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Polymorphic Superelasticity in Semicrystalline Polymers**

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Semicrystalline polymers may show elastic properties although they exhibit high crystallinity and high mechanical strength.[1] Syndiotactic polypropylene (sPP) is a superb example of this category of materials.[2] It is a low-cost, stiff, thermoplastic elastomer in which the elasticity is associated with a reversible and instantaneous crystal–crystal phase transition.[2] It has been argued, but never directly demonstrated, that this transformation is of first order and that elasticity in sPP is not merely entropic, as in conventional elastomers, but also partly a result of the enthalpy change associated with the stress-induced crystal–crystal phase transition.[2]

The reversible stress-induced crystal–crystal phase transition that occurs in sPP is illustrated in Figure 1. During elongation, when a given crystal experiences a stress higher than a critical value, a phase transition occurs from the stable form II, with chains in a twofold helical conformation[3] (Figure 1 a), into the metastable form III, with chains in a *trans*-planar conformation[4] (Figure 1 b). This transformation is accompanied by a 38 % increase in the size of the crystals along the chain-axis direction. When the tensile stress is released and a given crystal experiences a stress below a critical value, the *trans*-planar form III becomes unstable and transforms instantaneously into the more stable helical form II. Correspondingly, the crystals shrink by 38 % along the chain-axis direction.[2]

Herein, we present definitive evidence that the stress-induced phase transition between forms II and III in sPP fibers provides an enthalpic contribution to the elasticity, and suggest a method for the measurement of the phase-transition enthalpy. With this aim, X-ray fiber diffraction patterns of uniaxially oriented films of sPP were measured in situ, while the samples were cyclically stretched and relaxed at a controlled rate and at various temperatures, using the high X-ray flux available at the beamline 16.1 of the Synchrotron Radiation Source in Daresbury (UK). The stress–strain curves were recorded simultaneously.

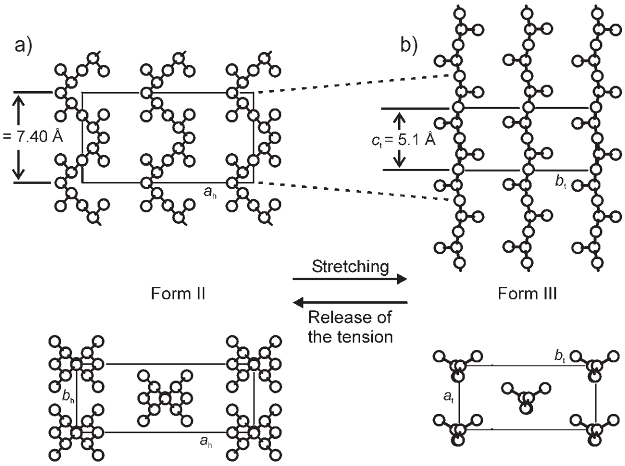

Figure 1. Packing models of limit-ordered forms II (a) and III (b) of sPP in projections parallel (top) and perpendicular to the chain axes (bottom). Form II is characterized by chains in a helical conformation packed in the orthorhombic unit cell with axes $a_h = 14.5$, $b_h = 5.6$, and $c_h = 7.4$ Å and space group $C222_1$.[3] In form III, the chains are in a *trans*-planar conformation and packed in the orthorhombic unit cell with axes $a_t = 5.2$, $b_t = 11.2$, and $c_t = 5.1$ Å and space group $P2_1cn$.[4] Upon stretching, the form II crystals increase in size by 38 % ($= (2c_t - c_h)/c_h$) along the chain-axis direction; upon release of the tension the form III crystals shrink by 38 % along the chain-axis direction.

Examples of X-ray fiber diffraction patterns, recorded during stretching and relaxing of sPP fibers at 273, 298, and 313 K, are shown in Figure 2. The corresponding diffraction profiles read along the equatorial layer line are reported in the Supporting Information. The stress–strain curves recorded simultaneously during consecutive cycles of stretching and relaxing at various temperatures are shown in Figure 3 a.

In the unstrained state ($\varepsilon = 0$) the samples are basically in the helical form II regardless of temperature. With increasing deformation, the intensities of reflections of helical form II gradually decrease, whereas the intensities of reflections of *trans*-planar form III gradually increase (Figure 2 b,e,h and the Supporting Information). The degree of crystallinity remains constant ($\approx 50\,\%$) during deformation and over the chosen temperature range, which indicates that crystals of form II gradually transform into form III with increasing deformation. At the maximum deformation achieved during stretching at the various temperatures (Figure 2 c,f,i and the Supporting Information) the sample is mostly in the *trans*-planar form III.

