

**Time Evolution of Hierarchical Structures
in Crystalline Polymers under Deformation
via Multiscale X-ray Analysis**

Masato ARAKAWA

2026

Contents

Chapter 1

General Introduction

1.1	Hierarchical Structures in Crystalline Polymer	1
1.2	Structural Evolutions under Strain	3
1.2.1	Deformation Modes of Amorphous Phases and Lamellae	4
1.2.2	Strain-induced Phase Transition	10
1.2.3	Deformation on the Fibrillar and Spherulitic Scales	12
1.3	Motivation and Outline of This Thesis	15

Chapter 2

Hierarchical Structure of LLDPE Spherulites Revealed through Integrated Molecular Orientation and Density Distribution Analysis

2.1	Introduction	23
2.2	Experimental Section	26
2.2.1	Sample Preparation	26
2.2.2	X-ray Scattering Measurements	27
2.2.3	Differential Scanning Calorimetry (DSC) Measurements	28
2.2.4	Light Scattering Measurement under H _v Polarization Condition	28
2.2.5	STXM Observation	29
2.3	Results and Discussion	31
2.3.1	X-ray and Light Scattering Measurements	31
2.3.2	STXM Measurements	35
2.3.2.1	Mapping of an Entire Spherulite	36
2.3.2.2	Mapping of the Center and Banded Structure within the Spherulite	38
2.3.2.3	Structural Origins of Density and Orientation Contrast	46
2.4	Conclusion	50

Chapter 3

STXM Studies on the Changes in the Spatial Distribution of Density and Chain Orientation of LLDPE with Strain

3.1	Introduction	55
3.2	Experimental Section	59
3.2.1	Sample Preparation	59
3.2.2	<i>In-Situ</i> X-ray Scattering Measurements	59
3.2.3	STXM Observation	60
3.3	Results and Discussion	63
3.3.1	X-ray Scattering Measurements	63
3.3.2	STXM Measurements	68
3.3.3	Hierarchical Structure at Each Stretch Ratio	73
3.4	Changes in the Hierarchical Structure under Stretching	76
3.5	Conclusion	78

Chapter 4

Differences in Hierarchical Structural Changes between Unoriented P(3HB) and P(3HB-co-3HH) under Stretching

4.1	Introduction	83
4.2	Experimental Section	86
4.2.1	Sample Preparation	86
4.2.2	<i>In-Situ</i> X-ray Scattering Measurements	87
4.3	Results and Discussion	88
4.3.1	S-S curves	88
4.3.2	Comparison of the Hierarchical Structures of Unstretched P(3HB) and P(3HB-co-11mol%-3HH)	89
4.3.3	Changes in the Hierarchical Structure under Stretching P(3HB)	91
4.3.4	Changes in the Hierarchical Structure under Stretching P(3HB-co-11mol%-3HH)	98
4.3.5	Hierarchical Structure in Each Region	101
4.3.6	Changes in the Hierarchical Structure and Difference between P(3HB) and P(3HB-co-11mol%-3HH) under stretching	104
4.4	Conclusion	106

Chapter 5

Enhancement of the Density Fluctuations of Polyamide-6 with Strain below Glass Transition Temperature

5.1	Introduction	111
5.2	Experimental Section	114
5.2.1	Sample Preparation	114
5.2.2	<i>In-Situ</i> X-ray Scattering Measurements	115
5.2.3	Differential Scanning Calorimetry (DSC) measurements	116
5.3	Results and Discussion	116
5.3.1	S-S Curves	116
5.3.2	Analysis of Hierarchical Structures before Strain	117
5.3.3	Case of PA6 at $T_c = 180\text{ }^{\circ}\text{C}$	124
5.3.3.1	USAXS and SAXS Analysis	126
5.3.3.2	WAXS Analysis	129
5.3.4	Case of PA6 at $T_c = 100\text{ }^{\circ}\text{C}$	134
5.3.4.1	USAXS and SAXS Analysis	134
5.3.4.2	WAXS Analysis	137
5.3.5	Changes in the Hierarchical Structures under Stretching	140
5.4	Conclusion	143

Chapter 6

Spatial Heterogeneity of Density and Orientation in Stretched Polyamide-6 Revealed by STXM

6.1	Introduction	149
6.2	Experimental Section	152
6.2.1	Sample Preparation	152
6.2.2	X-ray Scattering Measurements	153
6.2.3	STXM Measurements	153
6.2.4	Differential Scanning Calorimetry (DSC) Measurements	155
6.3	Results and Discussion	155
6.3.1	Analysis by USAXS, SAXS and WAXS Measurements	155
6.3.2	STXM Measurements	160
6.4	Conclusion	167

Summary	171
List of Publications	173
Acknowledgments	175

Chapter 1

General Introduction

1.1 Hierarchical Structures in Crystalline Polymer

Crystalline polymers are widely used in diverse products and are employed in a crystallized form for their various processability, mechanical properties, weather resistance, and chemical resistance.¹ Crystalline polymers, also called semi-crystalline polymers, never achieve 100% crystallinity and therefore have crystalline and amorphous regions.¹ In addition, crystalline polymers are generally polymorphic with one type of stable crystals and several other metastable crystals, each of which usually has different macroscopic properties.²⁻⁴ Hence, crystalline polymers exhibit a wide variety of mechanical properties in the same material. Polyethylene (PE), categorized as a commodity plastic,⁵ is used for containers and packaging films, while polyamide 6 (PA6), classified as an engineering plastic,⁶ is used for fibers such as fishing line and automotive parts. In recent years, researchers have also studied bioplastics,⁷ such as Poly[(R)-3-hydroxybutyrate] [P(3HB)], which have low environmental impacts with the aim of practical application. Extending the service life of these polymeric materials is expected to reduce the environmental burden. To achieve a longer service life of polymeric materials, it is necessary to investigate the hierarchical structure of crystalline polymers and the mechanical properties arising from the hierarchical structure.

When crystalline polymers crystallize from melts in a static field, they form hierarchical structures consisting of crystalline and amorphous phases on scales of Å to

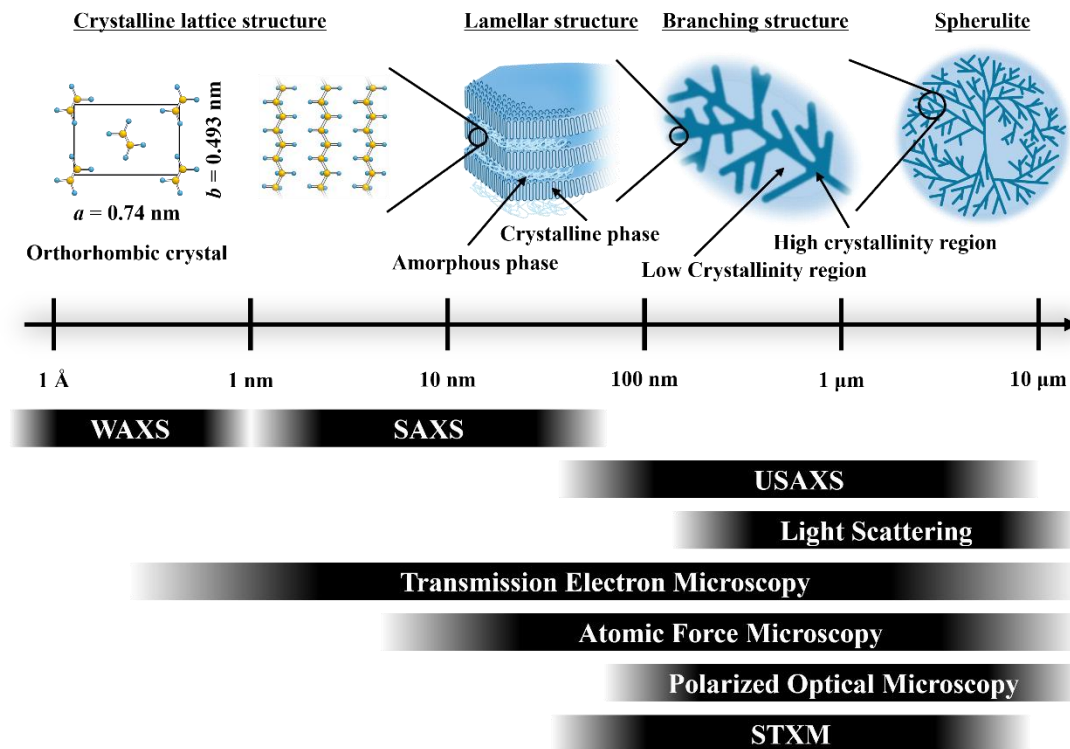


Figure 1.1. Hierarchical structures in crystalline polymers (example of PE) and typical observation techniques.

μm .⁸ Figure 1.1 illustrates the hierarchical structures. On the $\text{\AA}$ scales, polymer chains are regularly folded and packed,^{8,9} resulting in the formation of a crystal lattice structure that is energetically stable. On the 1 to tens nm scales, a lamellar structure is formed by alternating layers of crystalline phases and amorphous phases that cannot crystallize due to entanglements and tie chains.¹⁰ On the submicron scales, which are a few hundred nm scales, a branching structure is formed by the growth of lamellar structures. On the scales of 1 μm and larger, a spherulite structure is formed by the filling of branching and splaying fibrils.^{8,11} Each structure is typically studied by wide-angle X-ray scattering (WAXS) on the $\text{\AA}$ scales, small-angle X-ray scattering (SAXS) on the scales from 1 to tens nm, transmission electron microscopy, atomic force microscopy, and ultra-small-angle X-ray scattering (USAXS) on the submicron scales,

and polarized optical microscopy and light scattering on scales larger than μm . Complementing these methodologies, Scanning Transmission X-ray Microscopy (STXM) has developed as a powerful technique for the real-space characterization of crystalline polymers from the fibrillar to the spherulitic scale. By utilizing X-ray linear dichroism, STXM can simultaneously quantify local density and orientation of chemical bonds at sub-micrometer resolutions.¹²⁻¹⁵ This unique capability facilitates the direct observation of how the distribution of density and orientation correlate in real space, providing a critical perspective for revealing the hierarchical deformation mechanisms explored in this thesis.

To investigate the mechanical properties of crystalline polymers, it is essential to trace the mechanical response of each structure and the interactions within each hierarchy, and to clarify the contribution of these changes to the mechanical properties when the material is subjected to external forces, such as uniaxial stretching.

1.2 Structural Evolutions under Strain

The mechanical response and deformation behavior of crystalline polymers in the uniaxial stretching condition have been discussed with the experimental results obtained by SAXS and WAXS. A typical stress-strain (S–S) curve during uniaxial stretching of crystalline polymer is shown in Figure 1.2.¹⁶ The whole deformation process consists of several stages with different behaviors involved in each stage. Each stage is separated by critical strains associated with the onset of different structural changes. Deformation models and crystal phase transition mechanisms have been proposed to explain the mechanical behavior of crystalline polymers.

