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Mobility and relaxation of amorphous chains in drawn polypropylene: ^{2}H-NMR study

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Abstract

Mobility and orientation of amorphous chains in cold drawn films of isotactic polypropylene (PP) are studied by ^{2}H-NMR as a function of the annealing temperature. It is shown that the deformation is not affine. The relaxation of amorphous chains in materials annealed with free and clamped ends appears respectively at $T^* \approx T_g + 50$°C and at $T\alpha_c \approx 80$°C. Above these transition temperatures, corresponding to the onset of the chain mobility in the amorphous and crystalline states, the orientation of amorphous chains decreases linearly with the temperature. These reports show that the ^{2}H-NMR technique provides important information on the plastic deformation of semi-crystalline polymers. © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: Polypropylene; Glass transition; Secondary transition

1. Introduction

Isotactic Polypropylene (iPP) has been widely studied since three decades [1,2], but the mobility of the chains in the amorphous and crystalline phase is still not understood. It is well known that by differential scanning calorimetry (DSC) and dynamic mechanical thermal analysis (DMTA) various transitions are observed [3,4]. Above the glass transition temperature, T_g, another transition is detected at $T^* = 40$°C by DSC [5]. Various authors call it the upper glass transition T_{gu} [6,7]. By DMTA a secondary transition, called α_c is noticed above this temperature T^*; the loss curve (in the frequency range from1 to 100 Hz) begins to increase just above T^* and presents a maximum at $T\alpha_c$. The so-called α_c relaxation, observed in most of the semi-crystalline polymers, is considered to be mainly due to the crystalline phase [8–10] but as noted by various authors [11,12] this relaxation could involve different chain motions in both phases, amorphous and crystalline. Recently, by two dimensional NMR, Schaefer et al. [13] have shown that the chain motion in crystalline phase can be described as a limited number of helical jumps about the chain helix beginning at 80°C.

The aim of this note is to analyze the mobility of the amorphous chain appearing above T^* and to correlate it to the dimensionnal relaxation, appearing during annealing of cold drawn iPP in the domain of the α_c relaxation. The annealing treatment of drawn iPP was studied previously in different aspects [14–17]. ^{2}H-NMR is known to be well adapted and extremely sensitive to detect anisotropy in molecular motions. Oriented systems like rubber and recently semi-crystalline polymers (PA6 and polyamide–polyether block copolymers) swollen with deuterated solvent have been extensively studied by this technique [18–31]. This is because of the fact that the chains and the solvent have similar orientation.

2. Experimental

Isotactic PP of molecular weight: $M_N = 79\,300$, $M_W = 476\,000$ were supplied by Himont SPA. It is a high purity grade (ash residue 15–17 ppm) which contains about 3% of oligomers (measured by extraction at 100°C in *n*-decane). The films are drawn at room temperature (cold drawing) at deformation rate 1.3×10^{-3} s^{-1}. After yield the natural draw ratio is $\lambda_m^0 = 5$. Materials were then submitted to an annealing at temperature T_a and to a swelling at room temperature in deuterated *n*-decane. In some cases the swelling was done before the annealing. The equillibrium swelling rate of drawn and isotropic PP, $c = 7 \pm 0.2\%$, was not dependant of the annealing temperature. NMR measurements were performed with a AM250 spectrometer (^{2}H frequency 38.4 MHz) at room temperature or at annealing temperature T_a. The spectral width was limited to 20 kHz, the dimensions of the samples were 12 mm × 6 mm × 0.5 mm.

