N.m.r. studies of molecular motion in modified polypropylene

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N.m.r. proton spin-lattice relaxation measurements were performed on modified polypropylene at 88 MHz over a wide range of temperatures. The modification by ethylene acrylate copolymer produced compatibility between the polymer fibres and the dyestuff molecules. The influence of the modifier on the segmental motion and on the methyl group relaxation regions was studied, and a slight shift of the high frequency glass transition to lower temperatures and a change in the form of T_1 minima were found. Both effects are discussed in terms of a qualitative n.m.r. relaxation model.

(Keywords: ^{1}H nuclear magnetic resonance; relaxation; modified polypropylene; glass transition; methyl group reorientation)

INTRODUCTION

In recent years considerable attention has been devoted to research into compatible polymer blends. Frequently they were studied using n.m.r. methods, and it was shown that nuclear magnetic relaxation plays an important role for obtaining information about molecular motions and structural changes on a molecular level[1-6].

Another important problem in this field is the surface dyeing of the polypropylene fibres. The fibres prepared from pure polypropylene (PP) are not suitable for this purpose because they have a relatively compact structure and the chains of PP do not comprise of groups which are capable of binding securely the dyestuff molecules. It has been shown[7] that an effective solution of this problem is to modify PP with additives which alter the structure of PP so that the dyestuff molecules penetrate under the fibre surfaces and bind to its functional groups. For this purpose an ethylene acrylate copolymer with amine groups was chosen. The questions about the changes of the molecular motion processes and of the structure should be answered by the study of the temperature dependence of the spin-lattice relaxation time T_1.

THEORETICAL

The spin-lattice relaxation time T_1 characterizes a process of the establishment of the equilibrium between a spin system and its surroundings (lattice). It depends on the local, time dependent dipolar magnetic fields produced by the motion of neighbouring spins which cause transitions between nuclear spin states.

For the interpretation of the temperature dependence of the spin-lattice relaxation times the theory of magnetic relaxation is well known[8].

As a first approximation we used the isotropic rotational diffusion model considering a distribution of the correlation times[9].

This is possible, because the molecular motions in polymers are not uniform (distribution of conformations and configurations). But it is an open problem which distribution function has the best physical relevance. We have chosen the Cole–Davidson function[10,11].

EXPERIMENTAL

All samples were granulated materials. For the measurements pure PP and two blends with 4 (PP4) and 8 (PP8) wt% of modifier were used. The PP used was an isotactic polymer produced in Slovnaft Bratislava (TATREN 430) with a density of 888 kg m^{-3} and a crystallinity of about 0.5. The melting T_m and the glass transition T_g temperatures were 438 K and 268 K, respectively. The modifier was predominantly amorphous with a density of 904 kg m^{-3}. A broad glass transition and melting region were detected by differential scanning calorimetry (d.s.c.) at 226 K and 353 K, respectively.

Modified PP was prepared by melting both components at 473 K. To prepare samples suitable for n.m.r. measurements they were evacuated to remove the atmospheric oxygen and then sealed. The measurements of the spin-lattice relaxation time $T_1(^1\mathrm{H})$ were performed on the SXP 4-100 pulse spectrometer (Bruker Physik AG) with the well-known pulse sequence (π)-τ-$(\pi/2)$ at 88 MHz and in a temperature region from 120 K up to 420 K.

RESULTS AND DISCUSSION

From recent work dealing with the study of PP by n.m.r. relaxation it is known that the temperature dependence of the spin-lattice relaxation time has two minima. A high temperature minimum corresponds to the cooperative motion of the chains in the amorphous regions of the polymer corresponding to the glass transition (β process) and a low temperature minimum is connected with the rotation of the CH_3 groups[11,12]. The dependence of T_1 vs. temperature for our PP is shown in *Figure 1*.