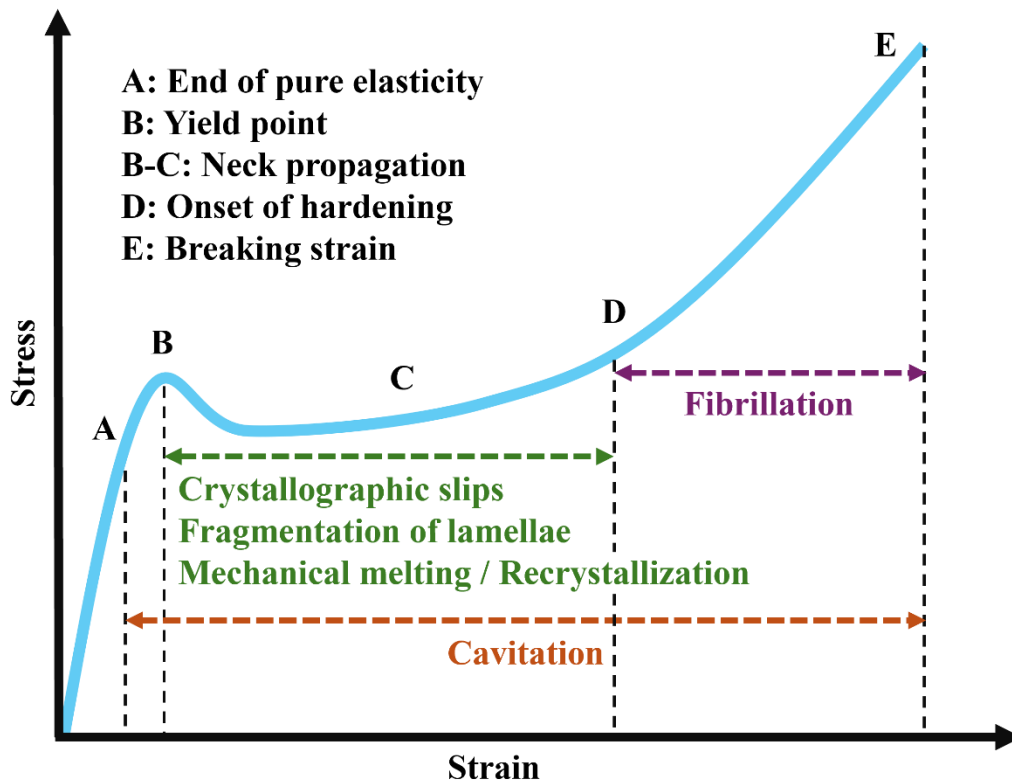


Figure 1.2. A typical true stress–strain curve of a semicrystalline polymer. A, B, C, D, E are the critical strains initiating different deformation mechanisms, respectively.

1.2.1 Deformation Modes of Amorphous Phases and Lamellae

There are three modes of amorphous deformation in crystalline polymers, as shown in Figure 1.3: interlamellar slip, interlamellar separation, and stack rotation.¹⁷

Interlamellar slip (or shear) involves mainly the shear of lamellae to each other, together with the amorphous layers. It is a relatively easy mechanism of deformation for the materials above the glass transition temperature (T_g). The elastic part of deformation can be almost entirely described by reversible interlamellar slip. Besides, interlamellar separation is caused by a component of tension or compression parallel to the lamellar surface. Finally, stack rotation represents the rotation of the lamellae under stress. For the stacks of lamellae to rotate freely, the stacks must be embedded in the amorphous matrix.

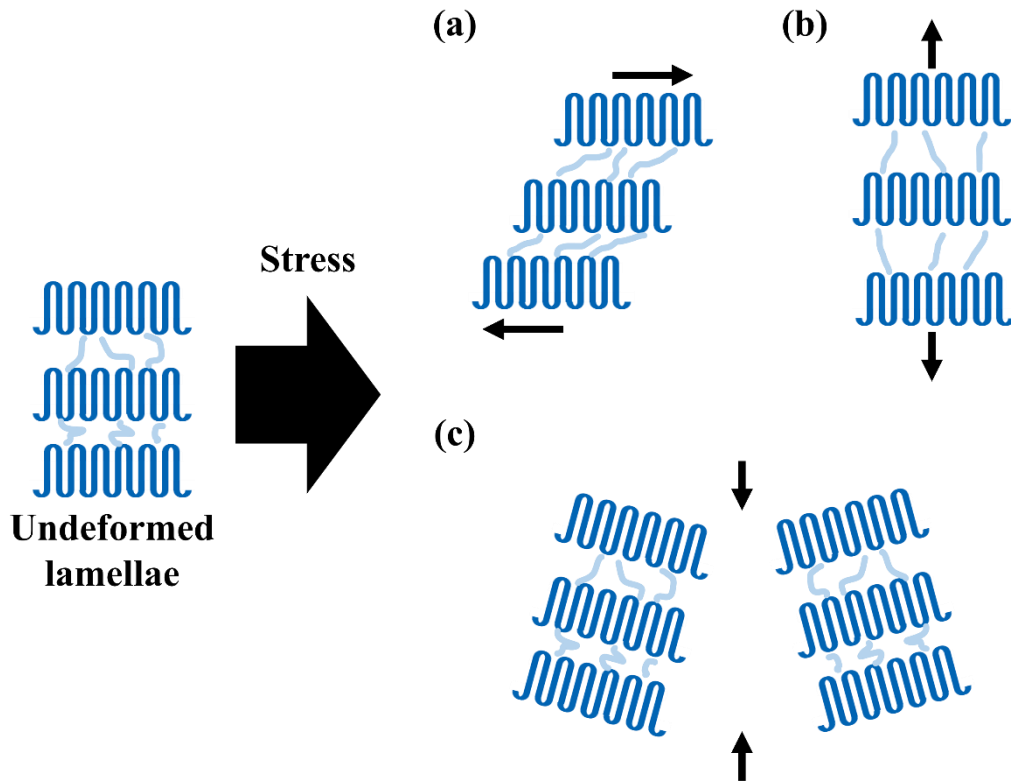


Figure 1.3. Deformation modes of the amorphous phase in crystalline polymers: (a) interlamellar slip, (b) interlamellar separation, (c) rotation of stacks of lamellae.

In contrast to the above, there are four fundamental bases of the deformation behavior established to describe the mechanical behavior of the lamellae with crystals involved during the multi-stage deformation process in S–S curve: crystallographic slipping model,^{17, 18} melting-recrystallization model¹⁹ and interpenetrated network model.^{20, 21}

The plastic deformation in polymer crystals is generally crystallographic, as in other materials, and occurs without destroying the crystal order around the yield point in the S–S curve. Polymer crystals can deform plastically by crystallographic slip, twinning, and phase transitions, such as a martensitic transformation.^{22, 23} The crystallographic slip mechanism is most important, as it is responsible for the largest plastic strain. A slip system, as shown in Figure 1.4a, is described as $(hkl)[h_1k_1l_1]$ where

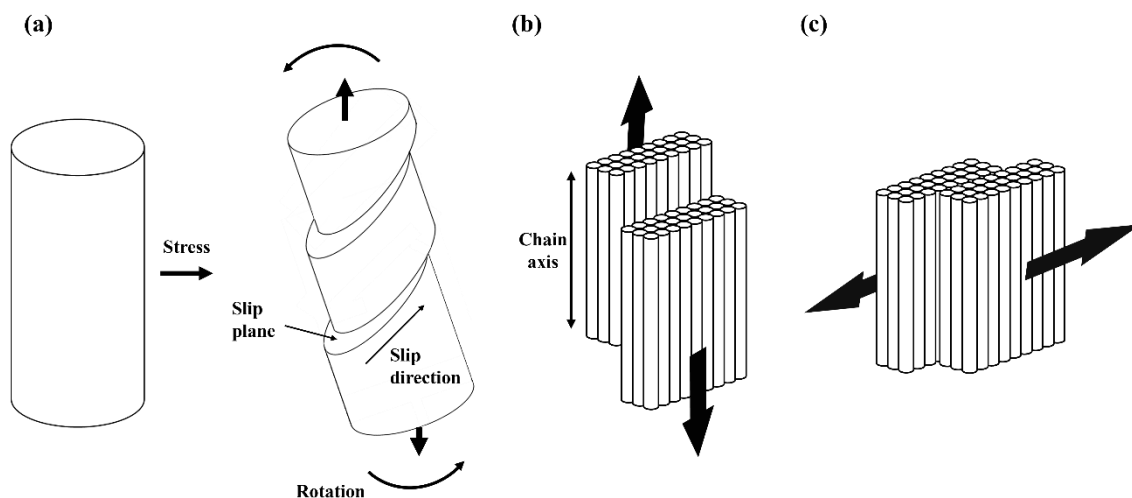


Figure 1.4. Slip mechanisms in polymer crystals: (a) slip system geometry and rotation during single slip, (b) chain slip modes, (c) transverse slip modes.

(hkl) is the slip plane containing a slip direction and $[h_1k_1l_1]$ is the slip direction.²¹ The geometry of the slip process implies that the orientation of a crystal undergoing a single slip rotates with respect to the stress axis, as shown in Figure 1.4a. The slip direction in the crystal rotates constantly toward the direction of maximum extension for a single slip,²² therefore, it rotates toward the tensile direction in the case of the uniaxial stretching, while it rotates away from the compression axis in the uniaxial compression.

In polymer crystals, the slip plane is a crystallographic plane parallel to the plane where the slip occurs and is limited exclusively to a plane containing the chain direction because covalent bonds are not broken during deformation. There are two types of slip: chain slip (slip along the chain direction) and transverse slip (slip perpendicular to the chain, both slips in the planes containing the chains, as shown in Figure 1.4b and c, respectively.²⁴ The plane of the easiest slip tends to be a close-packed plane in the structure, and the slip direction is a close-packed direction.

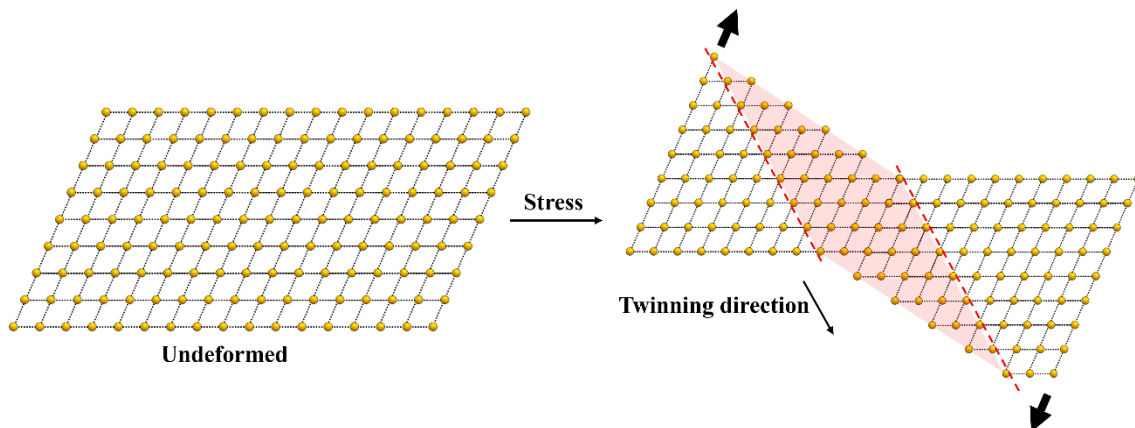


Figure 1.5. Schematic of twinning mechanism.

Incidentally, twinning as shown in Figure 1.5 may occur in crystals with sufficiently low symmetry.^{22, 23} For example, twinning does not occur in the cubic system but does occur in the orthorhombic system.