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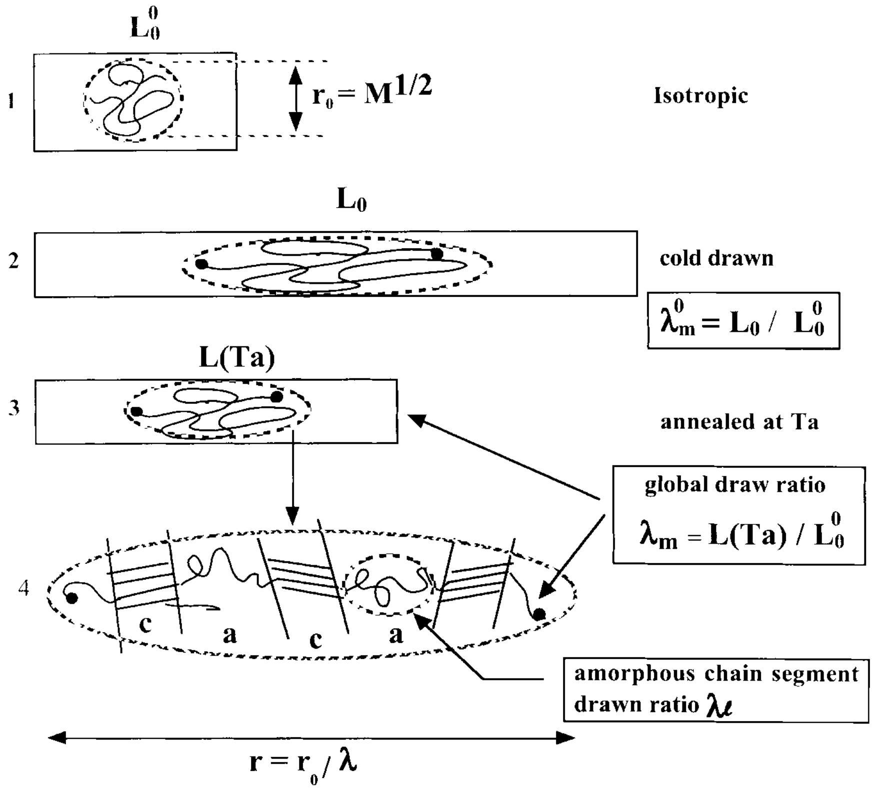

Fig. 1. Local and macroscopic deformations in drawn and relaxed iPP. r_0 and r are the coil dimensions of the chains in the isotropic (1) and drawn states (2,3). After the cold drawing the deformation is affine at the scale of the coil dimension, $\lambda_m^0 = 5$ and λ_l^0 (to be determined) are the macroscopic and local draw ratios of the cold drawn material. After annealing (3) the macroscopic deformation at the coils is still affine but the deformation of the amorphous chain segments between two crystallites is not. A drawn chain passing through the crystalline (c) and amorphous (a) layers is schematized in (4). The global λ_m and local λ_l draw ratios of the chains are not equal.

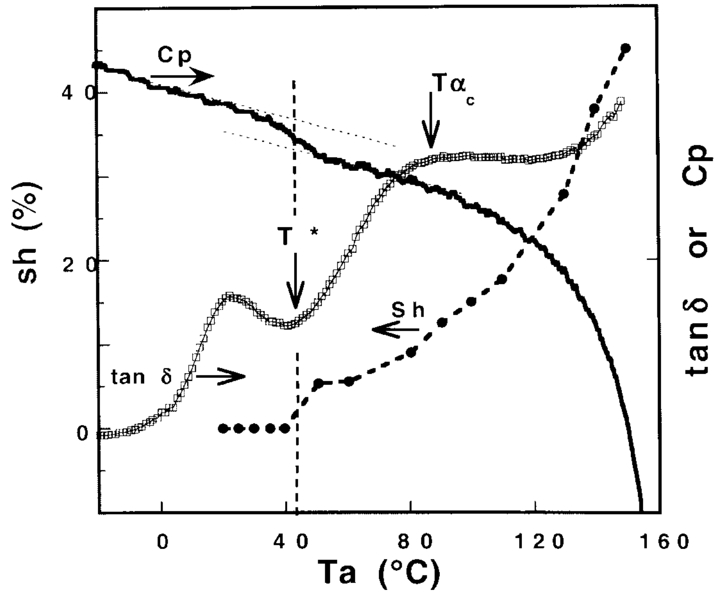

Fig. 2. Shrinkage (sh. %) of drawn iPP as function of the annealing temperature T_a (°C). In the same diagram are reported the DSC (heating rate 10°C/min) and DMTA (heating rate 3°C/min, at 1 Hz) thermograms of isotropic PP, showing, respectively, the mobility temperature (T^*) and the secondary transition temperature ($T\alpha_c$). The beginning of the α_c peak observed by DMTA occurs at the temperature T^* measured by DSC.

