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Stress induced changes in microstructure of a low crystalline Polypropylene investigated at uniaxial stretching

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Abstract

Novel asymmetric metallocene catalysts lead to low isotactic polypropylenes (iPP) with randomly distributed stereo irregularities. The polypropylenes are low crystalline and show elastic mechanical behaviour due to physical cross linking. The morphology of such iPP, responsible for mechanical properties observed is still sparsely resolved. In the present work a low isotactic, low crystalline metallocene iPP containing randomly distributed stereoerrors was investigated. The influence of the chain microstructure in the elastic properties was studied using two complementary investigation methods, X-ray diffraction and scanning force microscopy. This includes the efforts to come closer to the main question of the nature of the physical cross-links, as reason for the high elastic behavior.

For a better understanding of the unique mechanical properties microscopic changes in morphology and strain induced variation in chain orientation were monitored during uniaxially stretching using scanning force microscopy (SFM) and wide angle x-ray scattering (WAXS) measurements. For quantitative analysis and discussion the polymer chain orientations were calculated. The correlation between the orientation, the arrangements of the amorphous and crystalline phases observed by SFM and the mechanical properties of the material at different elongation ratios allows an interpretation of the macroscopic behavior on the microscopic scale. Interpretation are confirm with existing structural models, which proposed that small crystalline domains act as physical cross-links for the amorphous matrix.

Keywords: atomic force microscopy (AFM), WAXS, poly (propylene) PP, mechanical properties, elastomers,

Introduction

In the last decade, metallocene catalysts gained rapidly increasing interest in academic research as well as in industrial development [1], because these catalysts provide the control over the chain microstructures of polyolefines in contrast to conventional Ziegler-Natta catalyst [2-9]. When applied to propene polymerization [10, 11], depending on the symmetry of the catalyst and the polymerization conditions, a great variety of polypropene polymers with different stereo regularities and molecular weight distributions can be polymerized resulting in samples not only with different crystallinities but also with different morphologies and physical properties [7, 8, 12, 13]. Good examples for these variations are polypropene showing highly syndiotactic-, hemi-isotactic chains [7, 8] or atactic-isotactic block structures [9]. Especially low crystalline PP's have been attracted increasing amount of interest because these polymers exhibit elastomeric properties [6, 7, 14-16]. The elastic properties of these polypropylenes are assigned to a block structure of the chain where regular isotactic and irregular atactic sequences present [17]. Studies performed on stereoblock isotactic-atactic polypropylenes [18-21] confirm the model that regular (isotactic) segments form small stable, crystals, which are randomly distributed in a soft matrix composed of the atactic chain segments [5, 18]. The hard elements act as cross-links and build up the network necessary for the elastic deformation. For amorphous thermoplastic elastomers, such as styrene butadiene copolymers, it is well known that not only the total amount of hard segments but also their distribution within the chain determines the mechanical properties [22].

Although a broad variety of low isotactic polypropylenes have been synthesized [3, 8, 9, 19, 23-31] the influence of the distribution of regular segments in the morphology and elastomeric behavior is sparsely resolved. In this paper, the strain induced changes of a low isotactic polypropylene with statistically distributed stereo errors [8,13] were studied. Hence the isotactic blocks are short small lamellar domains were found, which form a randomly distributed forming a continuous network [32]. Properties, such as strength at elongation, are associated with rearrangement and deformation of the crystalline and amorphous domains. Therefore, the molecular understanding of the influence

of the chain microstructure on the deformation process of elastomeric semicrystalline materials is mandatory. Results of the mechanical studies on semicrystalline polymers clearly show that properties, such as tensile strength, elongation to break or reversible deformation, are associated with the rearrangement and deformation of the hard segment domains and amorphous domains. Based on many studies on highly oriented semicrystalline polymers the microscopic process of tensile deformation was proposed to proceed within several regimes [33-42]. At first, intra-lamellar slipping of crystalline blocks occurs at small deformation (deformation rates below yield strain). At a strain larger than the yield strain a stress-induced crystalline block disaggregation-recrystallization process takes place. In contrast for low crystalline thermoplastic elastomers (TEP) a deformation process reminiscent of that observed for naturally occurring fibrous proteins such as silks [43] was proposed, where the breakup of crystallites and their orientation into fibrils were suggested to be the determine processes during mechanical deformation [3, 44-46]. Based on WAXS [3] and SFM [45] studies three stages in the deformation were discriminated [3, 44-46]. In the unstrained state randomly distributed crystalline domains are connected by flexible amorphous chains. Under low deformation the amorphous regions are extended and due to local stress the crystalline domains break up. The rotation of domains and selective breakup of hard domains at various orientations results in a structure consisting of small blocks aligned in the stretching direction at higher elongation. Thus, a fibrillar superstructure is formed where chains are oriented parallel to the stress direction, and the soft segment chains undergo stress-induced crystallization. Releasing the stress, preferably the amorphous domains are retracted to reach the entropically favored disordered random coil conformation. Thus, the entropic effect is responsible for the elastic recovery [44].