Propagation of slip is mainly characterized by three types: the interlamellar slip, as shown in Figure 1.3, the fine slip, and the coarse slip, as shown in Figure 1.6.^{17, 25} The fine and coarse slips are classified as intralamellar slips and are related only to the deformation of crystal lamellae. Fine slip is a homogeneous slip process where chains in crystals orient along the deformation direction, and the angle between the direction normal to the slip plane and the chain axis changes. Coarse slip is a heterogeneous shear proceeded by sliding a crystal block one after another with the normal direction of the slip plane and the chain direction oriented in the same direction. Unlike fine slip, the deformation by coarse slip can lead to the fragmentation of lamellae, eventually forming the fibrillar structures at large strains. With respect to tensile deformation, intrinsic defects inside polymers, the treatment before deformation, and experimental conditions can result in coarse slips, which sometimes coexist and even compete with fine slips. The crystallographic slipping model is important as a

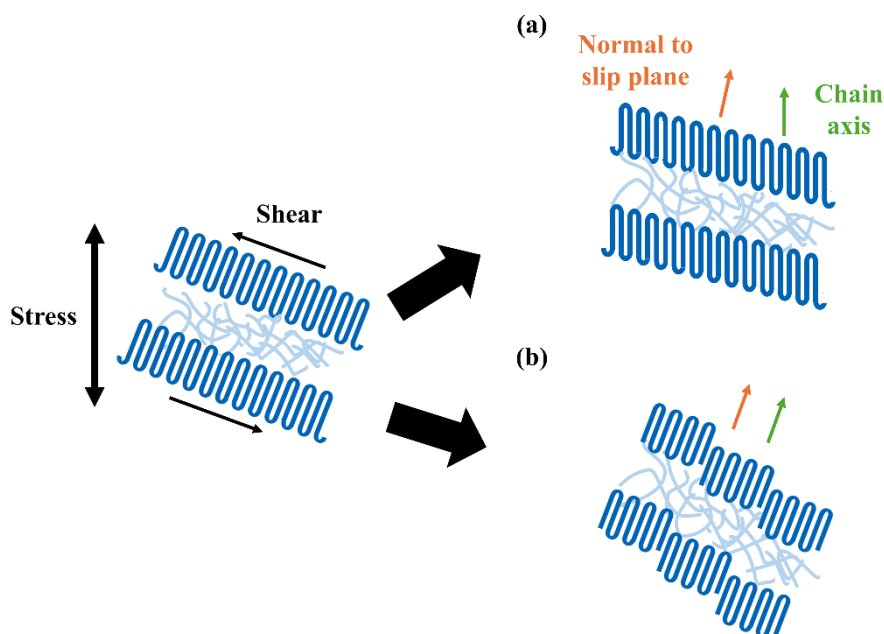


Figure 1.6. Schematic of (a) fine slip and (b) coarse slip.

fundamental molecular process for establishing some of the following models.

The melting-recrystallization model (Figure 1.7) is proposed by Flory and Yoon¹⁹ as an assumption that local strain-induced melting occurs in crystals under deformation from point B to point C in Figure 1.2, resulting in a highly disordered intermediate like melts. The melt regions recrystallize with strains, which form new crystallites such as fibrillar structures with preferred chain orientation along the stress direction.

Figure 1.8 illustrates the interpenetrated network model proposed by Strobl *et al.* to describe the whole deformation in the S–S curve.^{20,21} The polymer system in this model is built by two penetrated networks, which contain the skeleton network consisting of the rigid crystallites and the entangled network with an elastic amorphous phase. This model illustrates the following structural change in the multi-stage in S–S curves. Firstly, pure elasticity is observed up to critical strain A, which is the beginning

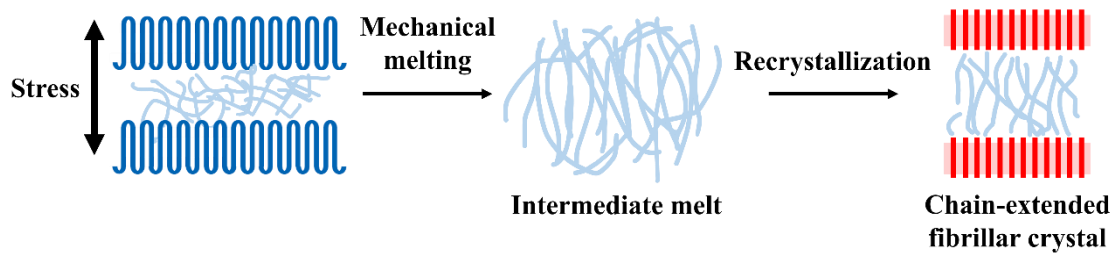


Figure 1.7. Schematic of melting-recrystallization model.

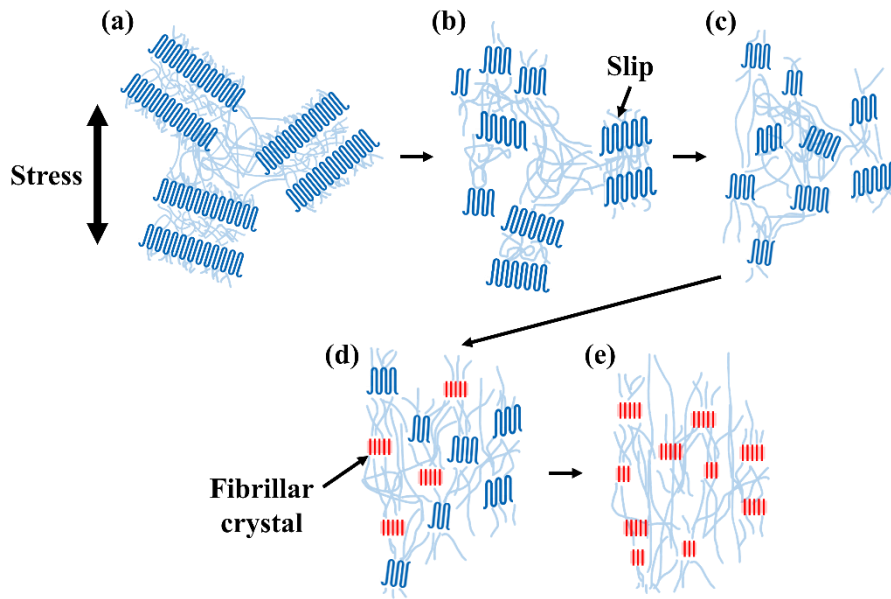


Figure 1.8. Schematic of deformation mechanisms in the interpenetrated model.

(a) Isotropic lamellae, (b) crystallographic slip, (c) lamellae fragmentation, (d) fibrillation, and (e) highly oriented network. The stages (b), (c), (d), and (e) correspond to the critical strains A, B, C, and D in Fig. 1.2, respectively.

of cooperative events of crystallographic slip and interlamellar shear after point B, a yield point. From critical strain B to point C, the S–S curve evolves into a plateau region where the fragmentation of crystals occurs. Finally, the hardening stage develops at critical strain D and reflects an increase in stress due to the fibrillation process, which is the rearrangement of the crystals. Besides, this model is also summarized into a two-step process. One is the crystallographic slip process at small strain, and the other is the

stress-induced disaggregation/melting-recrystallization at large strain, shifting the former to the latter depending on both the stability of slipped crystals and the state of the entangled network.

1.2.2 Strain-Induced Phase Transition

Mechanical deformation of crystalline polymers can induce changes in chain conformation and interchain packing, leading to the formation of crystal structures with a lattice different from the original structure. This process is known as strain-induced phase transition, which is generally distinguished into reversible and irreversible transitions.

The reversible phase transition, as shown in Figure 1.9a represents a solid-solid transition process induced by conformational change or martensitic transformation without conformational change, which occurs reversibly between two crystal phases under the application of stress and its removal.²⁶⁻²⁹ The change of *gauche* conformers to *trans* conformers is a very common type of conformational transition in the phase transition.

By contrast, the irreversible phase transition as shown in Figure 1.9b is associated with a transition of a stable crystal phase into a metastable phase with a higher-energy-state conformation and interchain packing or its opposite under strain. The factors of this transition are mainly classified into the change of intra- and intermolecular ordering.

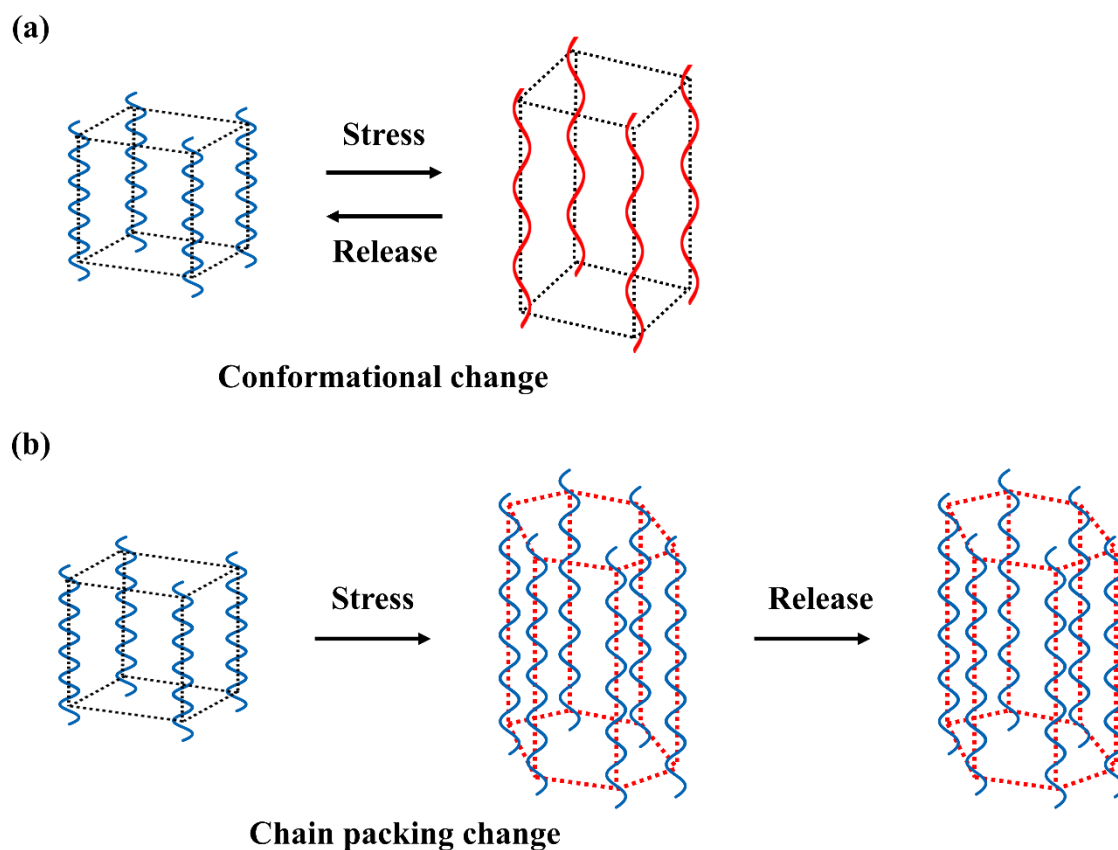


Figure 1.9. Illustration of (a) reversible and (b) irreversible phase transitions under stress. (a) shows the change in chain conformation using blue and red colors. (b) demonstrates the evolution of the crystal lattice from an orthorhombic arrangement (black dots) to a hexagonal one (red dots).