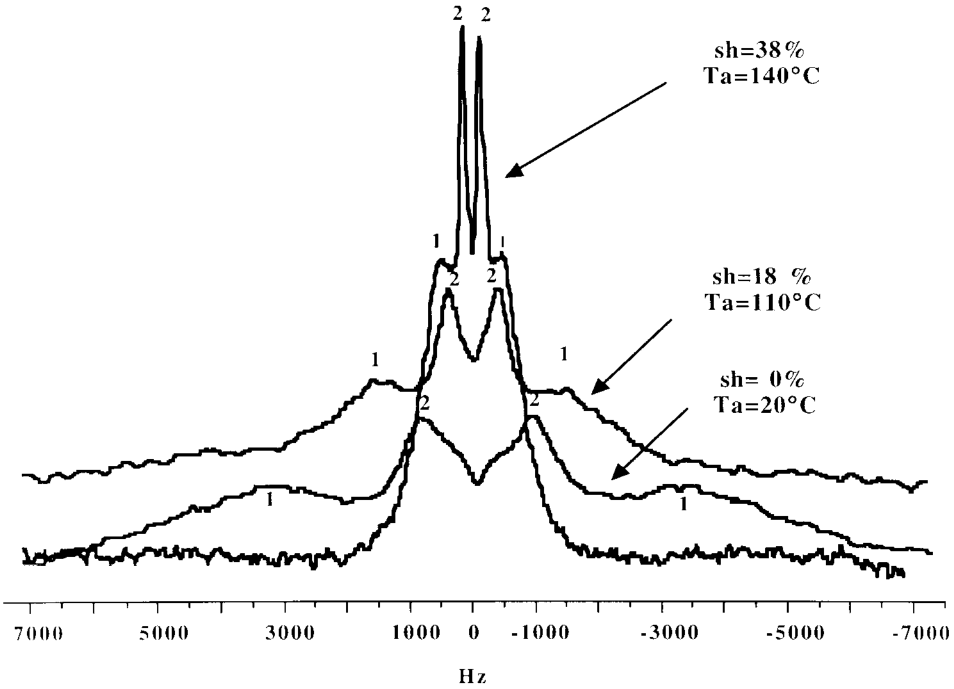

Fig. 3. NMR spectra of drawn iPP samples swollen with deuterated *n*-decane (7%) and annealed at different temperature T_a (°C). The corresponding level of shrinkage (sh. %) is indicated. The two doublets 1 and 2 due to the CD_2 and CD_3 groups of *n*-decane are marked.

3. Results and discussion

It has been verified that no flow occurs during the drawing process; this is different from the fiber production technology when the semi-crystalline material is drawn near the melting temperature (T_m). When the drawn iPP is re-melted, just above T_m, the material, like an elastomer, relaxes entirely; i.e. recovers its initial length. If the deformation is affine, at the scale of the whole chain of dimension $r_0 \approx M^{1/2}$ (*M* being the molecular weight), the local deformation $\lambda_{\mathrm{l}}^0 = r/r_0$ is equal to the macroscopic draw ratio $\lambda_{\mathrm{m}}^0 = L_0/L_0^0$, the macroscopic dimensions of the starting isotropic and drawn samples being L_0^0 and L_0. In oriented semi-crystalline polymers the orientation factors of the amorphous and crystalline chains are very different, this has been demonstrated by WAXS and birefringence measurements [32,33]. There is no reason to believe that the deformation of the amorphous chain segments linking two consecutive crystalline layers is also affine. Obviously, the same conclusion applies for the drawn material which has been subsequently annealed and relaxed.

