

STUDY OF MODIFIED POLYPROPYLENE FIBRES BY BROAD-LINE ^1H NMR SPECTROSCOPY

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Both changes of a supermolecular structure of the polypropylene fibres and macromolecular chains mobility caused by modifications of polypropylene were studied using the broad-line ^1H NMR spectroscopy. The following modifications were carried out: the addition of the high-molecular modifier into a polypropylene and stretching the fibres prepared from material modified in the way mentioned above. The information on the influence of these modifications was obtained by Bergmann's decomposition of the spectra into three components, corresponding to the crystalline, intermediate and amorphous regions and by the analyses of the temperature dependences of the second moment M_2 . The NMR spectra were measured in a temperature range from 190 K up to 390 K. It follows from the experimental data analysis that the presence of the high-molecular addition gives rise to the increase of chains mobility within the amorphous regions. The stretching produces an increase of the relative mass fraction of the chains motionless from the viewpoint of the NMR experiment used. These chains were ascribed to the crystalline regions of the polymer. In addition to that, the stretching results in an increase of the chain mobility in the intermediate regions. The NMR results were compared with the optical birefringence and crystallinity estimated using the infrared absorption spectroscopy.

I. INTRODUCTION

At present the regulation of classical polymer properties through physical and chemical modifications has been given priority in the preparation of new polymer materials. According to Penisson the modifications may be divided as follows: chemical, e.g., the change of molecular weight, end-groups modifying, polymer blends preparation, addition of convenient polymer modifiers, etc. These are realized in the phase of preparation of the polymer material from which fibres are prepared. Physical modifications, e.g., spinning, stretching, annealing etc. are aimed at changes of fibre properties due to specific technologies during their production [1].

The nuclear magnetic resonance (NMR) techniques are shown to be advantageous for the study of changes produced by modifications mentioned above. By the use of these techniques many chemical [2-6] and physical [7-10] modifications of polypropylene (PP) have been investigated.

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In this paper changes of the PP supermolecular structure and macromolecular chain motion arising from modifications like the addition of the polymer modifier into the PP and the stretching of the fibres to the various stretching ratios λ are studied. We have supposed that the individual modifications have given rise to changes of the molecular motion and the arrangement of the main chains in the monocrystalline regions of PP. For this reason we aimed at the glass transition temperature range of this polymer.

II. THEORETICAL PART

The shape of broad-line NMR spectra depends on the magnetic dipole-dipole interaction. Because these depend on the spatial configuration and motion of the resonating nuclei the NMR spectra measured over a certain temperature range provide information about the structure and molecular motions in the considered temperature range.

To obtain this information the NMR spectra were analysed according to the Bergmann method [11-14]. In accordance, the broad-line NMR spectrum is a superposition of three elementary spectra corresponding to the different kinds of macromolecular chain mobility. The broad elementary spectrum y_b derived from the low temperature experimental spectrum was attributed to the chains motionless from the viewpoint of the broad-line NMR experiment. The middle elementary spectrum y_m expressed by the product of the Gaussian and the Lorentzian function corresponds to the chains performing the hindered rotational motion about C-C bonds. And finally, to the chains performing a quasi free micro-Brownian motion the narrow elementary spectrum y_n expressed by the Lorentzian function is ascribed. The spectrum calculated y_c can be expressed as follows

$$y_c(x) = w_b y_b(x, s, B_m) + w_m y_m(x, \beta_G^m, \beta_L^m, B_m) + w_n y_n(x, \beta_L^n, B_m) \quad (1)$$

where w_b, w_m, w_n are the relative mass fractions of the chains carrying out the individual types of motions. The mass fractions fulfil the condition $w_b + w_m + w_n = 1$. $x = B - B_0$ is a deflection of the applied magnetic field induction B from the resonance value B_0 . B_m is the amplitude of the modulation magnetic field. The parameters of the elementary spectra w_i, β_i ($i = b, m, n$) and s , reflecting the structure and chains mobility, were estimated by the least square method. In the computing of these parameters the influence of the modulation field on all elementary spectra was considered.

