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Rotating frame ^{1}H n.m.r. spin–lattice relaxation studies of modified isotactic polypropylene

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Rotating frame ^{1}H n.m.r. spin–lattice relaxation times $T_{1\rho}$ have been used to study relaxation processes in partially crystalline polypropylene and polypropylene modified by a copolymer of ethylene and alkylaminoacrylate. Measurements were carried out within the temperature range of 250–420 K. Three relaxation times $T_{1\rho}$ were detected over the whole temperature range. α_c relaxation in the crystalline regions of the polymer, relaxation processes β(U) and β(L), associated with an apparent double glass transition, and α_a relaxation process, which was ascribed to a free reorientation of the whole chains in the amorphous regions, were observed by temperature dependences of these relaxation times. In addition to the α_c relaxation, another relaxation process with relatively low molecular mobility was found in crystalline regions. The influence of the polymer modifier on the observed relaxation processes greatly depends on its amount.

(Keywords: nuclear magnetic resonance; spin–lattice relaxation; modified polypropylene)

INTRODUCTION

In the past, considerable attention has been devoted to the research of polypropylene (PP), and many questions concerning its structure and molecular motion have been studied by n.m.r. techniques. Pulse n.m.r. experiments show that in the temperature range from the temperature of liquid nitrogen up to the melting point of partially crystalline PP, three notable relaxation processes, connected with the rotation of the CH_3 groups, glass transition and motion of the main chain groups of the crystalline regions, are effective. All these processes can be studied by means of the rotating frame spin–lattice relaxation times $T_{1\rho}$[1–4].

The individual relaxation processes can be influenced by several factors. Different chemical and physical modifications, such as the change of molecular mass, addition of a suitable polymer modifier, preparation of polymer blends, spinning in different conditions, and stretching, produce some changes of the molecular motions. One of these modifications was studied in our previous work[3]. Using the spin–lattice relaxation times T_1, the effect of polymer addition on both the relaxation process connected with the CH_3 group rotation and the β relaxation was investigated.

The technique of the rotating frame spin–lattice relaxation times $T_{1\rho}$ is, owing to the low frequency and the restriction of spin diffusion over the much shorter $T_{1\rho}$ times, more sensitive to the structural changes and molecular motions than that of the laboratory frame spin–lattice relaxation times T_1. By means of the $T_{1\rho}$ times we try to explain the influence of polymer additive on the molecular processes in PP which are effective in the temperature region above the glass transition of PP.

EXPERIMENTAL

The pulse ^{1}H n.m.r. measurements were performed on the PP sample (Mosten D3) and on two samples of modified PP with different amounts of the polymer modifier.

Crystallinity, flow index and number-average molecular weight of unmodified PP were 0.50, 2.50 g min^{-1} and 184.6 kg mol^{-1}, respectively.

The polymer modifier, PFDA 522, is an ethylene aminoalkylacrylate copolymer of predominantly amorphous character[5]. The melting temperature, detected by differential scanning calorimetry, was 360 K.

Samples of the modified PP were prepared by melting and blending Mosten D3 and polymer modifier PFDA 522 at 473 K. The modified samples are designated PP-X, where X (the percentage of PFDA 522 in modified PP) $=2$ and 8. All samples were provided by the Research Institute of Man-Made Fibres in Svit (Slovakia).

Relaxation times $T_{1\rho}$ were detected by the spin-locking technique[6] at the resonant frequency $f_0 = 30$ MHz, high frequency magnetic field amplitude $B_1 = 1.68$ mT over the

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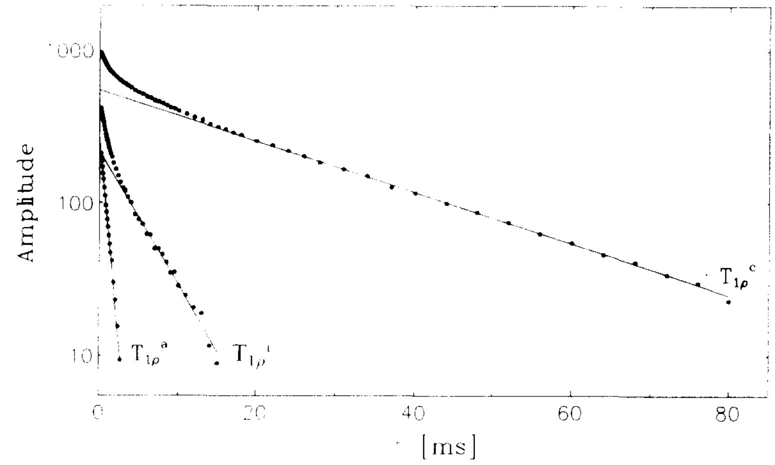

