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NMR STUDIES OF STRUCTURE AND MOLECULAR MOTION IN POLYPROPYLENE

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Using spin-lattice relaxation times in laboratory (T_1) and rotating ($T_{1\varrho}$) frames the molecular motion and the structure of the partially crystalline polypropylene have been investigated. Measurements of both spin-lattice relaxation times have been performed on the granulated sample in the 140—430 K temperature range. The temperature dependence of the T_1 has two minima corresponding to the glass transition of the polymer and to the rotation of the CH_3 groups, respectively. In the rotating frame spin-lattice relaxation time experiments in the temperature range above 250 K three relaxation times $T_{1\varrho}$ have been observed. The individual relaxation times are connected with crystalline, intermediate and amorphous phases of the polymer. The minima of the temperature dependences of the considered relaxation times reflect the α-relaxation process in crystalline regions and the double glass transition in noncrystalline regions of the studied material. The β-relaxation process connected with the glass transition in intermediate regions is shifted about 10 K toward higher temperatures as compared with the β-process in amorphous regions.

I. INTRODUCTION

In solids the spin-lattice relaxation in the rotating frame is substantially faster than that in the laboratory frame. Consequently, the spin-diffusion processes do not effect the rotating frame spin-lattice relaxation times $T_{1\varrho}$ to such an extent as the laboratory frame relaxation times T_1. In heterogeneous systems as, e.g., partially crystalline polymers in many cases especially at higher temperatures during $T_{1\varrho}$ measurements there has not been observed any formation of the spin temperature equilibrium between phases of a heterogeneous system. In such experiments it is possible to detect the flow of the energy from individual spin systems corresponding to the given phases to the lattice. Therefore the experimental data $T_{1\varrho}$ in comparison with the data T_1 reflect better the heterogeneity of the investigated partially crystalline polymer.

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In the present work in measurements of the T_1 on polypropylene at every temperature one relaxation time was observed [1, 2]. At the $T_{1\varrho}$ measurements at temperatures lower than 200 K only one relaxation time was observed. Above this temperature two relaxation times $T_{1\varrho}$ were detected. They were ascribed to crystalline and amorphous phases of the polymer, respectively [2, 3]. Unlike these works we have obtained three spin-lattice relaxation times $T_{1\varrho}$. We have briefly mentioned the temperature dependences of these relaxation times in [4]. Now we shall try to interprete these temperature dependences on the basis of established concepts of the structure and the molecular motion.

II. THEORETICAL PART

To interprete the spin-lattice relaxation times T_1 the theory of nuclear magnetic relaxation was developed [5]. This theory is frequently applied also to estimating experimental data obtained on polymers. A relatively simple relation between the spin-lattice relaxation time T_1 and the correlation time of molecular motion τ_c was derived. This dependence can be expressed in the form

$$\frac{1}{T_1} = \frac{2}{3} \mathrm{M}_2 \left(\frac{\tau_c}{1 + \omega_0^2 \tau_c^2} + \frac{4\tau_c}{1 + 4\omega_0^2 \tau_c^2} \right), \tag{1}$$

where M_2 is the second moment for the rigid lattice and ω_0 is the circular resonant frequency.

By extending this theory to the rotating frame spin-lattice relaxation time the relation

$$\frac{1}{T_{1\varrho}} = \frac{1}{3} \mathrm{M}_2 \left(\omega_e^2 \frac{3\tau_c}{1 + 4\omega_e^2 \tau_c^2} + \frac{5\tau_c}{1 + \omega_0^2 \tau_c^2} + \frac{2\tau_c}{1 + 4\omega_0^2 \tau_0^2} \right) \tag{2}$$

was obtained [6]. The effective circular frequency ω_e is determined by the amplitude of the r. f. field B_1 and by the local dipol magnetic field B_L and it is expressed according to the relation

$$\omega_e = \gamma (B_1^2 + B_L^2)^{1/2} \tag{3}$$

where γ is the gyromagnetic ratio of the resonant nuclei. In the case of polymers at higher temperatures there can be $B_L \ll B_1$ and then we can substitute for ω_e the circular frequency $\omega_1 = \gamma B_1$. Since in the experiments the condition $\omega_0 \gg \omega_1$ is always fulfilled the expressions with ω_0 in eq. (2) can be omitted and the $T_{1\varrho}$ can be written as

$$\frac{1}{T_{1\varrho}} = M_2 \frac{\tau_c}{1 + 4\omega_1^2 \tau_c^2}. \tag{4}$$