To learn more about the structural changes and crystal orientations of a low isotactic polypropylene containing statistically distributed stereoerrors the presented study was performed using both WAXS and SFM experiments. Interpretations of the macroscopic mechanical behavior on the bases of chain orientations recorded from WAXS measurements on low crystalline, high molecular weight metallocene PPs obtained so far [47] give no final explanation of the mechanical behavior of

those unique materials but a number of publications showed that scanning force microscopy has an excellent potential for studying polymers under macroscopic deformation. [44, 45, 48-51]. One advantage of this method is that no thin film sectioning, staining and sputtering is required as in TEM. Macroscopically thick samples can be studied *on-line* at different elongations. The results are directly relevant to the in-use properties. Therefore, we investigated such a sample with SFM in non-stretched state and during stretching in order to correlate those results with WAXS observations, allowing better knowledge on the network responsible for the elasticity. Therefore, stress induced changes of the existing crystals in the α - and γ - modification, how it was worked out in [13], were calculated from WAXS records by the orientation function and arrangements of the amorphous and crystalline phases was observed in the SFM images. The discussion of the orientation in terms of the main present net planes, arrangements of the phases and stress strain measurements showed that the network, which is responsible for the elasticity, is mainly composed of strain-induced morphology changes combined to chain orientations.

Experimental section

Materials

Sample preparation

A low isotactic polypropylene has been prepared in toluene at 315 K using a C_1 -symmetric *ansa*-zirconocene catalyst as described in [8]. Molecular weight and molecular weight distributions were determined by gel permeation chromatography (Alliance GPC 2000, Waters, Millford, USA), 420 K in 1,2,4-trichlorobenzene) universal to polystyrene and relative to polypropylene standards. For the presented sample a molecular weight of 160000 g/mol with M_w/M_n of about 1.8 has been determined. NMR spectra have been used to calculate the concentration of isotactic pentads. For this purpose 15 mg of the sample were dissolved in 500 μ l toluene in a 5 mm tube. ^{13}C NMR

spectra were recorded on a Bruker AMX 500 spectrometer (Bruker GmbH, Rheinstetten, Germany) operating at 353 K. The analyzed sample contains 36 % of isotactic pentads.

Film preparation

Different types of films were used for the various analysis techniques. For DSC and WAXS investigations as well as for mechanical testing melt pressed films with a thickness of about 1 mm were used (Series A). The surface of these films was rough because of the casting of the pressing tool. Therefore, these samples are not suitable for SFM experiments. For SFM experiments a second set of film was fabricated by the combination of solvent casting and heat-treating (Series B). All films were stored for 6 month at room temperature under ambient conditions (30% humidity, 278 K) before further investigations to ensure that the samples were in thermal equilibrium (fully crystallized).

Melt pressed films

To prepare melt pressed films (Series A) 10 g granulated polymer were placed in between two glass plates covered with PTFE foils with a spacer of 1 mm. The polymer was heated under constant low pressure (2kN) to 390 K. When the temperature was reached and the sample was molten the pressure was increased up to 5 kN. After leaving the sample for 30 min, the pressure was increased up to 20 kN. After another 30 min the sample was cooled down to room temperature with a cooling rate of 1.5 K/min. The thickness of the film was 1 ± 0.01 mm determined using a micrometer screw.

