

PROTON MAGNETIC RESONANCE STUDY OF DRAWN POLYAMIDE-6 FIBRES

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SUMMARY

The orientation of macromolecules in a solid polymer may have a profound influence on the macroscopic physical properties of the polymer. The influence of drawing on molecular chains mobility in polyamide-6 (PA-6) at room temperature was studied in this paper by means of broad-line NMR experiments. PA-6 fibres were drawn at two different temperatures: 20 °C and 190 °C, respectively, with a different drawn ratio $\lambda=1, 2, 3, 4$.

The influence of drawing on molecular chains mobility is based on the variations of the second moment NMR that varies its shape with temperature and drawing process. The obtained broadline ^1H NMR spectra were analysed by modified Bergmann method supposing that spectra may be expressed as a sum of three elementary spectra: y_n (narrow), y_m (middle) and y_b (broad), with the weight factors w_i (i -stands for n, m and b , respectively).

The narrow component, corresponding to the chains with the highest mobility was taken as Lorentzian function, the middle one, y_m , corresponding to the chains of non crystalline regions with hindered mobility was chosen as the normalized product of the Gaussian and Lorentzian functions, and the broad component y_b , representing rigid chains, was derived from the low temperature spectrum measured at -140 °C. The weight factors w_i and parameters of individual spectral components were calculated from experimental spectra by means of the least square method. NMR spectra differ from each other in shape and corresponding parameters, referring to a different mobility of chains in different regions in connection with the sample processing. At room temperature both ordered and disordered regions contribute to the broad component of the NMR curve. Any narrow component which is due to the presence of polymer-water complex units in the sample becomes sharp for highly drawn fibres. The broad component increases at the expense of decreasing of the fraction w_m .

Keywords: Nuclear Magnetic Resonance, polyamides, Bergmann decomposition analysis.

1. INTRODUCTION

Physical and mechanical properties of polymers are related to molecular mobility. Our previous study of relaxation processes in drawn PA-6 fibres has shown different behaviour in different temperature regions [2,3,4]. The influence of drawing on the relaxation processes in polyamide fibres have been studied by means of the broadline ^1H NMR experiments and the storage and loss components of the dynamic modulus. The materials used in this studies were PA-6 fibres drawn at two different temperatures: 20 °C and 190 °C, respectively, with different draw ratio $\lambda=1,2,3$, and 4. Manifestations of multiple molecular processes in the temperature range 143-373 K in NMR and free torsion vibration were studied in our papers [2,3,4]. Polyamides exhibit some properties at room temperature which are not consistent with the temperature range for T_g . As it was shown by Bergmann [1] the phase structure of polymers may be revealed from NMR spectra measured at room temperature.

2. EXPERIMENTAL

Broad-line ^1H NMR spectra were measured by means of a spectrometer RJa-2301 which operates at the constant resonant frequency $f = 14.1$ MHz. The

measurements were carried out at the room temperature (293K). The sweep of the external magnetic field, time constant of the phase detector, amplitude of the modulating field were $5 \mu\text{T s}^{-1}$ or $10 \mu\text{T s}^{-1}$, 1 s and $0.99 \cdot 10^{-4}$ T, respectively. The frequency of the modulating field was 35 Hz. There were several spectra of the differential form at the linear increasing and linear decreasing magnetic field.

The materials used in this study were PA-6 fibres prepared in the Research Institute for Chemical Fibres in Svit, which were drawn at two different temperatures 20 °C and 190 °C respectively. The starting undrawn fibre was manufactured by extrusion from the melted polymer. The drawn fibres with different draw ratio λ ($\lambda = l/l_0$, where l_0 resp. l is the length of the fibre before and after drawing) were prepared by a standard procedures. Fibres with $\lambda = 1, 2, 3$, and 4 have been studied in this work. The samples were prepared in the form of small solenoid with densely wound coils on a teflon rod and placed into thin wall glass tubes. The content of the moisture at ambient conditions does not exceed 3 wt %.

Parameters such as drawn ratio λ , birefringence Δn , density ρ and crystallinity β are stated in Tab. 1. The values of birefringence and density were taken from over [5].

Tab. 1 The parameters characterizing PA-6 fibres

sample	desig- nation	Δn $\times 10^3$	ρ [kgm ⁻³]	β [%]
1 (20)	1 U	7.3	1123	31.4
2 -"	2 S	36.8	1128	34.9
3 -"	3 S	45.0	1130	36.3
4 -"	4 S	53.2	1133	38.7
1 (190)	1 U	7.3	1123	31
2 -"	2 T	34.3	1129	35.6
3 -"	3 T	47.4	1135	39.7
4 -"	4 T	53.5	1140	43

The crystallinities (β) were calculated from densities according to the formula

$\beta = [(\rho - \rho_c)/(\rho_c - \rho_a)] \cdot \rho_c/\rho$. Using the crystal density $\rho_c = 1230 \text{ kgm}^{-3}$ and the amorphous density $\rho_a = 1080 \text{ kgm}^{-3}$, ρ is the measured density [3]. Our fibres are medium crystallinity polymers. The higher values of these characteristics with increasing of the drawn ratio and drawing temperature show that there is a higher degree of macromolecular orientation both in the crystalline and noncrystalline regions.

