

A Microscopic Insight into the Deformation Behavior of Semicrystalline Polymers: The Role of Phase Transitions

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The deformation behavior of semicrystalline polymers associated with polymorphic transformations under tensile deformation is discussed in the case of syndiotactic polypropylene. We report a phase diagram of this polymer where the regions of stability of the different polymorphic forms are defined as a function of the degree of stereoregularity and deformation. The values of critical strain corresponding to the structural transformations depend on the stereoregularity that affects the relative stability of the involved polymorphic forms and the state of the entangled amorphous phase.

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Crystalline polymers present a unique morphology. At variance with other crystalline materials, such as metals, polymers crystallize only partially. They are generally composed of crystalline lamellae embedded into an amorphous phase. The polymeric chains in the amorphous phase are highly entangled. The lamellar crystals usually have thickness of the order of tens of nanometers, whereas the lateral dimensions are much larger. Since the polymer chains in the crystalline phase are generally oriented perpendicular to the lateral dimension of the lamellae and the length of the chains is much larger than the lamellar thickness, each chain may run through several crystalline and amorphous regions. Therefore, semicrystalline polymers are characterized by a peculiar architecture, where lamellar crystals alternate to amorphous regions in a highly interconnected network [1].

The peculiar semicrystalline character of polymers largely determines their outstanding physical and mechanical properties. In particular, polymers exhibit large plastic deformation when stretched above the glass transition temperature. During deformation, the initial isotropic structure, characterized by the random orientation of the polymer segments in both amorphous and crystalline regions, is gradually transformed into a highly anisotropic fiber morphology, characterized by preferential orientation of the chains aligned along the stretching direction [2]. The development of a fibrillar morphology starting from the spherulitic structure is an irreversible process, the original spherulitic morphology can be reobtained only by melting of the fibrous material and successive recrystallization. Therefore, the stretching of crystalline polymers inevitably involves large plastic (irreversible) deformations.

The mechanism of plastic deformation in polymers is rather complicated and involves different phenomena, which occur on the same time scale of applied stress and on different length scales. The global deformation behavior of semicrystalline polymers at temperatures higher than the glass transition temperature may be regarded as the stretching of two interpenetrated networks, made by the interlocked crystalline lamellae and the entangled amorphous

phase [3], characterized by a large nonlinear internal viscosity. Deformation is accomplished by slip processes within the lamellae, intralamellar mosaic block slips, and, at larger strain, when the stress acting on the crystallites reaches a value at which the crystalline blocks are no longer stable, by stress-induced melting and recrystallization in new oriented crystallites, whose assembly forms fibrils [3]. The principal modes of deformation on the crystallographic length scale may be slips, twinings [2,3], martensitic transformations [4], stress-induced melting [5], and recrystallization [6], and formation of nanoblocks in the amorphous phase [7]. Collective intralamellar slip processes, collective motions of lamellar stacks [2,3,8,9], and formation of microvoids [4,7] may occur at a larger length scale.

This picture may be further complicated by the occurrence of polymorphic transformations during plastic deformation at large degrees of deformation, that is, after the yield point. In fact, in many polymers the crystalline form that develops upon stretching may be different from the stable form present in the melt-crystallized undeformed samples. Moreover, in some cases, stretching may cause the disruption of lamellar crystals through the pulling out of chains from the crystals, leading to the formation of a mesophase [10,11], i.e., a solid phase characterized by a large amount of structural disorder that may be considered as intermediate between amorphous and crystalline phases [12]. When the crystalline form that develops by stretching is metastable, it may transform back into the more stable form previously present in the unoriented sample, or into another polymorphic form, by removing the tensile stress. In some highly crystalline polymers the polymorphic transition occurring upon releasing the tension is reversible and is associated with a nontrivial elastic recovery [10,11,13,14]. The entity of plastic versus elastic deformation experienced by the material upon releasing the stress, may critically depend on the relative stabilities of the two crystalline phases that develop during successive cycles of stretching and relaxation. The enthalpic gain of the reversible crystal-crystal phase transition occurring upon releas-

ing the tension may play a key role in the elasticity of these materials [13].

The nontrivial role of the crystalline phase in the deformation behavior of semicrystalline polymers may be nicely illustrated by syndiotactic polypropylene (sPP) that shows unexpected long-range elasticity in spite of high modulus and crystallinity. The mechanical properties of sPP depend on the crystallization behavior, which in turn depends on the chain microstructure and, in particular, on the stereoregularity [14,15].