Since PP forms the predominant part of the polymer blends (the relative proton intensities of PP component is

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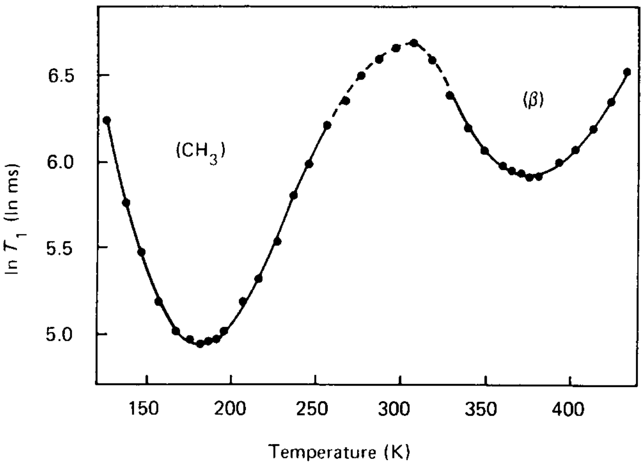

Figure 1 Temperature dependence of spin-lattice relaxation times (T_1) at 88 MHz of pure PP. The solid lines were calculated with parameters in text

96.7% for PP4 and 93.4% for PP8) our attention has been directed at the modified motion of PP chains.

During the blending process by melting and mechanical mixing we expect in principle that the modifier can be inserted into the structure of PP in one of the two following manners:

1. Both PP and modifier regions separated from one another can be present within the blend, and there are no interactions among macromolecules of the two components.
2. The modifier can be dispersed in the amorphous regions of PP in such a manner that the microdomains of the modifier interact strongly with the PP matrix.

In the first case a separated relaxation behaviour exists, but in the second only one averaged relaxation process. Because in our samples the concentration of modifier is too small to observe this different behaviour, we concentrated our studies on the influence of the modifier upon the segmental motion and the local CH_3 group reorientation which are reflected in the minima of the averaged T_1 times.

Figure 2 presents the temperature dependence for the pure PP and the two blends in the region of the dynamic glass transition. The dependence for pure PP has a relatively simple shape with one minimum at 380 K. In the case of the blends we see a shift by about 10 K of the minima to lower temperatures and a shoulder at the position of the minimum of pure PP. Such a course of the dependence in which there is a double minimum may be expected in a system with two different dynamic molecular processes for instance.

To evaluate whether or not this is some qualitatively new molecular process in the amorphous regions of modified PP we have calculated the parameters depending on the molecular motion of the polymer. By means of the Arrhenius relation $\tau_c = \tau_\infty \exp(E_a/RT)$ and a computer fitting procedure we have determined the activation energy E_a of the considered molecular process, the width parameter β of the Cole–Davidson distribution, the preexponential factor of Arrhenius relation τ_∞ and the constant C, which is related to the second moment of the n.m.r. spectrum. The calculations show that the values of these parameters for pure PP and both blends are practically the same because they vary only within intervals $E_a \sim (38.2\text{–}38.4)\,\text{kJ mol}^{-1}$, $\tau_\infty \sim (0.98\text{–}1.04) \times 10^{-14}\,\text{s}$, $\alpha \sim (0.53\text{–}0.56)$, $C \sim (0.44\text{–}0.46)\ 10^9\,\text{s}^{-2}$ and they are consistent with ref. 11. The shift of the minima by about 10 K towards lower temperatures can be explained by quasi plastification process caused by the more flexible modifier molecules. They are capable of penetrating into the amorphous regions of PP and influencing the molecular motion in the intermediate (im) and amorphous (am) phase in the sense of the three-phase structural model for partially crystalline polymers (amorphous, hindered amorphous or intermediate and crystalline phase)[13].

These phases are reflected for instance in the $T_{1\rho}$ relaxation behaviour (*Figure 3*)[12,17]. Consequently a decoupling of glass transition occurs. A possible model for the molecular description of this effect is presented by Boyer[14]. In this model the upper glass transition $T_g(U)$ corresponds to the amorphous material restrained by crystallites and the lower glass transition $T_g(L)$ corresponds to amorphous material relatively free from these restraints. As a rule $T_g(U) \approx 1.1\text{–}1.3 T_g(L)$ for frequencies in the region <1 Hz. But in our high frequency case of the T_1 relaxation ($\nu \approx 10^8$ Hz) we observed only a difference of about 10 K. It is very probable that we unmasked the double glass transition in PP by our modification procedure and measurement conditions. The slight decrease of the T_1 values at the minimum for the modified samples can be discussed in the same way as in ref. 15.