The X-ray fiber diffraction patterns recorded during sample relaxation are practically coincident with those recorded at the same strain during stretching (Figure 2 and

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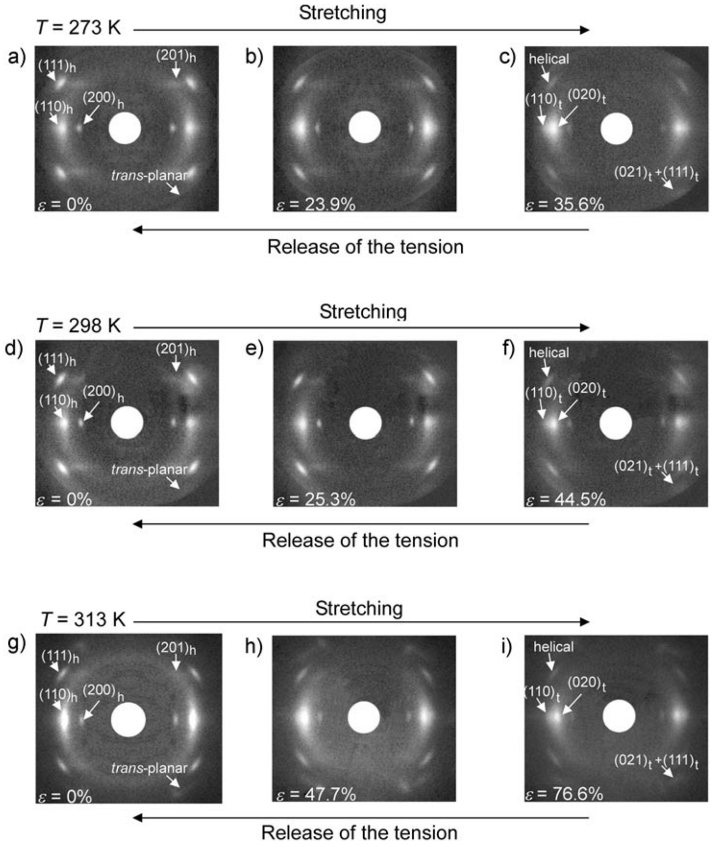

Figure 2. Selected sequences of two-dimensional X-ray fiber diffraction patterns of uniaxially drawn sPP films recorded in situ during stretching the sample within the elastic deformation range. Measurements performed during stretching at 273 (a–c), 298 (d–f), and 313 K (g–i) at the indicated ε values are reported. The X-ray fiber diffraction patterns of samples strained up to the same elongation during stretching and relaxing are practically coincident. The $(200)_h$, $(110)_h$, $(201)_h$, and $(111)_h$ reflections at $d = 7.24$, 5.22, 5.18, and 4.29 Å, respectively, of the helical form II[3] and the $(020)_t$, $(110)_t$, $(021)_t$, and $(111)_t$ reflections at $d = 5.43$, 4.88, 3.75, and 3.45 Å, respectively, of the *trans*-planar form III[4] are indicated. In the patterns without strain (a,d,g) and at the maximum value of strain achieved for each temperature (c,f,i) the characteristic reflections of the helical form II and the *trans*-planar form III, respectively, on the first layer line are also indicated with arrows.

the Supporting Information). This finding indicates that the structural changes occurring during stretching are reversible. Crystals in the *trans*-planar form III gradually transform back into the helical form II as the applied tension is gradually released. At the same time the sample recovers its initial dimensions upon releasing the tension (Figure 3a).

The critical value of strain at which form II starts transforming into form III was found by plotting the integrated intensity of the $(200)_h$ reflection of the helical form II, at $d = 7.24$ Å, as a function of strain (Figure 3b–d). The values of critical stress σ_{cr} corresponding to the critical strain ε_{cr} were determined from the stress–strain curves of Figure 3a. The values of the critical stress–strain parameters are reported in Figure 3e as a function of temperature. It is apparent that the structural transformation of form II into form III during stretching starts occurring at well-defined values of the stress–strain parameters (Figure 3b–d), and that the values of these parameters depend on the temperature (Figure 3e). Upon releasing the tension, the content of form II initially present in the sample is fully recovered only for values of deformation below a critical value. However, while the critical values of strain recorded during stretching and releasing the tension, associated with the reversible crystal–crystal phase transition, are coincident, the critical values of stress are different because of the small but significant hysteresis of the stress–strain curves recorded during consecutive cycles of stretching and releasing the tension (Figure 3a).