Fig. 1 summarizes the drawing and annealing process studied in this note and defines the different macroscopic and microscopic dimensions describing the structure of the materials.

Fig. 2 gives the shrinkage, $\mathrm{sh} = (L_0 - L(T_a))/L_0$, of the PP films as a function of the annealing temperature; L_0 and $L(T_a)$, respectively, the length of the cold-drawn and relaxed samples. As it is well known, the DSC thermograms of isotropic and oriented PP show two transitions in the domain $-10 < T < 70$°C, often called lower and upper glass transitions [6]. The temperatures where the capacity jumps are observed (at heating rate, 10°C/min) are called here T_g and T^*. In DMTA these temperatures correspond to the beginning of the so-called α and αc loss peaks [6,8,10]. The essential point to note is that the shrinkage process begins at the characteristic temperature T^*. It is emphasized that such a structural relaxation implies a certain mobility of the chains in both phases, crystalline and amorphous, therefore one cannot claim that T^* is the glass temperature (or an upper glass temperature) of the amorphous phase. Above T_g a change of the microstructure implies necessarily a certain mobility of the chain in the crystalline layers.

Fig. 3 shows typical quadrupolar NMR spectra of drawn PP relaxed at different annealing temperature T_a and then swollen with deuterated *n*-decane at room temperature. The samples were held parallel to the magnetic field. In each spectra one observes two doublets 1 and 2; the splittings $\Delta\nu_i$ and the widths W_i decrease when the shrinkage increases, that is to say when the orientation of the amorphous chains decreases and when the mobility increases. The absence of any central component in the spectra shows that there are no isotropic segmental reorientations on the NMR time scale, the uniaxial character of the dynamics of the probe (and then of the chains) is directly checked by tilting the sample drawn direction at an angle $\Omega = 55°$ (the magic angle) from the magnetic field, in that case the splitting disappears. The doublet 1 is because of the orientational motions of the four different methyl groups of the probe, and the doublet 2 to the methyl end groups (the 4 CH_2 groups give 4 doublets which, in the experimental conditions, cannot be resolved).

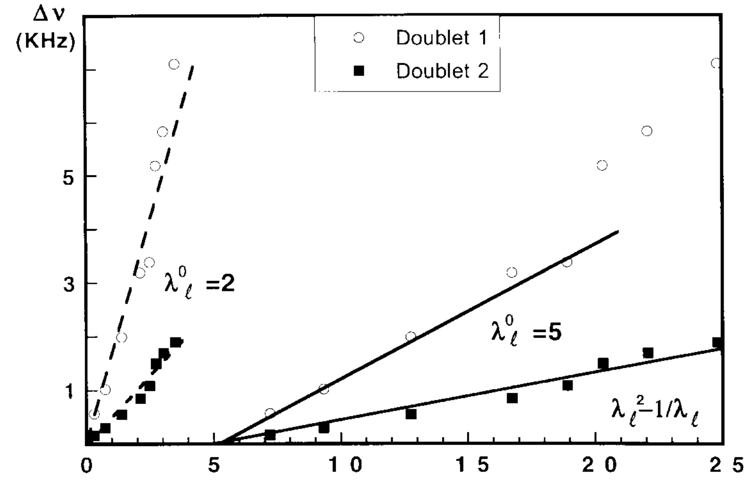

Fig. 4. Variation of the quadrupolar splitting $\Delta\nu_1$ and $\Delta\nu_2$ of the annealed drawn iPP swollen with deuterated *n*-decane, as function of the elasticity term $\lambda_\ell^2 - 1/\lambda_\ell$. The drawn ration λ_ℓ^0 in relation (2b) is assumed to be 5 (continuous line) and 2 (dashed line).

