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SHORT COMMUNICATION

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# On the plastic deformation of bulk syndiotactic polypropylene

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**Abstract** The plastic deformation of syndiotactic polypropylene (sPP) bulk samples has been investigated. A structural comparison of the initial states before and after plastic deformation by necking is carried out by X-ray diffraction observations. Independent of the initial states (amorphous, semi-crystalline with different crystal phases), only the planar all-*trans* crystal form of sPP is present in the deformed samples after necking. Form these results, molecular mechanisms of the plastic deformation in the neck zone of semi-crystalline polymers will be discussed.

**Key words** Semi-crystalline polymers – X-ray diffraction – necking – phase transformation – molecular mechanisms

## Introduction

The plastic deformation of polymers by necking has been a subject of intense investigations since 40 years. Several models have tried to explain the macroscopic visible necking during cold drawing of semi-crystalline bulk polymers by different molecular mechanisms in the necking region. A reorganization of crystals in a continuous, liquid-like matrix [1] or the deformation of complete spherulites [2–4] have been assumed in early publications.

Further investigations have resulted in observations of inhomogeneous deformations of spherulites and transformations of the lamellar to a fibre morphology in the necking region [5, 6]. Such transformations are explained by a local quasi-melting in the necking region, followed by recrystallization [7, 8]. Also, observations of twinning after deformation of polymer single crystals [9] and of a stress-induced martensitic phase transformation of polyethylene [10, 11] are found as special cases of plastic deformation of semi-crystalline polymers.

On the basis of the results obtained, two basically different types of molecular mechanisms have been proposed for the transformation from the homogeneously deformed pre-necked to the necked zone. Peterlin has suggested a model [12], which is based on lamellae tilting and crystal shearing along the chain axes [13, 14], to explain the deformation induced spherulitic-lamellar to oriented-fibrillar transformation. However, other models have explained the observed results by complete destruction of lamellar crystals in the necking region followed by fibrillar recrystallisation [15, 18].

Our experiments are carried out on sPP samples. Two different chain conformations in the crystalline state of sPP are known. Based on a twofold helical $(ttgg)_2$ conformation (Fig. 1A), three different crystal structures have been observed, one with isochiral chains packed in a c-centred unit cell (cell I, Fig. 2A) [19, 20], one with antichiral chains packed along the *a*-axis of the unit cell (cell II, Fig. 2B) and the third with antichiral chains packed along *a*- and *b*-axes of the unit cell (cell III, Fig. 2C) [21–24]. Potential energy calculations [25, 26] have indicated that nearly equivalent conformational energies of sPP chains are represented by the planar all-*trans* (tttt) conformation (Fig. 1B). Samples, which are cold-drawn below the glass transition temperature exhibit

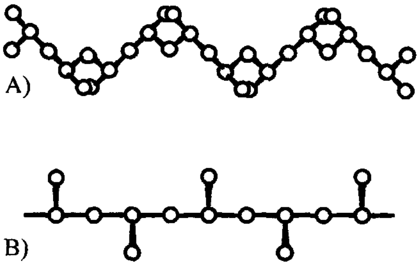


**Fig. 1** Molecule conformations of sPP: (A) twofold helical (ttgg)$_2$ conformation; (B) Planar all-*trans* (tttt) conformation

a crystal structure containing the zigzag chains (Fig. 2D) [27–29].

It is the purpose of this paper to report results of a structural study of plastic deformed bulk sPP samples.

## Experimental

The sPP used in the experiments was kindly supplied by the Fina Oil and Chemical Company. Samples with different crystal phases were prepared by melting the sPP in a hot press mould followed by isothermal crystallization at 130 °C for one week (cell III), 100 °C for one day (cell II), or by quenching from the melt to room temperature (mixture of cell I and II). Some samples were quenched into liquid nitrogen and kept below −20 °C in order to keep them in the amorphous glassy state. The deformation experiments were performed in a tensile testing machine, equipped with a cooling chamber, at room temperature for the semi-crystalline and, immediately after quenching, at −20 °C for the amorphous samples with a deformation rate of 5%/min.

For wide angle X-ray scattering (WAXS) investigations, the samples were fixed between clamps under constant strain conditions after the drawing. The measurements were carried out at room temperature using a Philips pinhole camera (X-ray generator operating at 30 kV and 20 mA, emitting Ni-filtered Cu $K_\alpha$ radiation) and a Philips wide angle goniometer (X-ray generator operating at 40 kV and 30 mA, emitting Ni-filtered Cu $K_\alpha$ radiation, scanning speed 0.01°/s.