The spin-lattice relaxation times T_1 and $T_{1\varrho}$ have the minimum when

$$\omega_0 \tau_c = 0.62 \ (T_{1,min}), \quad \omega_1 \tau_c = 0.5 \ (T_{1\varrho,min}) \tag{5a, b}$$

and

$$T_{1,min} = \omega_0 / M_2, \quad T_{1\varrho,min} = 4\omega_1 / M_2. \tag{6a, b}$$

From the eq. (5a, b) it results that the relaxation processes are most effective when the correlation frequencies of the molecular motion f_c ($f_c = 1/2\pi\tau_c$) are close to the laboratory frame resonant frequency $f_0 = \omega_0/2\pi$, respectively to the rotating frame resonant frequency $f_1 = \omega_1/2\pi$.

Generally in the case of polymers the assumptions (one correlation time τ_c, intermolecular dipol-dipol interactions between two identical spins, an isotropic stochastic motion) for the derivation of eqs. (1—6) are not fulfilled. In some cases it is possible to consider the distribution of the correlation times [1, 4, 7] and the influence of the intermolecular interactions [8], however, for some considerations [9, 10] the above mentioned simplified approach is sufficient.

III. EXPERIMENTAL PART

The investigated polypropylene denoted as TATREN 430 is the product of Slovnaft Bratislava (Czechoslovakia). It is the isotactic partially crystalline polymer with a density of 888.5 kg m^{-3}. According to [11] a crystallinity corresponding to this value of density is 0.43. The melting T_m and the glass transition T_g temperatures are 436 K and 268 K, respectively.

The NMR measurements have been performed at the Institute of Physics of the Technical University in Merseburg (GDR) on the SXP 4—100 pulse spectrometer (Bruker Physik AG). The spin-lattice relaxation time T_1 has been measured using the pulse sequence $\pi - \tau - \pi/2$ at the resonant frequency $f_0 = 88$ MHz. The spin-lattice relaxation times $T_{1\varrho}$ have been determined by means of the spin-locking experiment. In these measurements the amplitude of the radiofrequency magnetic field $B_1 = 1$ mT. Both spin-lattice relaxation times were measured within a temperature region from 140 K up to the melting point of the sample.

IV. RESULTS AND DISCUSSION

In the temperature dependence of the spin-lattice relaxation time T_1 we observe two, for polypropylene characteristic minima (Fig. 1). The high temperature minimum is reached at the temperature of 380 K ($10^3/T = 2.63$ K^{-1}) and the value of $T_{1,\min}$ is 0.635 s. The low temperature minimum is at the temperature of 179 K ($10^3/T = 5.59$ K^{-1}) and the value of the spin-lattice relaxation time at this temperature is $T_{1,\min} = 0.12\,\mathrm{s}$. The course of this temperature dependence is essentially consistent with the dependences in contemporary works [1, 2]. In accordance with the quoted papers the high and the low temperature minima are associated with the β—relaxation and the rotation of the CH_3 groups, respectively.