In anisotropic fluid, the quadrupolar interactions attached to a C–D bond are only partially averaged, and this effect splits the liquid-like NMR line into a doublet whose splitting is:

$$\Delta\nu = \frac{3}{2}\nu_q P_2(\cos\Omega)\langle\overline{P_2\cos\theta(t)}\rangle \sim k\nu_q(\lambda_\ell^2 - 1/\lambda_\ell) \qquad (1)$$

P_2 being the second Legendre polynomial. The quadrupolar frequency ν_q (C–D) is about 170 kHz, and in all the experiments hereafter, the angle between drawn direction and magnetic field is $\Omega = 0$. The overbar in the second factor denotes a time average over motions faster than the quadrupolar time $t_q \sim 1/\nu_q$. This term is the orientation order of the C–D bond with respect to the symmetry axis, and is proportional to the term $(\lambda_\ell^2 - 1/\lambda_\ell)$, with λ_ℓ the local drawn ratio of the amorphous chains. In rubber, at the scale of the distance between entanglements the local draw ratio is equal to the global draw ratio $\lambda_\ell = r/r_0 = L/L_0$. In semicrystalline polymers, see Fig. 1, the local draw ratio λ_l of the amorphous chains (at the scale of the distance between crystalline layers), is different from the macroscopic draw ratio $\lambda_m(T\text{a}) = L(T\text{a})/L_0^0$. The two draw ratios λ_m and λ_ℓ after annealing at T_a are given by the relations (Fig. 1):

$$\lambda_m = (1 - \text{sh})\lambda_m^0 \qquad (2a)$$

$$\lambda_\ell = (1 - \text{sh})\lambda_\ell^0 \qquad (2b)$$

In relation 2b, λ_ℓ^0 is the local draw ratio of the cold drawn PP ($\lambda_\ell^0 < \lambda_m^0 = 5$). One has postulated that during annealing, the relaxation of the chains involves essentially a shrinkage of the amorphous chains segment; by WAXS and SAXS studies it is found that the crystalline phase does not change its orientation conspicuously [32,33].

In Fig. 4 one reports the two quadrupolar splitting $\Delta\nu_i$ due to the deuterated probe as function of the elasticity term $(\lambda_\ell^2 - 1/\lambda_\ell)$ of the polymer chains, the sample is not

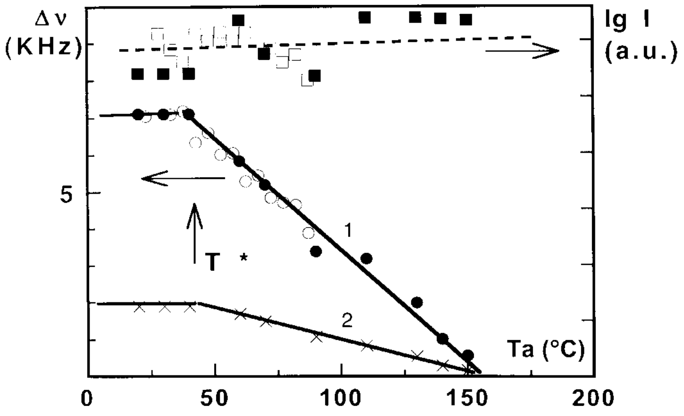

Fig. 5. Total intensity (*I*, a.u.) and splitting ($\Delta\nu$, KHz) of the two doublets 1 and 2 of the NMR quadrupolar spectra of drawn iPP swollen with *n*-decane as function of the temperature of annealing T_a (°C): (a) The sample has been drawn at 20°C, annealed at T_a and then swollen at room temperature. NMR spectra have been obtained at room temperature (filled symbols); (b) The sample has been drawn and swollen at 20°C, the NMR spectra have been obtained at the annealing temperature (empty symbols).