## Results

Depending on the preparation, different crystal phases or only the amorphous phase is found in the initial state of the investigated bulk samples. Figure 3 represents X-ray goniometer traces of samples prepared as described above. Quenched from the melt in liquid nitrogen and kept below −20 °C, the trace exhibits the typical shape of an amorphous polymer (Fig. 3A). For samples, which were isothermally crystallized from the melt at 130 °C for one week, the trace exhibits intensity maxima typical for the

**Fig. 2** Proposed unit cells of sPP: (A) C-centered cell I; (B) cell II with antichiral packing of chains along the *a* axis; (C) cell III with antichiral packing of chains along the *a* and *b* axes; (D) unit cell containing molecules with all trans conformation (R right-handed helices; L left-handed helices)

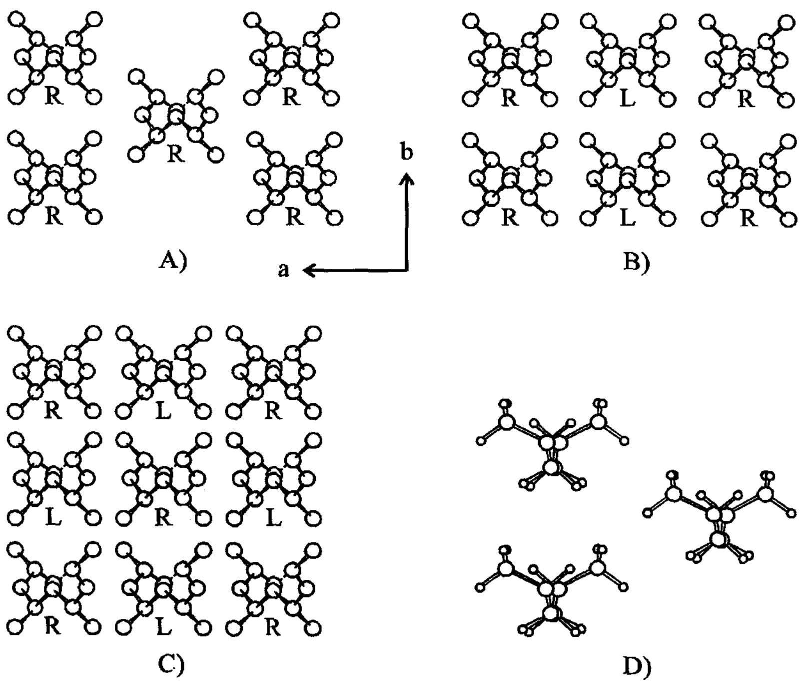
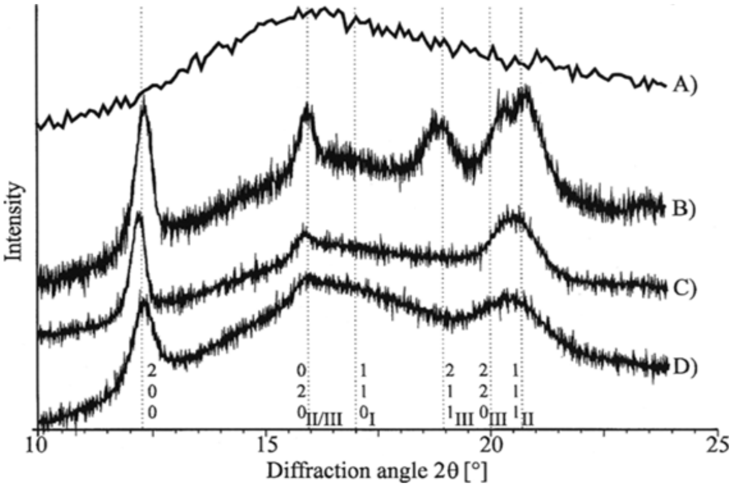


**Fig. 3** X-ray goniometer traces of sPP samples: (A) amorphous phase; (B) cell III phase; (C) cell II phase; (D) phase containing molecules with all-*trans* conformation



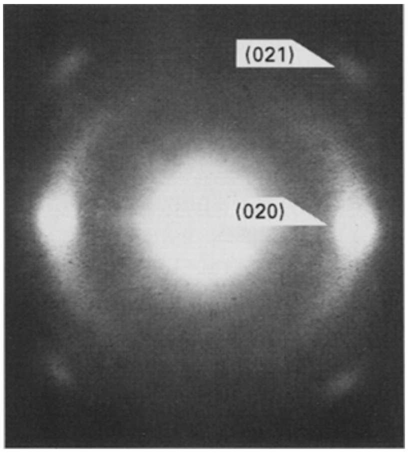


**Fig. 4** X-ray pinhole fibre diffraction pattern after the deformation of sPP from the necked region

cell III crystal form of sPP (Fig. 3B). Crystallized from the melt at 100 °C for one day, the samples contain cell II crystals (Fig. 3C). The absence of the cell III intensities at $2\theta = 18.9°$ and $2\theta = 20.0°$ and the narrow shape of the intensity maxima at $2\theta = 15.9°$ indicate the cell II phase. Samples crystallized from the melt at room temperature show a high amount of cell I crystals mixed with the cell II from (Fig. 3D). The scattering maxima at $2\theta = 15.9°$ for the cell II phase and at $2\theta = 17.0°$ for cell I crystals result in a broad, superposed intensity maximum.

