ANALYSIS OF ^{13}C NMR SPECTRA OF ISOTACTIC POLYPROPYLENE MATERIALS

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1. Introduction

Isotactic polypropylene (iPP) is a stereoregular polymer with chains crystallizing in helical form. The chains of iPP may be ordered into regions with different arrangement and different mobility and the microstructure of the iPP and its physical properties are strongly affected by the preparation technique [1]. Isotactic PP belongs to an important engineering plastic used in various application areas and many efforts are still put into improveming its mechanical, optical, thermal, and environmental properties. The chains of iPP consisting of three functional groups canform amorphous and crystalline domains. Many polymer properties are determined by the relative amountof crystalline regions in polymer structure which is called the degree of crystallinity. The same functional group within different domains produces different lines in the ^{13}C NMR spectra and the degree of crystallinity of iPP sample can be then estimated by the deconvolution ^{13}C NMR spectra [2]. The ^{13}C NMR measurements at two different delay times [3]were used for the estimation of the degree of crystallinity of two iPP samples.

2. Experimental details

Two samples of granulated predominantly isotactic PP were studied. The first one denoted as TATREN HG 1007 (ZN-iPP) was prepared by polymerization using classical Ziegler–Natta catalyst. The second sample denoted as METOCENE HM 562 N (m-iPP) was prepared by metallocene-catalysed polymerization.

The high-resolution solid-state single pulse^{13}C NMR measurements were carried out on a 400 MHz Varian solid-state NMR spectrometer. The spectra were recorded at the resonance frequency of approximately 100 MHz with the use of 4 mm rotors and magic angle spinning (MAS) frequency of 10 kHz. The measurements were performed at 98°C with delay timeof 1 s and 240 s and dipolar decoupling (DD) field of 45 and 75 kHz, respectively.

3. Results and discussion

Three resonance lines related to the CH_2, CH and CH_3 groups were observed in the ^{13}C CP NMR spectra measured on iPP sample crystallizing in the hexagonal β-form at room temperature (Fig. 1).These lines are observed atthe chemical shifts of 44.5, 26.6 and 22.2 ppm and they are related to the carbons in CH_2, CH and CH_3 groups, respectively.

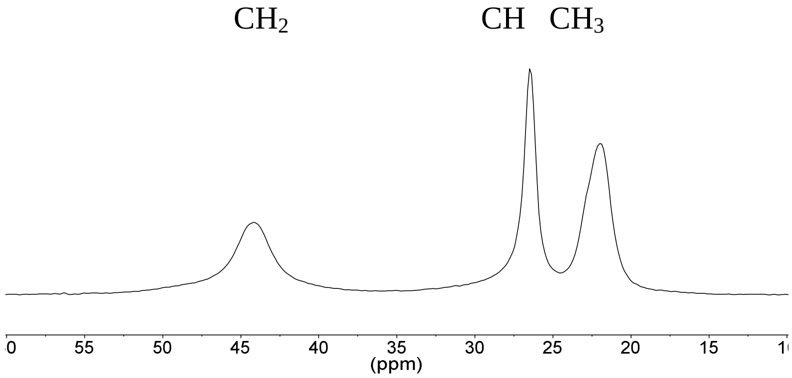

Fig. 1: *^{13}C CP NMR spectrum measuredat the room temperaturefor m-iPP.*

With increasing temperature the lines related to the CH_2 and CH groups split into doublets. This splitting appeared in NMR experiments carried out with CP as well as without the application of the CP technique[4-6].The new lines were assigned to the carbons within the chains of amorphous regions [5, 6].The main characteristics of the spectra measured for ZN-iPP exhibit a similar behavior as those shown for m-iPP confirming that both iPP samples crystallize in the hexagonal β-form [4, 5, 7].However, small differences between the spectra measured at the same temperature can be found.In spectra measured at elevated temperatures the resonance lines related to the CH_2 and CH carbons in amorphous regions of m-iPP are better resolved than those of ZN-iPP [2].Theresolution of lines related to the amorphous and crystalline domains was sufficient at the temperature of 98°C [2].That's why the degree of crystallinity was established using ^{13}C NMR measurementsat this temperature.The measurement with a short delay time (1 s) shows three lines at the chemical shifts of 46.6, 28.9 and 22.4 ppm which were assigned to the CH_2, CH and CH_3carbons, respectively, within amorphous domains.

