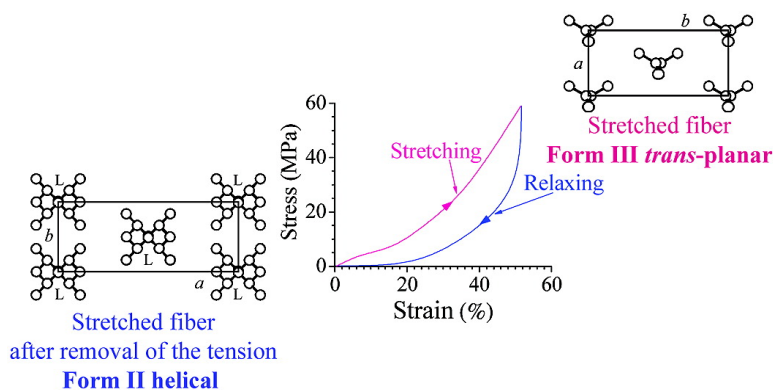Article

New Concepts in Thermoplastic Elastomers: The Case of Syndiotactic Polypropylene, an Unconventional Elastomer with High Crystallinity and Large Modulus

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New Concepts in Thermoplastic Elastomers: The Case of Syndiotactic Polypropylene, an Unconventional Elastomer with High Crystallinity and Large Modulus

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Abstract: Syndiotactic polypropylene (sPP), despite high crystallinity, shows unusual elastic properties, associated with a reversible crystal−crystal phase transition. The mechanism behind the crystal−crystal phase transition involved during cyclic elongation and recovery and the time scale of this process is here investigated, to unravel the origin of the elasticity of such an unconventional elastomer. The structural transformation of fibers of sPP during deformation has been studied by wide-angle X-ray diffraction measurements, using the high flux available on the beamline ID11 at the European Syncrotron Radiation Facility (ESRF), Grenoble, France, performing a time-resolved analysis of structural changes occurring while cyclically stretching and relaxing sPP fibers. This analysis indicates that the stress-induced phase transition is a martensitic transformation. As in martensitic phase transitions it occurs readily and directly, supporting the idea that elasticity in sPP is partially of enthalpic nature.

Introduction

Elastic polymers are, generally, entropic systems characterized by a network structure including flexible segments of chain, which act as springs, connected by chemical or physical cross-links, which act as knots.[1] The flexible segments, which are generally in the disordered random coil conformation in the unstretched state, assume extended conformation upon stretching. The presence of network knots prevents the material from flowing during application of the tensile stress. When the stress is released, the flexible segments tend to return to the disordered coil conformation and recover the initial dimensions. Correspondingly, the whole material tends to recover shape and size assumed in the undeformed state.

A wide class of thermoplastic elastomers includes poorly crystalline or amorphous polymers with glass transition temperatures much below the room temperature, which partially crystallize under stretching.[1] The small number of small crystals act as knots of the elastomeric network. When the applied tensile stress is removed, the crystals melt, providing a positive enthalpic contribution to the Gibbs free energy change involved during the elastic recovery of the material; therefore, the elasticity in these materials is merely of entropic nature, due to the conformational changes occurring in the amorphous "tie-chains".

In the late 1980s the discovery that metallocene catalysts, characterized by complexes of transition metals having C_s symmetry, are able to polymerize propylene to a highly stereoregular syndiotactic polymer with high molecular mass and without regio-irregularities,[2] has refocused the interest in syndiotactic polypropylene (sPP). Samples of sPP previously obtained with vanadium-based Ziegler−Natta catalysts, showed a low degree of crystallinity[3] and poor mechanical properties, because of the high content of defects of stereo- and regio-regularity.[4] The "novel" sPP produced with C_s symmetric metallocene catalysts, instead, presents high crystallinity and melting temperature (∼150 °C) and shows interesting mechanical properties.[5]

The complex polymorphism of sPP has been clarified, and several aspects concerning the relationships between structure and physical properties have been explained.[5−9] However, some basic aspects related to the unusual properties of this novel material are still unclear. Recent studies have pointed out that highly stereoregular sPP shows good elastic properties in a wide deformation range, despite the high crystallinity, thus behaving as a "thermoplastic elastomer" with values of the modulus several order of magnitude higher than that observed in conventional elastomers.[8,9]

The origin of the nonconventional elastic response of sPP is still a dilemma. Semicrystalline polymers are, indeed, generally

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not elastic because they undergo permanent plastic deformations under mechanical stress fields.[10] A study of the origin of elasticity in sPP is of great importance not only because of the potential applicative interest for this novel material but also because it may address basic questions concerning general possible mechanisms of elasticity. In other terms, should the current theories about elasticity of rubber be revised in order to include also this highly crystalline material, or elasticity of sPP is merely of entropic origin like in conventional elastomers?

