Polymer Communication

Confined intra-molecular clustering in orientated polyethylene after annealing

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Dedicated to the memory of Professor Baotong Huang on the first anniversary of his death.

Abstract

Deuterated polyethylene tracer molecules with small amount of branches (12 C_2H_5- branches per 1000 backbone carbon atoms) were blended with a hydrogenated polyethylene matrix to form a homogenous mixture. The conformational evolution of the deuterated chains in a stretched semi-crystalline film was observed via online small angle neutron scattering measurements during annealing at high temperatures close to the melting point. Because the sample was annealed at a temperature closely below its melting point, the crystalline lamellae were only partially molten and the system could not fully relax. The global chain dimensions were preserved during annealing. Recrystallization of released polymeric chain segments allows for local phase separation thus driving the deuterated chain segments into the confining inter-lamellar amorphous layers giving rise to an interesting intra-molecular clustering effect of the long deuterated chain. This clustering is deduced from characteristic small angle neutron scattering patterns. The confined phase separation has its origin in primarily the small amount of the branches on the deuterated polymers which impede the crystallization of the deuterated chain segments.
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Keywords: SANS; Polyethylene; Deformation

1. Introduction

Linear polyethylene (PE) − a material widely used for packaging, pipes, fibers, etc. − is also a model polymer for many fundamental studies because of its simple chemical structure. PE normally crystallizes only partly due to the kinetic hindrance of entanglements that cannot be disentangled during the course of crystallization. When being quenched from the randomly entangled melt state to lower temperatures, PE crystallizes into stacked lamellar crystallites of about 10 nm in thickness [1]. Together with the amorphous phase between the crystalline lamellae they yield a spherulitic morphology [1]. It is well known that the global conformation of single chains above a certain molar mass does not vary after the quench crystallization process implying that the PE chains must be incorporated into several lamellae [2,3]. Solid PE can be stretched typically to more than 400% in uniaxial extension [4,5]. Tensile stretching transforms the original spherulitic morphology into a fibrillar one where polymeric chains are preferentially orientated along the stretching direction [4−8].

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In the fibrils, stacks of crystalline lamellae with their normal close to the fiber axis are realized [9,10]. In-between these crystalline lamellae, partially orientated chains form the amorphous phase. The long spacing, i.e., the average separation between adjacent crystalline lamellae, of drawn polyethylene is typically of the order of some tens of nanometers — depending on the thermal history [9]. It is also known that the single chains deform roughly affinely with respect to the macroscopic deformation [11–15]. From this it is deduced that the elongated polymeric chains were incorporated into more different lamellae than in the isotropic state.

The conformational behavior of a single polymeric chain can be obtained by small angle neutron scattering (SANS) when mixing a few percent of deuterated polymer into the hydrogenated matrix where the high neutron scattering length difference between the deuterium and hydrogen is exploited [16].

In this work we report a local (confined) phase separation phenomenon leading to intra-molecular clustering in long polymeric chains in drawn partially deuterated PE (dPE). The effect was observed by SANS during annealing drawn PE specimens at a temperature close to but below its final melting point.

2. Experimental section

dPE tracer molecules (3 wt%) of molecular weight $M_w = 6.5 \times 10^5$ g/mol were dispersed into a hydrogenated matrix of average molecular weight 3.4×10^5 g/mol via the solution precipitation method as discussed elsewhere [15]. The dPE contains randomly distributed 12 C_2H_5- side groups per 1000 carbon atoms on the polymeric chain as was determined by nuclear magnetic resonance spectroscopy. Fig. 1 shows the differential molecular weight distribution of the dPE. The polydispersity of the dPE (M_w/M_n) is 2.26. Films of about 0.3 mm in thickness were obtained via melt pressing the dry precipitant between two aluminum foils at 160 °C for 2 min and quenched into ice water. According to literature no phase separation occurs during this preparation process [11–14]. Drawn PE samples were obtained by stretching a 15 mm strip of the PE film up to its natural draw ratio at room temperature (where the neck has propagated over the whole sample area resulting in an extension ratio of 450%).