The molecular motion can be studied also by means of the temperature dependence of the second moment M_2 . The motion of the chains excited within certain temperature range often results only in the partial averaging of the dipole interactions. It causes the second moment to decrease from the value M_{2H} to M_{2H}

corresponding to the value of the second moment at lower and higher temperatures, respectively, than the temperature range of the second moment decrease. In this case the dependence of the second moment on molecular motion can be written by the relation [15]

$$M_2 = M_{2n} + (2/\pi)(M_{2n} - M_{2m}) \arctg(\gamma M_2/\nu_c) \quad (2)$$

where ν_c is the correlation frequency characterizing molecular motion and γ the gyromagnetic ratio for resonating nuclei. Using the Arrhenius equation

$$\nu_c = \nu_0 \exp(-E_a/RT) \quad (3)$$

the dependence of the second moment vs. temperature can be expressed. Then the activation energy E_a and the preexponential factor ν_0 in eq. (3) may be evaluated.

III. EXPERIMENTAL PART

The broad-line NMR spectra were measured on the samples prepared in the Research Institute of Man-Made Fibres in Svit. The sample of the unmodified partially crystalline granulated PP denoted MOSTEN D3 was used as a reference sample. The modified samples were in fibre form and have been prepared by melting PP with 8 wt% of the high-molecular additive, which is the copolymer of ethylene and alkylaminoacrylate with a predominantly amorphous character [16]. The spinning was realized at the temperature of 270 °C and a spinning speed of 400 min^{-1} . The unidirectional deformation was made at 130 °C at various stretching ratios λ . In accordance with the quantity of modifier (8 wt%), the spinning speed v and the stretching ratio λ , the samples will be denoted PP8/ v/λ . The crystalline X_c established by the infrared absorption spectroscopy and the values of optical birefringence Δn of the samples are introduced in Tab. 1. During the NMR measurements the fibres were densely wound on a thin teflon rod and inserted into the glass tube of a 10 mm diameter. The measurements were made by the Soviet spectrometer RYa-2301 in the temperature range from 190 K to 390 K at the resonant frequency $f_0 = 14.1 \text{ MHz}$. To obtain the optimal spectra the operating parameters of the spectrometer were as follows: the sweep of the external magnetic field $\Delta B/\Delta t = 5 \mu\text{T/s}$ or $10 \mu\text{T/s}$, the time constant of the phase detector $\tau = 1 \text{ s}$ or 5 s , the frequency of the modulating field $f = 35 \text{ Hz}$ and the amplitude of this field B_m either 0.75×10^{-4} or $1.20 \times 10^{-4} \text{ T}$. From the spectra of the differential form, alternatively at the increasing and decreasing of the magnetic field, were recorded at every temperature.

IV. RESULTS AND DISCUSSION

As mentioned above, the investigated fibres were modified by addition of a polymer additive and by stretching. These modifications will be evaluated on the

basis of the results obtained by Bergmann's decomposition of NMR spectra and by the analysis of the temperature dependences of the M_2 . Our considerations are based on ideas of the three phase model of the partially crystalline polymer the chains of which are contained in the crystalline, intermediate and amorphous regions. In the case of PP the model was confirmed also by measurements of the spin-spin relaxation times T_2 [3, 8, 9] and the spin-lattice relaxation times $T_{1\rho}$ [16].

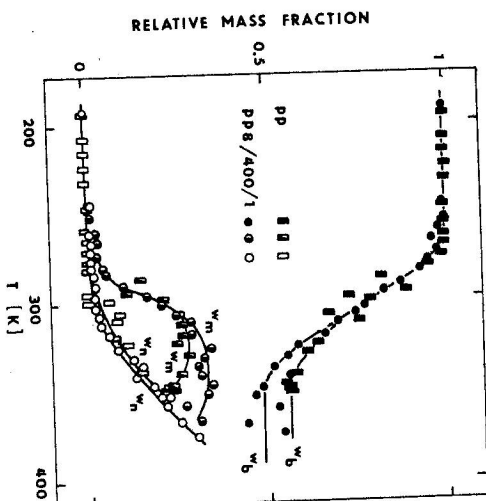


Fig. 1. Temperature dependences of relative mass fraction w_i ($i = b, m, n$) for unmodified PP and modified PP8/400/1 samples.