The change in intramolecular order is based on a change in chain conformation^{30, 31} (Figure 1.10a) or in the interchain interactions^{32, 33} (Figure 1.10b). Chain conformational change is the same as the mechanism for the reversible phase transition. The change in interchain interactions is caused by the application of stress to some polymers exhibiting strong intermolecular interaction (e.g., H-bonding). Stress induces the change of interchain (or intramolecular) arrangement in the crystal unit cell, resulting in a phase transition.

The phase transition by intermolecular change is dominated by crystallographic

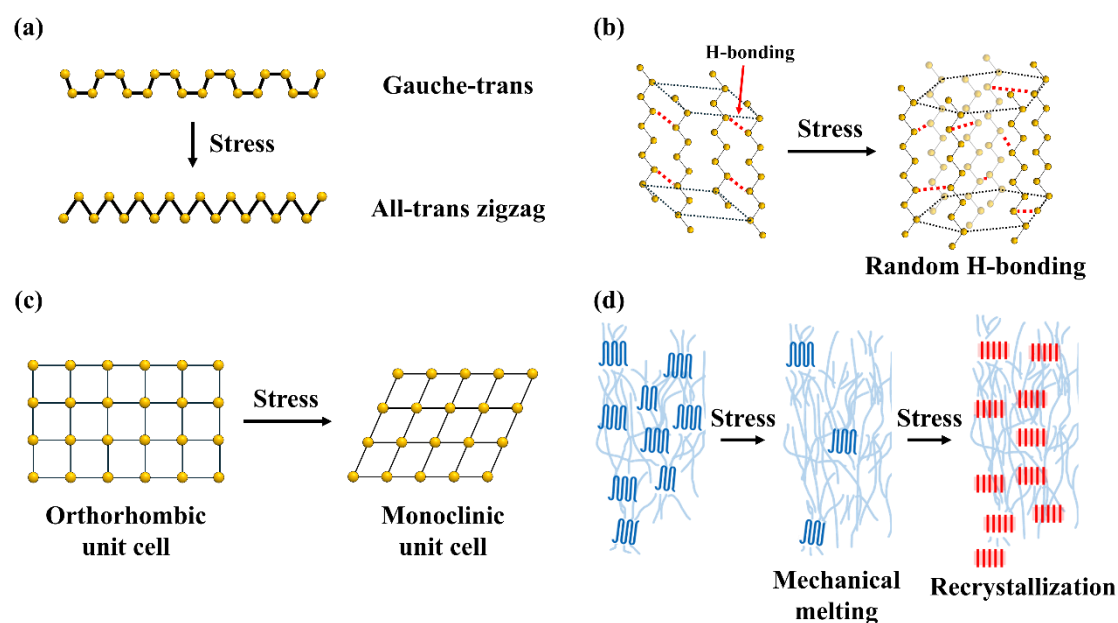


Figure 1.10. Four mechanisms of strain-induced crystal phase transitions at the chain level: (a) conformational change, (b) interchain H-bond rearrangement, (c) crystallographic slip, and (d) melting-recrystallization.

slipping³⁴⁻³⁶ (Figure 1.10c) or melting-recrystallization^{19, 37, 38} (Figure 1.10d). The crystallographic slipping modifies the chain packing mode within the crystal lattice, and then a phase transition occurs. On the other hand, the phase transition dominated by melting-recrystallization concerns the process of mechanical melting in original crystals to produce an intermediate melt and then recrystallization of the melt into another crystal form.

1.2.3 Deformation on the Fibrillar and Spherulitic Scales

The above chapters focus on the deformation and phase transition on the scales from Å to tens of nm. In this section, the styles of deformation on larger scales than lamellae are mentioned. An elastic deformation of crystalline polymers changes into a viscoelastic one before the yield point in the S–S curve. The structural changes that

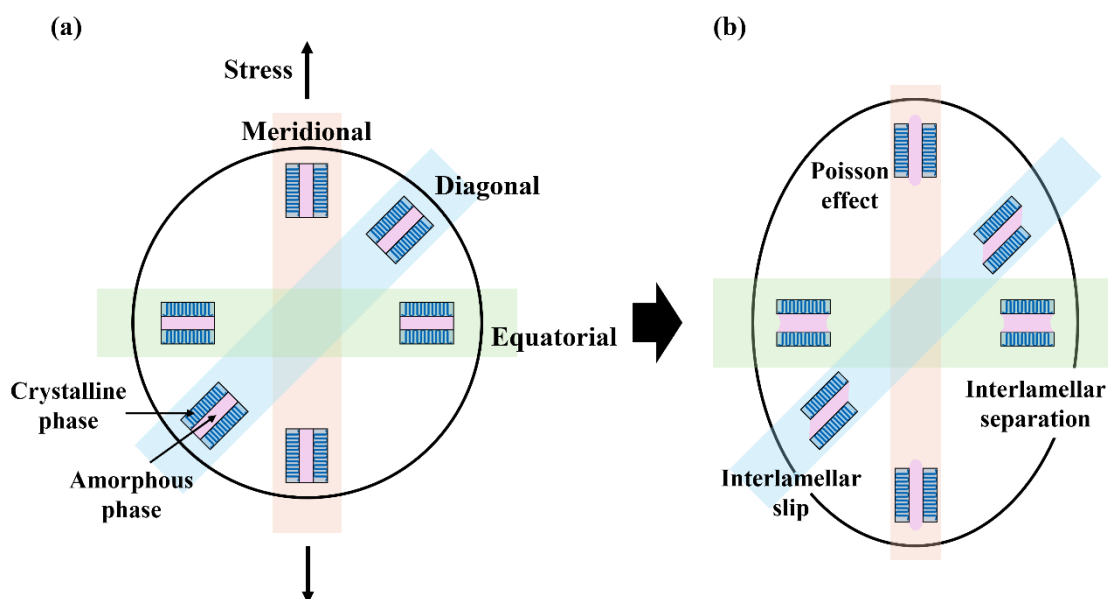


Figure 1.11. Schematic of deformation mechanisms of lamellar structure within a spherulite. (a) Lamellar stacks before stretching a spherulite, (b) structural deformation of lamellae under small strain.

occur near the yield point affect the viscoelastic response of the polymer and play an important role in the modification of hierarchical structures.

The lamellar structure in the fibril structures, which spreads out radially from the center of the spherulite before deformation, is generally set, as shown in Figure 1.11a. Figure 1.11b illustrates that the lamellae at the meridional (parallel to the stretching direction), diagonal (inclined to the stretching direction), and equatorial (perpendicular to the stretching direction) deform in different manners at small strain, respectively. With respect to the meridional direction, it is reported that the lamellae are compressed due to the Poisson effect.^{39, 40} In contrast, the interlamellar separation is supposed to occur for lamellar stacks in the equatorial region.¹⁷ In the small-strain regime prior to the yield point, these deformations are consistent with affine deformation.⁴¹ Finally, the lamellae in the diagonal direction deform by interlamellar shear.¹⁶ The above physical behavior is based on the result obtained by SAXS and

WAXS.

Recently, however, USAXS has been developed and enabled the study of the correlation between structure and physical properties on the sub-micrometer scales. By USAXS, information on the fibril structures in crystalline polymers is obtained. Takenaka *et al.* observed an ‘abnormal’ butterfly pattern reflected in heterogeneous deformation by the difference in mechanical properties between fibrils and non-fibril parts in stretched PE by USAXS.⁴² In the abnormal butterfly pattern, the scattering intensity is highest along the elongational direction near the yield point. Experimentally, the abnormal butterfly patterns are obtained in the swollen chemical gels having the inhomogeneous spatial distribution of the crosslinking points, which was calculated by Bastide *et al.*^{43, 44} In addition, researchers observed the abnormal butterfly patterns in semidilute polymer solution consisting of polystyrene and dioctylphthalate under shear,⁴⁵ slide-ring gels under uniaxial drawing⁴⁶ and stretched mixtures of short and long polystyrene homopolymers.⁴⁷ Doi and Onuki theoretically proved that the coupling between the fluctuation of concentration and that of the stress originating from the difference in mechanical properties between constituent components in the systems, which results in the abnormal butterfly pattern observed in semidilute polymer solution and polymer blend under shear flow.⁴⁸ Subsequently, Furukawa and Tanaka theoretically prove that the coupling between the flow and density fluctuations, taking the contribution of the density dependence of the viscosity into account, can lead to mechanical instability such as cavitation.⁴⁹ This theory is consistent with the abnormal butterfly patterns observed in the bulk of PE under a uniaxial deformation and describes the strain-induced density fluctuation in crystalline polymers under stretching. In summary, Doi and Onuki, and Furukawa and Tanaka proved that density fluctuation

increases under deformation, accompanied by the gradient of the stress field in connection with density dependence.

The crystalline polymers have a spatial heterogeneity of crystallinity due to their hierarchical structure consisting of crystal and amorphous regions. Therefore, the original density fluctuations and mechanical properties related to crystallinity lead to the spatial inhomogeneity in the stress field under uniaxial stretching, resulting in inhomogeneous deformation that induces spatial inhomogeneity of the density. In heterogeneous deformation, the non-fibril regions between fibrils are deformed more than the fibrils.

1.3 Motivation and Outline of This Thesis

Crystalline polymer materials exhibit a range of mechanical properties that depend on molecular characteristics, processing conditions, and polymorph. As described above, researchers have investigated the changes in crystalline lattice structure and lamellae under strain and proposed the deformation models based on small-scale structural transformations. The recent development of USAXS has enabled the study of the correlation between structure and physical properties on the sub-micrometer scale and the observation of an abnormal butterfly pattern in stretched PE. I investigated the role of crystallinity-dependent orientation of polymers on not only the scales from Å to tens of nm but also the submicron scales.

In Chapter 2, LLDPE spherulites were investigated by integrating dual-polarization STXM with multi-scale scattering. I quantified the local density and the orientation order parameters of C-H and C-C bonds to analyze their spatial correlations by STXM. The STXM analysis revealed a 180-degree phase shift between C-H bond

orientation and fluctuations in density and C–C bond orientation, explained by a geometric model of lamellar twisting around the *b*-axis. These results clarify how ordered crystallographic twisting coexists with stochastic fibril packing, bridging local orientations of chemical bonds and macroscopic morphologies.

In Chapter 3, I investigated the evolution of density and C-C bond orientation in stretched linear low-density polyethylene (LLDPE), which exhibits two yield points. By combining STXM with *in-situ* X-ray scattering, I quantified both local density and the orientation order parameters across different strains. The results reveal crystallinity-dependent inhomogeneous deformation, where molecular orientation develops preferentially in low-density regions. This integrated approach provides new insight into the hierarchical deformation mechanisms in crystalline polymers, particularly the role of crystallinity-dependent mechanical melting and orientation dynamics.

In Chapter 4, I investigated the hierarchical structural changes in the biodegradable homopolymer P(3HB) and a copolymer poly[(*R*)-3-hydroxybutyrate-*co*-(*R*)-3-hydroxyhexanoate] [P(3HB-*co*-3HH)] during uniaxial stretching. Using *in-situ* USAXS, SAXS, and WAXS, I clarify how the introduction of 3HH comonomer units improves ductility. The results demonstrate that copolymerization suppresses the regularity of crystals and facilitates stress dispersion, thereby reducing the sub-micrometer inhomogeneous deformation characterized by "abnormal" butterfly patterns in USAXS. By comparing these two systems, this study identifies the structural origin of improved mechanical properties, highlighting the role of hierarchical structural control in governing macroscopic ductility.

