# BROAD LINE $^1$H NMR STUDY OF POLYMER BLEND COMPOSED OF ISOTACTIC POLYPROPYLENE AND ETHYLENE-PROPYLENE-DIENE TERPOLYMER

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## SUMMARY

*The study of the polymer blend composed of isotactic polypropylene (i-PP) and ethylene-propylene-diene terpolymer and of the components of this blend was made with the use of the broad line $^1$H nuclear magnetic resonance technique. Experiments were carried out within the broad temperature range of 160 – 370 K that covers the glass transition regions of all investigated polymers. Interpretation of the experimental results is based on analysis of the variation of the second moments $M_2$ with temperature and on decomposition of the NMR spectra into elementary components related to the amorphous, intermediate and crystalline regions of partially crystalline polymers.*

*The temperature dependences of the second moment of the spectra measured on the terpolymer and i- PP show drops in the temperature ranges 200 – 250 K and 270 – 320 K, respectively, which are related to the glass transitions of the particular polymers. A double glass transition was revealed on the blend by means of the second moment temperature dependence whereby the observed transitions are located in the glass transition temperature regions of the components of the blend. A chain penetration of one polymer into the region of the second one and mutual restriction of the chain mobility were concluded from the fact that the second moment $M_2$ of the measured spectra differs from that calculated using the additivity principle.*

*Some conclusions concerning the relaxation processes in the particular phases of the PP and blend were drawn from the temperature dependences of the mass fractions of the structural phases. The relaxation process related to the lower glass transition was found to be associated with activation of the hindered chain motion and then with its transformation into “free” motion. The lower crystallinity and the higher fraction of intermediate regions of the blend, compared with those of neat i-PP, were found.*

**Keywords:** *Isotactic polypropylene, EPDM rubber, polymer blend, glass transition, broad line $^1$H NMR.*

## 1. INTRODUCTION

Isotactic polypropylene is an important commodity polymeric material with favourable price/performance ratio and many applications. Intensive research has revealed a remarkable complexity of its crystalline structure. Isotactic polypropylene is a partly crystalline material with crystalline domains embedded in amorphous matrix. The glass transition temperature $T_g$ of the amorphous phase is about 260 K. The molecular architecture of isotactic polypropylene is the key to controlled superstructure formation and, consequently, to macroscopic mechanical properties, such as stiffness, toughness, drawability and optical clarity. Besides, the resulting morphology depends on thermal history, mechanical treatment and possible presence of nucleation agents. The application of neat isotactic polypropylene is limited by its tendency to brittle fracture at lower temperature. It has been found that blending with suitable ethylene-propylene rubbers can decrease the temperature of brittle transition and enhance the low-temperature toughness considerably [3]. In this case, the concentration and type of the rubber, distribution of rubber particles in the polypropylene matrix and interfacial adhesion are the factors controlling the resulting properties, toughness in particular. From the point of view of structural micromechanics, molecular motions in the individual structural components are responsible for the dissipation of mechanical energy of an impact and therefore also for macroscopic toughness.

The aim of this work is to study the relaxation processes in a blend of isotactic polypropylene with ethylene-propylene-diene terpolymer by broad-line $^1$H nuclear magnetic resonance. A special attention has been devoted to the interphase between the polypropylene and rubber components.

## 2. THEORETICAL

The shape and width of the broad line $^1$H NMR spectra depend on the magnetic dipole – dipole interactions that depend on the spatial configuration of hydrogen protons and their motions. To obtain information about structure and molecular motions of the investigated polymers the second moment $M_2$ was calculated from the measured NMR spectra. Furthermore, to get information about molecular motions in particular phases of the partially crystalline polymers, a decomposition of the spectra was made.