Figure 1 The $T_{1\rho}$ relaxation curve measured on PP-2 at 298 K and its decomposition into three components. The relaxation times $T^{c}_{1\rho}=25.8$ ms, $T^{i}_{1\rho}=4.95$ ms and $T^{a}_{1\rho}=0.81$ ms and intensities $p_c=0.53$, $p_i=0.21$ and $p_a=0.26$ correspond to the individual components. For the minimization process, a method similar to the Marquardt method[28] was used, which is a combination of the Newton and the gradient method. Reliability of decomposition is guaranteed by the convergence stability of minimization, which is stable only when the number of the fitted components does not exceed the number of the real components. The initial values of the relaxation times and intensities entering into the fitting procedure were estimated by the graphical interactive linear regression

temperature range 250–420 K. The locking pulse length could be set from 0.2 to 120 ms. To reach reliable results, each relaxation curve was detected by at least 60 points, and every point is an average of 10 measurements. Experiments were carried out by the computer-controlled n.m.r. spectrometer constructed in our department by Dr L. Ševčovič and his co-workers[7]. As in some previous papers[3,8], three $T_{1\rho}$ components were obtained from the measured non-exponential relaxation curves. The decomposition of the relaxation curve is shown in *Figure 1*.

RESULTS AND DISCUSSION

The present rotating frame spin–lattice relaxation time $T_{1\rho}$ measurements were carried out on unmodified PP and on samples PP-2 and PP-8 of modified PP. In all cases, the relaxation curves were decomposed into three exponentials over the whole temperature range. The relaxation times and intensities corresponding to the individual components are denoted as $T^{c}_{1\rho}$, $T^{i}_{1\rho}$, $T^{a}_{1\rho}$ and p_c, p_i, p_a, whereby the designation is related to the three-phase model of the partially crystalline polymers with crystalline, intermediate and amorphous phases, respectively[3,4,9]. The three-phase structure of the partially crystalline PP was also observed by means of the spin–spin relaxation times T_2 [10–15] and the broad-line n.m.r. spectra[16,17].

The temperature dependences of the relaxation times $T_{1\rho}$ measured on unmodified PP undergo several minima (*Figure 2, Table 1*) corresponding to the relaxation processes in the structurally different regions of PP. In agreement with the previous work, in the temperature region close to the minimum $T^{c}_{1\rho,\min}$ at temperature 382 K this dependence is associated with the α_c relaxation process in crystalline regions of PP[1,2,4]. A broad and flat minimum of the $T^{i}_{1\rho}$ dependence is observed in the temperature region from 300 to 350 K. The relaxation process corresponding to this minimum is related to the upper glass transition and so it has been ascribed to the PP intermediate chains, the motion of which is restricted by crystallites. The minimum at 309 K is related to the

