

Proton Spin–Lattice and Spin–Spin Relaxation Times in Isotactic Polypropylene. II. Effects of Stretching Ratio and Temperature*

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Synopsis

Proton spin–lattice, T_1 , and spin–spin, T_2 , relaxation times of uniaxially stretched polypropylene film were measured at 40°C using a wide line pulse spectrometer operating at 19.8 MHz. T_{1l} , the longer T_1 , increases almost linearly with increasing stretching ratio, and T_{2a} , T_2 of the amorphous region, decreases gradually as the stretching ratio is increased. These results can be interpreted in terms of the increased constraints to molecular motion in the amorphous region. The fraction of the rigid protons in the sample, F_c , increases with increasing stretching ratio, while the crystallinity calculated from the density, X_d , does not change largely. The difference between F_c and X_d , therefore, increases as the stretching ratio is increased. This indicates that the physical structure of the highly stretched sample is far from the ideal two-phase model. The influence of the stretching temperature was also investigated. There are only slight increases in T_{1l} and in F_c for the samples stretched in a temperature range from 80°C to 150°C, whereas the considerable increase in T_{2a} occurs. The most notable change introduced at a high temperature stretching is the increase in the chain mobility in the amorphous region.

INTRODUCTION

In recent years the application of nuclear magnetic resonance to the study of the solid polymers has received considerable attention and the relaxation phenomena in polymers have been investigated extensively by utilizing the spin–lattice, T_1 , spin–spin, T_2 , and rotating frame, $T_{1\rho}$, relaxation times.^{1,2} Relatively few systematic investigations of relaxation effects, however, in the oriented isotactic polypropylene films and fibers have been made. Hyndman and Origlio³ have reported on the anisotropy of the proton derivative line shapes for cold drawn polypropylene fibers at room temperature, and McBrierty et al.⁴ have reported on the temperature dependence of T_1 , T_2 , and $T_{1\rho}$ for the oriented commercial fibers using a pulse technique. The samples employed in these studies were not so well characterized and the stretching conditions were also not known. The present paper describes the effects of stretching ratio and temperature on the magnetic relaxation times. As is similar in the previous study,⁵ the measurements of the relaxation times were performed at a constant temperature of 40°C. Nevertheless, in this case too, data obtained are expected to provide some useful information on the physical structure of the uniaxially stretching isotactic polypropylene films under various stretching conditions.

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EXPERIMENTAL

Materials

The sample film used in this study was an isotactic polypropylene film which contained no plasticizers and was characterized by $M_n = 45,000$, $M_w = 270,000$, and the tacticity of 94.4% (determined by extraction with boiling *n*-heptane).

Preparation of the Sample for Stretching

Sample films of about 0.30 mm thick were formed by compression molding at 230°C and subsequent quenching in ice water.

Stretching of the Sample

Two series of stretching were performed as follows.

In series 1, a piece of the quenched sample which was allowed to attain the stretching temperature by leaving it in a poly(ethylene glycol) bath for 5 min prior to stretching was uniaxially stretched at 140°C at a rate of 0.4 mm/s followed by quenching in ice water. The stretching ratios were determined from the ink marks printed on the sample before stretching.

In series 2, a quenched sample film was stretched in a variety of temperatures ranging from 80°C to 150°C with a constant stretching ratio, $\lambda = 4$. Other stretching conditions were the same as those in series 1.

Measurements of Magnetic Relaxation Times

The experimental apparatus and procedures used in this work have been described in detail elsewhere.⁵ In brief, spin-lattice, T_1 , and spin-spin, T_2 , relaxation times were measured at 40°C using a Bruker P 20 wide line pulse spectrometer operating at a frequency of 19.8 MHz and the results obtained were analyzed by the method reported by Fujimoto et al.⁶ The sample was cut in a shape of the slender strip and packed in a simple tube so as to align the stretching direction perpendicular to the applied magnetic field direction unless specifically noted. Some of the samples were finely cut and packed in a sample tube in order to eliminate the effects of orientation.