The broad line NMR spectrum measured on the partially crystalline polymers can be expressed as a superposition of three elementary spectra, $y_n$ (narrow), $y_m$ (middle) and $y_b$ (broad), which are related to the amorphous (micro – Brownian motion), intermediate (hindered motion) and crystalline (rigid chains) regions, respectively [1]. Usually, the narrow component $y_n$ is the Lorentzian function, the middle one $y_m$ is the product of the Gaussian and the Lorentzian and the broad elementary spectrum $y_b$ is derived from the measured low temperature spectrum. The spectrum $y_c$ calculated in terms of the elementary spectra $y_n$, $y_m$ and $y_b$ can be expressed by the equation

$$y_c = w_n\, y_n\, (\Delta B, \beta^L, B_{\mathrm{mod}}) + w_m\, y_m (\Delta B, \beta_m^L, \beta_m^G) + w_b\, y_b (\Delta B, S) \qquad (2)$$

in which $\Delta B = B - B_0$ is a difference between the applied magnetic field induction $B$ and the resonance magnetic field $B_0$. The relative mass fractions $w_i$ $(i = n, m, b)$ and parameters of the elementary spectra $\beta_i$ and $S$ were obtained by the least square method. Influence of the modulation field $B_{\mathrm{mod}}$ on the narrow elementary spectrum $y_n$ was considered in our previous computations [4].

## 3. EXPERIMENTAL

The broad line $^1$H NMR experiments were made on the samples of isotactic polypropylene, ethylene-propylene-diene terpolymer (further terpolymer only) and on PP/terpolymer blend containing 22.5% of the terpolymer.

Isotactic polypropylene is a commercial partially crystalline material Mosten 58.412 produced in the Czech Republic. The density of the polymer determined by the flotation technique is 899 kgm$^{-3}$. Crystallinity $X_c$ of the sample calculated by means of the density according to the formula

$$X_c = \frac{\rho - \rho_a}{\rho_c - \rho_a} \qquad (1)$$

with densities of crystalline ($\rho_c$ =936 kg m$^{-3}$) and amorphous ($\rho_a$ = 853 kg m$^{-3}$) domains [2] is $Xc = 0.55$.

The ethylene-propylene-diene terpolymer (EPDM rubber), the trade mark of which is Keltan 512, a product of DSM, the Netherlands, is an amorphous polymer. It contains 55, 41 and 4% of carbon atoms in ethylene, propylene and diene units, respectively. The glass transition of the terpolymer is about - 40 °C.

The *i*-PP/terpolymer blend contains 22.5 % of the amorphous terpolymer. The density of the blend is 892 kgm$^{-3}$.

The samples of *i*-PP and *i*-PP/terpolymer blend were prepared in the form of 4 x 10 x 50 mm plates and then they were cut into small pieces and inserted into a glass tube of a 10 mm diameter.

The broad line $^1$H NMR measurements were performed with the continuous wave spectrometer that operates at the resonant frequency $f_0$ = 14.1 MHz in the temperature range 160 – 370 K. The operating parameters of the spectrometer were the same within the whole temperature range. The sweep of the magnetic field $\Delta B / \Delta t = 10\ \mu T\ s^{-1}$, the time constant of the phase detector $\tau = 1 s$, the frequency of the sinusoidal modulating field $f_m = 35 Hz$ and the amplitude of the field was $B_m = 1 \times 10^{-4}\ T$.

## 4. RESULTS AND DISCUSSION

Three relaxation processes that are related to the rotation of CH$_3$ groups, segmental motion in noncrystalline regions and local motion in crystalline regions, can be detected on isotactic polypropylene in the broad temperature range by means of the broad line $^1$H NMR. Within the temperature range 200 – 370 K that we are interested in, only molecular motions related to the glass transition can be investigated. Different shapes of the spectra measured at temperatures far below, in the region of, and far above the glass transition can be seen in Fig. 1. The broad structurless spectrum detected at the low temperature reflects the rigid chain structure within both the crystalline and amorphous domains. On the other hand, besides the broad component also the narrow component appears in the spectrum detected at the high temperature. The narrow component arises from the mobility of the chain segments in amorphous regions and the broad one relates to the rigid chains in crystalline regions. The narrowed spectrum without appearance of the narrow peak was measured at 300 K.