In measurements of the $T_{1\varrho}$ in the temperature range from the lowest operating temperature of the spectrometer (130 K) up to 225 K we have been also measured only one relaxation time. However, at temperatures higher than 260 K three relaxation times have been determined. We have denoted them by $T^a_{1\varrho}$, $T^b_{1\varrho}$ and $T^c_{1\varrho}$ their temperature dependences are depicted in Fig. 2. Since the spin-lattice relaxation time $T^a_{1\varrho}$ is connected with the short component of the FID, we have ascribed it to the crystalline phase of the polymer. In agreement with [2, 3] we ascribe the $T^a_{1\varrho}$ minimum reached at temperature of 375 K ($10^3/T = 2.67\,\mathrm{K}^{-1}$) to the motion of the main chains in the crystalline regions of polypropylene (α-relaxation). It is obvious that the temperature dependences $T^b_{1\varrho}$ and $T^c_{1\varrho}$ are connected with the noncrystalline phase of the polymer. The noncrystalline phase of the partially crystalline polymers is divided by crystallites into a lot of regions differing in local volumes and physical restrictions. For this reason the noncrystalline phase can exhibit several of the glass transitions. In many partially crystalline polymers two glass transitions were observed for which Boyer introduced the term "apparent double glass transition" (in the following "double glass transition" only). It assumes the existence of upper and lower glass transitions at temperatures $T_g(U)$ and $T_g(L)$, respectively [12]. The upper glass transition is caused by noncrystalline material in which the motion is restricted by crystallites and the lower arises from noncrystalline regions not influenced by the crystalline part of the polymer.

The temperature dependences $T^b_{1\varrho}$ and $T^c_{1\varrho}$ corresponding to motions in noncrystalline regions of polypropylene can be explained in terms of Boyer's model of glass transition. The minima of these temperature dependences are shifted by about 10 K from each other. We suppose that by means of the temperature dependence $T^b_{1\varrho}$ with the minimum at the higher temperature of 325 K ($10^3/T = 3.075\,\mathrm{K}^{-1}$) and by the temperature dependence $T^c_{1\varrho}$ with the minimum at the temperature of 315 K ($10^3/T = 3.175\,\mathrm{K}^{-1}$) we have detected the relaxation processes connected with the upper and lower glass transitions, respectively. The corresponding relaxation processes have been denoted as $\beta(U)$ and $\beta(L)$ (Fig. 2). This intepretation is in agreement with the three-phase model of partially crystalline polymers [13—15]. According to this model the noncrystalline part consists of the amorphous and the intermediate phases. In the amorphous phase there appears in the temperature range of the glass transition a free microbrownian motion of chains; however, a motion in the intermediate phase is considerably restricted owing to its linkage with the crystalline regions. For this reason the minimum of the temperature dependence $T^b_{1\varrho}$ in comparison with the $T^c_{1\varrho}$ minimum is shifted toward higher temperatures. Therefore, the relaxation times we have measured correspond to the crystalline ($T^a_{1\varrho}$), intermediate ($T^b_{1\varrho}$) and amorphous ($T^c_{1\varrho}$) phases of the polymer.

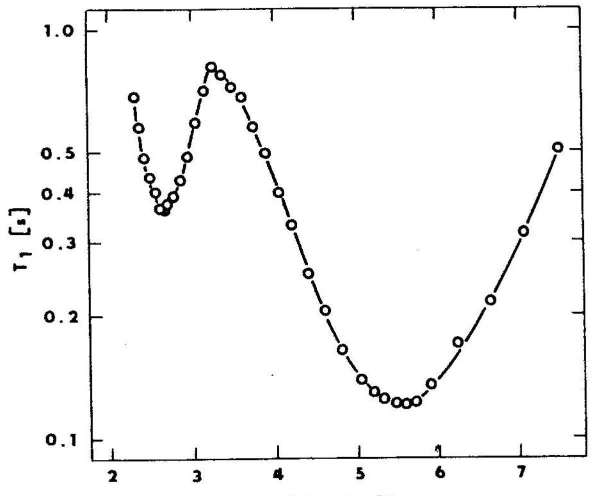

Fig. 1. Temperature dependence of the spin-lattice relaxation time T_l measured on the polypropylene sample.

We have measured the spin-lattice relaxation time $T^c_{1\varrho}$ also at some temperatures above the range of 350—430 K [4]. The intensities of these relaxation times acquire very small values which are in the 0.00—0.15 range. We suppose that the dependence $T^c_{1\varrho}$ near the minimum occurring in this temperature range corresponds to the high-temperature α-process in the intermediate regions of polypropylene similarly as in the case of polyethylene [3]. From the above values it follows that this process is effective in a very small part of the sample.