Figure 4 shows a X-ray pinhole fibre diffraction pattern after the deformation from the necked region with indicated main diffraction reflexes, typical for all four initially different types of samples. In order to avoid shrinkage of the necked part of the samples, they were clamped into a rigid frame. The diffraction patterns are explained in terms of the orthorhombic unit cell with cell constants $a = 0.522$ nm, $b = 1.117$ and $c = 0.506$ [28]. These oriented crystals contain chains with all-trans conformation.

## Discussion

Several molecular models of the plastic deformation via necking of semi-crystalline bulk polymers have been discussed in the literature, as described above. According to the general experimental evidence, only the models explaining the plastic deformation by a lamellar to fibrillar transformation will be discussed here. Peterlin describes this transformation by a lamellae tilting and crystal shearing along the chain axes, followed by the oriented rearrangement of these crystalline fragments [12]. A complete destruction of the crystalline structure, followed by fibrillar recrystallization [15–18] is suggested in other models.

From transmission electron microscopic results (TEM, dark field mode), Peterlin has demonstrated, that the single fibrils show a fragment-like, interrupted crystalline morphology [30, 31]. Also, the calculation of the shear forces along the chain axes during plastic deformation has indicated that the shear is more likely than the fracture of the lamellae [10]. On this basis, Peterlin's model is a possible explanation of the lamellar to fibrillar transformation after necking. But in many subsequent investigations it is demonstrated, that the fragment thickness does not necessarily coincide with the original lamellar thickness.

Furthermore, in an excellent performed experiment, Fujiwara et al. have demonstrated, that the isotactic polypropylene (iPP), which is crystallized in its hexagonal $\beta$-modification, transforms into the monoclinic $\alpha$-modification after "neck" deformation [32–34]. The authors conclude, that Peterlin's model is invalid to interpret their experimental results, because the unit cell of the $\beta$-iPP contains two helical chains with opposite handedness, while the $\alpha$-modification contains two helical chains per unit cell with the same handedness, and no shear mechanism can change the handedness of a helical chain.

It is also known since long, that the piezoelectric active $\beta$-polyvinylidene flouride (PVDF) phase can be processed by high drawing of the piezoelectric not active $\alpha$-phase [35]. During the drawing, the $[\mathrm{ttgg}]_2$ chain conformation of the PVDF transforms into the all-*trans* chain conformation of the $\beta$-phase. Additionally, the chiralities of the two chains in the unit cells of the $\alpha$- and $\beta$-PVDF are of opposite or the same sign in the two respect unit cells. It is also hard to explain these tranformations by Peterlin's model.

The results obtained from our investigations on the deformed sPP directs to the same conclusions: independent of the "phase-state" of the non-necked material – glassy or crystal phases with different chain chiralities – the necked region in the deformed material contains a different crystal phase with a different chain conformation compared to the non "transformed" phases. From these observations we conclude, that the final molecular process in the lamellar to fibrillar tansformation during necking involves the loss of the memory of the chains about their physical state from the non transformed material to the "necked" material. While lamellar shear and rotation, and crystal shear may occur before necking, these molecular processes cannot be responsible for the lamellar to fibrillar transformation occuring in the "necking" zone.

A similar conclusion was drawn in Ref. [18], where ultra thin films of crystalline and amorphous isotactic polystyrene/atactic polystyrene (iPS/aPS) blends were deformed and investigated by TEM and electron diffraction. While in these ultra thin films (deformed at RT, 70 °C below the glass transition temperature of polystyrene), the transformation occured in an area of nanometer size, we cannot give any clue on our bulk samples of sPP about the size of this transformation zone (Fig. 5). We assume, that in this transformation zone the molecules have disordered but highly strained chain conformation, either resulting from strain energy or from thermal energy. When passing this transformation zone, the non ordered material can recrystallize under the high strain conditions into a fibrillar morphology.

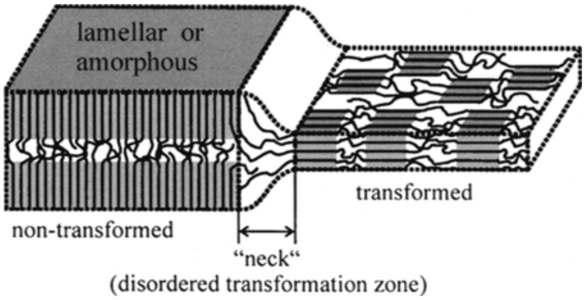


**Fig. 5** Sketch of a deformed sample with indicated transformation zone

## Conclusion

SPP tensile test samples containing different crystal modifications, or being amorphous can be highly deformed via the necking process. The crystal modification as well as the chain conformation in the necked regions are different from non necked areas. This leads us to the conclusion, that the Peterlin model cannot be applied for the molecular process occuring in the transformation zone between non necked and necked material. A transformation zone is postulated, in which the memory of the molecules to their initial state (non transformed) gets lost.

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