In this Letter we analyze the polymorphic transitions occurring during tensile deformation and the mechanical properties of sPP samples of different stereoregularity. We show that, depending on stereoregularity, different polymorphic transitions are involved during stretching, and that stress-induced phase transitions are strain controlled rather than stress controlled. A phase diagram of sPP is built up where the regions of stability of the different polymorphic forms are defined as a function of stereoregularity and degree of deformation.

We have analyzed sPP samples prepared with different metallorganic catalysts, which produce polymer chains of different stereoregularity [16–20]. The samples present, indeed, concentration of the fully syndiotactic *rrrr* pentad in the range 26%–96%, and melting temperatures variable between 153 °C and 45 °C. A fully amorphous slightly syndiotactic sample with $[rrrr] = 26\%$ has also been studied.

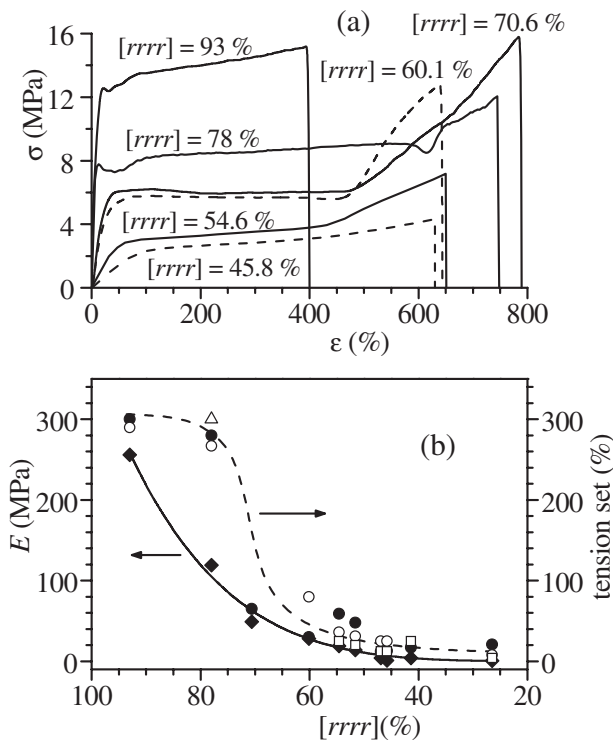


FIG. 1. Stress-strain curves (a), values of Young's modulus (E) (\blacklozenge), and residual deformation (tension set) after 200% (\square), 400% (\circ), 600% (\triangle) strain and breaking (\bullet) (b) of sPP samples as a function of stereoregularity [21].

The stress-strain curves of compression-molded films of some sPP samples are reported in Fig. 1(a). In view of the large uncertainty in the true stress-strain relationships, especially for the more stereoregular samples (with $[rrrr]$ in the range 78%–93%) that exhibit nonuniform stretching behavior and deform via necking, only the engineering stress-strain curves are reported [21]. The Young's modulus and the residual deformation (tension set) after deformation of 200%, 400%, and 600%, and after breaking decrease with decreasing stereoregularity [Fig. 1(b)]. This indicates that poorly stereoregular samples show good elastic behavior even in the state of unstretched compression-molded film. Furthermore, the residual deformations do not depend on the value of the strain and are identical, within the experimental error, to that measured after breaking.

The polymorphic transitions occurring during plastic deformation have been studied for all samples as a function of stereoregularity by recording the x-ray diffraction patterns during stretching. Examples of diffraction patterns are reported in Fig. 2 for samples having $[rrrr] = 93\%$ (a–c) and 78% (a'–c'). Two benchmarks have been placed on the test specimens and used to measure elongation. During deformation the focused x-ray beam always illuminates the same position of the film, between the two benchmarks. Therefore, the measured strain, correlated to the structural transformations, basically corresponds to the true strain [21].