Fig. 3 represents the temperature dependences of the intensities p_a, p_b and p_c corresponding to the spin-lattice relaxation times $T^a_{1\varrho}$, $T^b_{1\varrho}$ and $T^c_{1\varrho}$, respectively. We have observed that in the range above 300 K the intensity p_c decreases and at temperatures higher than 350 K for the above reasons it can be regarded as zero. Therefore, above the latter temperature practically we observe only two relaxation times $T^a_{1\varrho}$ and $T^b_{1\varrho}$. From the increase of the intensity p_b and the constant values of the p_a within the interval of 300—380 K it results that above 380 K the p_b represents both the amorphous and the intermediate phases of the studied polymer. Consequently, at temperatures higher than 380 K the same values of the relaxation times $T^b_{1\varrho}$ and $T^c_{1\varrho}$ correspond to the both phases. From this conclusion and from the assumption of validity of eq. (4) it results that above the temperature 380 K the chains of both discussed phases perform the motions with the same correlation times, respectively with the same correlation frequencies. Hence, for the excitation of the motion with the correlation frequency of 85 kHz (resulting from eq. (5b)) in the intermediate phase a temperature about 10 K higher is desirable than that in the amorphous phase. At temperatures over 380 K motions with the same correlation frequencies are excited at the same temperatures. This statement is based on the connexion with the motion in the crystalline phase of the polymer. In Figs.. 2 and 3 we can see that in the temperature range in which the intensity p_b increases the α-relaxation process is activated. The temperature range with the constant p_b ($p_b \doteq 0.62$) and with one relaxation time for amorphous and intermediate phases is above the temperature of 375 K at which $T^a_{1\varrho}$ has the minimum. From this we conclude that the loosening of the chain motion in the intermediate phase is due to the activation of the motion in the crystalline phase. In consequence of the considered loosening the motion in the intermediate phase acquires the character of the motion in the amorphous phase.

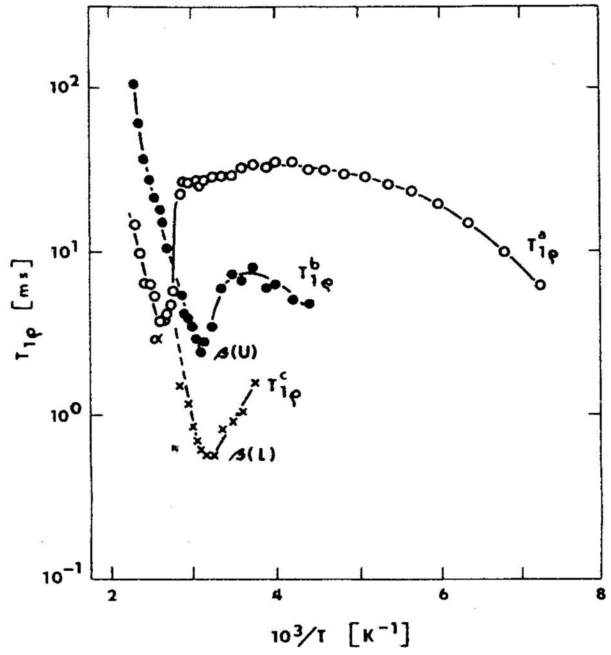

Fig. 2. Temperature dependence of the rotating frame spin-lattice relaxation times $T_{1\varrho}$ measured on the polypropylene sample.