To characterize the thermal behavior of the stretched specimen, differential scanning calorimetric (DSC) measurements were performed with a TA Instruments DSC-2920. During the DSC heating run, the specimen was put into a special sample holder to prevent macroscopic shrinkage till melting. The heating rate was 5 K/min.

Online SANS experiments were performed at the instrument D11, ILL Grenoble. A wavelength of 0.6 nm and a sample to detector distance of 5 m were used. The SANS patterns were corrected for background and normalized using water as a standard [17]. Before being tightly squeezed between two quartz glass windows of a thermal stage the drawn sample was wrapped in layers of aluminum foil to prevent macroscopic shrinkage during high temperature annealing.

Complementarily, the morphology and crystalline orientation of the samples were measured by small- and wide-angle
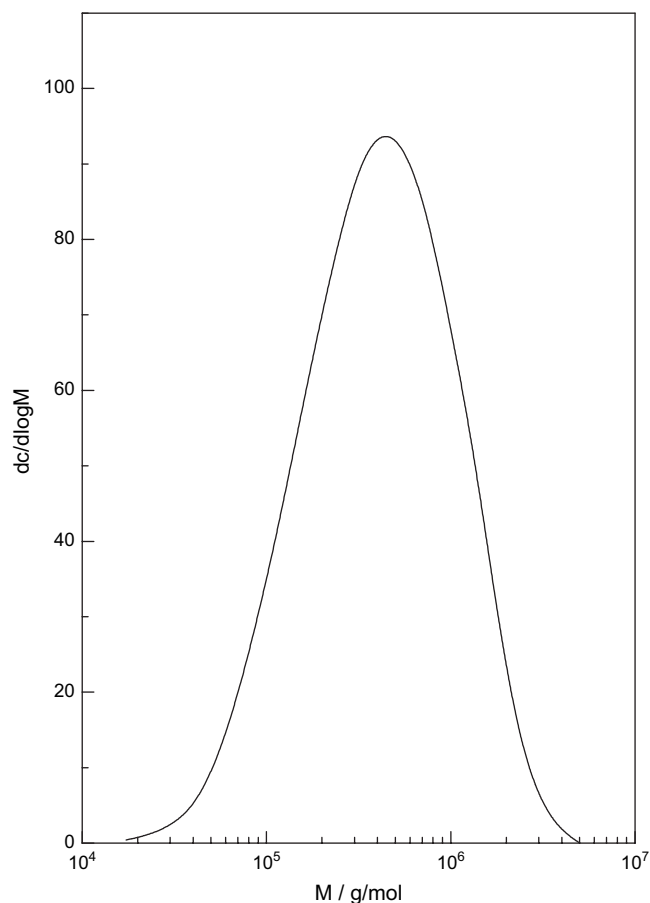

Fig. 1. Differential molar mass distribution of the dPE.

X-ray scattering (SAXS, WAXS) with a Nanostar AXS system of Bruker, Germany. The sample to detector distances for SAXS and WAXS were 647.5 and 92 mm, respectively.

3. Results and discussions

Fig. 2 shows the thermal behavior of the PE specimen stretched at room temperature during heating as detected by the DSC diagram of a heating run. An integration of the DSC curve in Fig. 2 yields a crystallinity value of 62% where a value for the heat of fusion of 100% crystalline PE of $\Delta H_{id} = 293$ J/g was used [18]. The temperature of maximum heat flow ("the melting point") of this specimen is 131 °C. SANS online annealing experiments were carried out at 130 °C, i.e., at a temperature where the sample is partially molten. The evolution of the conformational behavior of the deuterated chains was followed by two-dimensional SANS measurements.