Measurement of Density and Calculation of Crystallinity

The density of the sample was measured in a density gradient column made with the nonsolvents of water and *n*-propyl alcohol at 23°C. The crystallinity was calculated from the crystal density of 0.936 g/cm³⁷ and the amorphous density of 0.858 g/cm³.⁸

RESULTS AND DISCUSSION

Effects of Stretching Ratio

T_1 is plotted as a function of stretching ratio in Figure 1. As is similar to the annealed sample,⁵ the stretched sample also exhibits two T_1 's, T_{1l} and T_{1s} . Here

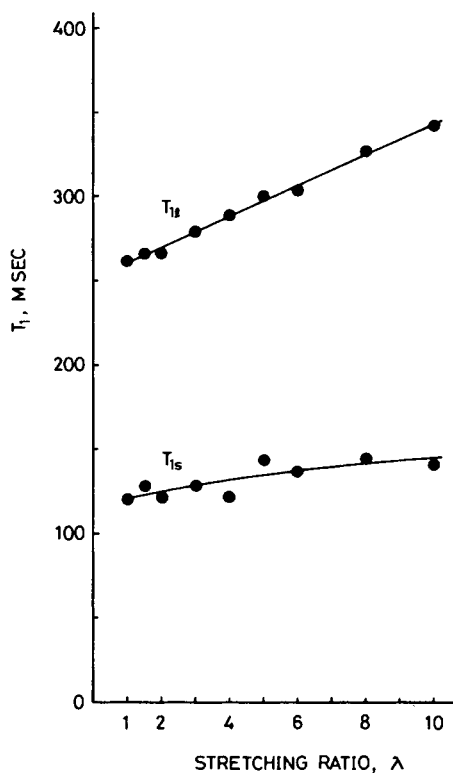


Fig. 1. Plots of T_{1l} and T_{1s} as a function of stretching ratio.

T_{1l} and T_{1s} refer to a longer and a shorter T_1 , respectively. The appearance of two T_1 's indicates the development of the mobile amorphous region which decouples with the immobile crystalline one.⁹ Apart from the appearance of two T_1 's the value of T_{1l} increases linearly with increasing stretching ratio. It is well known from the BPP theory¹⁰ that in the T_1 vs. temperature plot the T_1 minimum appears at a temperature where $\omega_0\tau_c \approx 1$. Here ω_0 and τ_c refer to the resonance frequency and the correlation time of internal motion of the material, respectively. The T_1 minimum for the segmental motion of isotactic polypropylene locates around 80–100°C^{4,11–14} though the temperature is frequency dependent.¹⁴ It has already been reported that the T_1 minimum shifts to higher temperature as the constraints to the segmental motion is increased.^{9,11} Taking the measurement temperature of 40°C used in this study into consideration, the increase in T_{1l} with increasing stretching ratio can be explained in terms of the increased constraints to the segmental motion in the amorphous region. It has also been shown that the value of T_1 minimum becomes longer as the mobile mass fraction is decreased.^{9,11,15–17} As is shown later (in Fig. 3) the mobile mass fraction F_a decreases with increasing stretching ratio. Therefore, the decrease in F_a also contributes to the increase in T_{1l} . The relatively small increase in T_{1s} indicates that the mobility of the amorphous chains which decouple with the crystalline one is gradually restricted as the stretching ratio is increased.

In Figure 2 T_{2a} , T_{2m} , and T_{2c} are plotted against stretching ratio, where T_{2a} , T_{2m} , and T_{2c} refer to the spin-spin relaxation times of mobile (amorphous), intermediate, and rigid (crystalline) regions, respectively. As the shape of the