3. RESULTS AND DISCUSSION

The NMR spectrum varied its shape with temperature and drawing process. The cause of these variations were the motions which may be attributed to „crankshaft mechanism“ at low temperatures, to segments of the main chain and to onset of much more general motions as the temperature is raised. The NMR spectra were analysed by modified Bergmann's method [1,6] supposing that they may be expressed as a sum of three elementary spectra: y_n (narrow), y_m (middle) and y_b (broad), with the weight factors w_i (i-stands for n, m and b, respectively) according to relation:

$$y(x) = w_n \cdot y_n(x, B_m, \beta_L) + w_m \cdot y_m(x, \beta_{mL}, \beta_{mG}) + w_b \cdot y_b(x, S), \quad (1)$$

where abscissa $x=B-B_0$ is the deflection from the resonance field B_0 and parameters β_L , β_{mL} , β_{mG} and S relate to the widths δB_i of the elementary spectra. The narrow component, corresponding to the chains with the highest mobility was taken as Lorentzian function, the middle one, y_m , corresponding to the chains of non crystalline regions with hindered mobility was chosen as the normalized product of the Gaussian and Lorentzian functions, and the broad component y_b , representing rigid chains, was derived from the low temperature spectrum, measured at -140°C . The weight factors w_i and parameters of individual spectral components were

calculated from experimental spectra by means of the least square method [1,6]. The analysis described above is illustrated in Fig.1. on the sample PA 3T. Results of our analysis are summarized in Tab.2.

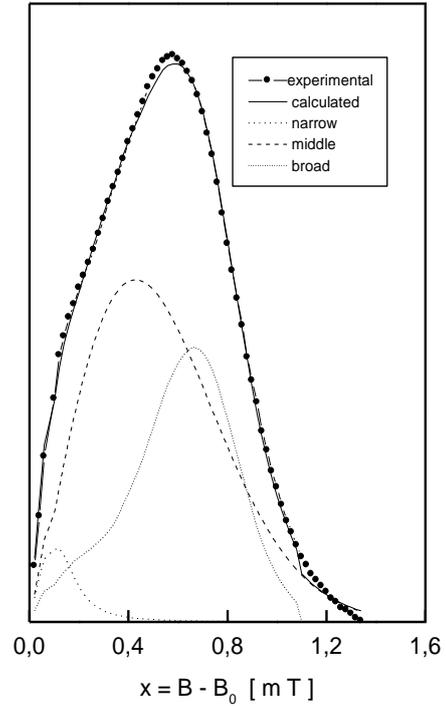


Fig.1 The decomposition of the broad line NMR spectrum measured on the drawn PA 3T fibres at 293 K.

4. CONCLUSION

As can we see from Tab.2 NMR spectra differ from each other in shape and corresponding parameters, referring to a different mobility of chains in different regions in connection with the sample processing. At room temperature both ordered and disordered regions contribute to the broad component of the NMR curve. Any narrow component which is due to the presence of polymer-water complex units in the sample becomes sharp for highly drawn fibres. The broad component increases at the expense of decreasing of the fraction w_m . We also observed the decrease of the second moment in all samples at the temperature $T > 293 \text{ K}$.

Tab.2 The parameters characterizing PA-6 fibres analysed by Bergmann method

SAMPLE	$\lambda=1$	$\lambda=2$ (20 ⁰ C)	$\lambda=2$ (190 ⁰ C)	$\lambda=3$ (20 ⁰ C)	$\lambda=3$ (190 ⁰ C)	$\lambda=4$ (20 ⁰ C)	$\lambda=4$ (190 ⁰ C)
w _n [%]	8.1	7.4	1.3	4.2	1.0	2.6	0.3
w _m [%]	62.1	62.6	64.7	62.6	61.3	61.8	59.0
w _b [%]	29.8	30.0	34.0	33.2	37.7	35.6	40.7
M _{2n} [G ²]	5.22	5.04	3.61	4.67	5.38	4.9	4.76
M _{2m} [G ²]	13.58	13.84	14.37	14.68	15.4	14.96	14.96
M _{2g} [G ²]	14.04	14.04	13.64	14.30	15.61	14.03	18.24
δB_n [G]	0.96	0.919	0.75	0.69	0.54	0.79	0.21
δB_m [G]	16.94	16.52	16.85	16.89	17.62	16.69	16.78
δB_b [G]	5.7	5.59	5.82	5.87	5.92	5.60	5.88
M _{2exp} [G ²]	13.1	13.53	14.52	14.24	15.21	14.45	15.83
M _{2num} [G]	13.02	13.24	13.97	14.13	15.37	14.36	16.25

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BIOGRAPHY

Kamila Jelšovská was born on 4.8.1952. In 1975 she graduated (MSc.) the Faculty of Science of University of P.J. Šafárik in Košice. She defended her PhD. in the field of magnetic and NMR study of paramagnetic monohydrates in 1992; her thesis was "Magnetic and NMR study of the same paramagnetic monohydrates". Her scientific research is study of properties of polymers by NMR methods.