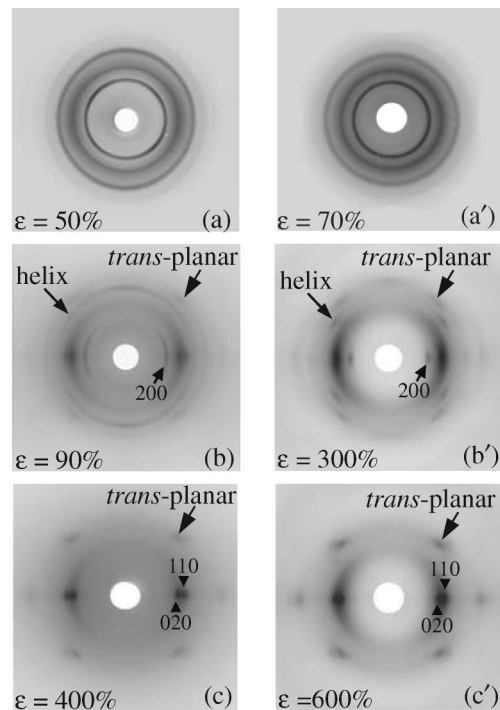


FIG. 2. X-ray fiber diffraction patterns of fibers of sPP samples of different stereoregularity, with $[rrrr] = 93\%$ (a–c) and 78% (a'–c'), stretched at deformation ϵ . The 200 reflection of the helical form I and 020 and 110 reflections of the *trans*-planar form III are indicated.

These data reveal that the plastic deformation is associated with a polymorphic transition. For the more stereoregular sample, when a critical value of the strain $\epsilon_c = 90\%$ – 100% is achieved, the stable form I with chains in twofold helical conformation, present in the unoriented compression-molded films [Fig. 2(a)], gradually transforms into the *trans*-planar form III [Figs. 2(b) and 2(c)]. Fibers in the pure form III are obtained only at higher deformation [Fig. 2(c)]. The value of the critical strain ϵ_c increases with decreasing stereoregularity. In addition, different structural transformations are observed for samples of lower stereoregularity, having $[r_{rrrr}]$ in the range 70% – 87% [Figs. 2(a')–2(c')]. The helical form I [Fig. 2(a')] partially transforms into the *trans*-planar mesomorphic form upon stretching at deformations higher than the critical value ϵ_c [Fig. 2(b')], and only at higher deformations the mesomorphic form transforms into form III [(Fig. 2(c')]. For poorly syndiotactic samples having $[r_{rrrr}]$ in the range 45% – 70% , the ordered *trans*-planar form III does not form by stretching even at very high deformation [20]. The helical form I transforms at high deformation into the *trans*-planar mesomorphic form and the crystalline form III never forms.

It is worth noting that in all cases the degree of crystallinity does not change during stretching [21]. The transformation of form I into form III for more stereoregular samples (with $[r_{rrrr}] > 90\%$), and into the mesomorphic form for samples of lower stereoregularity (with $[r_{rrrr}] < 90\%$), is probably originated by mechanical melting of form I lamellae, with consequent formation of a disentangled amorphous, followed by fast recrystallization into the *trans*-planar form III or mesomorphic form, and only marginally by crystallization of the amorphous phase during stretching.

The structural analysis have allowed building the phase diagram of sPP at room temperature (Fig. 3), where the regions of stability of the different polymorphic forms of sPP in oriented fibers are defined as a function of stereoregularity and degree of deformation ϵ .

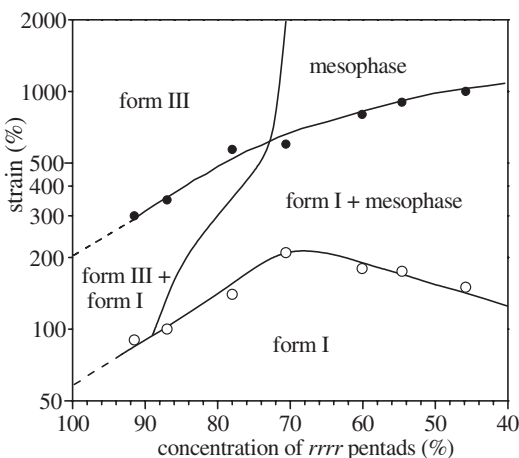


FIG. 3. Phase diagram of sPP as a function of strain and stereoregularity.

The different phases are not considered from thermodynamic standpoint but from the structure standpoint, based on the x-ray diffraction observations. For all the analyzed samples the boundary lines between the different regions have been determined by the emergence or disappearance of x-ray reflections typical of the different polymorphic forms of sPP, including the mesophase [21]. The values of the critical strain at which the polymorphic transitions start and at which the transformation is complete depend on the stereoregularity. The critical values of the stress instead also depend on other parameters as, for instance, the degree of crystallinity of the sample, the amount of structural disorder present in the crystals and on the method of preparation of the test specimens. It is worth noting that although the phase diagram of Fig. 3 is given from a dynamic perspective rather than from a thermodynamic perspective, the critical values of strain are not affected by the deformation rate. In fact, the samples are kept in tension for two hours during recording the x-ray fiber diffraction patterns, allowing full relaxation of the test specimen, and the observed polymorphic form probably corresponds to the equilibrium modification, thermodynamically stable at those values of stereoregularity and deformation [21].