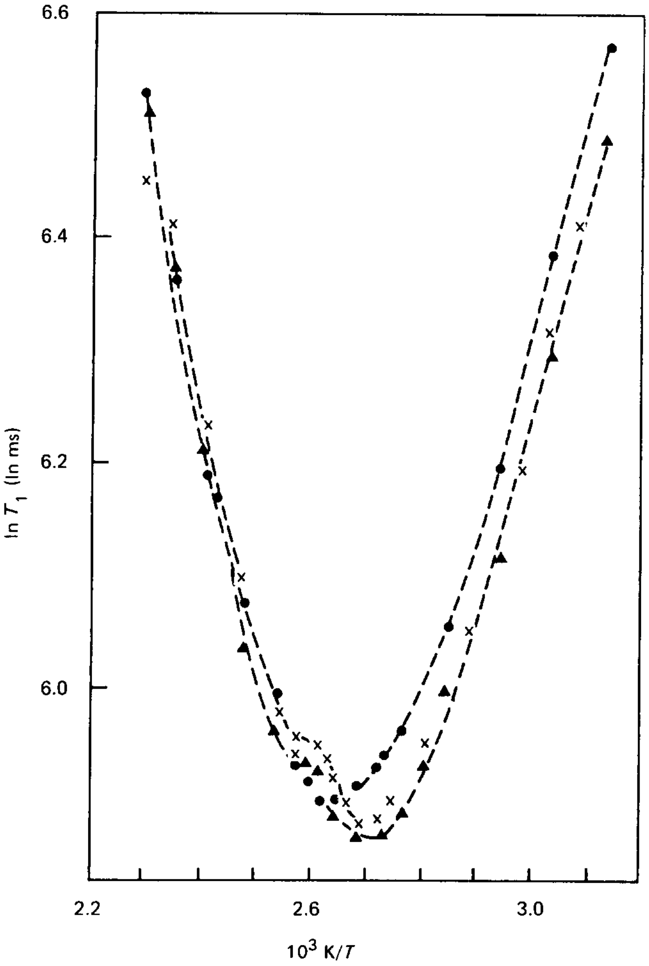

Figure 2 Temperature dependence of spin-lattice relaxation times (T_1) at 88 MHz of pure PP and both blends measured in the temperature region of β process ((●): pure PP; (×): PP4; (▲): PP8)

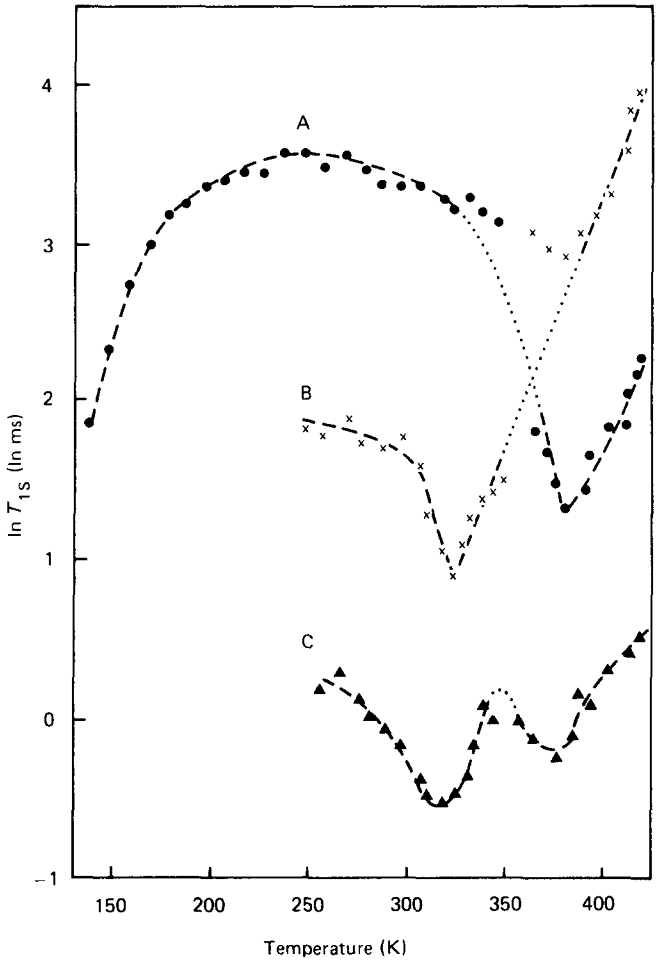

Figure 3 Temperature dependence of the rotating frame relaxation times ($T_{1\rho}$) for pure PP measured with spin-locking field $B_1 = 1$ mT. (●): $T_{1\rho}$ values correspond to the short component in free induction decay (FID) and $T_{1\rho}$ values (×), (▲) correspond to the long component in FID. Curve A: crystalline; curve B: amorphous; and curve C: intermediate relaxation regions

The influence of the modifier molecules on the methyl group relaxation can be seen in *Figure 4*. Two aspects are of interest:

1. with an increasing content of modifier the $T_{1\mathrm{min}}$ values are greater.
2. in modified PP a small shoulder appears at the high temperature site of the minimum.