To elucidate some basic structural features we present in Fig. 3 the SAXS and WAXS patterns of the isotropic PE film, of the specimen drawn at room temperature and of the specimen used in the online SANS measurements where it was kept at 130 °C for 3 h. The original film had no preferential orientation with respect to lamellar and chain orientations as indicated by the homogenous scattering intensity distribution along the SAXS ring (Fig. 3a) and the Debye rings in the
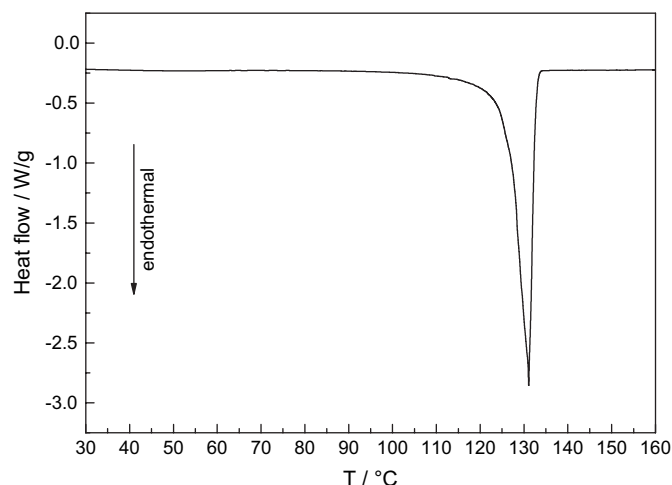
Fig. 2. DSC heating run of the PE specimen stretched at room temperature to its natural draw ratio of 450%. During heating the sample was fixed in order to prevent macroscopic shrinkage. Heating rate is 5 K/min.

WAXS pattern (Fig. 3d). The position of the intensity maximum in a SAXS pattern (q_{max}) for semi-crystalline polymeric system is related to the long spacing of crystalline lamellae (d_{ac}) by [1,19,20]:

$$d_{ac} = \frac{2\pi}{q_{max}} \qquad (1)$$

The X-ray data taken on the stretched sample show that the original isotropic morphology of the film was transformed into a highly orientated structure after stretching at room temperature. The SAXS pattern of Fig. 3b shows characteristic features of a tilted lamellar structure [21]. Annealing (online SANS measurements) at 130 °C for 3 h leads to a shift of the location of the maximum intensity in SAXS pattern towards a smaller angle (Fig. 3c) and a splitting of the WAXS intensity into two parts on the Debye rings along the azimuthal angle (Fig. 3f). Moreover, the SAXS pattern in Fig. 3c suggests a well-ordered periodical lamellar structure because the second order scattering peak of the long spacing is clearly seen [10]. The splitting of the corresponding WAXS data along the Debye ring indicates a tilting of the polymeric chains in the crystalline phase. The values of the long spacing for the isotropic sample, the specimen stretched at room temperature and the specimen after high temperature annealing are 20, 15 and 36 nm, respectively. The variation of the lamellar long spacing is known due to the stress induced melting and recrystallization (from 20 to 15 nm) [8] and the reorganization of the system during annealing (from 15 to 36 nm) [15].

X-ray scattering measurements are sensitive to the electron density differences between the phases [20]. No information about single chain conformation is available from such experiments. In order to obtain information about the averaged conformational behavior of single polymeric chains during high temperature annealing, we consider now the SANS results. Fig. 4 shows the SANS patterns on the stretched sample in real time during annealing at 130 °C. The exposure time for each SANS pattern was 10 min. The pattern for PE stretched