According to a generalized view the mechanism that governs the process of tensile deformation of semicrystalline polymers at low and moderate deformations appears strain controlled, rather than stress controlled [3]. This may be evidenced by the fact that along the true stress-strain curves of several polymeric materials different regimes are discernible, corresponding to changes in the differential compliance that take place at defined critical points [3]. These critical points have been interpreted as (i) the onset of isolated interlamellar and intralamellar slip processes after the initial Hookean elastic range (point A); (ii) change into a collective activity of slip motions at the yield point (point B), and (iii) the beginning of the destruction of crystal blocks followed by recrystallization with formation of fibrils (point C) [3,9]. The values of the strain at each critical point are constant, for each class of polymer, when varying crystallinity, temperature, strain rate, and crystal thickness [3]. The position of the critical strain at the point C, at which a critical network stress is reached that starts destructing the crystal blocks, depends on the interplay between the entanglement density of the amorphous phase and the intrinsic stability of crystals [3]. A higher entanglement density implies a higher stress that is generated when the sample is stretched. The more stable the crystallites, the higher the stress needed for their destruction [3]. When polymorphic transformations occur during plastic deformation, as in the case of sPP, also the phase transitions are probably strain controlled rather than stress controlled. Since the critical value of deformation at which the polymorphic transitions start are higher than the deformation values at point C, the structural transformations presumably always correspond to the destruction of the original lamellae of a given crystalline form, and recrystal-

lization with formation of fibrils in a new crystalline form. Moreover, the dependence of the critical strain on the stereoregularity (Fig. 3) suggests that the two factors that govern the location of the critical strain corresponding to the formation of fibrils, that is, the modulus of the entangled amorphous and the stability of the crystal blocks [3], depend on the stereoregularity. Chains of different stereoregularity possess, indeed, different flexibility. In fact, the relative configuration of consecutive stereoisomeric centers along the chain affects the space correlation among skeletal bonds and the rotational energy barriers around the C-C bonds [22]. Since the dynamics of macromolecular chains is largely controlled by these parameters, which can be defined as “the internal viscosity” [23], different degrees of stereoregularity produce a different entanglement density of the amorphous phase. The stereoregularity also affects the stability of crystals (besides the degree of crystallinity) and may influence the relative stability of the different polymorphic forms involved in the structural transformations. In the case of sPP, it has been shown that the presence of stereodefects destabilizes the *trans*-planar form III, because *mm* triad and *m* diad stereodefects, typical of sPP chains, are more easily tolerated within the lattices of the crystalline modifications of sPP with chains in helical conformation [13,20], so that the formation of the *trans*-planar form III by stretching becomes more difficult (Fig. 3) and is prevented in poorly stereoregular sPP. The relative importance of the crystal stability driven by stereoregularity and the network modulus driven by entanglement density, is probably different depending on the stereoregularity and degree of crystallinity. For more crystalline and stereoregular samples the influence of crystal stability is dominant and the critical strain where the helical form I starts transforming into the *trans*-planar form III increases with increasing concentration of defects due to the reduced stability of the *trans*-planar form III. For poorly stereoregular and crystalline samples the further decrease of plastic resistance of the preexisting highly defective crystals of the helical form I, the increased flexibility and reduced network modulus are more important and produce a slight decrease of the critical strain.

In summary, the nontrivial role of the crystalline phase in the deformation behavior of semicrystalline polymers at large deformations has been illustrated. When the results of the present analysis are jointly examined with the up-to-date results concerning the deformation mechanism of semicrystalline polymers at low and moderate deformations [3], a quite unified picture may be outlined. Polymorphic transitions occurring during tensile deformations involve breaking of preexisting lamellae of the original crystalline form and formation of fibrils of the new crystalline form. These transitions, for a given sample, appear strain controlled rather than stress controlled. The values of the critical strain linked to the polymorphic transi-

tions are, indeed, namely, affected by the chain microstructure, whereas the corresponding values of the stress depend on the degree of crystallinity, the amount of structural disorder present in the crystals and on the relative stability of the two involved crystalline forms. Direct crystal-crystal phase transitions may instead occur upon stretching and relaxing oriented fibers, that is, specimens that have already undergone plastic deformation. In these cases the structural transition may play a key role in the elastic recovery of the sample, when the crystalline form obtained upon stretching is less stable than the crystalline form that develops upon releasing the tension [13,14].

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