We presume that the hindered rotation of the methyl groups is modified by the strong interactions with the modifier molecules. Consequently, two different surroundings exist for the CH_3 groups of PP. A broader distribution of the correlation times for this local motion process can describe this change[15]. Our fitting calculations performed in the same manner as for the segmental motions gave the results in *Table 1*, which agree well with these ideas and with results of ref. 11.

For pure PP we have calculated the second moment for the case of isotropic reorientation of the CH_3 groups with the experimental value of $T_{1\mathrm{min}}$ (120 ms), the width parameter α ($\alpha = 0.50$) and the correlation time τ_c calculated from the condition for the minimum $\omega_0\tau_c = 0.62$. The value $M_2^{\mathrm{exp}} = 1.52 \times 10^{10}$ s^{-2} which in the limits of accuracy is equal to the second moment calculated including the intraproton distance $r_{\mathrm{H\text{-}H}} = 1.786 \times 10^{-10}$ m of the methyl group ($M_2(CH_3)^{\mathrm{cal}} = 1.57 \times 10^{10}$ s^{-2}).

Spin diffusion can also influence the T_1 values at the minimum of the modified PP analogous to other polymer blends[5], but this is not sufficient to explain the increasing $T_{1\mathrm{min}}$ values with increasing concentration of modifier in PP. Thus this first simple qualitative discussion (without consideration of the anisotropy of the CH_3 groups reorientations) gives a satisfying interpretation of the observed effects in our PP blends.

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Table 1 Fitting data for the minima of the methyl group relaxation

	E_a/kJ mol^{-1}	α	τ_∞ (s)
PP (pure)	11.78	0.48	8.3×10^{-13}
PP8	11.75	0.53	8.9×10^{-13}

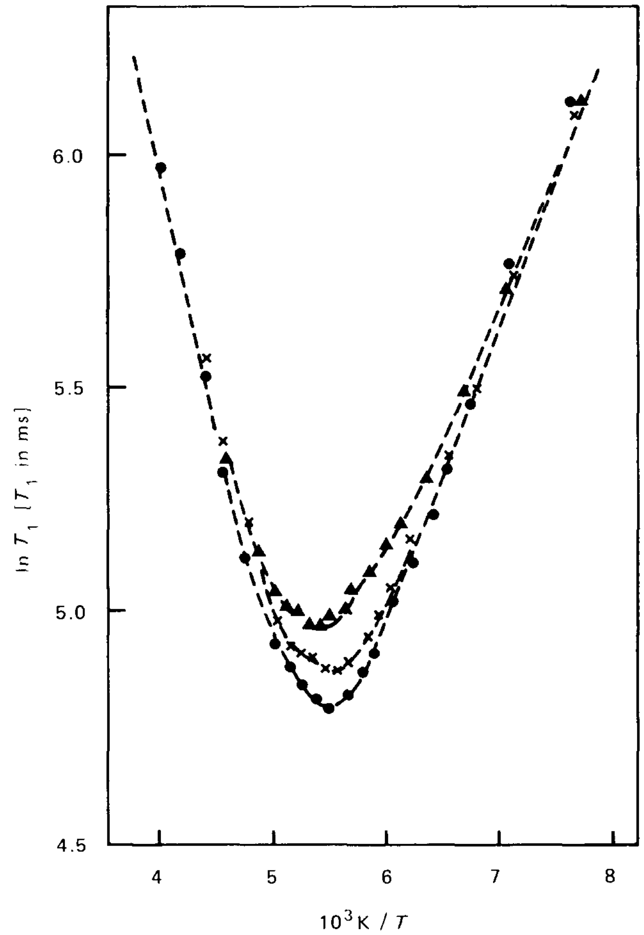

Figure 4 Temperature dependence of spin-lattice relaxation times (T_1) at 88 MHz of pure PP and both blends measured in the temperature region of methyl groups relaxations ((●): pure PP; (×): PP4; (▲): PP8)

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