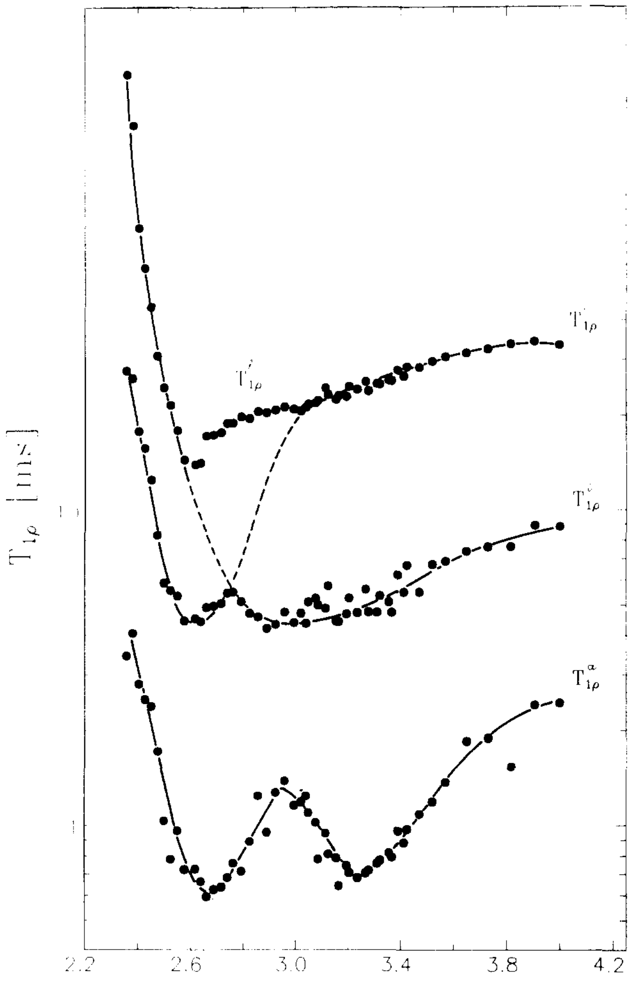

Figure 2 Temperature dependences of the rotating frame spin–lattice relaxation times $T_{1\rho}$ measured on unmodified PP. $T^{c}_{1\rho}$, $T^{i}_{1\rho}$ and $T^{a}_{1\rho}$ relate to the crystalline, intermediate and amorphous regions of PP, respectively. The specification of the $T^{1}_{1\rho}$ is given in the text

Table 1 Positions of minima T_{min} and $T_{1\rho,\mathrm{min}}$ of the temperature dependences of the rotating frame spin–lattice relaxation times $T_{1\rho}$ related to the different relaxation processes in PP, PP-2 and PP-8

	α_c relaxation		α_a relaxation		β(U) relaxation		β(L) relaxation	
Sample	T_{min} (K)	$T^{c}_{1\rho,\mathrm{min}}$ (ms)	T_{min} (K)	$T^{a}_{1\rho,\mathrm{min}}$ (ms)	T_{min} (K)	$T^{i}_{1\rho,\mathrm{min}}$ (ms)	T_{min} (K)	$T^{a}_{1\rho,\mathrm{min}}$ (ms)
PP	382	4.30	375	0.60	335	4.30	309	0.70
PP-2	380	4.70	375	0.60	325	4.10	305	0.70
PP-8	330	4.35	355	1.35	305	4.50	305	0.66

lower glass transition in the amorphous regions of the polymer investigated, and so it reflects the relaxation processes associated with the motion of the chain segments free of the restriction by crystallites[4,18,19]. Next, we will denote the relaxation processes connected with the upper and lower glass transitions as β(U) and β(L), respectively. The $T^{a}_{1\rho}$ temperature dependence also reveals the relaxation process in the amorphous regions of PP, which occurs in the temperature region of the α_c relaxation process. Because of both the temperature and structural regions we denote it the α_a relaxation process.

Our assignment of the α_c and β(L) relaxation process is also supported by the relaxation map of isotactic PP. From the condition $\omega_1\tau_c = 0.5$ (refs. 20, 21) it follows that the correlation frequency f_c of the molecular motion at temperatures corresponding to $T_{1\rho}$ minima is 1.43×10^5 Hz ($f_c = 1/2\pi\tau_c$). This frequency, together with temperature T_{min} of the α_c and β(L) relaxation processes for PP (*Table 1*), fits the data determined from dielectrical, mechanical, electron spin resonance and n.m.r. experiments[22].

The temperature dependences of the spin–lattice relaxation times $T_{1\rho}$ measured on modified sample PP-2 (*Figure 3, Table 1*) are almost the same as those for unmodified PP. In both cases two common problems exist.