In Chapter 5, I attempted to clarify the universality of sub-micrometer heterogeneous deformation by stretching PA6 in its glassy state. Through *in-situ* X-ray

scattering measurements, I analyze samples crystallized at different temperatures to identify the differences of polymorphism and initial morphology. I reported the observation of "abnormal" butterfly patterns below its T_g , demonstrating that strain-induced density fluctuations persist even when amorphous chains are in a glassy state. Furthermore, I clarify how crystal stability and fibril branching dictate the competition between cavitation and shear banding, broadening the understanding of plastic deformation in semi-crystalline polymers.

In Chapter 6, I visualized the structural deformation on the submicron scales of PA6 using STXM. While NEXAFS-based orientation analysis is established for PE, I applied this methodology to PA6 for the first time to quantify fluctuations in density and C-C bond orientation. A comparative analysis with PE reveals that glassy PA6 restricts amorphous chain orientation, causing crystalline domains to align more readily than the amorphous network. This study clarifies how a glassy state dictates the microscopic response of hierarchical structures, providing a fundamental distinction between rubbery and glassy crystalline polymers.

References

1. Strobl, G. R., *The Physics of Polymers*, 3rd ed.; Springer: Berlin, 2007.
2. Wunderlich, B. *Macromolecular Physics: Crystal Melting*, Vol. 1; Academic Press: New York, 1980.
3. Holmes, D. R.; Bunn, C. W.; Smith, D. J. *J. Polym. Sci.* **1955**, *17* (84), 159–177.
4. Arimoto, H.; Ishibashi, M.; Hirai, M.; Chatani, Y. *J. Polym. Sci., Part A* **1965**, *3* (1), 317–326.
5. Vasile, C., Ed. *Handbook of Polyolefins*, 2nd ed.; CRC Press: Boca Raton, FL, 2000.
6. Herzog, B.; Kohan, M. I.; Mestemacher, S. A.; Pagilagan, R. U.; Redmond, K.; Sarbandi, R., R. Polyamides. In *Ullmann's Encyclopedia of Industrial Chemistry*, 7th ed.; Wiley-VCH: Weinheim, 2013.
7. Chen, G.-Q., Ed. *Plastics from Bacteria: Natural Functions and Applications*; Microbiology Monographs, Vol. 14; Springer-Verlag: Berlin, 2010.
8. Keller, A. *Prog. Phys.* **1968**, *31*, 623–704.
9. Keller, A. *Philosophical Magazine* **1957**, *2*, 1171–1175.
10. Claver, G. C.; Buchdahl, R.; Miller, R. L. *J. Polym. Sci.*, **1956**, *20* (94), 202–205.
11. Keith, H. D.; Padden, F. J. *J. Appl. Phys.* **1963**, *34*, 2409–2421.
12. Fu, J.; Urquhart, S. G. *J. Phys. Chem. A* **2005**, *109*, 11724–11732.
13. Ade, H.; Hitchcock, A. P. *Polymer* **2008**, *49* (3), 643–675.
14. Wang, Y.; Zou, Y.; Araki, T.; Lüning, J.; Kilcoyne, A. L. D.; Sokolov, J.; Ade, H.; Rafailovich, M. *Macromolecules* **2010**, *43* (19), 8153–8161.

15. Arakawa, M.; Kishimoto, M.; Uchida, K.; Nakanishi, Y.; Takenaka, M. *Macromolecules* **2026**, *59* (1), 369–378.
16. Xu, S.; Zhou, J.; Pan, P. *Progress in Polymer Science* **2023**, *140*, 101676.
17. Bowden, P. B.; Young, R. J. *J. Mater. Sci.* **1974**, *9*, 2034–2051.
18. Bartczak, Z.; Galeski, A. *Macromolecular Symposia* **2010**, *294* (1), 67-90.
19. Flory, P. J.; Yoon, D. Y. *Nature* **1978**, *272*, 226-229.
20. Schultz, JM.; *Polymer materials science*; Englewood Cliffs: Prentice-Hall, 1974.
21. Fua, Q.; Men, Y.; Strobl, G. *Polymer* **2003**, *44*, 1927–1933.
22. Kelly, A.; Groves, G. W. *Crystallography and Crystal Defects*; Longman: London, 1970
23. Peterlin, A., *J. Mater. Sci.* **1971**, *6*, 490–508.
24. Bartczak, Z.; Argon, A. S.; Cohen, R. E. *Macromolecules* **1992**, *25*, 5036–5053.
25. Galeski, A.; Bartczak, Z.; Argon, A. S.; Cohen, R. E. *Macromolecules* **1992**, *25*, 5705–5718
26. Tashiro, K.; Nakai, Y.; Kobayashi, M.; Tadokoro, H. *Macromolecules* **1980**, *13*, 137–145.
27. Auriemma, F.; De Rosa, C. *Macromolecules* **2003**, *36*, 9396–9410.
28. Tashiro, K.; Cheng, J.; Ike, M. *Macromolecules* **2003**, *36*, 359–367.
29. Liu, G.; Zheng, L.; Zhang, X.; Li, C.; Jiang, S.; Wang, D. *Macromolecules* **2012**, *45* (13), 5487–5493.
30. Liu, G.; Zheng, L.; Zhang, X.; Li, C.; Jiang, S.; Wang, D. *Macromolecules* **2012**, *45* (13), 5487–5493.
31. Chelakara Satyanarayana, K.; Bolton, K. *Polymer* **2012**, *53* (14), 2927–2934.

32. Xu, J.-R.; Ren, X.-K.; Yang, T.; Jiang, X.-Q.; Chang, W.-Y.; Yang, Shuang.; Stroeks, A.; Chen, E.-Q. *Macromolecules* **2018**, *51* (1), 137–150.
33. Pepin, J.; Gaucher, V.; Rochas, C.; Lefebvre, J.-M. *Polymer* **2019**, *175*, 87-98.
34. De Rosa, C.; Auriemma, F.; De Lucia, G.; Resconi, L. *Polymer* **2005**, *46* (22), 9461–9475.
35. Bao, R.-Y.; Ding, Z.-T.; Liu, Z.-Y.; Yang, W.; Xie, B.-H.; Yang, M.-B. *Polymer* **2013**, *54* (3), 1259–1268.
36. Wang, H.; Zhang, J.; Tashiro, K. *Macromolecules* **2017**, *50* (8), 3285–3300.
37. Liu, Y.; Cui, K.; Tian, N.; Zhou, W.; Meng, L.; Li, L.; Ma, Z.; Li, L. *Macromolecules* **2012**, *45* (6), 2764–2772.
38. Wang, Y.; Jiang, Z.; Wu, Z.; Men, Y. *Macromolecules* **2013**, *46* (2), 518–522.
39. Xiong, B.; Lame, O.; Chenal, J.-M.; Rochas, C.; Séguéla, R.; Vigier, G. *Polymer* **2014**, *55* (5), 1223–1227.
40. Xiong, B.; Lame, O.; Chenal, J.-M.; Rochas, C.; Séguéla, R.; Vigier, G. *Macromolecules* **2015**, *48* (7), 2149–2160.
41. Kishimoto M.; Mita K; Ogawa H.; Takenaka M. *Macromolecules* **2020**, *53*, 9097–9107.
42. Takenaka, M.; Shimizu, H.; Nishitsuji, S., *Phys. Rev. E* **2007**, *75*, 061802.
43. Bastide, J.; Leibler, L.; Prost, J. *Macromolecules* **1990**, *23*, 1821– 1825.
44. Mendes, E., Jr.; Lindner, P.; Buzier, M.; Boué, F.; Bastide, J. *Phys. Rev. Lett.* **1991**, *66* (12), 1595–1598.
45. Hashimoto, T.; Fujioka, K. *J. Phys. Soc. Jpn.* **1991**, *60*, 356–359.
46. Karino, T.; Okumura, Y.; Zhao, C.; Kataoka, T.; Ito, K.; Shibayama, M. *Macromolecules* **2005**, *38*, 6161– 6167.

- 47. Hayes, C.; Bokobza, L.; Boué, F.; Mendes, E.; Monnerie, L. *Macromolecules* **1996**, 29, 5036– 5041.
- 48. Doi, M.; Onuki, A. *J. Phys. II* **1992**, 2, 1631–1656.
- 49. Furukawa, A.; Tanaka, H. *Nat. Mater.* **2009**, 8, 601–609.

Chapter 2

Hierarchical Structure of LLDPE Spherulites Revealed through Integrated Molecular Orientation and Density Distribution Analysis

2.1 Introduction

Polyethylene (PE) represents one of the most widely used thermoplastic polymers and serves as a primary model for studying the crystallization of crystalline polymers. The hierarchical structure of PE is characterized by multiple length scales, ranging from the crystal lattice structure where molecular chains are regularly folded, to lamellar structures of alternating crystalline and amorphous phases, fibrillar structures formed by growth of lamellae, and finally, macroscopic spherulites.¹⁻³ When quenched from the melt, PE typically forms an orthorhombic crystal lattice with parameters $a = 0.740$ nm, b (growth direction) = 0.494 nm, and c (chain axis) = 0.253 nm.⁴ During the formation of spherulites, it is well established that lamellar crystals and fibrils undergo periodic twisting around the b -axis growth direction.^{5,6} These spherulites are formed by the branching and splaying of fibrils that radiate from a central nucleus, resulting in the characteristic banded structure with concentric extinction rings observed under polarized optical microscopy (POM).⁵

The hierarchical structure of PE has been extensively investigated using various analytical techniques. Wide-angle X-ray scattering (WAXS) provides

information on the crystal lattice,⁴ while small-angle X-ray scattering (SAXS) yields statistical averages for the lamellar long period and crystal thickness.^{7, 8} Ultra-small-angle X-ray scattering (USAXS) has been employed to evaluate the mass-fractal dimension of spherulites, which serves as an indicator of fibril packing density and branching frequency.^{9, 10} Furthermore, small-angle light scattering (SALS) provides macroscopic data on the average spherulite size, band periodicity, and the sign of birefringence, as well as orientation fluctuations.^{11–14} In addition to these reciprocal-space techniques, real-space observations by POM and atomic force microscopy (AFM) have been used to characterize the band periodicity and the surface morphology in spherulites.^{5, 15–17}

Recently, Scanning Transmission X-ray Microscopy (STXM) has emerged as a powerful tool for probing the local structure of polymers. STXM is an X-ray microscope in which synchrotron radiation X-rays are focused on a sample by a Fresnel zone plate, and the transmitted X-rays I at the focus position are mechanically raster scanned to obtain a spatial image of the I distribution.^{18–20} By acquiring the incident X-ray intensity, I_0 , the optical density (OD) is obtained by the following equation:

$$OD = -\ln \frac{I}{I_0} \quad (2.1)$$

Since STXM provides images of transmitted X-rays at several different energies, 2D images are acquired at various energies near the X-ray absorption edge of the atom of interest, and the near-edge X-ray absorption fine structure (NEXAFS) spectrum of the atom is obtained from the value of the OD at each pixel of the 2D images. Peaks corresponding to chemical bonds appear in the NEXAFS spectrum, the intensities of which depend on the angle between the transition dipole moment (TDM) of the chemical bond and the direction of polarization of the X-ray (electric field).