Recent investigatons have shown that in fiber samples of sPP a reversible crystal−crystal phase transition occurs along with the elastic deformation.[7b] Above a critical stress, sPP fibers are mainly crystallized in form III, characterized by chains in *trans*-planar conformation.[7b,8,9,11] This crystalline form is metastable and transforms into the more stable form II upon the release of the tension.[8,12] Form II is characterized by chains in helical conformation and is more stable than the *trans*-planar form III in the unstrained state[8,12] by 0.52 kcal/mol of monomeric units.[13] This transition is reversible; form III and form II transform each other in successive stretching and relaxing of sPP films.[8,12] Only a partial elastic recovery is instead observed when the transition of the helical form into the *trans*-planar form III is prevented.[12]

The amount of direct participation of crystalline domains to macroscopic elastic recovery of the material may be roughly estimated from the variation of the chain periodicity during the stretching and relaxing process. sPP chains in helical conformation present periodicity $c = 7.4$ Å including 4 monomeric units/period,[3] whereas the chain periodicity of sPP chains in *trans*-planar conformation is 5.1 Å, including 2 monomeric units/period;[14] during the transition from the helical form into the *trans*-planar form III, the crystal dimensions increase along the chain axis direction by a factor proportional to $0.70(= (5.1/2) - (7.4/4))$ Å/monomeric units (38% strain). In the hypothesis that only the polymorphic transition occurring in the crystalline domains is responsible for the elastic response of sPP, so that the average dimensions of chains in the amorphous regions do not change, the shrinkage of a perfect elastic sample (r) corresponds to the ratio between the net increase of the crystal dimensions along c over the initial dimensions of the sample:[15] $r = (100x_c 0.70)/[2b(1 - x_c)(C_\infty)^{1/2} + x_c(7.4/4)]$ where $C_\infty(\approx 6)$ is the characteristic ratio of polypropylene in the unperturbed state in the limit of infinite chain,[16] $b(= 1.54$ Å$)$ the C−C bond length, and x_c the degree of crystallinity. According to this formula, the elastic recovery would be 38% for a single crystal ($x_c = 1$) and ∼5% for a sample with 40% crystallinity. Since crystalline sPP experiences fully elastic

recovery in a much wider deformation range, the role of crystals in the elasticity of sPP should be more subtle.

On the basis of these considerations, it was suggested, that crystals in sPP participate indirectly to the elasticity of sPP, via the enthalpy gain achieved when the tension is removed, due to the metastability, in the unstrained state, of the *trans*-planar form, which transforms into the more stable helical form.[8,12] As in conventional elastomers, the highly entangled amorphous chains also experience a reversible conformational transition between the coiled and the extended conformations, during the stretching and relaxing process. Therefore, while the driving force leading conventional elastomers to recover the initial dimensions is merely entropic, in the case of sPP, the elasticity is possibly also assisted by the enthalpic gain achieved when the sample is relaxed.[8,12]

The ideas behind elasticity of sPP are simply hypotheses, and direct experimental evidences have not been given so far. In particular, it is still not clear whether the reversible polymorphic transition is a direct crystal−crystal transformation or involves transition through a third, disordered, intermediate phase. In this paper, the study of the time scale of this crystal−crystal phase transition during stretching−relaxation mechanical cycles is presented. The influence of this phase transition on the elasticity of sPP is also analyzed.

In situ X-ray diffraction measurements have been performed on uniaxially oriented films of sPP, while the samples are cyclically stretched and relaxed at a controlled rate, using the high flux available on the beamline ID11 at the European Syncrotron Radiation Facility (ESRF), Grenoble, France. During the experiments the stress−strain curves were also recorded.