Problem 1. The question of the molecular mechanism of the α_a relaxation process should be answered. We suppose the amorphous transition under consideration corresponds to that which was observed by several methods in amorphous, atactic polystyrene; it was denoted $T_{l,l}$ indicating the liquid–liquid transition from the amorphous state characterized by the hindered chain rotation in consequence of the interactions with the surrounding chains to another amorphous state, in which the relatively free rotation of the whole chains can occur[19,23]. Overlapping of the molecular process, discussed above, with the relaxation process in the crystalline regions makes it difficult to observe it in partially crystalline polymers. We suppose that splitting of the $T_{1\rho}$ relaxation curves into three components made it possible to reveal this process in partially crystalline PP. However, it would be necessary to carry out other $T_{1\rho}$ experiments on PP samples with different molecular mass in order to confirm our standpoint[19].

Problem 2. The relaxation times $T^{c}_{1\rho}$ and $T^{i}_{1\rho}$ measured in the temperature range ≈340–385 K could be expected to follow the dashed lines in *Figures 2* and *3* (ref. 2). But instead of the rate increase of the energy transport from the spin system of the crystalline region of the polymer to the lattice, a drop of p_c and rise in p_i are observed, as shown in *Figure 4* for PP-2. The spin diffusion producing the energy transport from the spin system of the crystalline regions into that of intermediate regions may be one of the reasons for the considered changes of intensity. In that case the increase of $T^{i}_{1\rho}$ and decrease of $T^{c}_{1\rho}$ should be observed in the measured temperature dependences. Obviously, there is a disagreement between the dependences of the relaxation times $T_{1\rho}$ and the concept presented. So, there is the question of interpretation of the points of the longest $T_{1\rho}$ components which were attributed neither to the temperature dependence $T^{c}_{1\rho}$ nor to $T^{i}_{1\rho}$. Two relaxation processes within crystalline regions of PP with different relaxation times could give an explanation. We assume that one of them has a relaxation time comparable in this temperature range with that of $T^{i}_{1\rho}$ and the other one

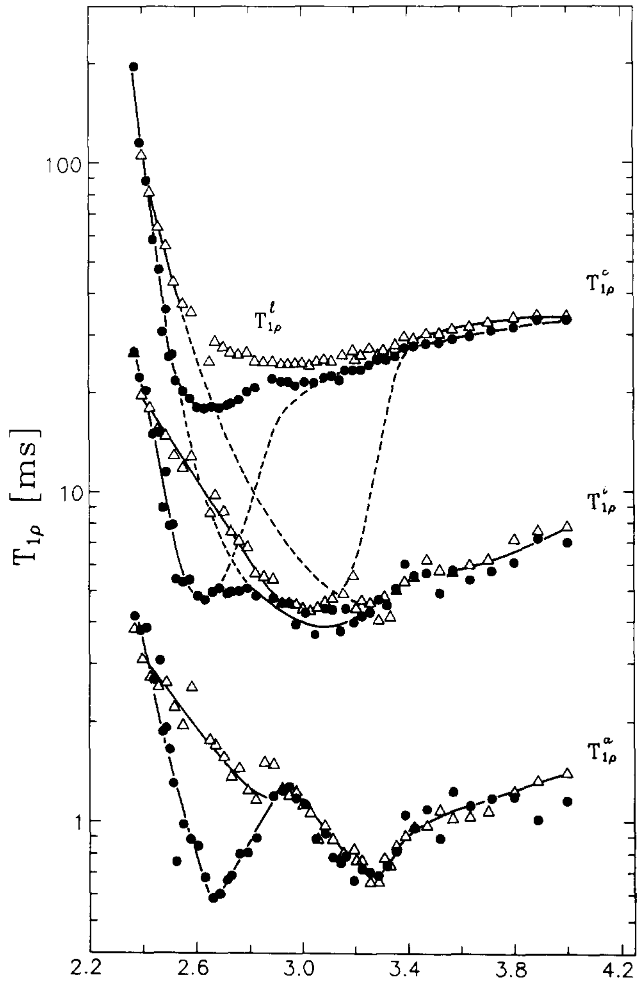

Figure 3 Temperature dependences of the rotating frame spin–lattice relaxation times $T^{c}_{1\rho}$, $T^{i}_{1\rho}$ and $T^{a}_{1\rho}$, measured on PP-2 (●) and PP-8 (△)