Furthermore, the critical values of deformation at which form II starts transforming into form III during stretching (and equivalent critical values on releasing the tension) do not depend on the deformation rate, but merely on the degree of stereoregularity of the sample and the temperature[2,5] (Figure 3e). However, the values of critical stress also depend on the deformation rate: the higher the deformation rate, the higher the apparent critical value of stress.

To determine the stability of the crystal, we kept a fiber in tension at a fixed value of deformation for a long time (hours) while recording the X-ray diffraction patterns every ten minutes. The distribution of diffraction intensity does not change with time, which indicates that the crystals of form II (form III) that transformed into form III (form II) do not transform back into form II (form III). During this time, however, the stress relaxes and reaches a final plateau value. Our knowledge of the viscoelastic nature of polymeric materials, as demonstrated by numerous experiments on various polymers, reveals that the final value of stress does not depend on the applied strain rate, but only on the imposed strain.[6] This suggests that the equilibrium value of strain experienced by the crystals in a sample stretched up to the critical value of strain ε_{cr} may be found by performing stress-relaxation experiments (see the Supporting Information).

The enthalpy difference associated with the reversible crystal–crystal phase transition between forms II and III, $\Delta H_{(\mathrm{II}\leftrightarrow\mathrm{III})}$, was evaluated from the equilibrium values of the critical stress σ_{cr} experienced by the crystals at various temperatures (found by stress-relaxation experiment) using the Flory–Oth equation [Eq. (1)].[7]

$$\left[\frac{\partial(\sigma_{cr}/T)}{\partial(1/T)}\right]_P = \frac{\Delta H_{(\mathrm{II}\leftrightarrow\mathrm{III})}}{A\,\Delta L} \qquad (1)$$

Herein, P is the pressure, A is the cross-sectional area per monomeric unit of crystals of form II, and ΔL is the difference between the advance lengths of each monomeric unit parallel to the chain axis in the *trans*-planar form III and those in helical form II. In the case of sPP, $\Delta L = 0.7$ Å and $A = 10.15$ Å^2 (see the Supporting Information). From the linear plot of Figure 4 we obtained a value of the transition enthalpy of (2.6 ± 0.1) kJ mol^{-1} of monomeric units, in good agreement with energy calculations which indicate that the helical form II is more stable than the *trans*-planar form III in the unstrained state by 2.2 kJ mol^{-1} of monomeric units.[8] It is

