

STUDY OF MELTING PROCESS IN ISOTACTIC POLYPROPYLENES BY MEANS OF SPIN-LATTICE RELAXATION TIMES $T_1(^1\text{H})$

Peter Duranka, Magdaléna Uhrínová, Viktor Hronský, Dušan Olčák

*Department of Physics, Faculty of Electrical Engineering and Informatics,
Technical University of Košice, Park Komenského 2, 042 00 Košice, Slovakia*

E-mail: peter.duranka@tuke.sk

Received 09 May 2013; accepted 16 May 2013

1. Introduction

Isotactic polypropylene is nowadays an important material often used in technical areas because of its properties formed thanks to its chains being crystallized in helical forms. It does have a crystal structure and physical characteristics that are strongly dependent on the preparation process [1].

NMR techniques are very appropriate for purposes of analyzing morphology and molecular motion of studied materials, due to their high sensitivity. Therefore, they are widely used for studies of order characterization, orientation or alignment of molecular chains and their dynamics [2-4]. The ^1H laboratory frame spin-lattice relaxation time $T_1(^1\text{H})$ was frequently used to study molecular dynamics in iPP with the use the broad-line NMR. The spin-lattice relaxation time T_1 is sensitive to molecular motions of the frequency of the order of 10-100 MHz [3].

The aim of this paper is to study the molecular dynamics of iPP samples within a broad temperature range which covers the temperature interval of the glass transition relaxation, α -relaxation and melting process.

2. Experimental

Two samples of granulated iPP prepared by different polymerizations were the subject of this study. The first of them known as TATREN HG 1007 (ZN-iPP) was prepared by the polymerization using classical Ziegler-Natta catalysis. Crystallinity and melting temperature of this sample, which were estimated by DSC technique, are 55 %, 163.6°C, respectively, and glass transition temperature $T_g=10^\circ\text{C}$ was estimated from DMTA measurements. The other one known as METOCENE HM 562 N (m-iPP) was prepared by metallocene-catalysed polymerization. Degree of the crystallinity, melting temperature and glass transition temperature 52 %, 145.2°C and 12°C, respectively.

All NMR measurements were performed by Varian solid state NMR spectrometer at the resonant frequency of 400 MHz in the temperature range of 80 – 190°C. The NMR experiments were carried out with a probe-head using the 4 mm rotor under the magic angle spinning conditions at the spinning rate of 10 kHz. Spin-lattice relaxation times in the laboratory frame $T_1(^1\text{H})$ were measured using the inversion recovery method. Calculations were done using Varian VnmrJ 3.2 software.

3. Results and discussion

The spin-lattice relaxation process detected by inversion recovery technique is illustrated in Fig. 1. The time dependence in this figure, which was obtained from the ^1H NMR spectra measured for m-iPP at 135°C , shows an exponential course of the spin-lattice relaxation.

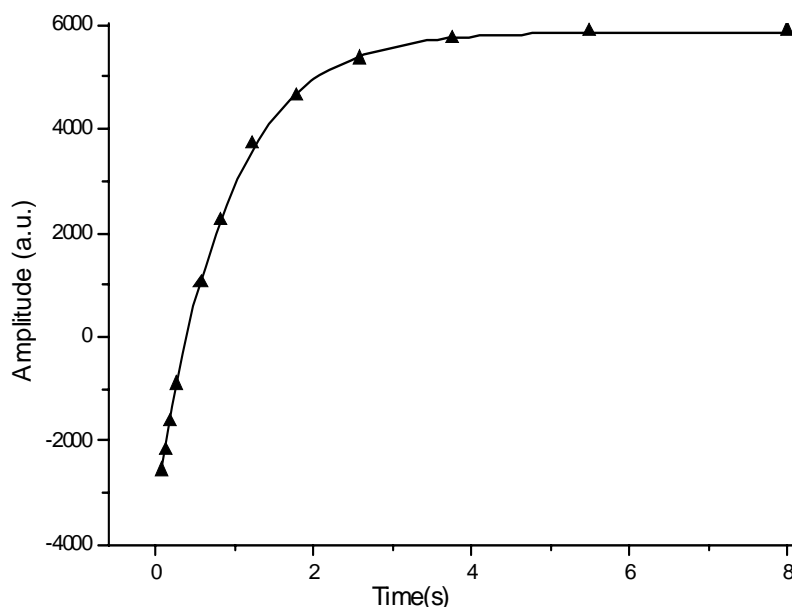


Fig. 1 The time dependence of the amplitude of the ^1H NMR lines detected during inversion recovery experiment performed for m-iPP at 135°C . The points represent the amplitudes of the ^1H NMR lines related to the CH_3 groups. The solid line shows the fitted exponential course of the spin-lattice relaxation process.

Measurements presented in this paper were performed at higher frequency, which was 400 MHz, than those which has been used in previous papers [4 - 6] and therefore, the minimum associated with the glass transition can be expected to be shifted towards the melting process. Fig. 2 shows the temperature dependences of the spin-lattice relaxation times $T_1(^1\text{H})$ for both samples m-iPP and ZN-iPP. The splitting of the spectrum measured at temperatures above 70°C enables to estimate the spin-lattice relaxation times $T_1(^1\text{H})$ for protons giving peaks with chemical shifts of 1.61, 1.30 and 0.91 ppm, which are assigned to the methine, methylene and methyl protons. The flat and sharp minima associated with the glass transition relaxation and melting process, respectively, can be observed in Fig. 2. In this paper our attention will be concentrated to the minima related to the melting process.