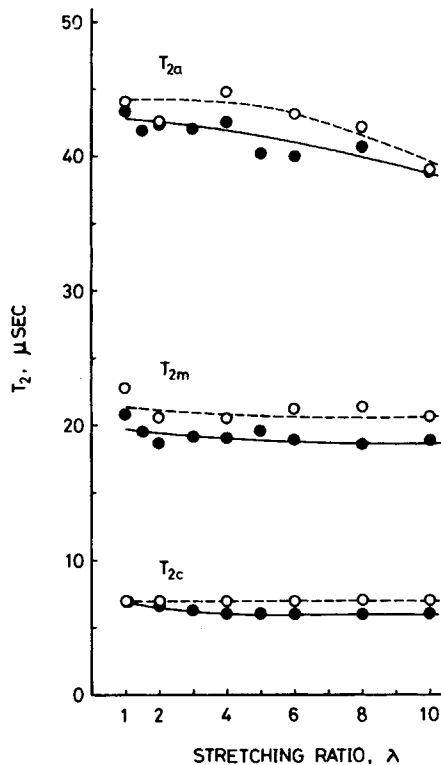


Fig. 2. T_{2a} , T_{2m} , and T_{2c} plotted against stretching ratio: (●) sample placed perpendicular to the magnetic field; (○) finely cut sample.

nuclear magnetic resonance spectrum depends on the orientation angle γ ,³ where γ is the angle between the stretching direction and the applied magnetic field direction, the measurements of the FID traces on the finely cut samples also carried out to eliminate the orientation effects, although it has been reported that the effects of orientation angle on the value of T_2 are relatively small for the isotactic polypropylene fiber.⁴ Solid circles indicate the data for the sample placed with its stretching direction perpendicular to the applied magnetic field direction and the open circles those for the finely cut sample.

Although there is some scatter in the data, T_{2a} decreases gradually as the stretching ratio is increased. The difference in the value of T_{2a} between two samples is thought to be a reflection of the orientation effects. It has already been shown that the rapid motion in the amorphous region is responsible for the longer value of T_{2a} .¹⁸ The decrease in T_{2a} , therefore, can be attributed to the restricted molecular motion in the amorphous region owing to the generation of the microparacrystals during stretching. The value of T_{2a} for an ultrahighly stretched sample ($\lambda > 15$), however, is not so very small,¹⁹ suggesting that the small fraction of the sample which is undergoing considerable molecular motion still exists even for the ultrahighly stretched sample. This is in agreement with the results on the ultrahighly drawn polyethylene reported by Smith et al.²⁰

There is no significant change in T_{2m} with increasing stretching ratio, though it seems that T_{2m} slightly falls in the initial stage of stretching. Furthermore, it can scarcely be recognized that there is a difference in the variation of T_{2m}

between the finely cut sample and the sample placed perpendicular to the magnetic field, though the difference in the absolute value of T_{2m} exists. T_{2c} , however, shows a definite difference in these two samples; the finely cut sample gives virtually the same T_{2c} for all stretching ratios covered in this work, while T_{2c} of the sample placed perpendicular to the magnetic field decreases definitely in the range of $\lambda = 1-5$. As was discussed in the earlier paper,⁵ one cannot expect to obtain precise value of T_{2c} because the dead time of the instrument is the same order of magnitude as T_{2c} . Nevertheless, a definite difference was observed in T_{2c} values of these two samples. It has been shown from the X-ray investigation for the stretched sample that the orientation of the crystallites is almost completely accomplished at a rather low stretching ratio such as $\lambda = 5-6$.²¹ The lowering in T_{2c} at the initial stage of stretching for the sample placed perpendicular to the magnetic field is believed to be related to the orientation of the crystallites. The details of these observations are in need of further examination.

Figure 3 shows the variations of F_a , F_m , and F_c as a function of stretching ratio, where F_a , F_m , and F_c refer to the fractions of mobile (amorphous), intermediate, and rigid (crystalline) regions, respectively. F_a decreases and F_c increases as the stretching ratio is increased, though F_c for the sample placed perpendicular to the magnetic field is rather constant at a low stretching ratio. It is believed that the closer chain packing and the generation of the microparacrystals in the amorphous region result in the substantial decrease in F_a and the increase in F_c .