at room temperature (Fig. 4a) presents typical SANS scattering of samples containing elongated chains [13,14]. As was discussed elsewhere [15], a precise determination of the averaged dimensions of the chains (radii of gyration) requires a wider q-range; but this is not the purpose of this work. However, one can roughly estimate the dimension of the chains along the stretching direction by considering the molecular weight and draw ratio [15,22]. As is shown in Fig. 1, the molar mass of the dPE used in this study has a distribution starting from around 2×10^4 to 5×10^6. It has been observed that for chains having an average molar mass of about 4×10^4 stretching till the natural draw ratio yields a chain dimension of about 45 nm along the stretching direction. The fraction of dPE chains having such a molar mass ($<4 \times 10^4$) is only about 1% in the present case. On average, the dPE chains must possess a dimension of about 150 nm in the stretching direction [15,22]. It has been shown by means of SAXS data that after high temperature annealing the lamellar long spacing increased from 15 to 36 nm suggesting that a rearrangement of the lamellae and/or amorphous layers occurs on a length scale of at most 25 nm. This size is much smaller than the dimension of the stretched dPE chains so that a larger scale liberation of the stretched dPE chains is prevented. With this in mind, we look for an interpretation of the temporal evolution of the SANS patterns recorded during high temperature annealing (Fig. 4b–f). First, there is no significant variation of the anisotropic original peak stemming from the stretched (deuterated) chains indicating that the global dimension of most of the elongated chains does not change. Secondly, new scattering "bands" appear along the stretching direction meaning that a periodical distribution of the deuterated chain