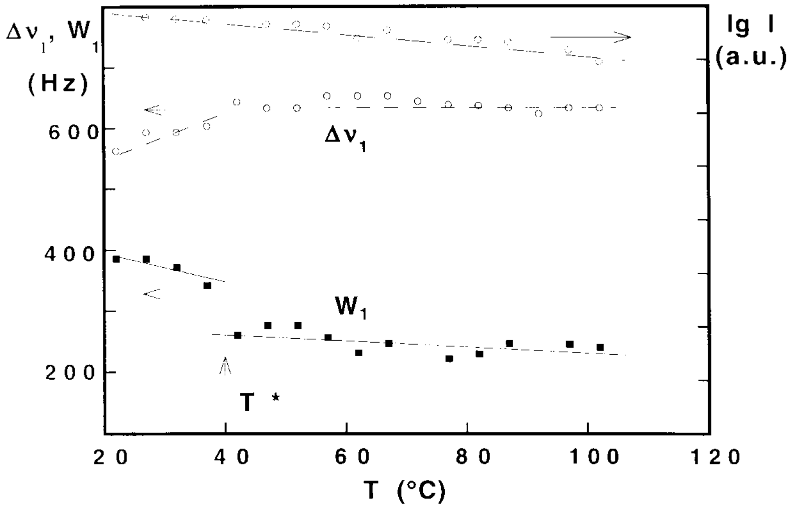

Fig. 6. Line width W_1 and splitting $\Delta\nu_1$ of the peak 1 as function of the temperature T (°C). The drawn material PP, $\lambda_m^0 = 5$,, has been partially relaxed at 150°C, near the melting temperature and then swollen with deuterated *n*-decane at room temperature ($c = 7\%$). The total intensity of the NMR quadrupolar spectra is also given.

clamped so shrinkage occurs during annealing. If one postulates that the local draw ratio λ_ℓ is equal to the macroscopic draw ratio $\lambda_m = L/L_0^0$, the local draw ratio λ_ℓ is then given by relation (2b) with $\lambda_\ell^0 = \lambda_m^0 = 5$; in that case $\Delta\nu_i$ is linear with $(\lambda_\ell^2 - 1/\lambda_\ell)$ (continuous line) but the lines do not pass through the origine as predicted by relations 1. This indicates clearly that this assumption is wrong.

If one assumes that the draw ratio of the amorphous chain segments is given by relation (2b), but with λ_ℓ^0 being equal to two, one finds that both splittings verify relation (1) (dashed lines in the figure). Therefore one concludes that the initial cold drawn PP has amorphous chains with local draw ratio, $\lambda_\ell^0 = 2$, much less than the natural draw (or global) ratio, $\lambda_m^0 = 5$. Also from the figure, comparing the variations of $\Delta\nu_1$ and $\Delta\nu_2$ one notes that C–D bonds of the CD_2 groups of the probe are three times more oriented than those of the end groups.

In Fig. 5 one reports the splitting $\Delta\nu_1$ and $\Delta\nu_2$ as function of the annealing temperature of the same samples analyzed in Fig.4. During the experiments the NMR integrated intensity (in the windows ± 10 000 Hz) remains quasi-constant. When the drawn samples are relaxed at T_a and then swollen at 20°C, the splitting $\Delta\nu_1$ measured at 20°C (filled circles) starts decreasing at $T^* = 40°$, decreases linearly with temperature T_a and extrapolates to zero at the melting temperature $T_m = 158$°C ($T_m = 160$°C, measured by DSC at 10°C/min). When the drawn samples are swollen first and then annealed at T_a, the splitting measured at that temperature (open circles) varies exactly in the same manner (measurements cannot be done above 80°C, solvent evaporates above this temperature). Same behavior is observed for