The temperature dependences of the second moment $M_2$ calculated from the NMR spectra measured on the *i*-PP, terpolymer and blend are depicted in Fig. 2. In the case of *i*-PP the second moment takes up the values about 16x10$^{-4}$ T$^2$ at temperatures below 270 K. It is known that the CH$_3$ side group rotations and rigid main chains are responsible for this value. A drop of the second moment that is seen in the region 270 – 320 K is related to the glass transition. The plateau above this temperature range shows that an excitation of the motion within the whole noncrystalline part of *i*-PP takes place.

A deep drop of the second moment related to the amorphous terpolymer is observed above 200 K.

Apparently, the decrease observed up to 250 K is associated with the glass transition of terpolymer. An extrapolated zero value of the second moment $M_2$ is reached at 260 K.

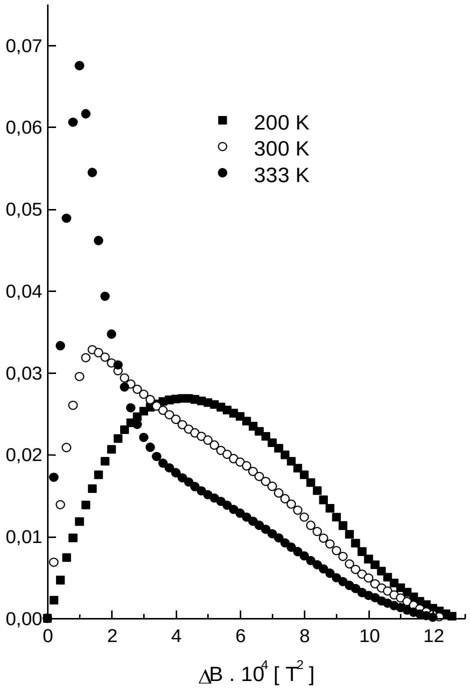

**Fig. 1** The derivations of the broad line NMR absorption spectra measured on i-PP at temperatures as indicated. Due to the symmetrical shape of the spectra only their halves are depicted.

The blend exhibits two steps of the second moment decrease in the temperature dependence of the second moment $M_2$. They differ in their slopes and are located in the glass transition temperature regions of the terpolymer and *i*-PP. The first drop is observed in the region of 230 – 260 K and a relaxation process in this temperature range seems to be managed by molecular motions within the terpolymer domains. The temperature region of the second decrease, which is observed above 260 K, is about the same as that revealed on *i*-PP. Then, the chain motion in the noncrystalline domains of *i*-PP could be responsible for relaxation process in this temperature range. Generally, in both discussed temperature regions each polymer component within the blend can influence the chain mobility of the other component. In order to estimate interactions of the *i*-PP and terpolymer chains the values of the second moment $M_2$ for the blend were calculated according to the equation

$$M_2 = (1-p)M_2^{(PP)} + p\,M_2^{(terpolymer)} \tag{3}$$

in which $p$ is a percentage of the number of the terpolymer hydrogen protons in the blend. With regard to the composition of the ethylene-propylene-diene terpolymer, the percentage $p$ takes up the value of 0.2205 that differs very slightly from the mass percentage of terpolymer in the blend. The solid line in Fig. 2 represents the temperature dependence of the second moment $M_2$ calculated according to Eq. (3). Besides the narrow temperature region above 260 K, in which no change of the second moment $M_2$ is supposed for both polymers, the experimental data are higher than calculated. The difference observed in the region 230 – 260 K can be explained by a restriction of the mobility of the terpolymer chains by the *i*-PP chains.

The higher crystallinity and/or lower chain mobility of the noncrystalline chains in the blend could explain discrepancy between experimental and calculated second moments in the region of high temperature plateau. On the other hand, the lower second moments for blend as compared with those for *i*-PP exclude the former possibility. Therefore, a penetration of the terpolymer chains into intermolecular regions of *i*-PP and hindering effect should be supposed.

The relaxation processes observed on the blend within the broad temperature range through the second moment decreases with different slopes provide an evidence of the existence of the double glass transition.