segments was formed in the process. Due to the shadowing effect of the beamstop these two bands together with the original equatorial scattering intensity look like stemming from a hexagonal structure at first sight, but a closer look reveals that typical SANS long-period scattering maxima have been formed − qualitatively similar to the SAXS maxima in Fig. 3b and c being also a four-point pattern indicating a tilted lamellar structure. A detailed analysis revealed that the scattering intensity along the stretching direction increases with the prolonged annealing time but the location of the intensity maximum with respect to the scattering angle hardly changes. A straightforward calculation using Bragg's law yields a characteristic length of 39 nm along the stretching direction. This value is in good agreement with the long spacing of the crystalline lamellae as determined by the SAXS measurement (36 nm) if one takes into account that the SAXS measurement was carried out at room temperature where thermal shrinkage of the specimen and possible secondary crystallization during cooling reduce the SAXS long spacing. Given the structural information we have from WAXS and SAXS it is safe to assume that only an enrichment of the deuterated segments in lamellar or amorphous phase is able to yield similar SANS patterns shown in Fig. 4b–f. It was derived above that no global dimensional change of elongated chains occurs, so that the enrichment of the deuterated segments must occur at an intra-molecular level. The main features occurring in the
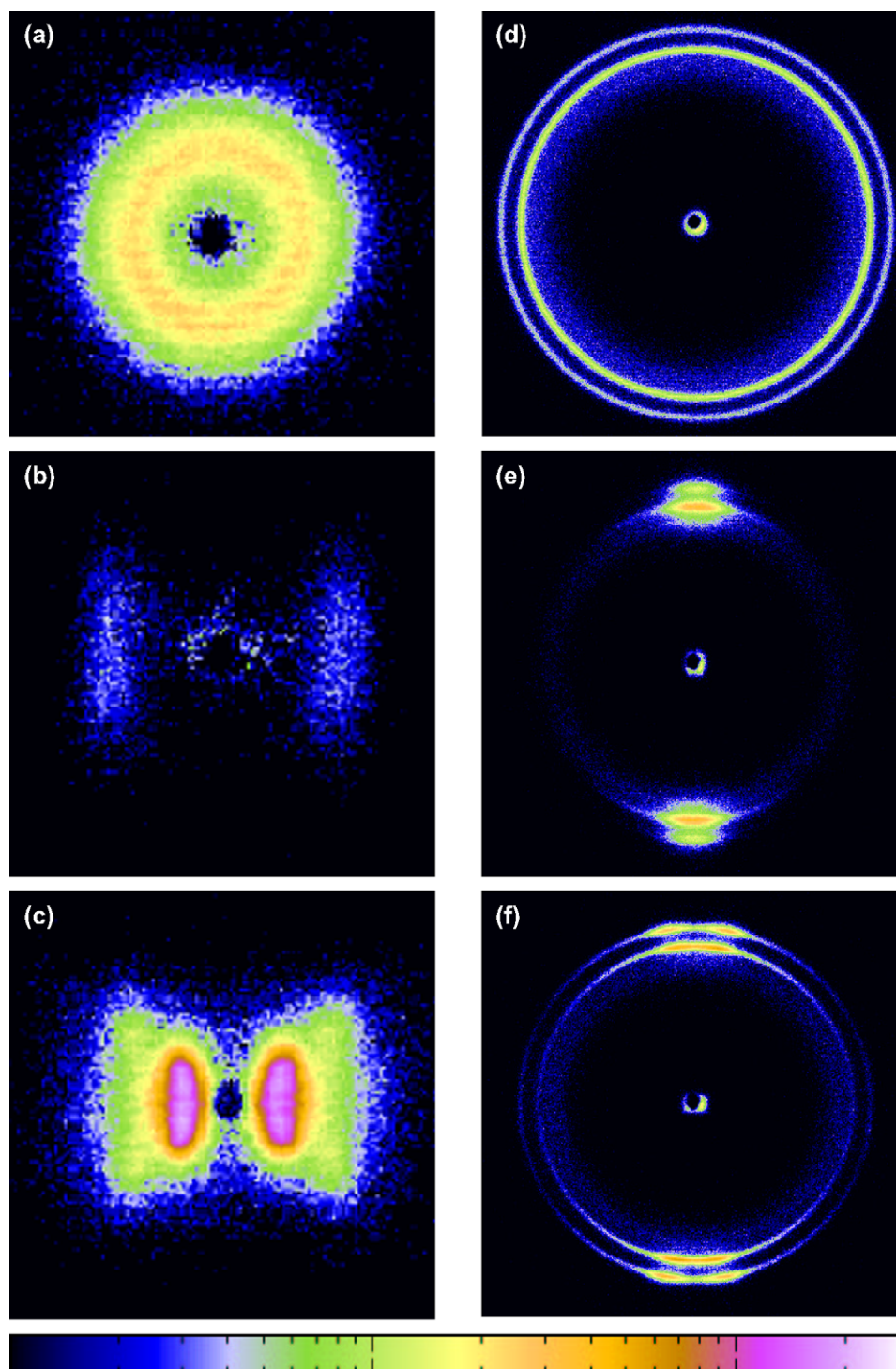
Fig. 3. Small (a, b and c) and wide-angle (d, e and f) X-ray scattering patterns of melt quenched polyethylene film (a and d), after room temperature stretching to 450% (b and e) and after annealed at 130 °C for 180 min (c and f). Stretching direction is horizontal.