Previous STXM studies have successfully evaluated the linear dichroism of n-alkanes, which are saturated hydrocarbons composed of methylene units similar to PE, as well as the inhomogeneous deformation in stretched PE at the sub-micrometer scale, and have observed the PE spherulites grown on substrates.^{17, 21, 22}

Among these studies, the pioneering work by Wang *et al.*¹⁷ observed the morphology of linear low-density polyethylene (LLDPE) thin films using NEXAFS spectroscopy, providing insightful visualizations of the orientation distribution within spherulites. While they utilized the dichroic contrast between C-H and C-C resonances to perform quasi-compositional mapping, their analysis was largely qualitative, relying on the comparison of images acquired at specific sample rotations.

Since the *OD* in STXM represents an integration of both local density and molecular orientation through the entire film thickness, it remains a significant challenge to quantitatively decouple these two factors. Specifically, Wang *et al.* demonstrated orientation patterns but did not derive a thickness-independent orientation order parameter at a pixel-by-pixel level. Therefore, there remains a critical need to fully decode the physical meaning of STXM contrast by performing dual-polarization quantitative analysis.

In this study, I acquired STXM images at both horizontal and vertical polarization directions for the exact same sample area. This approach allows for the pixel-wise calculation of the orientation order parameter, effectively normalizing out the effects of local thickness and density fluctuations. By integrating real-space observations by STXM with reciprocal-space data from multi-scale scattering techniques (USAXS, SAXS, and SALS), I aim to verify the structural origin of the observed contrast. This study evaluates whether the periodic fluctuations in density and

orientation can be consistently explained by a geometric model of the orthorhombic unit cell undergoing lamellar twisting, thereby establishing a quantitative framework for interpreting the hierarchical structure of crystalline polymers through STXM.

2.2 Experimental Section

2.2.1 Sample Preparation

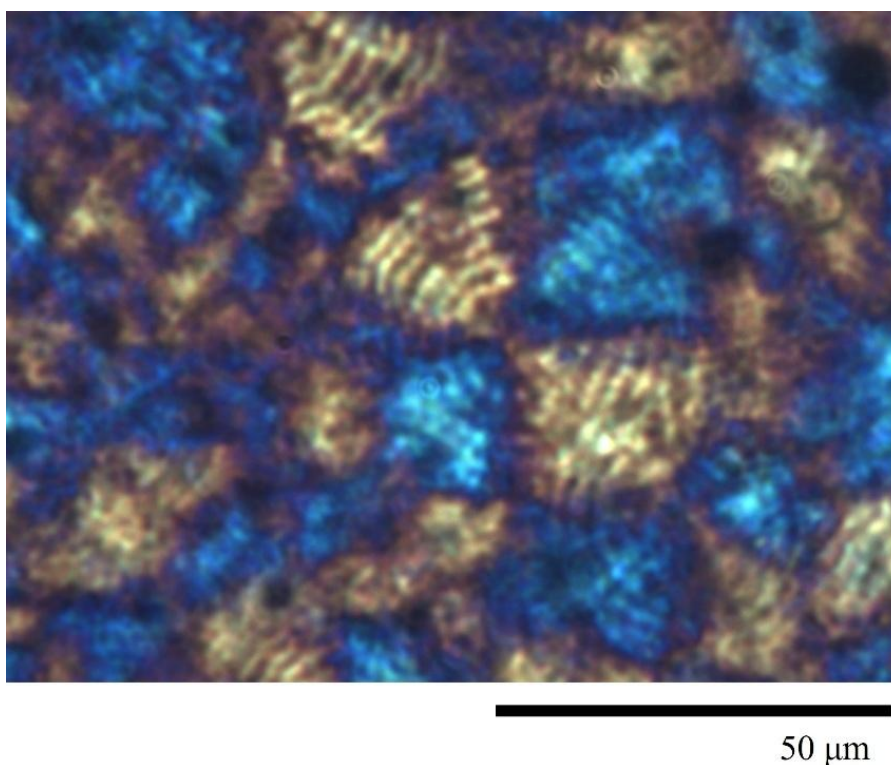


Figure 2.1. LLDPE spherulites in the press sheet observed by POM.

LLDPE (density: 0.920 g/cm³, content of 1-butene) was used in this study. The polystyrene-equivalent weight-average molecular weight (M_w) and molecular weight distribution (M_w/M_n) were 1.1×10^5 and 5.17, respectively, as determined by gel permeation chromatography (GPC). LLDPE sheets with a thickness of 220 μm were prepared using two press machines (a custom-made model and IMC-180C, Imoto Machinery Co., Ltd.). First, the LLDPE pellets were melted at 180°C (above the

melting point) for 10 min under pressure. The melt was then immediately transferred to another press machine set at 100°C to allow isothermal crystallization. Additionally, an LLDPE sheet crystallized at 0 °C, consisting of smaller spherulites to serve as a reference sample for NEXAFS spectra, was obtained using a similar method.

The morphology of the resulting sheets was observed using a polarized optical microscope (POM, BX50, Olympus). Figure 2.1 shows a representative POM image of the spherulites in the LLDPE sheet. The spherulites exhibited a characteristic banded structure with concentric extinction rings, which is attributed to the periodic twisting of lamellar crystals during growth.

2.2.2 X-ray Scattering Measurements

USAXS and SAXS measurements were conducted at the second hutch of beamline BL03XU at SPring-8 (Hyogo, Japan).²³ The beam size at the sample position was 100 μm (horizontal) $\times$ 300 μm (vertical), and a PILATUS-1M detector (Dectris Ltd.) was used for both measurements. For the SAXS measurements, the incident wavelength, camera length, and exposure time were 1.0 Å, 4.33 m, and 1 s, respectively, with a 20 μm -thick Mo attenuator. For the USAXS measurements, the incident wavelength, camera length, and exposure time were adjusted to 2.0 Å, 7.81 m, and 10 s, respectively, without an attenuator. In the data analysis, the obtained 2D scattering images were corrected for sample absorption, and background scattering from the air and the instrument was subtracted.

2.2.3 Differential Scanning Calorimetry (DSC) Measurements

Thermal analysis was performed using a DSC (PerkinElmer, Inc.) calibrated with indium. Samples of approximately 18 mg were scanned at a heating rate of 10 °C/min. The crystallinity of each sample was calculated from the enthalpy of the melting endotherm the theoretical melting enthalpy of 100% crystalline PE, $\Delta H_m^0 = 296$ J/g.^{24, 25}

2.2.4 Light Scattering Measurement under H_V Polarization Condition

Small-angle light scattering (SALS) measurement was performed on the PE sheet under H_V (depolarized) scattering condition using a red laser source ($\lambda = 633$ nm). The instrument utilized an indirect imaging method, where the scattering patterns were projected onto a translucent screen and captured by a CMOS camera (Basler ace acA1920-155um).²⁶ The camera length (R_{CL}), defined as the distance from the sample to the screen, was set at 35 cm, and the working distance (R_{WD}), the distance from the screen to the detector lens, was set at 45 cm. The exposure time was fixed at 1.2 ms for all measurements. The details of the instrument and the data treatment are described elsewhere.²⁶

2.2.5 STXM Observation

STXM measurements were performed at BL-19A of the Photon Factory, High Energy Accelerator Research Organization (KEK-PF, Japan).²⁰ For STXM observation, ultrathin sections of LLDPE press sheets were prepared using a cryo-microtome (EM UC7, Leica Microsystems). To preserve the original spherulites and prevent mechanical damage during sectioning, the specimens were cut below the glass transition temperature of LLDPE. The resulting ultrathin sections were placed on a grid for observation. In the STXM measurements, the incident X-ray energy was scanned from 280 to 320 eV, covering the carbon K-edge absorption region (approximately 285 eV). The exposure time was set to 2 ms per pixel. To analyze the orientation within the spherulites, the polarization direction of the X-rays was set to both horizontal and vertical directions relative to the observation area at the same sample position. To analyze the orientation of LLDPE crystallized at 100 °C, images were obtained with spatial resolutions of 200 nm/pixel and 30 nm/pixel, depending on the required field of view. In contrast, images for reference NEXAFS spectra (crystallized at 0 °C) were acquired at 100 nm/pixel resolution. All images used for orientation analysis were corrected for sample drift.

To visualize the density distribution within the LLDPE spherulites, the optical density (*OD*) images obtained at 319.5 ± 0.5 eV were converted into local density (ρ) maps. The *OD* at each pixel is defined as:^{22, 27}

$$OD = \mu \rho t \quad (2.4)$$

where μ is the mass absorption coefficient, and t is the sample thickness.

The energy region of 319.5 ± 0.5 eV was selected because it is sufficiently far from the carbon K-edge (≈ 285 eV). In this region, the *OD* is independent of the

transition dipole moment (TDM) orientation and depends solely on the mass thickness (ρt) of the sample. I, thus, estimated the sample thickness t from the spatial-average of the OD , $\overline{OD}$ at 319.5 ± 0.5 eV. It should be noted that the sample thickness is assumed to be uniform within the observed area. The sample thickness is estimated using $\overline{OD}/\mu\bar{\rho}$ with $\bar{\rho}$ being the average density of the sample. The value of μ of LLDPE at this energy was determined to be 3.40×10^4 cm²/g based on the X-ray attenuation length obtained from the Center for X-ray Optics (CXRO) database. The average density $\bar{\rho}$ of the LLDPE sample was first calculated from the average crystallinity determined by DSC, using the theoretical densities of the crystalline (1.00 g/cm³) and amorphous (0.855 g/cm³) phases. The local density ρ at each pixel was mapped by dividing the OD at 319.5 ± 0.5 eV by the product of μ and the estimated thickness t . While the sample thickness t was assumed to be uniform for the conversion to local density, it is worth noting that topographical artifacts, such as wrinkles and knife marks, could lead to local overestimation or underestimation of ρ .

2.3 Results and Discussion

2.3.1 X-ray and Light Scattering Measurements

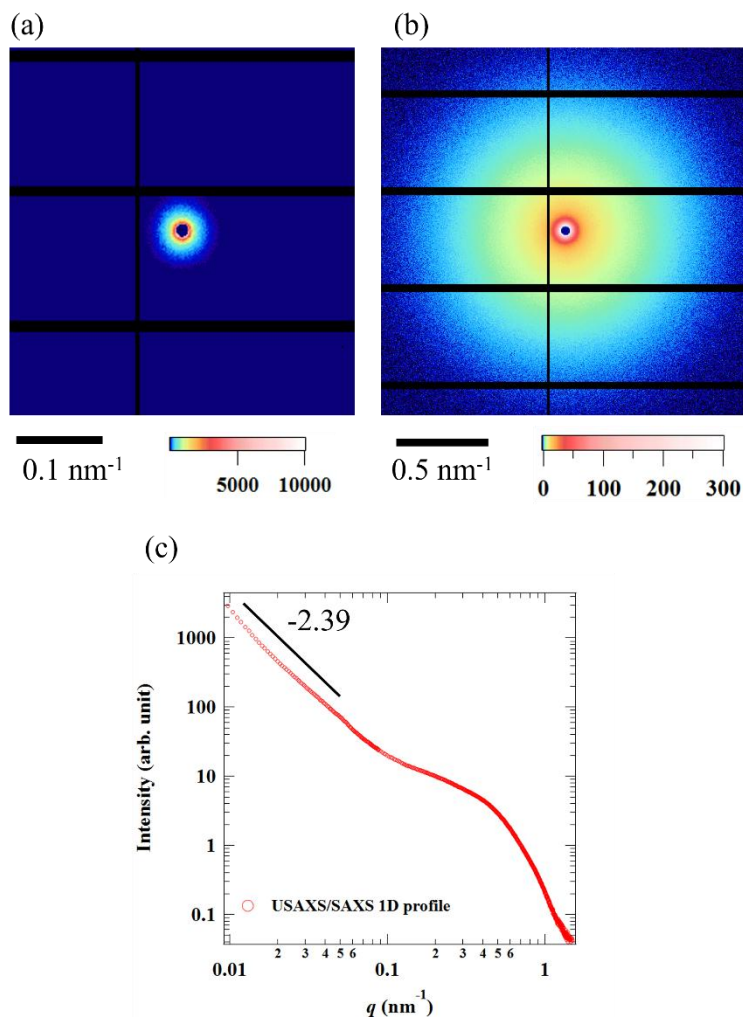


Figure 2.2. (a) USAXS and (b) SAXS 2D scattering patterns of LLDPE crystallized at 100°C and (c) combined USAXS and SAXS 1D scattering profile.