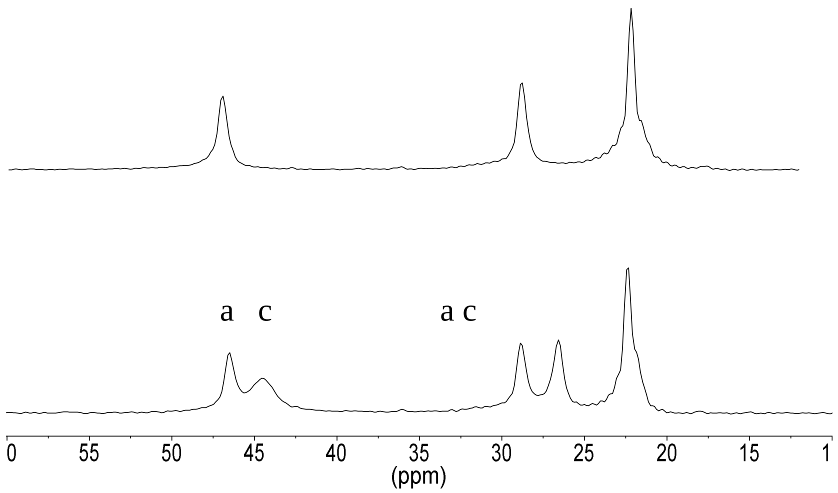

Fig.2: *^{13}C NMR spectra measuredat 98°C for m-iPP with delay time 1 s (top) and 240 s (bottom), (a-amorphous, c-crystalline)*

Due to a short delay time the spin system in crystalline domains does not have enough time for relaxation(Fig. 2 top).The linesproduced by the carbons in amorphous domains can be recognized in the spectrum measured with the delay time of 240 s (Fig. 2-bottom). The information about the amount of crystal and amorphous domainscan be obtained from the deconvolution ofthis ^{13}C NMRspectrum.

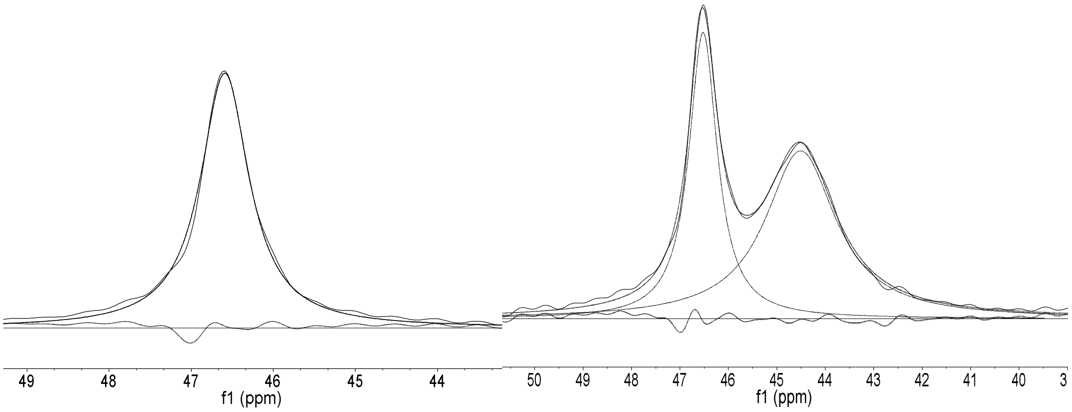

Fig.3:*The resonance line related to the* CH_2 *groups in* ^{13}C NMR *spectrum of m-iPP sample measured with delay time of 1s (left) and 240s (right), the latter was deconvoluted with two lines.*

The partial overlapping of lines related to the CH groups with those associated with CH_3 groups affects deconvolution. For this reason the degree of crystallinity was determined from the deconvolution of lines related to the CH_2 groups (Fig. 3).For deconvolution of the CH_2 line in the spectrum obtained from experiment with thelong delay time, the parameters of the line arising from amorphous domains in a spectrum recorded with theshort delay time, were used. These parameters are the position, width and shape of the line.The results of deconvolution are presented in Tab. 1.

Tab.1.*The values of degree of crystallinity for* m-iPP and ZN-iPP *samples determined from* ^{13}*C NMR spectra and DSC experiments.*

sample	Crystallinity of CH_2 (%)	
	NMR	DSC
m-iPP	58	52
ZN-iPP	62	55

4. Conclusion

The measurements performed with a short delay time enable to detectthe spectrum with lines associated only with groups in amorphous domains of iPP.The estimation of the degree of crystallinity for two samples of iPP was carried out fromdeconvoluted ^{13}C NMR spectra measured with a long delay times. These values are in good agreement with the values obtained from DSC experiments.

Acknowledgement
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