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Nuclear Magnetic Resonance Investigation of the Influence of Drawing and Drawing Temperature on Molecular Mobility in iPP Fibres

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A set of stretched isotactic polypropylene fibres prepared with the draw ratio $\lambda = 2.5$ at different temperatures was investigated by ^1H pulsed relaxation NMR method and continuous wave spectroscopy. Both, drawing and temperature of drawing influence physical properties of isotactic polypropylene fibres. NMR technique is shown to be advantageous for the study of these changes on molecular level since the shape of broad-line NMR spectra and processes of the NMR relaxation depend on the spatial configuration and motions of the resonating nuclei.

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1. Introduction

The physical properties of the isotactic polypropylene (iPP) fibres, as the semi-crystalline polymer, are affected by processing conditions, i.e. the stretching temperature and draw ratio λ , where λ is defined as the ratio of final length l to the original length l_0 of the fibres. The PP morphology has four different types [1]. When the semicrystalline polymers are drawn, the shear forces destroy the spherulites. Elongation of the iPP fibres causes the transformation of the molecular structure from spherulitic to fibrillar one. The influence of the processing conditions on the structure and on the macromolecular mobility in PP by solid-state NMR has been also studied [2, 3]. The transformation from spherulitic to fibrillar one is completed at the draw ratio about $\lambda \approx 2.5$ for iPP [4].

The aim of this paper is to study the influence of the stretching temperature and draw ratio upon the changes in structure and molecular mobility in isotactic PP fibres in the region where the transformation from spherulitic to fibrillar structure occurs.

2. Experimental

The broad-line NMR spectra were measured, in the temperature range of 200–400 K, with a RYa-2301 spectrometer operating at 14.1 MHz resonance frequency. Proton spin–lattice relaxation times T_1 were measured using a home made pulse spectrometer operating at a frequency of 30 MHz [2] by multiple-pulse saturation recovery method with a train of 90° pulses of 20 ms duration separated by 100 μs intervals in the temperature range of 280–420 K. The measurements were performed for both non-stretched and stretched PP fibres, prepared in the Research Institute for Chemical Fibres in Svit. Fibres were made from iPP, marked as Tatren 430, produced by Slovnaft Bratislava. iPP fibres were stretched at different temperatures T_S (293 and 373 K) to draw ratio $\lambda = 2.5$. In accordance with the quantities temperature

of stretching T_S and draw ratio λ the samples will be denoted $\text{PP}/T_S/\lambda$.

3. Result and discussion

Second moments M_2 were evaluated from the derivative records of the NMR spectra. The temperature dependences of the second moment M_2 for both non-stretched iPP fibre and for stretched iPP fibres are shown in Fig. 1. The temperature dependences of the second moment were estimated according to formula [5]

$$M_2(T) = M_{2\text{lt}} + \frac{2}{\pi} (M_{2\text{lt}} - M_{2\text{ht}}) \times \arctan \left[\gamma \tau_c \sqrt{M_2(T)} \right]. \quad (1)$$

Here γ is the gyromagnetic ratio of resonating nuclei, $M_{2\text{lt}}$ and $M_{2\text{ht}}$ refer to the second moments at temperatures below and above the transition range. The correlation time, τ_c , for corresponding molecular motion, may be expressed according to the Arrhénius formula

$$\tau_c = \tau_0 \exp \left(\frac{E_a}{RT} \right). \quad (2)$$

In above equation τ_0 is correlation time at infinite temperature, E_a is activation energy and R is the gas constant.

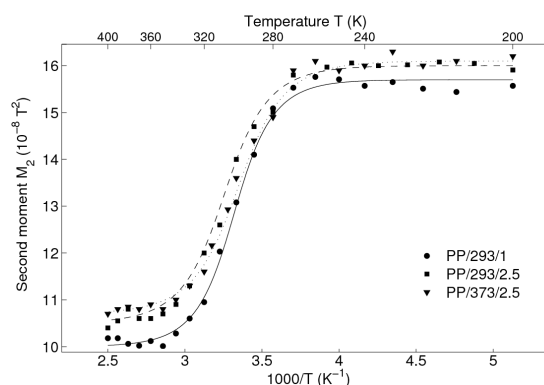


Fig. 1. Temperature dependences of the second moment of ^1H NMR spectra for non-stretched and stretched PP fibres. The lines represent line calculated according to Eqs. (1) and (2).

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The changes in the NMR spectra and decrease of the second moments (Fig. 1) are related to region above glass transition, which is equal for iPP to about $T_g \approx 273$ K. Decrease of the second moment could be ascribed to the motion of segments of iPP chains in the non-crystalline regions. The molecular motions in these temperature regions are in the literature referred to as β -relaxation processes. The decrease of the second moment for both stretched iPP fibres is shifted towards higher temperatures and widths of the transition region are larger than for non-stretched iPP fibre. Activation energy E_a of the molecular motion for stretched iPP fibres is lower than that for non-stretched iPP one (Table). The activation energies E_a for corresponding molecular motion above temperature T_g for non-stretched and stretched iPP fibres were calculated from Eqs. (1) and (2) and are presented in Table.