Solvent casted films

These films were prepared dissolving 2 g of the polymer in 75 ml toluene. The solution was heated in a water bath at 350 K for 60 min to ensure the total dissolution of the polymer. The solution was casted on top of a PTFE foil placed in a petri dish ($\varnothing = 10$ cm). The petri dish was covered with glass to enable the slow evaporation of the solvent. After 7 days films with a thickness 0.25 ± 0.05

mm were obtained. To simulate the heating process of the melt pressed film the solvent casted films were heated in a vacuum oven to 390 K for 60 min and cooled down to room temperature with a cooling rate of 1.5 K/min (Series B).

Mechanical characterization

To test the mechanical properties of the samples, stretching experiments have been performed on a commercial stretching device (Zwick 1445, Zwick GmbH + Co. KG, Ulm Germany). From both types of films (Series A and B) samples were punched using a dog-bone puncher with nominal dimensions of 20 mm in length and 5 mm in width. Areas on the films showing inhomogenities were excluded for the tests. To calculate the nominal stress the cross sectional area has to be determined. Therefore, additional to the width the exact thickness of the samples was estimated using a micrometer screw. The initial length of the sample as well as their elongation was measured by the optical detection system (accuracy of the method: ± 0.5 mm) of the used stretching device. For this purpose two optical markers were applied in the middle of the sample with a distance of around 15 mm. To determine the stress-strain behavior the samples were subjected to tensile testing with a stretching rate of 4 mm/min until the sample fails.

To determine the reversible deformation and to study the morphology of stress-relaxed specimen, the samples were stretched to a desired elongation $\lambda_{cyc} = 8$ using a strain rate of 4 mm/min, keeping the film under tension for 1 min at room temperature, then removing the tension with a controlled rate of 4 mm/min. Subsequently, the samples were removed from the stretching device and stored without strain for 24 h to allow them to recover totally before measuring their final length (l_{rel}). The elasticity of a sample can be defined as the amount of reversible deformation ε_{rev} after elongation to a given strain rate λ_{cyc} calculated by equation 1, where l_{cyc} = length of the sample stretched to λ_{cyc} and l_{rel} = length of the relaxed sample.

Wide angle x-ray scattering (WAXS)

For x-ray scattering investigations 1 mm thick melt pressed films were used similar to the other stretching experiments (series A). Wide Angle X-ray scattering (WAXS) measurements were performed at room temperature at the beamline A2 at HASYLAB at DESY in Hamburg (wavelength = 1.5 Å). Phosphor imaging-plate devices (IP) were used for recording the two-dimensional (2d) scattering intensities. For stretching the melt pressed films a custom made setup was used, which was implemented in the beamline. The sample was stretched stepwise from $\lambda = 1$ (non-stretched state) to $\lambda = 9.7$ ($\Delta\lambda \geq 1$). At each step, a 2d scattering record was taken. Sample elongation was determined using radiolucent markers on the strips and a caliper. Crystallinity of the sample in the non stretched state, where the existing crystals presents an isotropic distribution was determined according to the method described in [13]. Briefly the crystallinity is given by the ratio of the integral of the scattering curve subtracted by the amorphous halo to the integral of the whole scattering curve [13].

Constant azimuthally intensity distribution of 2d scattering images, assured that only initially isotropic samples were investigated. For a quantitative description of the orientation, radial intensity distributions were read out and the orientation functions were calculated. Procedure of the data acquisition and the calculation of the orientation function were performed as described in detail in [47]. Therefore, the azimuthally intensity distributions at the scattering angles of interest representing the main net planes (110_{α} , 040_{α} , and 202_{γ}) [sample P3 in 47]) were determined from the radial intensity distributions and the orientation functions were calculated for each elongation step. Briefly the orientation function is a function of the azimuthally intensity distribution. The notations of the reflections given herein correspond to the identification of the apparent crystal modifications in the presented sample as analyzed from Boger et al. [13].

Orientation functions are presented as functions of elongation. The co-domain of the orientation function ranges from -0.5 (net planes are perpendicular oriented to the reference axis) to 1 (net

planes are parallel oriented to the reference axis). Reference axis was the stretching direction indicated by $\varphi = 0^\circ$. Zero ($f = 0$) indicates an isotropic distribution of the net planes. A rotational symmetry can be assumed if the sample dimensions are several times bigger than oriented structures according to [52]. This is the case for the presented polymer, where the sample thickness was greater than 0.1 mm even at maximum elongations. Obtained orientation functions were compared and discussed to the SFM observation.