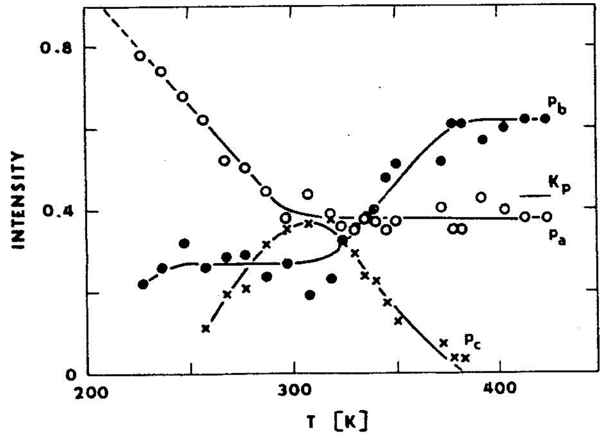

Fig. 3. Temperature dependence of the intensities p_a, p_b and p_c corresponding to the spin-lattice relaxation times $T^a_{1\varrho}$, $T^b_{1\varrho}$ and $T^c_{1\varrho}$, respectively. X_c is the crystallinity calculated from the density according to [11].

In the above interpretation of molecular motion it is assumed that in the discussed temperature range the values of the individual spin-lattice relaxation times and intensities are not influenced by spin diffusion. It is possible to estimate its influence by comparison of the experimental values $T_{1\varrho,min}$ with those calculated using eq. (6b). Because the second moment M_2 in this equation represents the part of dipol interactions averaged owing to motion [10], we can estimate by means of the temperature decrease of the second moment the competent value of $T_{1\varrho,min}$. From the temperature dependence of the second moment of the broad-line NMR spectra it results that the mentioned decrease corresponding to the β-process is 0.06 mT^2 [16]. The spin-lattice relaxation time $T_{1\varrho,min}(\beta)$ corresponding to this value is ≈ 0.25 ms. In regard of the polymer structure the most favourable conditions to fulfil the assumptions of derivation of eq. (4), respectively (6b), are in its amorphous regions. Despite of this the calculated value $T_{1\varrho,min}(\beta)$ is lower than the experimental value $T^c_{1\varrho,min}$ (0.5 ms) corresponding to the amorphous regions of polypropylene. The higher experimental value $T^c_{1\varrho,min}$ can be explained in terms of the correlation time distribution [17] which it is reasonable to suppose in such complicated systems as polymers.

Besides we have to consider that at temperatures lower than the temperature of the glass transition the arrangement of the chains in the amorphous regions is looser than that in the intermediate regions. Consequently, the amorphous regions contribute to the decrease of the second moment less than $0.06\,\mathrm{mT}^2$. Therefore, the theoretical value corresponding to the amorphous regions is a little higher than the calculated value 0.25 ms.

Temperature dependences of the intensities also do not testify to spin-diffusion processes in the discussed temperature range (over 300 K). The increase of the intensity p_b to the detriment of p_c with increasing temperature cannot be explained in terms of the spin diffusion. We would expect such a "merging" of phases in consequence of spin diffusion with decreasing temperature in the same way as it results from the course of intensities at temperature in the same way as it results from the course of intensities at temperatures lower than 300 K.

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ИССЛЕДОВАНИЕ СТРУКТУРЫ И МОЛЕКУЛЯРНОГО ДВИЖЕНИЯ В ПОЛИПРОПИЛЕНЕ МЕТОДОМ ЯМР

В работе исследовано молекулярное движение в изотактическом (частично кристаллическом) полипропилене, а также структура данного вещества при помощи метода спин-решеточных времен релаксации в лабораторной системе координат T_1 и во вращающейся системе координат $T_{1\varrho}$. Измерения обоих спин-решеточных времен осуществлялись на образце гранулированной пробки в интервале температур 140—430 K. Температурная зависимость T_1 в исследуемом диапазоне температур имеет два минимума, которые связаны с переходом полимера в стеклообразное состояние и с вращением CH_3-групп. При измерениях спин-решеточного времени релаксации во вращаящейся системе координат при температурах свыше 250 K обнаружены три релаксационных времени $T_{1\varrho}$, которые соответствуют кристаллической, переходной и аморфной фазам полимера. Эти минимумы времен релаксации обусловлены α-процессом в кристаллических состояниях полимера и двойным переходом в стеклообразное состояние в некристаллических фазах данного материала. При этом β-процесс релаксации, соответствующий стеклообразованию в переходных областях, происходит при температурах на 10 K выше, чем температуры, при которых происходит β-процесс в аморфных фазах полипропилена.