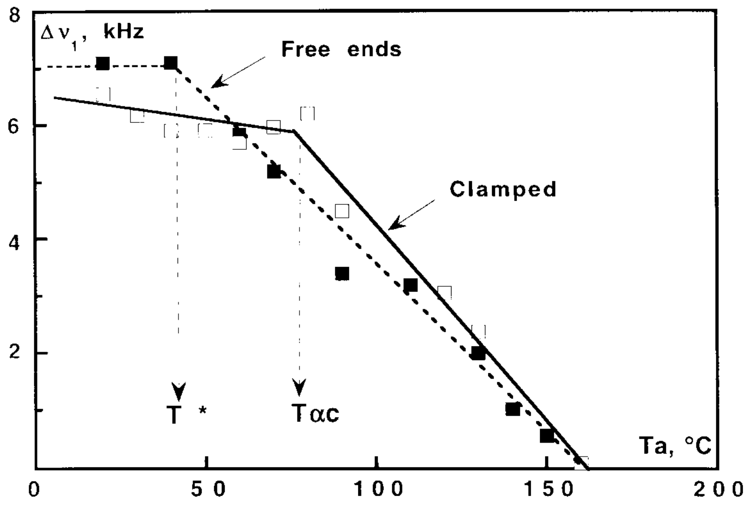

Fig. 7. Quadrupolar splitting $\Delta\nu_1$ in kHz of relaxed PP. Comparison between cold drawn PP annealed at T_a with free (filled squares from Fig. 5) and clamped ends (empty squares). Drawn samples have been annealed at T_a then swollen at 20°C with deuterated *n*-decane, NMR measurement at room temperature.

the splitting $\Delta\nu_2$. The comparison of the two sets of experiments shows that the small amount of deuterated solvent does not induce additional relaxation of the chains or dissolution when the temperature is changed; *n*-decane can be considered as a θ-solvent of PP.

In Fig. 6 the width W_1 of the NMR peak 1 is plotted as function of the temperature. The cold drawn sample has been annealed first at 150°C and then swollen at 20°C. The amorphous chain segments are nearly isotropic ($\Delta\nu_1 \sim 0.6$ kHz, instead of 7 kHz for the starting material), but the sample is still highly oriented, $\lambda = 2.8$, this orientation is due to the crystalline phase, which relaxes weakly during annealing. The width of the peak 1 (and also peak 2) presents a discontinuity at $T^* = 40°\text{C}$ and can be considered as constant between T^* and $T_a = 150°\text{C}$. This decrease in the width value at T^* indicates that the mobility of the chains in the probe environment increases. So, the T^* is a chain mobility temperature. It is important to note that T^* has the same value for all the materials: isotropic and drawn, dry and swollen (Figs. 5 and 6). This transition T^* often called upper glass transition will be discussed in a forthcoming article.

In Fig. 7 comparison of the orientational order of the chains in materials which have clamped ends with that of the preceding materials (with free ends) has been made. Same behavior is observed; this indicates again that the relaxation of the amorphous chains is gradual during annealing. The onset of the amorphous chains relaxation appears at a higher temperature, which corresponds to $T\alpha_c$ (80°C). At this temperature it has been shown by dielectric measurements [34] and NMR [13] spectroscopy that there is a certain mobility of the chains in the crystalline phase; in materials with clamped ends relaxation of the amorphous chains is possible only if the chains are able to slip in the crystalline lamellae.

4. Conclusion

Shrinkage and ^{2}H-NMR experiments provide important information concerning the mobility and the orientation of the amorphous chains in semi-crystalline polypropylene. The structural relaxation of cold drawn iPP with free ends begins at the temperature T^*. When the ends are clamped, the relaxation begins at $T\alpha_c$. During cold-drawing and annealing the deformation of the amorphous chains is not affine; ^{2}H-NMR allows one to measure the temperature dependance of the local draw ratio of the amorphous chains and to follow their microscopic deformation. The fact that the drawing does not shift the T^*-transition is a clear evidence that this mobility temperature is not influenced by the morphology in particular by the orientation, perfection and the thickness of the crystalline phase. This transition (often called T_{gu}) is not dependent on the amount of solvent; this indicates that it cannot be interpreted as a glass transition. The nature of this transition, independent on the local environment of the amorphous chains is puzzling and should be studied by others techniques.

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