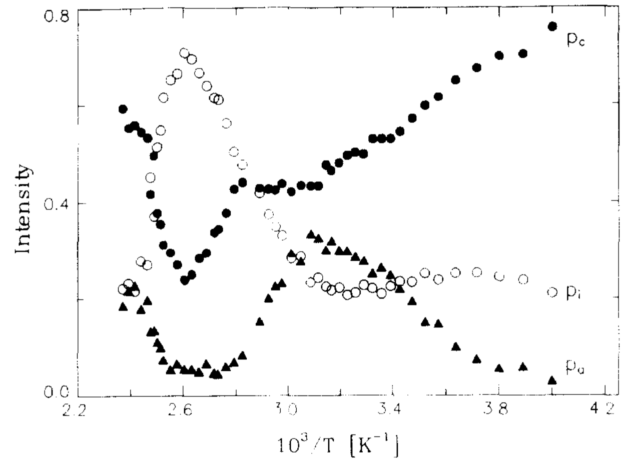

Figure 4 Temperature dependences of the intensities p_c, p_i and p_a associated with the rotating frame spin–lattice relaxation times $T^c_{1\rho}$, $T^i_{1\rho}$ and $T^a_{1\rho}$, respectively, measured on the sample PP-2. The intricate courses of the intensities reflect the multiple-phase structure of the polymer, molecular motions in the different phases, spin diffusion processes and overlapping minima in different phases. Owing to these phenomena only the intensity p_c measured at the highest temperature corresponds with the crystallinity of the sample

remains with an essentially longer relaxation time $T^l_{1\rho}$. The changes of intensities p_c and p_i, mentioned above, are in agreement with that interpretation. Also, without a close specification of the relaxation process we can state that the temperature dependence of the $T^l_{1\rho}$ relaxation times is related to the process with relatively low molecular mobility. Two transitions in the crystalline regions of PP were also found with the techniques of thermal expansion and thermally stimulated current[24].

From *Figure 3* it is obvious that the amount of polymer modifier considerably influences the relaxation behaviour of the polymer. As we have stated, the $T_{1\rho}$ dependences for PP-2 are generally in agreement with those measured on unmodified PP. We can conclude that neither such a small amount (2 wt%) of modifier nor melting and recrystallization have a substantial influence on the relaxation behaviour. The expressive changes were observed on the sample PP-8. The minimum related to the α_c relaxation is at 300 K, i.e. at a temperature 50 K lower than that of PP-2. The $T^i_{1\rho}$ minimum connected with the β(U) process occurs at the same temperature as the $T^a_{1\rho}$ minimum associated with the β(L) process. The temperatures at which the β(L) process is observed are practically the same for all samples investigated (*Table 1*). The α_a relaxation process in PP-8 is less expressive, and appeared more or less as a shoulder on the high temperature side of the minimum related to the β(L) relaxation process. As we can see from *Figure 3*, the dependences are rather complicated and on that account the temperatures at which some relaxation processes occur cannot be unambiguously determined. We believe that they are as in *Table 1*; however, the substantial point from which we conclude this is that the dependences for PP-2 are very close to those for PP, and on the other hand there are great differences between temperature dependences for PP-8 and those for PP and PP-2.

With regard to the course of the $T_{1\rho}$ temperature dependences measured on the modifier (*Figure 5*), and the relatively small content of this polymer in PP-8, we can state that changes mentioned above are caused by the modification of PP and they do not reflect the existence of the casual domains of the pure modifier in PP-8.