process of annealing thus derived are schematically summarized in Fig. 5. In the left schematic of Fig. 5, we sketch the fibrillar structure of a drawn PE. The chains in the crystalline lamellae are oriented along the stretching direction whereas the lamellar normal is tilted by some degrees as evidenced by the SAXS and WAXS results. The deuterated chain was elongated during uniaxial stretching and is homogenously embedded in

the fibrils. When the sample was heated up to 130 °C, a rearrangement of the structure of lamellae and amorphous layers occurred. At first, a large fraction of the lamellar crystallites (thinner ones located randomly in the system) melted according to the DSC data. Both hydrogenated and deuterated chain segments are assumed to be involved in the melting process. Further annealing results in a demixing of the deuterated
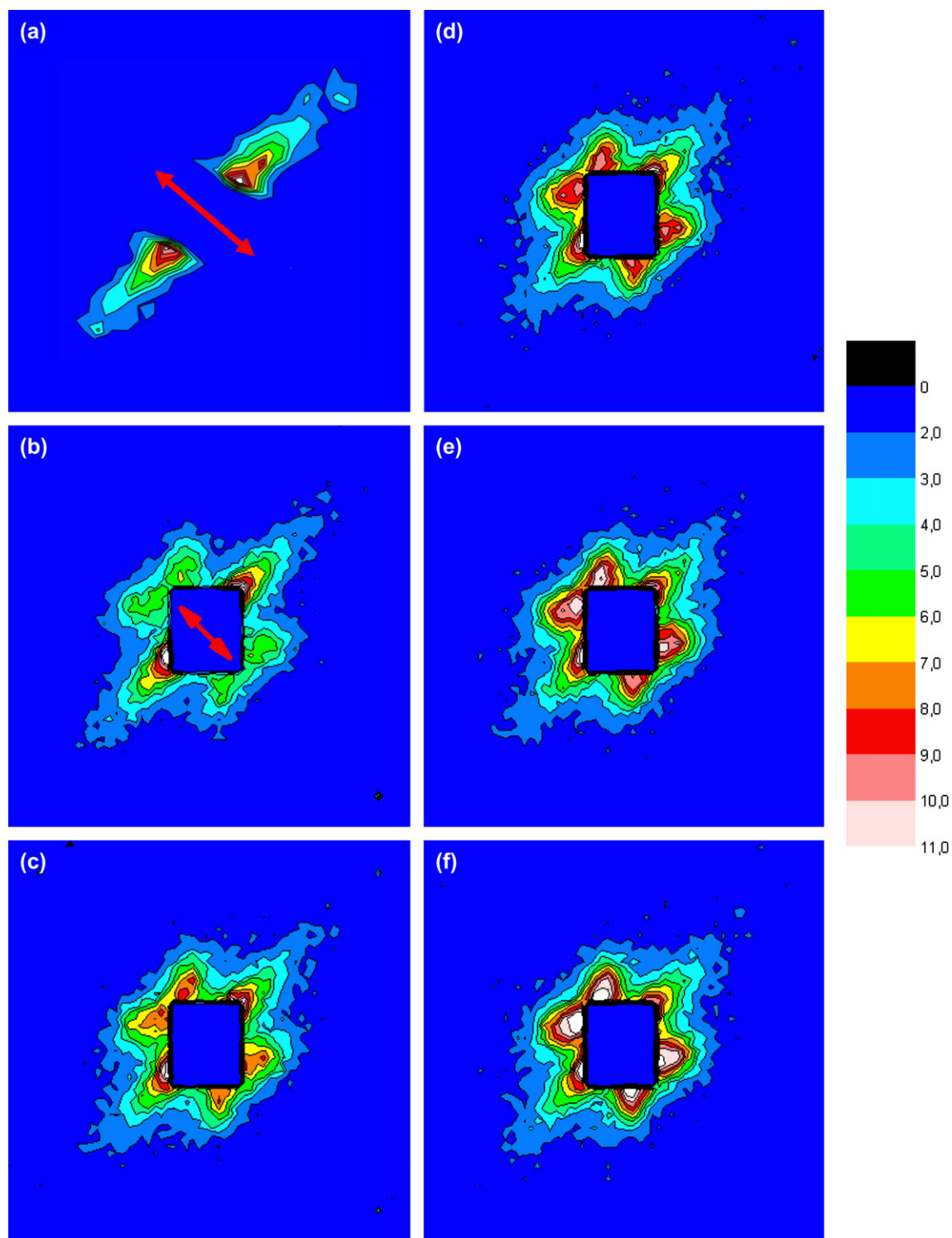
Fig. 4. Small angle neutron scattering patterns of drawn PE. Patterns taken at room temperature (a); at 130 °C annealed for 0–10 (b), 10–20 (c), 30–40 (d), 70–80 (e), and 170–180 min (f). The arrow indicates the fiber axis.