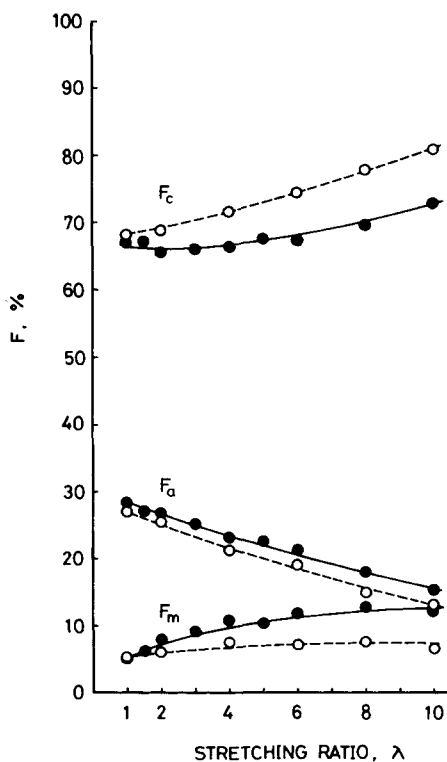


Fig. 3. Variations of F_c , F_m , and F_a as a function of stretching ratio: (●) sample placed perpendicular to the magnetic field; (○) finely cut sample.

The difference in the solid and broken lines for each fraction is probably due to the effects of orientation angle similar to the situation in T_2 .

F_c for the finely cut sample and the crystallinity calculated from the density, X_d , are plotted against stretching ratio in Figure 4. There is only a small change in X_d for $\lambda \leq 10$, while there is a monotonic, rather sharp increase in F_c , indicating that the physical structure of the stretched sample is far from the ideal two-phase model.

Effects of Stretching Temperature

In Figures 5–7 are shown the data for the samples uniaxially stretched to $\lambda = 4$ at various temperatures (80–150°C). The value of T_1 is plotted as a function of stretching temperature in Figure 5. Two T_1 's were observed for all samples irrespective of the stretching temperature. There is a slight increase in T_{1l} and a decrease in T_{1s} with increasing stretching temperature. The increase in T_{1l} is attributable to the slight increase in F_c as is shown in Figure 7. T_{1s} decreases slowly with increasing stretching temperature, indicating that the decoupling of the mobile amorphous chains with the immobile crystalline ones gradually proceeds and the molecular motion in the amorphous region becomes rapid, which is also reflected in the increase in T_{2a} , as is shown in Figure 6.

Figure 6 shows plots of T_{2a} , T_{2m} , and T_{2c} against stretching temperature. As is evident from the figure, the most notable features is the considerable increase in T_{2a} as the stretching temperature is increased. It is believed that the amorphous region achieves greater molecular mobility owing to the mechanical re-