Additionally, the superstructures of the samples were investigated under uniaxial deformation performing SAXS measurements. The SAXS records were made similar to the WAXS records with longer detector-sample distance and higher exposure time.

Scanning force microscopy

For scanning force microscopy (SFM) investigations, solvent crystallized films were used, because their surface had been shown to be relatively smooth and their macroscopic properties determined from stress-strain experiments are similar to the ones observed for thicker melt pressed films. To investigate the morphology of polypropylene samples the surface of the solvent casted films were imaged using a D3100 Scanning Force Microscope equipped with a Nanoscope IIIa controller (Veeco Instruments, Santa Barbara, CA) under ambient conditions. The microscope was operated in Tapping Mode (TM) using standard micro-fabricated silicon cantilever with aluminum reflex coating (OMCL 160TS, Olympus Corporation, Japan). The cantilevers have nominal spring constants of 40 N/m; typical resonance frequencies ranged between 275 and 315 kHz. In TM [53] the topography is measured as the constant distance of the tip normal to the surface by keeping the amplitude of the oscillating tip constant. The amplitude damping r_{SP} conditions the applied force. r_{SP} is defined as the ratio of the engaged amplitude A to the free air amplitude (A_0) of the oscillating tip. Amplitude and set point ratio were chosen such that the cantilever-tip assembly did not get trapped on the sample surface and that the imaging conditions warranted stiffness-dominated

contrast in the phase images. Typically, in phase images recorded under these conditions harder domains show higher phase shifts, thus appearing brighter than softer areas. For discussion of image contrast and its dependence on scanning conditions see also [54, 55]. In our studies the free amplitude A_0 has been set to 2 V, which is equivalent to 90 nm, and the set point amplitude A ranges between 1.325 and 1.35 V resulting in an amplitude damping r_{sp} of about 0.65 – 0.7. The phase images shown here were subjected to a first-order plane-fitting procedure to compensate for sample tilt. The magnitude of the phase signal is affected by various scan parameters, such as the precise amplitude of the free vibrating cantilever and the set point ratio. Since these values are given by the SFM software and cannot be absolutely controlled, the recorded values can only be considered as relative ones [54]. Thus, phase images are presented without an absolute color scale.

SFM images were performed on one sample (Series B) at different deformation states. Therefore a home-built stretching device was combined with a SFM to monitor deformation induced changes in the morphology of polymeric films on-line [56]. The compact setup of the stretching device fits in a Dimension 3100 SFM (Veeco, Santa Barabra, USA).

Two computer controlled stepper motors (MICOS GmbH, Eschenbach, Germany) are used for stretching. This balanced assembly was used to secure symmetric deformation of the sample. A strain gauge force sensor with maximum range of 5 ± 0.5 N (Submidget force sensor Type 8411, Burster, Gernsbach, Germany) equipped with an SEMMEG 9000 amplifier is integrated. The stretching device was controlled via custom-built software, which allows the simultaneous recording of the force. This enables either to measure force-elongation curves of the used samples or to control the force during SFM imaging. Latter has been shown an important parameter because deformation experiments of elastic materials showed that these samples relax when the stretching process was interrupted. To avoid relaxation induced changes in sample structure while scanning the specimen were left under a given deformation rate for at least 3 hours to relax. To retain relatively high surface smoothness and avoid films vibrations a moveable support has been mounted in the middle of the stretching device, where the height can be adjusted by a micrometer screw.

The morphological changes were recorded taking a series of phase shift images of the film surface after stepwise stretching from $\lambda = 1$ to $\lambda = 7$. The elongation was determined by the initial length (l_0) and the displacement (Δl) received from the calibrated step motor control (accuracy: ± 1 mm). Stress-relaxed specimen have been prepared by stretching the film up to $\lambda = 7$, keeping under tension for 1 min at room temperature, removing the tension and allowing the specimens to relax for 2 h.

The average distance between adjacent crystalline blocks was detected by means of line scans of SFM phase images (Figure 1a and b). The results are averaged over at least 10 crystalline domains. Performing SFM phase images of the samples on a scan range of 1 μm with 512 x 512 pixels per image, results in a accuracy of ± 2 nm for the observed features. Any quantitative determination of the lamellar dimensions from TM-SFM images leads to a considerable overestimation because of the finite tip radius.