and protonated chain segments of the freed polymeric chains and leading finally to a recrystallization of the protonated chain segments yielding a thickened lamellar structure. Before or during the recrystallization process, the crystallites rotated with respect to the stretching direction by several degrees due to a slight macroscopic shrinkage of the sample at high temperature with the accompanying local relaxation. It is

well known that co-crystallization of hydrogenated and deuterated PE to form a homogenous mixture can only be realized by quenching [3]. The recrystallization process in our case is different from the case of melt quenching. At 130 °C, hydrogenated PE chain segments are favored to crystallize whereas the deuterated chain segments are expelled to the amorphous layers. The main reason for this phenomenon is that the
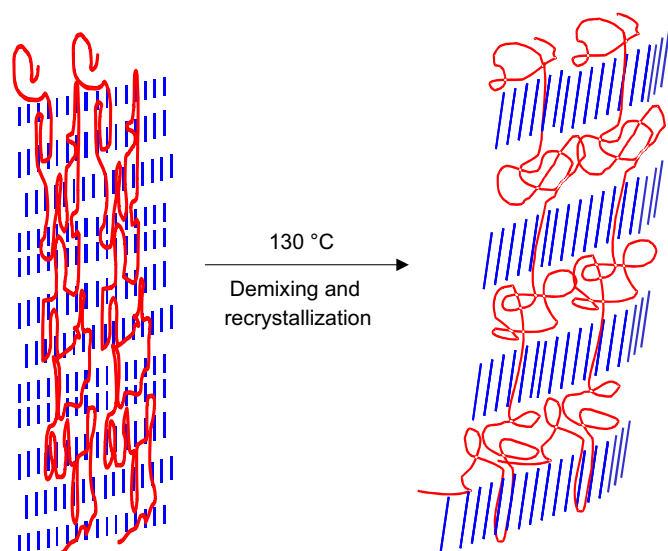
130 °C

Demixing and recrystallization

Fig. 5. Schematic representation of the crystallization induced nanosized phase separation resulting in an enrichment of the segments of deuterated chains in the amorphous phase during annealing which causes the butterfly neutron scattering patterns. Fiber axis is vertical. Only two representative dPE chains (in red color) are depicted in the sketch. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

deuterated PE used in this study contains 12 ethyl branches per 1000 backbone carbon atoms on the polymeric chain which lower the melting point of the pure branched dPE to about 115 °C [23]. It is thus obvious that the annealing temperature of 130 °C is high enough to impede the crystallization of dPE chains. In addition, it is also well known that deuteration lowers the melting point of polyethylene by another several Kelvin [3]. The elongated chains were only partially molten, i.e., the chains were still fixed by the orientated crystalline lamellae; global shrinkage of the chains and macroscopic phase separation were not possible. The recrystallization process thus yields an intra-molecular aggregation of deuterated chain segments in the amorphous layers between the crystalline lamellae. This situation is sketched in the right part of Fig. 5. This intra-molecular clustering of deuterated chains provides enough neutron scattering contrast to yield a scattering pattern from which the information about the lamellar long spacing in the direction of stretching can be evaluated — similarly to SAXS scattering being based on the density contrast between crystalline and amorphous layers. Another noteworthy feature in the SANS patterns in Fig. 4 is that the length of the scattering intensity due to lamellar structure perpendicular to the stretching direction is much smaller than that of the equatorial streak. To a first order of approximation, the dimension of the scattering intensity corresponds to the inverse of the width of the scattering object. The observed SANS patterns thus are indicative that the dPE segments in the inter-lamellar regions have a much larger dimension than the transverse thickness of a single stretched chain. This apparent contradiction can be explained as follows: although there was only 3 wt% of dPE mixed in the matrix, the dPE chains are close enough to each other in the system because of the dimension of the single chain. As was sketched in Fig. 5, two dPE chains were presented. After being annealed, the dPE segments in the inter-lamellar region from different chains interpenetrate with each other forming one single scattering object of much larger dimension than the transverse thickness of one single stretched chain.

In summary, we have elucidated a nanophase separation induced intra-molecular clustering of slightly branched deuterated PE chains after annealing PE specimen — stretched at room temperature — at elevated temperature close to its melting point. The results indicate that no global chain diffusion of the branched dPE is detectable in a drawn PE specimen albeit the drastic changes in the lamellar structure during high temperature annealing on the time scale of our experiments. The intra-molecular clustering effect in drawn PE opens new possibility to study the behavior of confined segments of a polymeric chain that is not easily obtainable by other procedures.

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