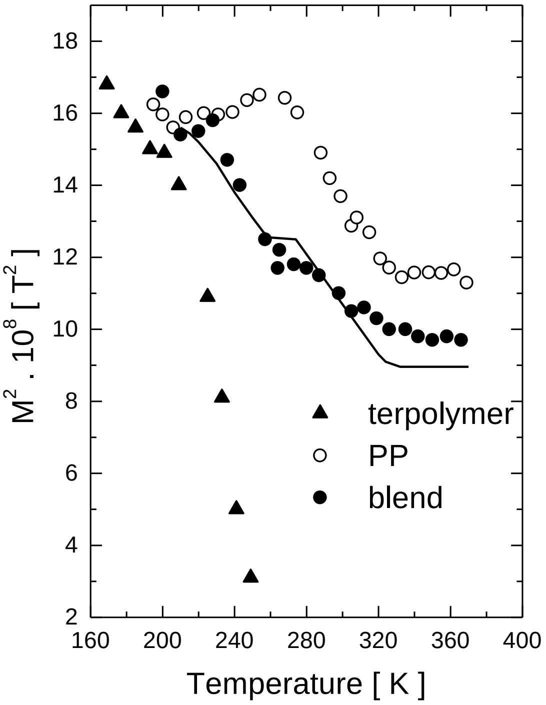

**Fig. 2** The temperature dependences of the second moment $M_2$. The solid line represents the values calculated according to Eq. 3.

The structure of partially crystalline PP is frequently interpreted as a three-phase system with amorphous, intermediate and crystalline phases.

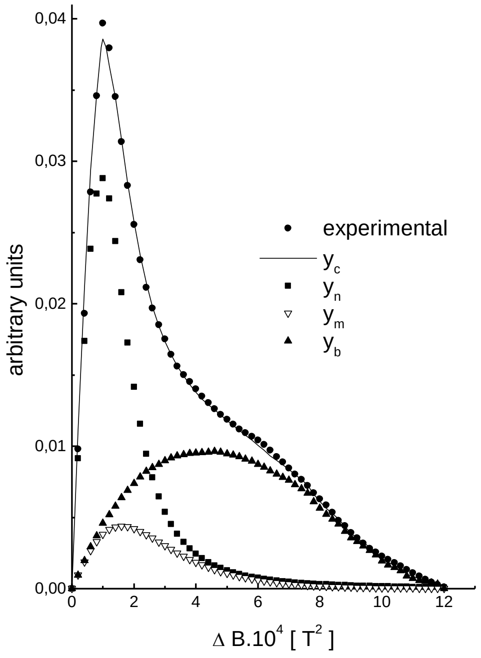

**Fig. 3** The decomposition of the NMR spectrum measured on *i*-PP at 321 K into elementary components as indicated. The computed parameters were as follows: $w_n = 0.23$, $w_m = 0.07$, $w_b = 0.70$, $\beta^L = 1.11 \times 10^{-4}\ T$, $\beta_m^L = 2.70 \times 10^{-4}\ T$, $\beta_m^G = 5.30 \times 10^{-4} T$, $S = 0.98$

Molecular processes in the particular phases of the polymer can be studied through the decomposition of the spectra according to Eq. (2). Fig. 3 provides illustration of the decomposition of the spectrum measured on *i*-PP.

As all chains of both the crystalline and non-crystalline regions are considered to be rigid below the glass transition temperature $T_g$, the mass fraction $w_b = 1$ in this temperature range. A drop of this value up to 0.65 is observed in the temperature range 275 – 325 K in the case of *i*-PP (Fig. 4). It is reasonable to suppose that molecular motion is activated within all noncrystalline domains at the temperatures far above $T_g$ and to consider the value 0.65 as the crystallinity of the *i*-PP sample. The increases of mass fractions $w_m$ and $w_n$ are observed simultaneously with the drop of mass fraction $w_b$. Then, above 325 K, the mass fraction $w_n$ that is related to the amorphous chains proceeds in its increasing at the expense of the small decrease of $w_m$. The values of the fractions at the highest temperatures exhibit that less than 10 % of the chains belongs to the intermediate regions with the hindered chain mobility and at least 25 % of the *i*-PP chains forms the amorphous domains.