Results & Discussion

Mechanical testing

Similar stress strain curves were obtained for melt pressed and solvent crystallized films when they were stretched until they failed (Figure 2a). The stress-strain curves show clearly that the samples can be assigned to the group of elastomers, because the obtained stress-strain curve does not show a pronounced yield point, but after reaching an elastic plateau the stress increases continuously until the sample fails after stretching up to 10 times of its initial length. Comparing melt pressed films and the ones obtained from solution crystallization, both types reached maximum draw ratios up to $\lambda = 10$ to 12 before the specimen fails at failure stresses σ_{max} of about 6 ± 1 MPa. Thus, the solvent crystallized films can be used as a model system for SFM experiments.

The reversible deformation (Figure 2b) was determined as described in the experimental section. A reversible deformation larger than 70% was observed for all the investigated samples indicating a high reversible deformation.

WAXS

Figure 3 (top) shows 2d WAXS-images of the sample at various states of elongations from $\lambda = 1$ to 8 and after stress release. The WAXS measurements showed very distinctive fiber textures for the sample presented. Orientation of the crystals could be obtained qualitatively by the scattering patterns which become anisotropic or in other words the azimuthally intensity distribution is not constant anymore. Additionally the equatorial radial intensity distributions at the several stretching steps are shown (Figure 3, bottom). The sample indicates reorientation and recrystallization at elongation lower than $\lambda = 4$, which could be seen qualitatively due to the alteration of the radial intensity distributions.

Quantitative orientations of the net planes are presented using the orientation function as function of the elongation (Figure 4). Orientation functions calculated for the sample of the main net planes $(110)_\alpha$, $(040)_\alpha$ and $(202)_\gamma$ are shown in Figure 4. An actual value of nearly zero in the unstretched sample ($\lambda = 1$) shows an initially isotropic state of the sample. When the sample is stretched to $\lambda = 2.5$ the change from zero indicates that the scattering gets anisotropic due to orientation of the existing crystals. During stretching the $(110)_\alpha$ net planes are orienting towards the stretching direction ($f < 0$) and becomes more accurate at higher elongations. Net planes corresponding to $(202)_\gamma$ show a slight orientation ($f_{(202)\gamma} = -0.06$, $\lambda = 9.7$) even at maximum elongation. Orientation function of the net planes $(110)_\alpha$ decreases continuously to -0.31 at maximum elongation indicating a medium orientation along the stretching direction. Most interestingly are the orientation observed from the net planes defined by $(040)_\alpha$. Those show initially a slight orientation perpendicular to the stretching direction ($f = 0.18$, $\lambda = 3$) and a decrease afterwards to ($f = -0.14$, $\lambda = 9.7$). The

orientation of the $(040)_\alpha$ net planes that should occur exclusively on the equator are not completely understood. In combination with the SFM observation this initial orientation towards perpendicular to the stretching direction supports the later interpretation according to the proposed model, that until $\lambda = 4$ a break up of the crystalline lamella occurs. Therefore these reflexes can be caused by tilted crystal structures (e.g. lath-like crystals). The authors would also like to mention that these reflexes can be overlapped with others at this scattering angle region (e.g. $(110)_\alpha$), which can be present in several orientation directions in the a_α - axis + c_α - axis orientation [57]). Separation of the WAXS reflexes belonging to different origins is very difficult, e.g. different sized lamella occurring during stretching as mentioned in the SFM results cannot be separated by presented WAXS investigations. Uniform chain orientation for $\lambda > 4$ where all blocks and tie chains are aligned towards the stretching direction, as an optimization of the fibrillar structure are consistent with SFM observations.

