a saturation state.

The foil EB 111 with the maximal draw ratio $\lambda = 6.8$ is an exception to this rule and the decrease of the value f_{2c} is observed when compared with the foil EB 111 with $\lambda = 6.0$. The decrease of f_{2c} for this foil is followed by a considerable increase of the parameter f_{2n} .

We ascribe the changes in the course of the parameter f_{2c} with the extension λ (an original decrease, when an increase of f_{2c} with the trend to saturation) in accordance with papers [6, 15], to transformations of the supermolecular structure of isotactic PP, which are realized during the drawing process.

It was experimentally confirmed [6, 15, 21] that PP has a spherulitic supermolecular structure. The changes in the form of spherulites and in the internal arrangements of the crystalline and noncrystalline components of the spherulites take place by drawing. When the draw ratio of the foil increases the spherulitic supermolecular structure transforms into a fibrillar [6, 20, 22] one, which is characterized by the high degree of macromolecular orientation in the crystalline regions. We suppose that the transformation from the spherulitic into the fibrillar structure for the foils studied by us ends at draw ratios $\lambda \leq 6$. For $\lambda > 6$ only a small increase of the orientation parameter f_{2c} could be observed. When the tensile strengths are close to their ultimate values defects in the crystalline structure may arise and as a consequence the parameter f_{2c} may decrease as it is observed at the foil EB 111 with $\lambda = 6.8$.

V. CONCLUSION

In the present paper the study of the macromolecular chain orientation is realized for the foils from isotactic polypropylene. On the basis of experimentally obtained angular dependencies of NMR spectra and birefringence the parameters f_{2c} and f_{2n} characterizing the degree of macromolecular chain orientation both in the crystalline and the noncrystalline regions are derived for every foil studied. Such a way of characterization of the oriented state is very important from the point of view of the understanding of the deformation processes of polymers on the molecular level. For a detailed description of the deformation process it is necessary to use besides the above mentioned methods also other methods which give the possibility to observe changes on higher morphological levels of the polymer structure (the X-ray method, light scattering, electron microscopy, etc.).

REFERENCES

- [1] Miller, M. L.: *The Structure of Polymers*. Reinhold Publ. House, New York 1966.
- [2] Roe, R. J., Kirgbaum, W. R.: *J. Chem. Phys.* 40 (1964), 2608.
- [3] Ward, I. M.: *Proc. Phys. Soc.* 80 (1962), 1176.
- [4] Stein, R. S.: *J. Polym. Sci.* C 15 (1966), 185.
- [5] Samuels, R. J.: *J. Polym. Sci.* A 3 (1965), 1741.
- [6] Samuels, R. J.: *J. Polym. Sci.* A 2, 6 (1968), 1101.
- [7] Nishijima, Y., Onogi, Y., Asai, T.: *J. Polym. Sci.* C 15 (1966), 237.
- [8] Roe, R. J.: *J. Polym. Sci.* A-2, 8 (1970), 1187.
- [9] Stein, R. S.: in Ke, B.: *Newer Methods of Polymer Characterization*, Interscience, New York 1964.
- [10] Heise, B., Kilian, H. G., Pietralla, M.: *Prog. Colloid Polymer Sci.* 62 (1977), 16.
- [11] Pietralla, M.: *Colloid & Polymer Sci.* 254 (1976), 249.
- [12] Murin, J.: *The Study of Orientation of Macromolecules in Drawn Polypropylene Films by NMR*. Dissertation, Košice 1979.
- [13] Murin, J.: *Czech. J. Phys.* B 31 (1981), 62.
- [14] Pinnock, P. R., Ward, I. M.: *Brit. J. Appl. Phys.* 17 (1966), 575.
- [15] Samuels, R. J.: *J. Polym. Sci.* C 20 (1967), 253.
- [16] Slichter, W. P., Mandell, E.: *J. Appl. Phys.* 29 (1958), 1438.
- [17] Woodward, A. E., Odajima, A. J., Sauer, J. A.: *J. Phys. Chem.* 65 (1961), 1384.
- [18] Kienzle, U., Noack, F., Schütz, J.: *Kolloid-Z. u. Z. Polymere* 2 (1970), 129.
- [19] McBrierty, V. J., Douglass, D. C., Falcone, D. R.: *JCS Faraday Trans. II* 68 (1972), 1051.
- [20] Hashimoto, T., Kawasaki, H., Kawai, H.: *J. Polym. Sci.* A 16 (1978), 271.
- [21] Natta, G., Gorradini, P.: *Suppl. d. Nuovo Cimento* XV (1960), 40.
- [22] Peterlin, A.: *J. Appl. Phys.* 48 (1977), 4099.
- [23] Rákoš, M.: *Exp. Techn. d. Phys.* XV (1967), 197.
- [24] Rákoš, M., Šimo, R., Varga, Z.: *Czech. J. Phys.* B 16 (1966), 112.

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