Experimental Section

The sPP sample analyzed here was kindly supplied by Dr. A. Razavi (ATOFINA Petrolchemical Research). The sample ($M_w = 1.93 \times 10^5$, $M_w/M_n = 4.5$) was prepared using homogeneous metallocene-based catalytic system and is characterized by fully syndiotactic pentad content [$rrrr$]=78% and melting temperatures of 124 °C.

Compression molded films (0.3 mm thick) were obtained by slowly cooling the melt to room temperature. Oriented films were obtained by stretching at room temperature compression-molded films. Rectangular strips 10 mm long, 5 mm wide, and 0.3 mm thick were cut from freshly prepared unoriented films and hence uniaxially drawn and relaxed several times, to achieve a fully elastic recovery.

X-ray diffraction experiments were performed on these oriented films after checking to ensure that they experience a fully elastic recovery in the deformation range applied in our stretching runs. Wide-angle X-ray diffraction measurements were performed using monochromatic X-rays of wavelength $\lambda = 0.718$ Å and the high flux available on the beamline ID11 at the European Syncrotron Radiation Facility (ESRF), Grenoble, France. The oriented films were mounted on a homemade dynamometer, provided with two mobile clamps, which were moved back and forth, cyclically stretching and relaxing the material at a controlled rate of 5 mm/min, within the elastic deformation range of the samples. The mechanical apparatus allowed the automatic recording of the stress−strain ($\sigma - \epsilon$) curves during the experiments. The deformation ϵ of the material is defined as $\epsilon = (l - l_0)/l_0$, with l_0 being the initial gauge length of the sample and l the length of the sample in the strained state.

The X-ray diffraction patterns were recorded in situ, while deforming the material. Each diffraction pattern was exposed 2 s on a two-dimensional CCD detector, and 12 frames were recorded every minute during stretching−relaxation cycles. The two-dimensional data were corrected for curvature of the detector using the diffraction pattern of

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$$C_\infty = \lim_{n \to \infty} (\langle r_0^2 \rangle_n / nb^2)$$
with n being the number of bonds in the backbone, b the bond length, and $\langle r_0^2 \rangle_n$ the mean square length of the chain in the unperturbed state. See, for instance: Flory, P. J. *Statistical Mechanics of Chain Molecules*; John Wiley & Sons: New York, 1969; Chapter 1.
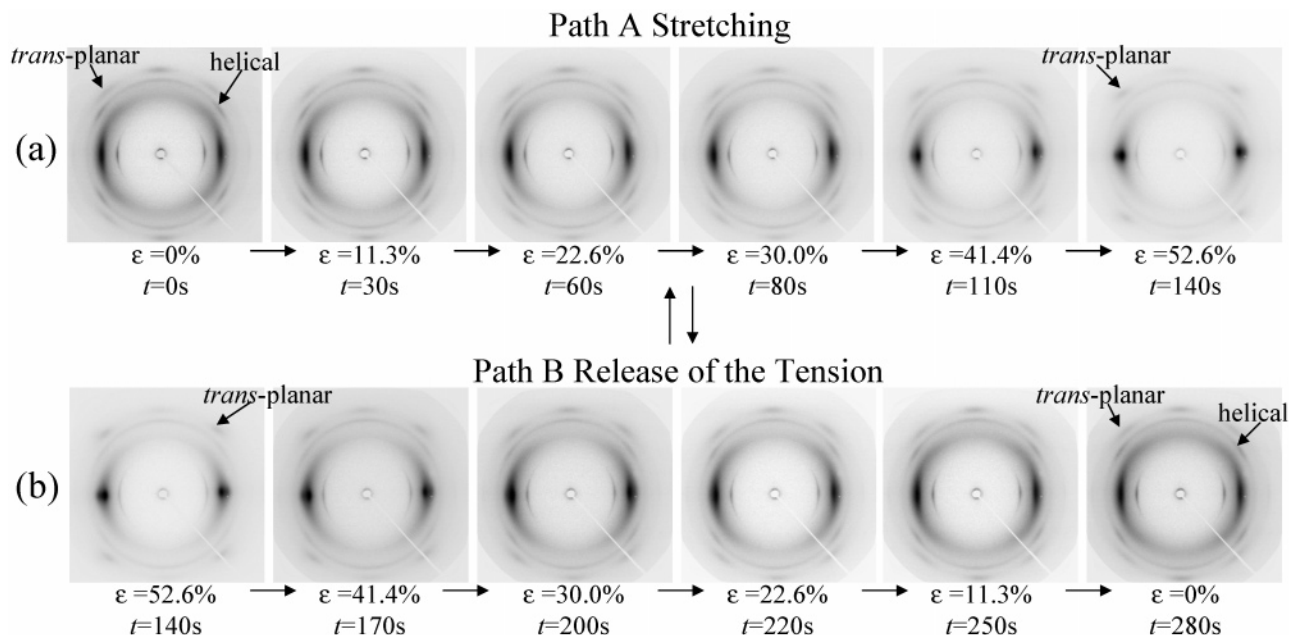
Figure 1. Two-dimensional X-ray fiber diffraction patterns of uniaxially drawn sPP films, recorded in situ, while stretching (a) and relaxing (b) the sample within its elastic deformation range at the indicated values of the strain ϵ. The sample was cyclically stretched (path A) and relaxed (path B) at a controlled rate of 5 mm/min. The patterns were recorded using syncrotron radiation (monochromatic X-rays of wavelength $\lambda = 0.718$ Å, 2 s exposure time, 12 frames/min). In the figure, only the most significant frames are reported. Values of the time during the mechanical cycle starting from the initial unstretched state, $t = 0$, $\epsilon = 0$, are also indicated. The characteristic reflections of the helical form II and the *trans*-planar form III of sPP on the first layer line are indicated with arrows.