The stress-strain curve of the sample (Figure 2) shows a steadily increase in strength after reaching $\lambda = 3$. Comparing the slope in the stress-strain curve and the orientation it can be concluded, that the increase in crosslinking density (increasing slope / material stiffness) is associated with constant increasing orientation of the $(110)_\alpha$ net planes, which consists mainly of α - crystals [13]. This indicates that these oriented crystals mainly cause the driving force, which is the reason for the elasticity after stress is released. Those oriented crystals could be only a part of all crystals, especially only the small crystals, which are formed during stretching as mentioned in the SFM results & discussion section. Thus, they are the building blocks of the network responsible for material elasticity. According to the findings described in [47], the sample showed a parallel chain axis-orientation of the disordered α/γ - crystals according to the calculations from Auriemma and De Rosa [57]. Changes of the orientation function belonging to net planes called $(040)_\alpha$ showed also a high correlation to the stiffness of the material and have to be analyzed and understood in more detail.

WAXS record performed in the relaxed state after stretching to $\lambda = 8$ is shown in Figure 3. This investigation shows that if the stress is released, the crystals are stable but relaxed in the orientation. Orientation functions calculated for the main net planes (not shown) in the relaxed state decreased to $f = -0.1$ and $f = -0.08$ for the netplanes defined by $(110)_\alpha$ and $(040)_\alpha$, respectively. Orientation function for the $(202)_\gamma$ net planes remained constant after releasing the stress ($f = -0.05$). Keeping the sample under tension at high elongation over longer time, further crystallization appears which can qualitatively be observed as an increase of the peak height and therefore of the reciprocal integral width which is directly related to the crystal size [13].

SAXS records showed no discrete scattering reflexes and therefore no indication on existing superstructures could be observed by the x-ray scattering investigations.

Scanning force microscopy

The sequence of SFM images of solvent crystallized sample under deformation and in the relaxed state is shown in Figure 5a - i.

The phase shift image of the unstretched sample (Figure 5a, $\lambda = 1$) shows isotropic dispersed but discontinuous hard domains consisting of rodlike crystalline lamellae and smaller crystalline blocks immersed in a continuous softer amorphous phase. Determined amount of hard phase was about $18 \pm 2\%$ of the surface. These data suggest that owing to the relatively low isotacticity the crystalline lamellae and blocks form a network-like structure [32]. Stretching to $\lambda = 1.5$ results in the re-orientation of some of the crystalline lamellae parallel to the stretching direction, but most of them remain unoriented (Figure 5b). Similar trends can be observed at $\lambda = 2$, but here the orientation of larger crystalline domains (Figure 5c) becomes more obvious. Tilting of the lamellae occurs in such a way that the chain folds are aligned with the tensile axis. This parallel alignment of the chain is supported by the x-ray experiments as mentioned already.

At further elongation to $\lambda = 3$ only small increase in stress was recorded (Figure 2). This suggests that at this state of deformation mainly tie chains within the amorphous regions become extended. When a distinct level of stress was reached, additionally the separation between crystalline segments occurs as shown in Figure 5d. Only a few large lamellae remain unchanged, preferably those aligned parallel to the stretching direction. Almost no crystal retains its original length. Therefore, at this draw ratio the stress was sufficient to break up the initial ribbon-like crystals into small blocks. The constant increase in stress observed in the stress strain curve (Figure 2) points out that the local stress required to break a given crystallite becomes higher when the crystallite size decreases. When the sample is stretched to $\lambda = 4$ almost all of the original crystallites are destroyed (Figure 5e). However, they are not all transformed separated in small blocks with an average width of 7 ± 2 nm until a draw ratio $\lambda = 5$ is reached (Figure 5f).

The images taken at a draw ratio $\lambda = 6$ (Figure 5g) show blocks aligned in the stretching direction resulting in fibrillar structures which are seen to span more than a few hundred nanometers. These fibrils are reminiscent on a beads-on-a string structure where the crystalline blocks are detected as the slightly wider regions (beads) connected by slightly darker fibrils having a width in the narrow direction about half of the block width. These thinner microfibrils oriented in the strain direction might consist of originally amorphous sequences. [33, 58] Since SFM phase shift images are sensitive only to changes in local stiffness, lamellar crystals as well as oriented soft segments could both appear to be “stiff” enough to provide contrast. In the final stage of elongation ($\lambda = 7$) almost all blocks and tie chains are aligned along the direction of the tensile axis resulting in a highly oriented fibrillar structure depicted in Figure 5h. Since the fibrils are perfectly straight, they have to be under stress. This structure is very similar to the load-bearing microfibrils imaged by electron microscopy in highly oriented ultra-thin polyethylene. [39, 40] Thus, at high elongation a morphology has been formed similar to the fibrillar structure observed for higher crystalline samples.