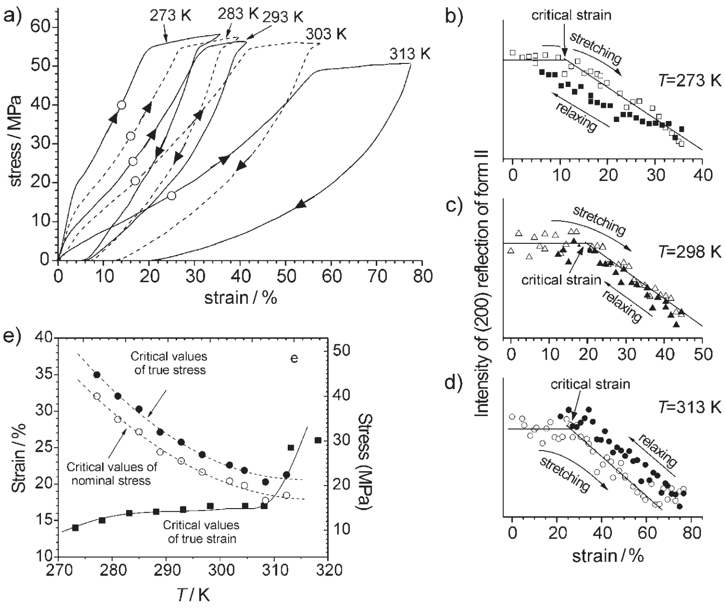

Figure 3. Stress–strain curves recorded while cyclically stretching the sample and releasing the tension at a controlled rate of 4.83 mm min^{-1} according to the direction of the arrows, at the indicated temperatures. a) The critical values of stress along the stress–strain curve recorded during the stretching step are indicated by ○. b–d) Intensity of the $(200)_h$ reflection of the helical form II evaluated from X-ray diffraction patterns (Figure 2 and Supporting Information) as a function of strain at b) 273, c) 298, and d) 313 K. e) Critical values of strain ε_{cr} (■) and apparent values of nominal (○) and true critical stress σ_{cr} (●) as a function of temperature. The apparent values of critical stress σ_{cr} (○) correspond to those read along the stress–strain curves recorded during stretching. The corresponding values of true stress (●) are evaluated by the product of the nominal stress σ_{cr} and the corresponding draw ratio λ ($=l/l_0$, with l_0 the initial gauge length and l the length of the sample in the strained state).

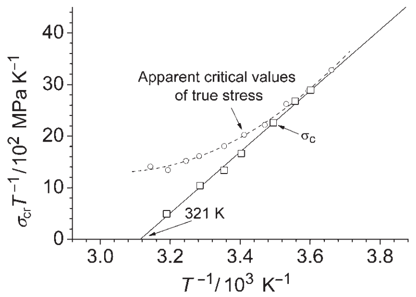

Figure 4. Plot of equilibrium values of stress (σ_{cr}) experienced by the crystal skeleton of sPP fibers stretched up to the values of critical strain ε_{cr} at which transformation of form II into form III starts occurring, according to Flory–Oth theory[7] [Eq. (1)]. The values of σ_{cr}/T (□) are reported as a function of reciprocal temperature $1/T$. The linear fit of σ_{cr}/T data allows evaluation of the enthalpy difference of the crystal–crystal phase transition between forms II and III from the slope of the straight line. The extrapolation of the straight line to $\sigma_{cr}/T=0$ gives a value of temperature corresponding to the spontaneous transformation of form II into form III under free tension of 321 K. The apparent critical values of true stress σ_{cr} determined from the stress–strain curves recorded during stretching are also reported (○).

apparent that the spontaneous transformation of form II into form III without tensile deformation ($\sigma_{cr}=0$) is expected to occur at 321 K, which corresponds to the extrapolated point of the straight line to $\sigma_{cr}T^{-1}=0$. From the value of $\Delta H_{(II\leftrightarrow III)}$ and the equilibrium transition temperature of 321 K, a value of the transition entropy of $\Delta S_{(II\leftrightarrow III)}=8.1\ \mathrm{J\,mol^{-1}\,K^{-1}}$ was derived.

In conclusion, fibers of highly stereoregular sPP samples show elastic behavior over a substantial deformation range and in a wide temperature range despite the high degree of crystallinity. This behavior occurs as a result of a first-order crystal–crystal phase transition, which provides an enthalpic contribution to the elastic recovery of the sample, when the applied stress is removed. Herein, we provide for the first time a value of the polymorphic transition enthalpy change responsible for the elastic recovery.

sPP is not an isolated case. Other examples of polymers that show long-range elasticity despite exhibiting a high degree of crystallinity are oriented fibers of poly(tetramethylene terephthalate)[1b] and some naturally occurring protein fibers, such as keratin, resilin, and spider silks.[1a] However, the case of sPP is of particular interest because the presence of high levels of crystallinity and the active role of crystals in the elastic recovery can be exploited for the development of low-cost, high-modulus, polypropylene-based thermoplastic elastomers characterized by a chain network with controlled stiffness, high strength and ductility, and elastic properties in a wide deformation range.[2,9]

The present study provides a basis to widen the concept of elasticity in thermoplastic polymers, as a phenomenon that involves retractive forces of enthalpic origin in addition to those of an entropic nature, as in conventional elastomers. In particular, elasticity in highly crystalline sPP is similar to the superelasticity of shape-memory alloys that undergo martensitic phase transitions during stretching.[10] We introduce the concept of polymorphic “superelasticity” as the property of some crystalline polymers to respond immediately to applied stress through a martensitic-like crystal–crystal phase transition, which provides for the macroscopic recovery of the dimensions of the sample upon releasing the applied tension. Introduction of such a concept in the field of thermoplastic elastomers may open new routes toward the development of novel elastomeric materials with enhanced mechanical properties, in terms of high modulus and stiffness that do not impair the ductility and elastic performance.

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