a specific calibration grid placed in the X-ray beam. A silicon wafer was used as external standard for calibration of the sample−detector distance. The two-dimensional X-ray diffraction patterns were processed using the FIT2D program of Dr. Hammersley of ESRF.

The crystalline index has been evaluated from the X-ray fiber diffraction patterns. The two-dimensional diffraction patterns were transformed into one-dimensional profiles by performing integration along the azimuthal angle using FIT2D program. The circle coordinates of strong reflections of an unoriented film specimen of sPP were used to determine the correct beam center coordinates. The monodimensional diffraction profile of the amorphous phase was evaluated by performing the same procedure on a two-dimensional X-ray diffraction pattern of atactic polypropylene. The amorphous profile was then scaled and subtracted from the X-ray diffraction profile of the crystalline samples. The crystalline index was then calculated from the ratio of the so-obtained crystalline diffraction area and the total area of the X-ray diffraction profile.

Results and Discussion

X-ray fiber diffraction patterns, recorded during stretching and relaxing of sPP, and the corresponding diffraction profiles read along the equatorial layer line (after subtraction of the amorphous contribution) are reported in Figures 1 and 2, respectively.

The patterns of Figures 1 and 2 were collected while stretching the sample at 5 mm/min from 0 to 52.6% strain (path A, Figures 1a and 2a) and relaxing, at the same rate, the tension from 52.6% to 0 strain (path B, Figures 1b and 2b). The stress−strain curves recorded during the mechanical cycle are reported in Figure 2c. Fully elastic recovery of the sample dimensions are observed in this regime. The Bragg angles, 2θ, and the Bragg distances of the *hkl* reflections observed in the X-ray patterns of Figure 1 are reported in Table 1. The crystalline index of the sample remains constant through the cyclic paths A and B and amounts to $\approx$40%.

In the unstrained state ($\epsilon = 0$), the sample is mostly in the helical form II, as shown by the presence of the strong $(111)_{hII}$ reflection (hII stands for helical form II, this reflection is labeled "helical" in Figure 1a, $\epsilon = 0$) and by strong equatorial $(200)_{hII}$ and $(110)_{hII}$ reflections at $d = 7.20$ Å ($2\theta = 5.72°$) and 5.26 Å ($2\theta = 7.83°$), respectively (Figure 2a, profile for $\epsilon = 0\%$). The $(110)_{hII}$ reflection is typical of the C-centered form II of sPP, characterized by the isochiral packing of chains in 2-fold helical conformation.[3,5] The sample at 0% strain also includes a not negligible fraction of crystals in the *trans*-planar conformation as indicated by the presence of reflections on the first layer line corresponding to the chain periodicity $c = 5.1$ Å[14] (the strongest first layer line reflection arising from these crystals is labeled "*trans*-planar" in Figure 1a).