The closer examination of the microfibrillar structure points out that at increasing elongation the distance between adjacent crystalline blocks increases along the stretching direction. This suggests the continuous elongation of the amorphous domains at increasing draw ratios. To quantify the local deformation in stretching direction, the distance between crystalline blocks along the stretching direction was determined from cross-sectional plots (Figure 1). Plotting the distances versus the elongation, strain induced microscopic changes in morphology (filled circles, Figure 6) can be correlated to the macroscopic stress-strain behavior (line, Figure 6).

Within a deformation regime between $\lambda = 1 - 3$ the distance between adjacent crystalline blocks along the stretching direction is nearly unchanged. Based on SFM images (Figure 5a-c) the amorphous regions become elongated and rod-like lamellae are oriented parallel to the stretching direction. Within this stretching regime the local stress is insufficient to break up the crystalline lamellae. A substantial increase in the distance between adjacent crystalline blocks can be observed when the draw ratio increase from $\lambda = 3$ to 4. Thus, stress becomes high enough to break the lamellae apart and fractions are formed which start to align along the stretching direction. The fractions are displaced and their distance increases. The increase in stress can be attributed to the fact that the smaller, thus shorter, the lamellae are the higher the stress necessary to break them up.

When the draw ratio $\lambda > 4$, microblocks are formed all over the sample which aligned along the stretching direction revealing a fibrillar superstructure (Figure 5d). Now, the increase the draw ratio leads to a nearly linear increase in stress and block distance along the stretching direction. Since no further crystalline break up can be observed in the SFM images, it might be suggested that the amorphous chains connecting the microblocks are elongated in the same ratio as the macroscopic draw ratio increase. At higher elongation $\lambda = 7$ the flexible chain segments are nearly perfectly parallel aligned and forming a microfibrillar structure (Figure 5g). The aligned chains start to crystallize due to the applied stress and the increase in block distance is no longer linear (not shown here).

To learn more about the elastic recovery of the films, a stress-relaxed specimen have been prepared. An elastic recovery ε_{rev} of $75 \pm 5\%$ of the sample refers to irreversible changes in the polymer structure during deformation. SFM phase shift images of a relaxed sample (Figure 5h) confirm the results, which were mentioned already from the elastic recovery, that irreversible changes in the polymer structures occurred during deformation. In the image taken in the relaxed state the degree of reversibility of the structure orientation is visualized. After releasing the stress the extended amorphous domains contracts and the most part of the sample reveals randomly distributed crystalline blocks (Figure 5h). This result confirms the proposed structural model which was briefly mentioned in the introduction and will be described in the following paragraph, which proposed that small crystalline domains act as physical cross-links for the amorphous matrix.

Within some areas oriented fibrils with a beads-on-a string structure persist (Figure 7). Along the fibrils the average distance between the individual crystalline blocks is reduced compared to the stretched state ($\lambda = 7$) (open circle, Figure 6). Thus, the entropy driven relaxation of the amorphous interspaces can be proposed. The distance is larger than the one estimated in the unstretched state, it might be suggested that some fraction of the amorphous chains crystallized under stress and cannot entropically relax. Thus, for the relaxation also morphological changes due to melting and recrystallization might be taken into account. To proof this assumption further studies also concerning the thermal behavior are necessary.

The results of WAXS and SFM support the proposed a model for the deformation of thermoplastic elastic polymers [44-47] but in case of the homogeneous crystalline network some modifications are necessary (Figure 8): Under low deformation the amorphous regions are extended and crystalline lamellae rotate to become aligned with their long axis parallel to the stretching direction. Thus, the chains are oriented perpendicular to the stretching direction (Figure 8 B) At higher elongation (Figure 8 C) the lamellae are preferably oriented perpendicular to the stretching direction. Due to the local stress the crystalline domains break up and small blocks are formed.

Further elongation (Figure 8 D) a fibrillar superstructure is formed where chains oriented parallel to the stress direction, and the soft segment chains will undergo stress-induced crystallization). Releasing the stress (Figure 8 E), preferably the amorphous domains are retracted.

Orientation of the existing structures could be shown with both methods and also correlated to the macroscopically properties. However a strengthening effect on the interpretations by combining those methods could only partly observed.