Figure 2.2(a) and (b) are 2D patterns of USAXS and SAXS, respectively. They are isotropic. I, thus, obtained the combined USAXS and SAXS 1D intensity profile by averaging circularly as shown in Figure 2.2(c). Here q is the magnitude of the scattering vector and is defined by

$$q = \frac{4\pi}{\lambda} \sin\left(\frac{\theta}{2}\right) \quad (2.5)$$

where λ and θ are the wavelength of the incident X-rays and the scattering angles, respectively. The scattering peak corresponding to the long period of the lamellar structure was not clearly observed in the combined 1D profile. This lack of a well-defined peak indicates a broad distribution of the long period of the LLDPE spherulite.

To characterize the lamellar structures of the LLDPE spherulites, the crystal and amorphous thicknesses, as well as the long period, were estimated by calculating the one-dimensional correlation function from the combined 1D scattering profiles.^{7, 8} The one-dimensional correlation function, $K(z)$, as a function of distance z , is defined as:

$$K(z) = \frac{\int_{0.008 \text{ nm}^{-1}}^{5.00 \text{ nm}^{-1}} q^2 I(q) \cos qz \, dq}{\int_{0.008 \text{ nm}^{-1}}^{5.00 \text{ nm}^{-1}} q^2 I(q) \, dq} \quad (2.6)$$

The average d-spacing (l_d) of the lamellar structure, which accounts for the distribution of lengths, was estimated by the following equation:

$$l_d = \frac{\int_{\alpha}^{\beta} z K(z) \, dz}{\int_{\alpha}^{\beta} K(z) \, dz} \quad (2.7)$$

Here, α is defined as the value of z where $K(z)$ becomes positive for the second time as z increases from zero, and β is the value of z where $K(z)$ becomes negative for the second time. The crystal thickness is estimated by the intersection of the $K(z)$ minimum and the extrapolation of the linear part in the $K(z)$. Based on the crystallinity obtained from DSC results of 27.6%, the crystal thickness was determined as 3.32 nm and the average long period of lamellar structures was 8.20 nm. Based on characteristic parameters of the lamellae, the line crystallinity of the lamellar structures in fibril

bundles was estimated to be 40.4%. The difference may be due to the effects of the defects between the spherulites.

The mass-fractal dimension of the LLDPE spherulites was determined to be 2.39 from the slope of the 1D profile in the USAXS region. The power-law exponent between 1 and 3 in the USAXS region indicates that the long-scale density fluctuations within spherulites follow mass-fractal.^{9, 10} An exponent approaching 3 indicates that fibrils are packed more densely within the spherulite.

Figure 2.3 shows the SALS 2D pattern under H_V condition. A four-leaf clover pattern was observed in the 2D pattern, reflecting the formation of spherulites in the sample. The 1D intensity profile (Figure 2.3b) obtained by averaging the four sectors at $\varphi = 45^\circ \pm 5^\circ$, $135^\circ \pm 5^\circ$, $225^\circ \pm 5^\circ$ and $315^\circ \pm 5^\circ$ shows the peak at $0.16 \mu\text{m}^{-1}$. The definition of the azimuthal angle φ is shown in Figure 2.3a.

The peak position reflects the average spherulite size (R_{sp}) and we can estimate R_{sp} from^{11, 14}

$$R_{sp} = \frac{4.09}{q_c}. \quad (2.8)$$

R_{sp} is $25.4 \mu\text{m}$ of the samples. The result agrees with the size of the spherulite in POM.

Theoretically, the scattering intensity along the direction parallel and perpendicular to the polarization axes vanishes in ideal spherulites. On the contrary, the intensity along the extinction direction was measured as shown in Figure 2.3b. This existence of intensity arises from the optical heterogeneity along the radial direction, in other words, continuity and defects of fibrils within the spherulites and the density fluctuations along the tangential direction between fibrils. To estimate characteristic length relative to the factor of intensity along the polarization axes, the 1D profile in the

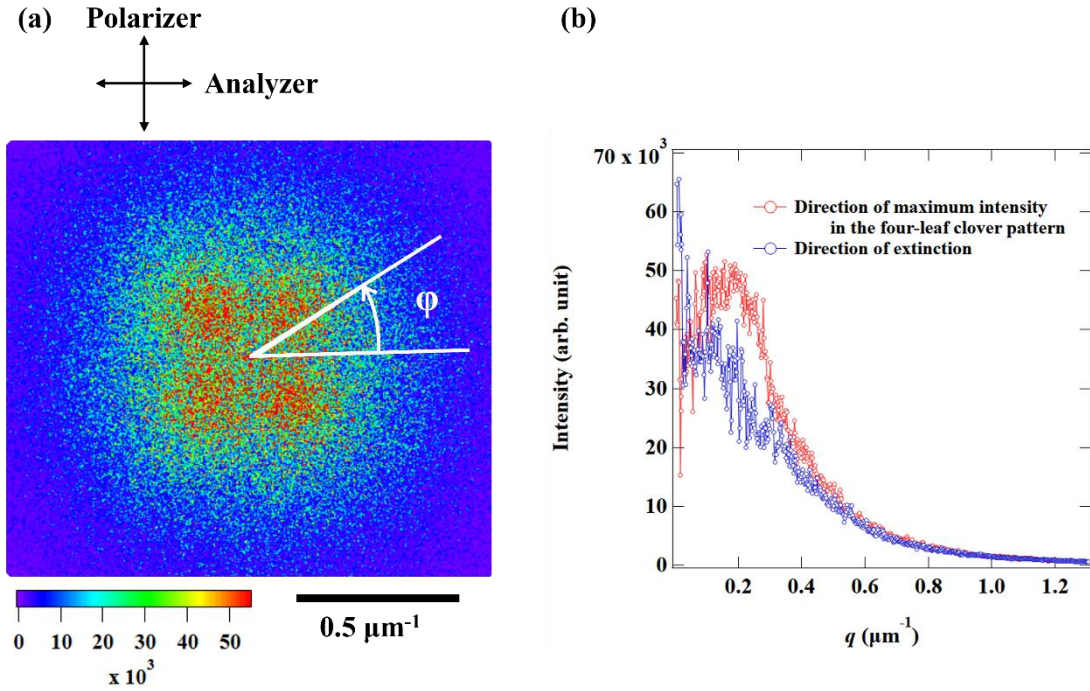


Figure 2.3. (a) 2D H_V light scattering pattern of the LLDPE spherulites. (b) 1D scattering intensity profiles.

extinction direction was analyzed by the Debye–Bueche function,²⁸

$$I(q) = \frac{I(q=0)}{[1 + (q\xi)^2]^2} \quad (2.9)$$

where ξ and $I(q=0)$ are the correlation length and the intensity at $q=0$, respectively.

The value of ξ , the length associated with the fibrils was estimated as 2.05 μm .

The spherulites, with an average crystallinity of 28.2%, are composed of a fibril structure formed by the growth of lamellae. These lamellae have the crystal thickness of 3.32 nm and the long period of 8.20 nm. The fibrils are packed with a mass fractal dimension of 2.39, resulting in an average spherulite diameter of 25.4 μm .

2.3.2 STXM Measurements

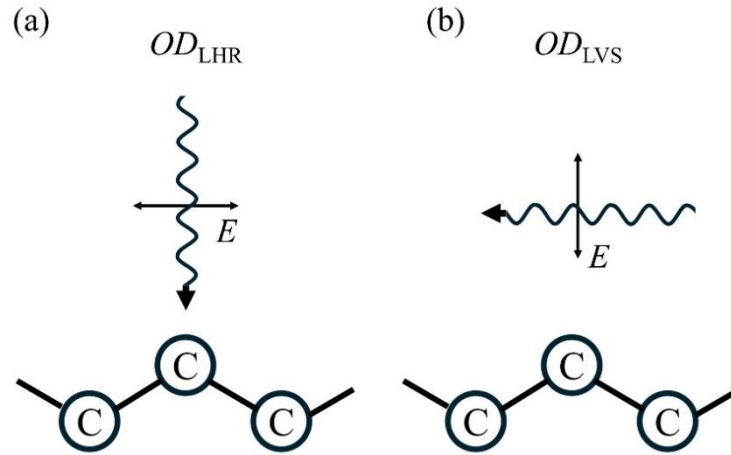


Figure 2.4. PE polymer chains oriented horizontally relative to the measurement field of view. (a) When the electric field vector (E) is parallel to the C–C bond (LHR polarization), the OD is maximized at the C-1s $\rightarrow \sigma^*_{C-C}$ transition. (b) When E is perpendicular to the C–C bond (LVS polarization), the OD is minimized at the same transition.

The OD near 288 eV and 292 eV correspond to C-1s $\rightarrow \sigma^*_{C-H}$ and C-1s $\rightarrow \sigma^*_{C-C}$ resonances, respectively.²⁷ OD of the chemical bond resonance is proportional to $\cos^2 \theta$, where θ is the angle between the electric field vector of incident X-rays (E) and the direction of TDM, μ_{if} ,²¹ such as

$$OD \propto |E\mu_{if}|^2 \propto \cos^2 \theta \quad (2.10)$$

In this study, the X-rays used in the STXM measurements were horizontally linearly polarized (LHR) and vertically linearly polarized (LVS) relative to the measurement field of view. Consequently, when numerous horizontally aligned C–C bonds, as shown in Figure 2.4, exist within the field of view, the OD under LHR X-rays increases. This occurs because the TDM of the C-1s $\rightarrow \sigma^*_{C-C}$ transition lies along the bond axis. The same principle applies to the C-1s $\rightarrow \sigma^*_{C-H}$ transition.

2D orientation maps for the C–H and C–C bonds were generated by calculating the orientation order parameter, $\langle P_2 \rangle$, defined by the following equation, respectively.²⁹

$$\langle P_2 \rangle = \frac{OD_{LHR} - OD_{LVS}}{OD_{LHR} + 2OD_{LVS}} \quad (2.11)$$

where OD_{LHR} and OD_{LVS} are the OD values at the energy relative to the chemical bond resonance obtained using LHR and LVS X-rays, respectively, after subtracting the background (the OD value at 319.5 ± 0.5 eV). A $\langle P_2 \rangle$ value of 1 represents perfect parallel alignment of the bonds in the horizontal direction, while -0.5 indicates perfect vertical alignment. A value of 0 corresponds to a random orientation of the chemical bonds.