For strain lower than a critical value, $\epsilon_c \approx 20\%$ (i.e., for $\sigma_c \approx 10$ MPa, Figure 2c), we do not observe any significant change in the X-ray diffraction patterns of Figures 1a and 2a. For higher elongation, $\epsilon > \epsilon_c$ ($\sigma > \sigma_c$), the intensity of $(200)_{hII}$ reflection gradually decreases with increasing ϵ, while the intensities of $(020)_t$ and $(110)_t$ reflections (at $2\theta = 7.55$ and $8.44°$, respectively, Figure 2a) typical of *trans*-planar form III[17] (t standing for *trans*-planar) increase. This indicates that the relative amount of crystals in the helical form II decreases with increasing deformation, while the content of *trans*-planar form III increases. Therefore, a stress-induced phase transition from the helical form II into the *trans*-planar form III occurs when the sample is stretched above a characteristic value of strain. At 52.6% deformation, 72% of the material originally in the helical conformation transforms into the *trans*-planar form III (Figures 1a and 2a). The degree of orientation of crystals in the helical form does not greatly increase while stretching the material (path

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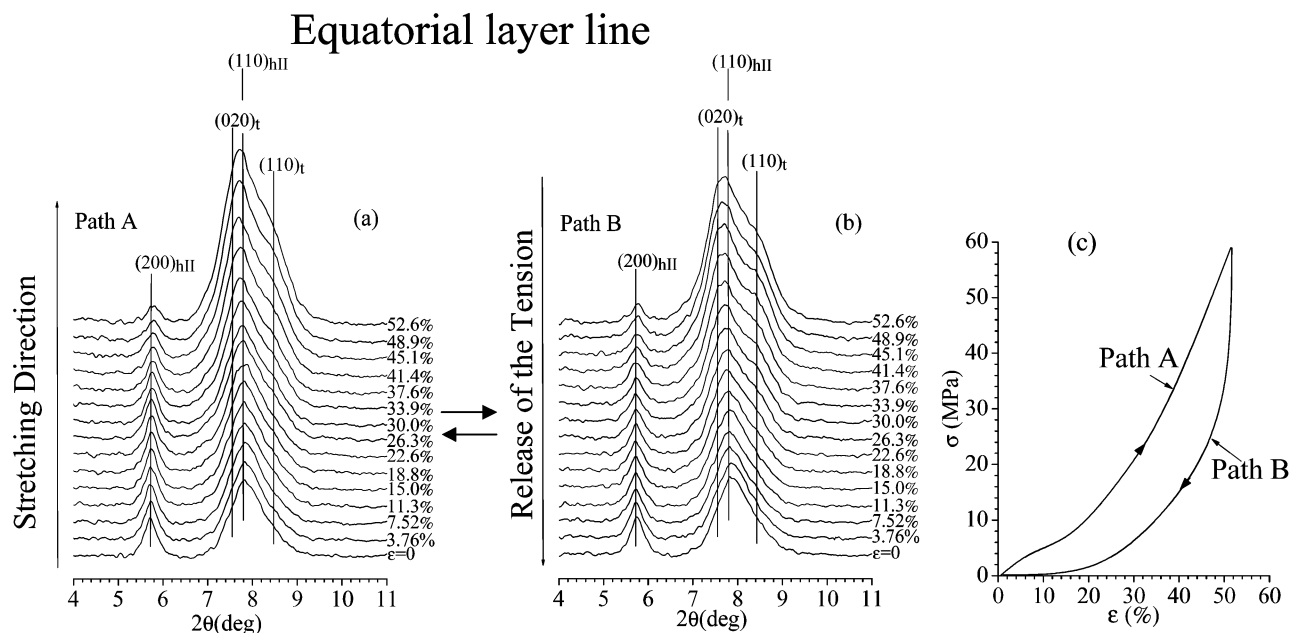
Figure 2. (a), (b) X-ray diffraction profiles read along the equatorial layer line of the two-dimensional fiber diffraction patterns of Figures 1a and 1b, after subtraction of the amorphous contribution. The label close to the profiles indicates the strain ϵ. The position of the most intense equatorial reflections of the helical form II and the *trans*-planar form III are also indicated. Profiles recorded every 10 s are reported. (c) Stress strain curves recorded while cyclically stretching the sample (path A) and releasing the tension (path B) at a controlled rate of 5 mm/min.