Figs. 1, 2 show the temperature dependences of the relative mass fractions w_i . We can see that the shapes of these dependences are similar in the basic features for all samples. At low temperatures the spectra consist only of a broad component ($w_b = 1$). It means that the macromolecular chains in the whole polymer are motionless from the point of view of the broad-line NMR experiment. By increasing temperature the chain motion in the noncrystalline regions is activated. It results in the rise of the narrow and middle components of the spectra. The middle component and the narrow one are related to the intermediate regions, i.e. to regions with limited mobility and to chains motion in the amorphous regions, respectively. The value of w_b decreases with increasing temperature until a constant value is achieved, which is denoted w_c (Tab. 1). The cause of the curve w_b in the temperature range where the w_b values do not change indicates that the motion of all chains in the noncrystalline regions of the polymer is activated. Thus the value w_c corresponding to the relative mass fraction of motionless chains, in the discussed

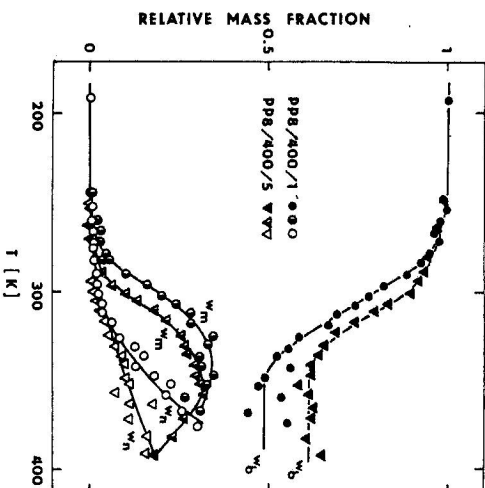


Fig. 2. Temperature dependences of relative mass fraction w_i ($i = b, m, n$) for unstretching PP8/400/1 and stretching PP8/400/5 samples.

temperature range, is considered to be the crystallinity of the sample. Indeed, the values of crystallinity X_c and w_c determined by infrared absorption spectroscopy and Bergmann's analysis of the measured spectra, respectively, are in a very good agreement (Tab. 1). At temperatures of about 330 K the temperature dependences w_m have achieved their maximum values. This may be explained by the activation of the motion of all chains in the intermediate regions of the polymer. Above this temperature w_m starts to decrease, because the motion in the intermediate regions begins to have the character of the motion in the amorphous regions. It results in an increase of the narrow component values w_n . The comparison of experimental results for modified and unmodified PP samples enables to judge the influence of the polymer modifier on molecular motion and PP supermolecular structure. The temperature dependences of relative mass fractions w_i in Fig. 1 indicate that the mixture of PP and polymer modifier produces a polymer with different fractions of mainly crystalline and intermediate regions. Although it is expected that this modification causes the decrease of crystallinity, the observed changes can be dependent on the preparation of sample, thus we cannot unambiguously ascribe them to the influence of the polymer modifier. However, the values of parameter β_L^* are connected with the width of the narrow component of the spectrum [17], so we can judge the mobility in amorphous regions of both samples (Tab. 1). The values of this parameter in modified PP are lower than in the unmodified one.

Thus the influence of the polymer modifier results in an increased mobility of chains in amorphous regions of the modified PP. The increase of mobility can be explained by interactions between the more flexible macromolecules of the modifier and the PP chains, as well as by the increase of the free volume, i.e. generating better conditions for the conformation changes [6].

By comparing the temperature dependences of relative mass fractions w_i for stretching and unstretching fibres (Fig. 2) we can characterize the changes caused by stretching. In the temperature range where we observe the narrow y_n and the middle y_m components of spectra (temperature higher than ≈ 250 K) at the stretching fibres the relative mass fractions w_b are higher and the relative mass fractions w_m, w_n are lower when compared to the unstretching fibres. This indicates a greater representation of motionless chains in the stretching fibres at each temperature of the discussed temperature range. The w_c values in Tab. 1 show that the motion restriction of the part of chains is caused by their arranging into crystalline domains. The w_b, w_m and w_n temperature dependences in the temperature range where the values of w_b are due to the crystallinity of the sample ($T \geq 300$ K) indicate that the increase of crystallinity caused by stretching is related to the decrease of the amorphous fraction of the sample. This final state probably rises by the decreasing chains mobility in amorphous regions until it is equal to the chains mobility in intermediate regions and new crystalline regions arise by a total disappearing of chain mobility in the intermediate regions.