Temperature dependences of the relaxation times $T_1(^1\text{H})$ relating to particular groups achieve sharp minima at about the same temperature, $162 - 166^\circ\text{C}$ for m-iPP and $175 - 180^\circ\text{C}$ for ZN-iPP (Tab. 1). These temperatures are higher than melting temperatures of the corresponding samples. The spin lattice relaxation times $T_1(^1\text{H})$ related to the positions of the minima are significantly different from one another, and the differences were also found between the relaxation times related to the same proton groups in different samples.

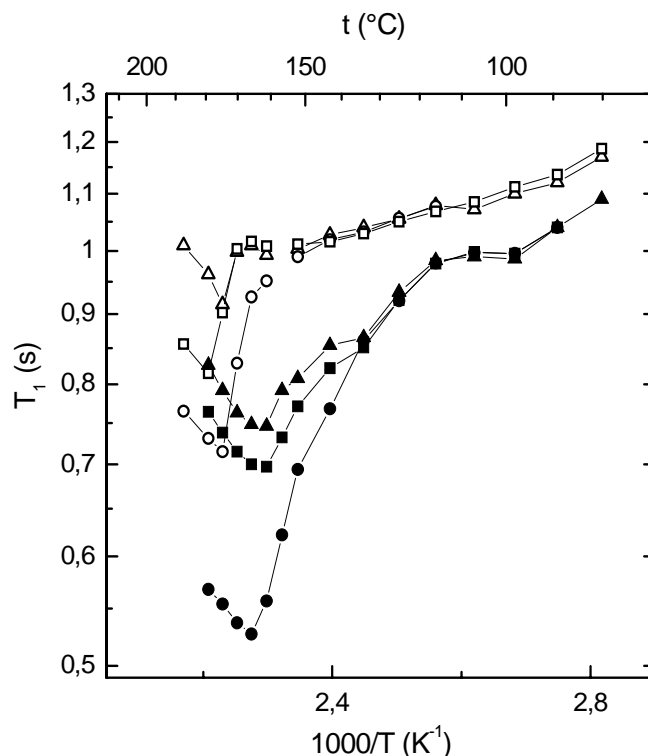


Fig. 2 The temperature dependences of the spin-lattice relaxation time $T_1(^1H)$ of m-iPP (solid symbols) and ZN-iPP (open symbols) related to methine, methylene and methyl groups estimated by the peaks observed at 1.61 (■, □), 1.30 (●, ○) and 0.91 (▲, Δ) ppm, respectively.

The experimental $T_{1,\min}$ values related to the particular groups of ZN-iPP are obviously higher than those related to m-iPP (Fig. 2, Tab. 1). An interpretation of the minima of the temperature dependences of the spin-lattice relaxation times related to the melting process can be based on the assumption that the magnetic dipole-dipole interactions between equal nuclei is predominant relaxation mechanism and the isotropic reorientation of two-spin system with a single correlation time is the main motional process [7 - 9]. The theoretical value $T_{1,\min}$ of 0.31 s was calculated for the methylene groups on the basis of the mentioned assumptions [10]. The difference between corresponding experimental and theoretical $T_{1,\min}$ values is larger for ZN-iPP than that for m-iPP. The comparison of the experimental $T_{1,\min}$ with theoretical values provides information not only about the motion of the individual groups but also about the polymer chain motions and in addition more severe restrictions of motions of polymer chains in melted ZN-iPP as compared with those in m-iPP can be inferred from the $T_{1,\min}$ data. The reason of the different restriction can be possible entanglement of the high molecular weight chains in molten samples and stronger entanglement of ZN-iPP chains could give an explanation of their more severe restrictions of motion as compared with m-iPP chains [2, 11, 12].

Tab. 1. The temperatures T_{min} and spin-lattice relaxation times $T_{1, min}$ related to the positions of the minima of the $T_1(^1H)$ temperature dependences associated with the melting process. The theoretical value $T_{1, min}$ for isotropic reorientations of the methylene groups was found to be 0.31.

Proton group	m-iPP		ZN-iPP	
	T_{min} (°C)	$T_{1, min}$ (s)	T_{min} (°C)	$T_{1, min}$ (s)
CH ₂	166	0.53	175	0.72
CH	162	0.70	180	0.82
CH ₃	162	0.74	175	0.92

Conclusions

The temperature dependences of the spin-lattice relaxation times $T_1(^1H)$ related to the particular groups of m-iPP and ZN-iPP were shown to reach minima associated with the melting process at 162-166°C and 175-180°C, respectively. The values of particular relaxation times $T_{1, min}$ related to the minima occurring above the melting temperature differ greatly from one another and differences were also found between relaxation times related to the same proton groups in different samples. The experimental $T_{1, min}$ reached above melting point was compared with theoretical value calculated for methylene groups. The theoretical $T_{1, min}$ value is lower than experimental one and it is in better agreement with corresponding experimental value for m-iPP than for ZN-iPP. More severe restrictions of chain motions arising from more strongly entangled polymer chains in melted ZN-iPP as compared with those in m-iPP were suggested to explain the differences between experimentally obtained $T_{1, min}$ values.

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