Table 1. Reflections Observed in the X-ray Diffraction Patterns of Figures 1a,b and 2a,b

Form II

d^a(Å)	$(2\theta)_{\lambda=1.5418}$ Å^b(deg)	$(2\theta)_{\lambda=0.718}{}^c$(deg)	$(hkl)_{hII}{}^d$
7.20	12.3	5.72	200
5.26	16.9	7.83	110
5.18	17.1	7.95	201
4.29	20.7	9.59	111
3.70	24.0	11.1	002
3.59	24.8	11.5	400

Form III

d^a(Å)	$(2\theta)_{\lambda=1.5418}$ Å^b(deg)	$(2\theta)_{\lambda=0.718}{}^c$(deg)	$(hkl)_t{}^e$
5.45	16.3	7.55	020
4.88	18.2	8.44	110
3.75	23.7	11.0	021
3.45	25.8	11.9	111

^{a} Bragg interplanar distances. ^{b} For readers more familiar with conventional X-ray sources, diffraction angles of the observed reflection for the CuKα ($\lambda = 1.5418$ Å) radiation. ^{c} Diffraction angles of the observed reflection for the wavelength of the used monocromatic X-rays ($\lambda = 0.718$ Å). ^{d} Miller indices of Bragg peaks of form II, orthorhombic unit cell, $a = 14.5$ Å, $b = 5.6$ Å, $c = 7.4$ Å.[3,5] ^{e} Miller indices of Bragg peaks of form III, orthorhombic unit cell, $a = 5.22$ Å, $b = 11.17$ Å, $c = 5.06$ Å.[17]

A, Figure 1a), while a high degree of orientation of the crystals in the *trans*-planar form III, parallel to the stretching direction, is achieved in the fully strained state.

The structural changes occurring during the stretching are reversible. The crystals in the *trans*-planar conformation gradually transform back into the helical form as the applied tension is gradually released (path B, Figures 1b and 2b). Along path B, indeed, the characteristic reflections of the *trans*-planar form III gradually disappear, while the intensities of the reflections of the helical form II increase. Below a critical strain ($\epsilon_c \approx 20\%$), the sample is almost fully in the helical form. The X-ray diffraction patterns of samples strained up to a same elongation along paths A and B are practically coincident. Furthermore, we have checked that the X-ray diffraction patterns of sPP

samples recorded in Figures 1a,b and 2a,b and the stress–strain curves of Figure 2c are practically coincident to those collected during 12 consecutive analogous stretching–relaxing cyclic tests.

The results of our experiments clearly indicate that the structural evolution of sPP is a fast process and occurs on the same time scale as the rate the material is deformed. Moreover, the reversible phase transition between the helical form II and the *trans*-planar form III is a crystal–crystal transition which occurs directly, without involving transformations through a third, disordered, intermediate phase. This transition is a cooperative process imposed by steric constraints involving conformational and structural rearrangements of bundles of neighboring chains[18] in a very short time. The cooperativity induces the formation of helical chains having the same chirality from chains in the *trans*-planar conformation.[18] Such types of phase transitions are rather common in alloys and steels and are generally defined martensitic transitions.[19] As in alloys, the martensitic phase transition in sPP is associated to characteristic values of stress–strain parameters which, in turn, depend on the temperature. At temperatures higher than 60 °C the helical form does not transform into the *trans*-planar form III upon stretching and the samples show no longer elastic behavior.[12]

It is worth noting that a reversible crystal–crystal phase transition between stretched and relaxed states has been found also in polyethers,[20,21] and in some aromatic[22-26] and ali-