TABLE

Summary of the estimated parameters from Eqs. (1)–(3). Estimated activation energy E_a^{BPP} was calculated according to BPP distribution function. The values given in paranthesis represent uncertainty in the last digit place. The mass crystallinity X_c^m of the samples was calculated by means of the density [2].

	PP/293/1	PP/293/2.5	PP/373/2.5
E_a [kJ/mol]	48(3)	43(2)	41(2)
E_a^{mFK} [kJ/mol]	37.6(3)	35.2(6)	37.3(4)
E_a^{BPP} [kJ/mol]	12.8(5)	13.2(7)	12.5(5)
T_{\min} [K]	353(1)	358(1)	361(1)
$T_{1,\min}$ [ms]	141(2)	150(2)	162(1)
α	0.17(1)	0.19(3)	0.18(2)
β	0.88(6)	0.94(16)	0.83(9)
crystallinity X_c^m [%]	51	51	63

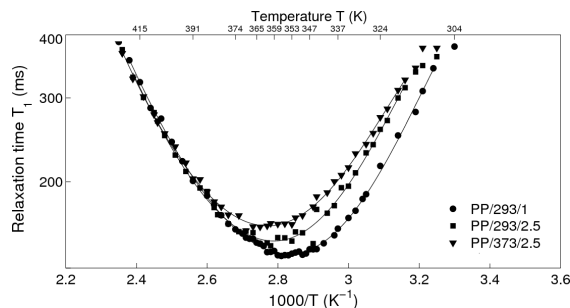


Fig. 2. Temperature dependences of the ^1H spin-lattice relaxation times T_1 for non-stretched and stretched PP fibres. The solid lines represent the best fit (with the lowest χ^2).

The pulsed ^1H NMR results are calculated using the modified Fuoss–Kirkwood (mFK) distribution. The dependence of the spin-lattice relaxation rate $1/T_1$ on the correlation time τ_c is expressed by Eq. [6]:

$$\frac{1}{T_1} = C[(\alpha + \beta)/(2\omega_0)] \sin(\alpha\pi/(\alpha + \beta)) \times \left[\frac{(\omega_0\tau_c)^\alpha}{1 + (\omega_0\tau_c)^{\alpha+\beta}} + 2 \frac{(2\omega_0\tau_c)^\alpha}{1 + (2\omega_0\tau_c)^{\alpha+\beta}} \right], \quad (3)$$

in which C is the relaxation constant, ω_0 is the circular resonant frequency and α and β are parameters of the mFK distribution ($0 < \alpha, \beta \leq 1$; β characterizing the distribution width in the low temperature region where $\omega_0\tau_c \gg 1$). It is seen that at $\alpha = \beta = 1$ Eq. (3) converts to the Bloembergen–Purcell–Pound (BPP) expression, i.e. to the isotropic motional model. The calculated values of the activation energy E_a^{mFK} and parameters α and β obtained by least-square fit of Eqs. (2) and (3) are given in Table.

The minima observed in the temperature dependences (Fig. 2) are related to the well known β relaxation process that is related to a segmental motion of macromolecular chains in non-crystalline regions polymeric materials. These minima are shifted to the higher temperature when the stretching temperature T_S increases. The shift of the $T_{1,\min}$ minimum to the higher temperature can be interpreted by restrictions of the segmental motions within the polymer chains due to an increase of molecular order in the non-crystalline and crystalline regions, e.g. it can be observed by the increase of the mass crystallinity X_c^m of the samples. The change in the value of $T_{1,\min}$ also leads to the difference in the effective interproton distance r .

4. Conclusion

The results show that changes in structure and molecular motion due to processing conditions (stretching temperature and draw ratio) in iPP fibres are detected by NMR measurements in the temperature region where β relaxation is dominant. The activation energy in this temperature region, estimated from CW and pulsed NMR measurements, for corresponding molecular motion is lower for stretched iPP fibres than that for non-stretched iPP fibre. Decrease of the activation energy value determined from CW measurements for draw ratio $\lambda = 2.5$ is lower than that for $\lambda = 4$ [2]. The shift of $T_{1,\min}$ to the higher temperature for $\lambda = 2.5$ is not so large than for $\lambda = 4$. It leads us to the assumption that the transformation from the spherulitic to fibrillar structure for the fibre PP/293/2.5 is not completed [1]. It is also assumed that the molecular motion activation is an Arrhenius process.

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