It is known that stretching at the stretching ratio $\lambda \approx 2.5$ already causes the transformation of the supermolecular structure from spherulitic to a fibrillar one [23, 24]. The fibrillar structure is characterized by a relatively high degree of the ordering of macromolecular chains in noncrystalline regions of the polymer, which can be observed as increasing optical birefringence values Δn (Tab. 1), [19]. Consequently, owing to the formed more ordered supermolecular structure the retardation effect of stretching would be expected also on the macromolecular chains mobility, which was observed in the case of other polymers [20, 21]. But the temperature dependences of the second moment M_2 (Fig. 3) as well as the values of activation energy E_a (Tab. 1) point to contrary effect of stretching. The M_2 decreasing is related to the glass transition of the investigated polymers, i.e. to motions in noncrystalline regions of these samples. We can see that at temperatures of up to 280 K the values of M_2 of the stretching fibres are lower and the decrease of M_2 starts at lower temperatures when compared with the unstretching ones. Besides we observe the lower values of activation energy E_a at the stretching fibres than at the nonstretching ones. Thus the stretching causes the increase of chain mobility in the noncrystalline PP regions. The atypical behaviour of the polymer, mentioned above, is connected with the helical structure of PP chains and with the presence of CH_3 side-groups. The helical structure of unstretching

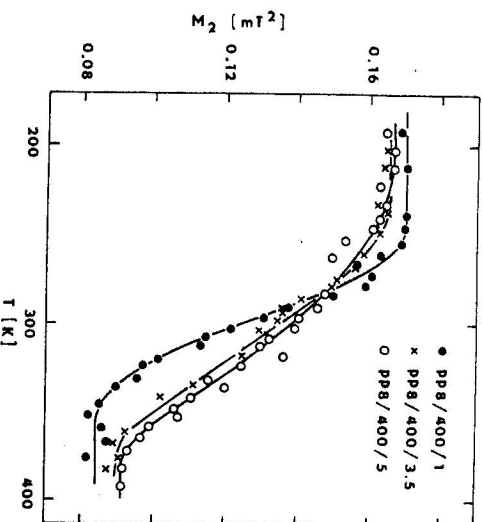


Fig. 3. The second moment M_2 temperature dependences of modified PP fibres: PP8/400/1, PP8/400/3.5, PP8/400/5.

fibres is resistant to the thermal motion due to the considerable overlapping of Van der Waals radii of CH_3 groups [20, 22]. During the stretching owing to the deformation of PP chains a mutual delaying of CH_3 groups arises, which causes the decrease of potential barriers and in this way the increasing of chains mobility. The question is whether the loss of motions connected with decreasing activation energy E_a and the discussed decreasing of the second moment M_2 occur in the whole noncrystalline regions of PP or only in some of their phases. The decrease of the second moment can be caused by molecular motion in amorphous regions as well as in intermediate ones. Thus neither by means of temperature dependences of the second moment nor by activation energy calculated from these dependences is it possible to solve the problem. The mobility of chains in the noncrystalline regions is characterized by a parameter of a narrow component β_L^2 and by two parameters of a middle component β_G^2 , β_L^2 . An unambiguous connection is only between the width of the spectra and the parameter β_L^2 . Since the values of this parameter are the same and independent of the stretching ratio and the temperature (Tab. 1), we arrive at a conclusion that the chain mobility in amorphous regions is not influenced. Hence it is possible to claim that the chains in intermediate regions of PP are responsible for the decrease of activation energy.

Table 1.

POLYMER	X_c [%]	w_c [%]	w_m max [%]	$\beta_L^2 \times 10^4$ [T]	$\Delta n \times 10^3$	E_a [kJ/mol]
PP	55.9	56.0	28.0	0.50-0.70	—	34.0
PP8/400/1	48.9	49.0	33.0	0.25-0.35	2.3	32.4
PP8/400/3.5	59.0	59.0	34.0	0.25-0.35	25.8	21.1
PP8/400/5	62.0	61.0	30.0	0.25-0.35	29.5	16.3

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ИССЛЕДОВАНИЕ МОДИФИЦИРОВАННЫХ ВОЛОКОН ПОЛИПРОПИЛЕНА И ПРИМЕНЕНИЕМ ЯМР НА ШИРОКОЙ ЛИННИИ ^1H

С применением электрооскопии ЯМР на широкой линии ^1H изучаются изменения супермолекулярной структуры волокон полипропилена и изменений подвижности макромолекулярных цепочек соответственно. Различные модификации полипропилена были вызваны высокомолекулярными добавками и при изготовлении волокон. Влияние модификаций определялось Бергмановской раскладкой спектров на три компонента, кристаллическую, промежуточную и аморфную соответственно. Температурная зависимость анализировалась с применением второго момента M^2 . Спектры ЯМР были измерены в температурном диапазоне от 190 К по 390 К. Из анализа экспериментальных добавок увеличивается подвижность цепочек в аморфной области. При вытяжке волокон увеличивается часть относительно массы, что с точки зрения ЯМР определяет неподвижность цепочек. Такие цепочки относятся к кристаллической части полимера.