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phatic[27,28] polyesters. In all cases, the chain conformation in the stable crystalline form in the unstretched state is not fully extended, whereas it is fully extended in the crystal form which develops upon application of a tensile stress.[22-28] In extensive studies,[22-26] the elastic properties of poly(tetramethylene terephthalate) have been associated with reversible strains of the crystalline lattices.[23] Probably, in all crystalline polymers showing unusual elastic properties, the molecular conformations in both the crystalline and noncrystalline regions play a key role in determining their mechanical behavior.[20-28]

Let us finally note that the other crystalline polymer from the same propylene monomer, isotactic polypropylene (iPP), shows a different mechanical behavior; iPP is a typical semi-crystalline polymer, which, indeed, undergoes permanent plastic deformation under mechanical stress-field. However, a structural transition is also involved. In a recent study the structural and morphological changes during the drawing process of iPP were followed using syncrotron small-angle scattering and wide-angle X-ray diffraction techniques.[29] It has been shown that the α form crystals in the initial iPP fibers transform into the mesomorphic modification by drawing at room temperature. The so-obtained mesomorphic form does not show any lamellar structure. The formation of the mesophase occurs through the destruction of the lamellar crystalline phase probably by pulling chains out of crystals.[29] Thus, while in sPP, application of a tensile strain induce transformation of form II crystals into form III, which transforms back into form II upon removing the stress, in the case of high stereoregular iPP the transformation of α form crystals into the mesophase modification is irreversible, because drawing completely destroys the morphological apparatus present in the sample, before the stretching.

Conclusions

The mechanism underlying the stress-induced, reversible, crystal−crystal phase transition associated with the elastic behavior of sPP and the time scale of this process has been investigated, to unravel the origin of the elasticity of such unconventional elastomer. The structural changes of uniaxially oriented films of sPP samples have been followed during deformation by wide-angle X-ray diffraction measurements, using syncrotron radiation.

The results of the present analysis clearly indicate that the structural transition of sPP between form II and form III is a fast and direct process, occurring on the same time scale as the rate the material is strained. The transition of form II into form III starts in correspondence to characteristic values of stress−strain parameters, during the stretching. As the strain increases, the relative amount of crystals in form II decreases, while the fraction of crystals in form III increases. Releasing the tension, the fraction of crystals in form III gradually decreases while the relative amount of crystals in form II increases; below the

characteristic strain, the sample is almost fully in the helical conformation, as in the initial, unstrained state. A complete recovery of the initial dimension of the specimen is observed. Since the total amount of crystallinity does not change during cyclic elongation and recovery, this result suggests that the reversible phase transition between form II and form III is a martensitic transformation and does not involve participation of any disordered, intermediate phase. As in martensitic phase transitions, it is a direct and cooperative process, implying conformational and structural rearrangements of large bundles of close neighboring chains and occurs instantaneously.

We propose a model for elasticity of sPP based on these data as "elasticity assisted" by the crystal−crystal phase transition. In this idea, both the crystalline and amorphous chains play key roles. The small crystalline aggregates actively participate to the elasticity of sPP, locally acting as microscopic engines. The chains in the amorphous regions are possibly well oriented and in extended conformation in the stretched state and experience a reversible conformational transition between disordered (coil) and extended conformations when the samples are repeatedly stretched and relaxed. These chains are also highly entangled and connect, as tie-chains, different crystals, which undergo the structural transition during the mechanical cycles.

During elongation, the chains in the amorphous regions assume extended conformations and tend to orient parallel to the stretching direction. The crystalline aggregates also tend to assume a preferred orientation with the chain axes parallel to the stretching direction; at the same time, when a given crystal experiences a stress higher than a critical value a crystal−crystal phase transition from the helical form II into the *trans*-planar form III occurs and the size of the crystal increases by 38% along the chain axis direction. During the relaxation step, when a given crystal experiences a stress below a critical value, the *trans*-planar form III becomes unstable and transforms instantaneously into the more stable form II; correspondingly, the crystal shrinks by 38% along the chain axis direction. Since the enthalpy change in this transition is negative, it, in turn, induces an abrupt conformational transition in the chains of the amorphous phase close to the crystals. These amorphous springs assume suddenly less extended conformations generating a sort of chain reaction, which rapidly extends to the whole material. Therefore elasticity in sPP is not merely entropic as in conventional elastomers but also enthalpic.

A deeper analysis of this topic will be reported soon.

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