It results from the dependences of the mass fractions in Fig. 4 that molecular motions in noncrystalline regions of the blend are excited at lower temperatures than are those in noncrystalline regions of *i*-PP. A decrease of $w_b$ is observed in two steps, the first is located at 220 - 260 K, and then the

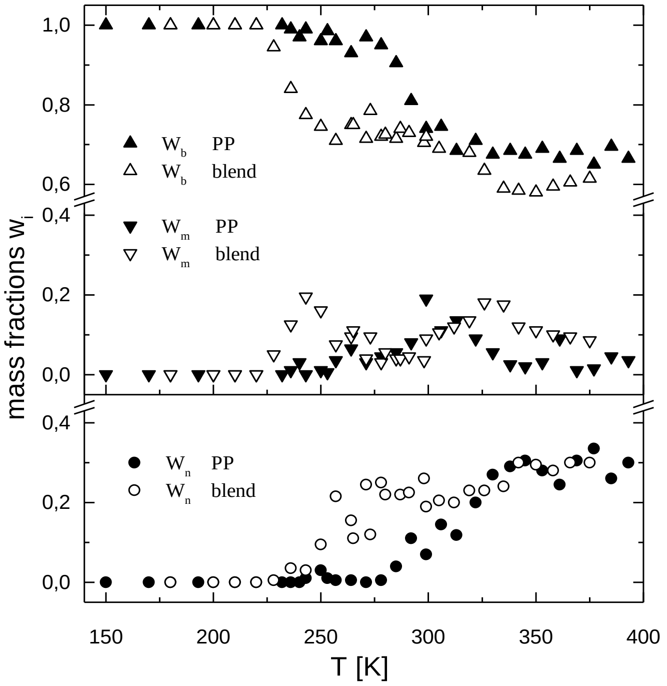

**Fig. 4** The temperature dependences of the mass fractions $w_i$ $(i = n, m, b)$ related to the samples of the *i*-PP and blend.

plateau can be seen above 260 K. The rise of the temperature in the mentioned temperature range results in the activation of motion of the chains, the amount of which is determined by the mass fraction $w_m$. The nature of this motion varies in the region of the mentioned plateau. An enhancement of the chain mobility can be deduced from the increase of the $w_n$ at the expense of $w_m$. It can be drawn from the data that this enhancement is due to a transformation of hindered motion of amorphous chains into free motion.

The second drop in the region of 300 – 330 K and the high temperature plateau are seen in the temperature dependence of $w_b$. The behaviour of all mass fractions in this temperature range is very similar to those calculated for *i*-PP. It is obvious from the data that crystallinity of the blend is lower and, on the other hand, the amount of the intermediate chains is higher than in *i*-PP.

## 5. CONCLUSIONS

The double glass transition was revealed in the blend composed of isotactic polypropylene and ethylene-propylene-diene terpolymer by broad line $^1$H NMR spectra. The relaxation process related to the lower glass transition is situated in the relaxation process temperature region of ethylene-propylene-diene terpolymer and that related to the upper one is located in the relaxation process temperature region of *i*-PP.

The interpenetration of the chains of the blend components was deduced from the analysis of the experimental data. The chains of each component of the blend effect the mobility of the chains of the other component. The *i*-PP chains hinder the motion of the terpolymer in the region of the lower glass transition and the mobility of the *i*-PP chains is affected by the terpolymer chains in the temperature region of the upper glass transition of the blend.

The relaxation process related to the lower glass transition is associated with activation of the hindered chain motion and then with its transformation into the “free” motion.

The relative mass fractions of the particular structural phases of both the PP and blend were determined in terms of decomposition of the broad line NMR spectra. Somewhat lower crystallinity and higher fraction of intermediate regions of the blend as compared with those of *i*-PP were found.

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## BIOGRAPHY

Dušan Olčák, associated professor, was born in 1950. He graduated at the Faculty of Natural Sciences of the P. J. Šafárik University in Košice and defended his PhD on Nuclear magnetic resonance study of modified polypropylene in 1986. His scientific research is focused on the physics of solid polymers

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