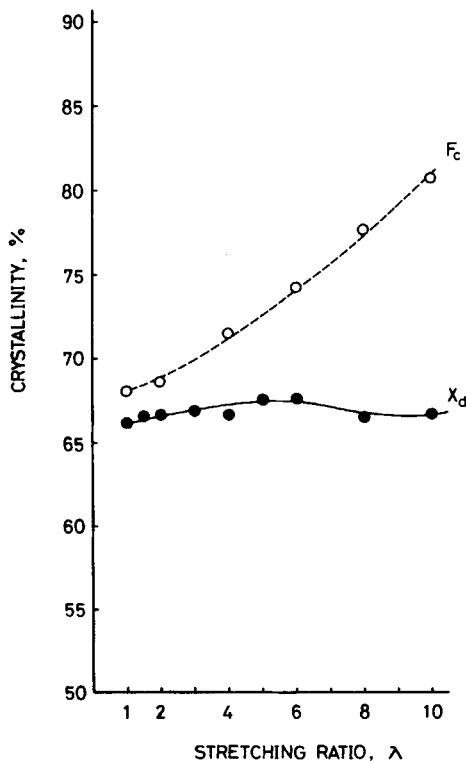
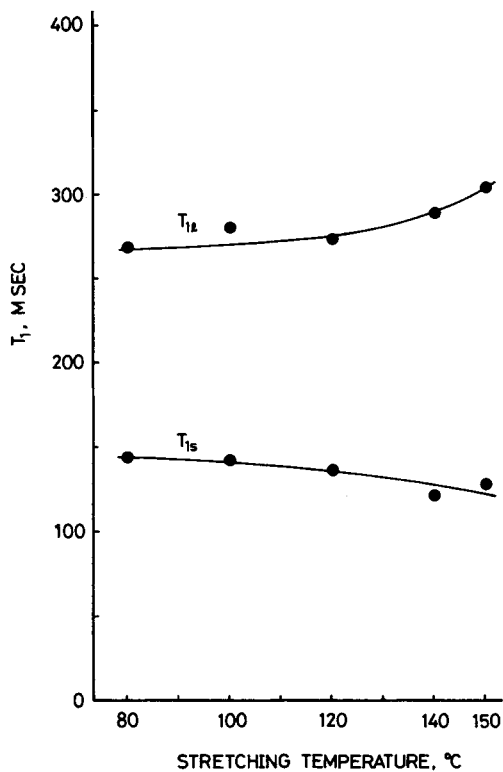
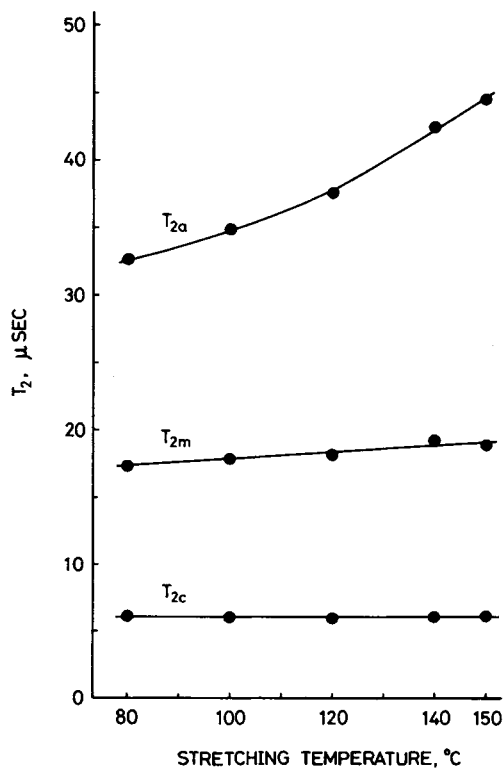


Fig. 4. F_c and X_d as a function of stretching ratio.

Fig. 5. T_{1l} and T_{1s} plotted against stretching temperature.Fig. 6. T_{2a} , T_{2m} , and T_{2c} as a function of stretching temperature.

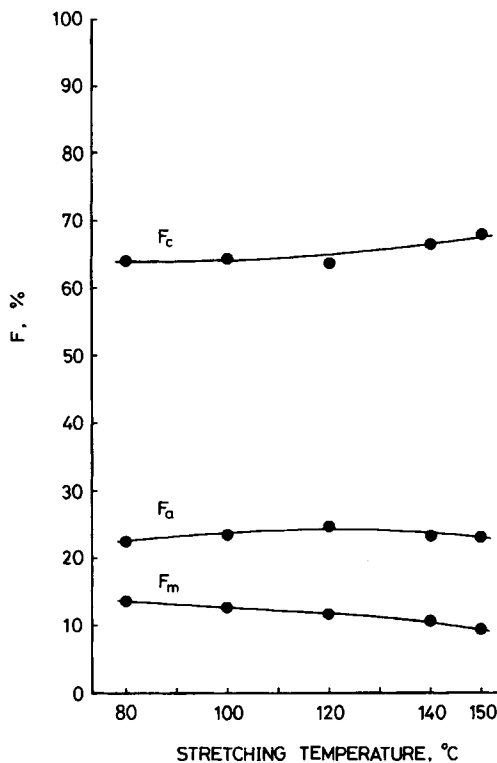


Fig. 7. Values of F_c , F_m , and F_a plotted against stretching temperature.

laxation which occurs significantly during high temperature stretching, resulting in the increase in T_{2a} . The variations of T_{2m} and T_{2c} are not so informative, though there is a slight increase in T_{2m} with increasing stretching temperature.

F_c , F_m , and F_a are plotted against stretching temperature in Figure 7. There is a slight increase in F_c and a slight decrease in F_m as the stretching temperature is increased. The increase in F_c at higher temperature stretching can be ascribed to the annealing effects during stretching. There is also no considerable change in F_a , indicating that the main change introduced in the amorphous region with increasing stretching temperature is the increase in the molecular mobility, not the amount of the mobile chains.

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