An improvement for the presented investigation could be to perform simultaneous SFM and x-ray microscopy records (small focus area, small radiated volume), in that way that the stepwise stretched sample is scanned by SFM and directly a x-ray microscopy record is taken.

Conclusion

These results obtained from WAXS studies in combination with the SFM experiments lead to the conclusion that the proposed structural model for the deformation of low crystalline polymers also fits for low isotactic polypropylenes with randomly distributed stereoerrors. WAXS results and discussion of the orientation in terms of unit cells and stress strain measurements showed that the network, which is responsible for the elasticity, is mainly composed of strain induced crystallites. Results of the present work support the interpretation of De Rosa et al. [6] about the origin of elasticity in poorly isotactic PPs. However the sample presented herein showed much higher elasticity and failure strain compared to the ones presented in the mentioned paper. It has to be taken into account that small randomly distributed crystalline domains are proposed to act as physical crosslinks for the amorphous matrix are not initially formed during crystallization from solution or melt, but generated by crystallite breakup and orientation of small crystalline blocks when the samples is stretched for the first time. Since the breakup of crystallites is essentially irreversible plastic deformation it contributes to the large degree of strain hysteresis observed as reduced elastic recovery between the first and second deformation cycle. When randomly distributed crystalline blocks have been formed, the samples show no further decrease in the elastic

recovery. Thus, chain segments belonging to the amorphous phase, connecting the crystalline regions are elastically deformed. These amorphous chains are entangled and connect, as tie-chains, the small crystalline domains. They act as springs between the crystals, which are in extended conformation in the stretched state and return in the disordered coil conformation when the tension is removed. The amorphous chains pass through a reversible conformational transition between the entropically favored disordered random coil conformation in the unstretched state and the extended conformation in the stretched state due to an entropic effect. Thus, the investigated low isotactic sample with a *mmmm* content of 36% can proposed that elastic recovery of TEP's occurs mainly due to the entropy driven relaxation of the amorphous segments.

Further SFM experiments where the morphology of relaxed samples was discovered give strong evidence that randomly distributed microblocks were generated when the polymer is stretched for the first time. In following stretching experiments these microblocks act as crosslinks. Thus suggests, that initially formed crystalline morphology has a limited influence in the elastic properties of propene based TEP's. The elasticity is mainly determined by the strain induced morphology. To proof this assumption further crystallization and deformation experiments with low isotactic polypropylenes, which have the same isotacticity, but different chain microstructures are necessary.

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$$\epsilon_{rev} = \left(\frac{l_{cyc} - l_{rel}}{l_{cyc}} \right) \bullet 100$$

Formula for the calculation of the reversible deformation ϵ_{rev} after elongation to a given strain rate λ_{cyc} , l_{cyc} = length of the sample stretched to λ_{cyc} and l_{rel} = length of the relaxed sample.

62x21mm (600 x 600 DPI)

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Illustration of the line scans from the SFM phase images to average the distance between adjacent crystalline blocks.
242x112mm (300 x 300 DPI)

Stress-strain diagrams of tensile test until failure (a) and cyclic tensile test (b) of the sample investigated.

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2d WAXS-images of the sample at elongations of $\lambda = 1, 4$ and 8 and in the relaxed state (top). Equatorial radial intensity distributions at elongations of $\lambda = 1, 4$ and 8 ; and in the relaxed state (bottom).
340x154mm (300 x 300 DPI)

Orientation functions on elongation from the (110)alpha, (040)alpha and (202)gamma net planes of the sample presented.

Sequence of SFM phase images of solvent crystallized sample at elongations of $\lambda = 1$ (a) to $\lambda = 8$ (h) and in the relaxed state (i).
232x235mm (300 x 300 DPI)

Averaged distance between adjacent crystalline/ lamellar blocks along the stretching direction as function of the strain (filled circles) and in the relaxed state (open circle).
Stress-strain diagrams of tensile test until failure (line).

191x135mm (600 x 600 DPI)

Illustration of the persisting beads-on-a string structure of the fibrils at sample relaxation (a) compared to the stretched state (b).

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Sketch describing the model about semi-crystalline polymers at uniaxial stretching.
370x175mm (600 x 600 DPI)