It is known from earlier work that the α_c process is intralamellar, and the temperature at which it is observed increases depending on the fold length growth of the chains and also on some other factors such as thermal treatment and crystalline defects[19]. The possible mechanisms of the α_c relaxation can be those denoted as the concerted helix transition and defect translation transition[25] introduced to explain the discrete jump motion observed by two-dimensional n.m.r. on isotactic PP[26]. In the former case, the activation energy should increase linearly with the chain length, and in the latter the activation energy is independent of the chain length. It was stated that only the defect translation transition mechanism is convenient to explain the mentioned jump motion in crystals of isotactic PP[25]. It is questionable, however, to what extent the motions observed in the scale of milliseconds and the results of the molecular mechanics approach can be applied to the present case under conditions of higher frequency. The lamellar sizes D established by the wide-angle X-ray analysis are independent of the percentage of the modifier (*Table 2*), and the reasons for changes observed in $T_{1\rho}$ temperature dependences cannot be interpreted by means of the fold length. The apparent activation energy E_a of the α_c relaxation process in PP-8, estimated from the slope on

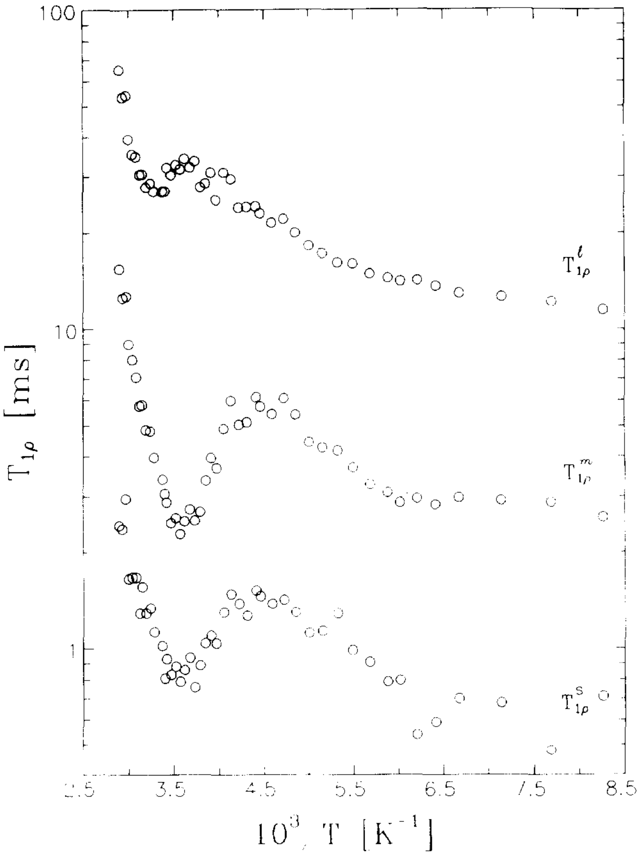

Figure 5 Temperature dependence of the spin-lattice relaxation times $T^l_{1\rho}$ (long), $T^m_{1\rho}$ (middle) and $T^s_{1\rho}$ (short) measured on modifier PFDA-522 over the temperature range 120–350 K. In the temperature range above the glass transition of PP, which is of interest, these dependences have minima at the temperatures $T^l_{min}=300$ K, $T^m_{min}=280$ K and $T^s_{min}=280$ K

Table 2 Crystallinities (X_c), lamellar thickness (D) and apparent activation energy (E_a) of the α_c relaxation process

Sample	X_c	D (nm)	E_a (kJ mol^{-1})
PP	50.2	12.65	110
PP-2	58.8	12.49	80
PP-8	59.1	12.32	25

the high temperature side of the $T^{c}_{1\rho}$ minimum, is essentially lower than those of PP and PP-2 and, as mentioned above, the expressive temperature shift of the minimum $T^{c}_{1\rho}$ was observed. Several phenomena can account for that behaviour. The crystalline defects arising from the crystallization of PP in the presence of another polymer can result in a fall of the energy barrier of the reorientational jumps. Besides, the drop of the slope, from which the apparent activation energy was estimated, can come from the broader distribution of the correlation times[27].

From the $T^{i}_{1\rho}$ temperature dependences, the polymer modifier is shown to have considerable effect on the chain motion in the intermediate regions. The shift of the $T^{i}_{1\rho}$ minimum towards the lower temperatures provides some evidence for the increase of the molecular mobility. We suppose that the polymer modifier PFDA 522, the chains of which (assuming a relatively low glass transition temperature of 225 K) are seen to be more flexible than those of PP, blends with PP on the molecular level. The interaction of the intermediate PP chains (tie molecules, loops) with the polymer modifier macromolecules can result in the increase of their mobility.

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