2.3.2.1 Mapping of an Entire Spherulite

Figure 2.5a represents the local density (ρ) 2D mapping of the overall spherulite with 200 nm/pixel resolution, and Figure 2.5b and c shows the orientation order parameter, $\langle P_2 \rangle$ 2D mapping of C–H bonds and C–C bonds corresponding to the local density (ρ) 2D mapping, respectively. In the ρ mapping, the ultrathin section had wrinkles and knife marks pointed by arrows in Figure 2.5a. The ρ mapping reflected density fluctuations arising from the local crystallinity, which is distributed isotropically from the center. The $\langle P_2 \rangle$ contrast in the image of C–H bonds is stronger than the density contrast. In the $\langle P_2 \rangle$ mapping of C–H bonds, $\langle P_2 \rangle$ changed values alternating between positive and negative along the radial direction, which is consistent with the periodic twisting. Notably, the $\langle P_2 \rangle$ contrast for the C–H bonds is more pronounced in the regions along the radial growth direction than in the central region, suggesting that the molecular orientation becomes more developed as the crystallization proceeds outward from the center. In contrast, the $\langle P_2 \rangle$ distribution of C–C bonds mapping did not exhibit clear periodic variation.

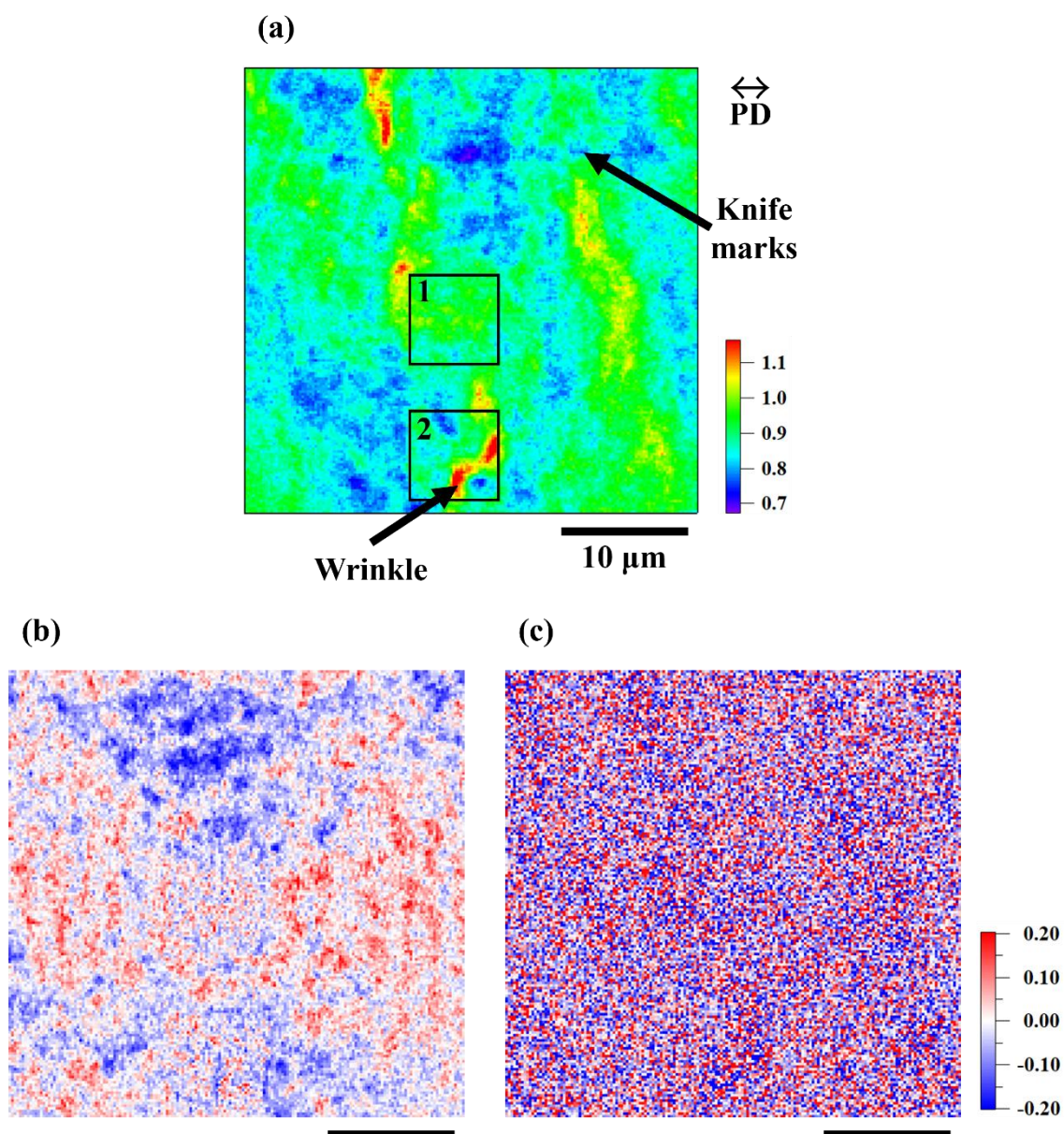


Figure 2.5. (a) Local density (ρ) and $\langle P_2 \rangle$ of (b) C–H bonds and (c) C–C bonds 2D mapping of the overall spherulite.

I analyzed the center of the spherulite (the region 1 in Figure 2.5(a)) and the region in the banded structure in the radial direction (the region 2 in Figure 2.5(a)) with high spatial resolution 30 nm/pixel to elucidate the local crystalline morphology.

2.3.2.2 Mapping of the Center and Banded Structure within the Spherulite

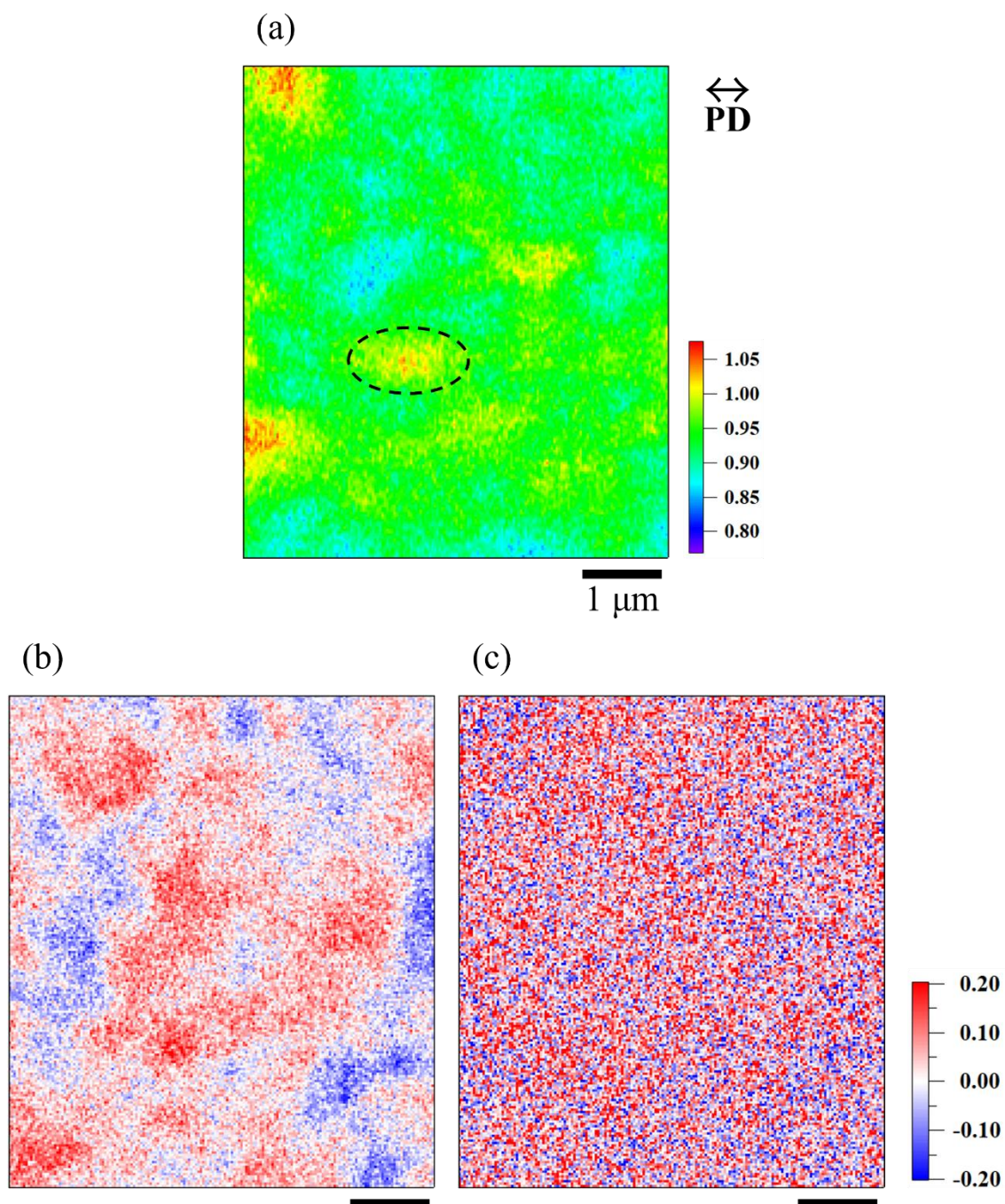


Figure 2.6. (a) Local density (ρ) and $\langle P_2 \rangle$ of maps for (b) C–H bonds and (c) C–C bonds at the center of the spherulite shown in Figure 2.5. The region enclosed by the broken line represents the nucleus of the spherulite, estimated based on the convergence of the periodic banded structure.

Figure 2.6 presents high-resolution STXM images taken at the center of the LLDPE spherulite or the region 1 in Figure 2.5(a). The local density map (Figure 2.6a) and the orientation order parameter maps for the C–H and C–C bonds (Figures 2.6b and c, respectively) were obtained with a spatial resolution of 30 nm/pixel. Within this central area (enclosed by the broken line in Figure 2.6a), high- ρ regions with diameters of approximately 600–800 nm were observed. The value of ρ in these regions is nearly identical to the theoretical density of the crystalline phase, suggesting that these regions correspond to nuclei.

Regarding the molecular orientation for C–H bonds, the $\langle P_2 \rangle$ map exhibits a mosaic-like assembly of distinct sub-micrometer domains. In this region, domains with horizontal orientation ($\langle P_2 \rangle > 0$) and vertical orientation ($\langle P_2 \rangle < 0$) were located adjacent to one another. This spatial distribution indicates that while the lamellae were locally aligned within each bundle, these individual bundles within the sheaf-like nucleus were oriented along various directions as they begin to splay from the central core. Notably, some of these central domains show spatial continuity with the larger-scale radial bands observed in Figure 2.5b, indicating that specific bundles in the nucleus serve as seeds for the subsequent development of fibrils.

While the $\langle P_2 \rangle$ map for C–H bonds clearly visualized these mosaic-like domains, equivalent spatial structures were less recognizable in the C–C bond mapping. Since the TDM of the $C-1s \rightarrow \sigma^*_{C-C}$ resonance is parallel to the c -axis (molecular chain axis), this relative lack of defined contrast suggests that these initial lamellar bundles were tilted in various directions and provides evidence that the initial splaying of bundles in the sheaf-like nucleus occurs three-dimensionally.

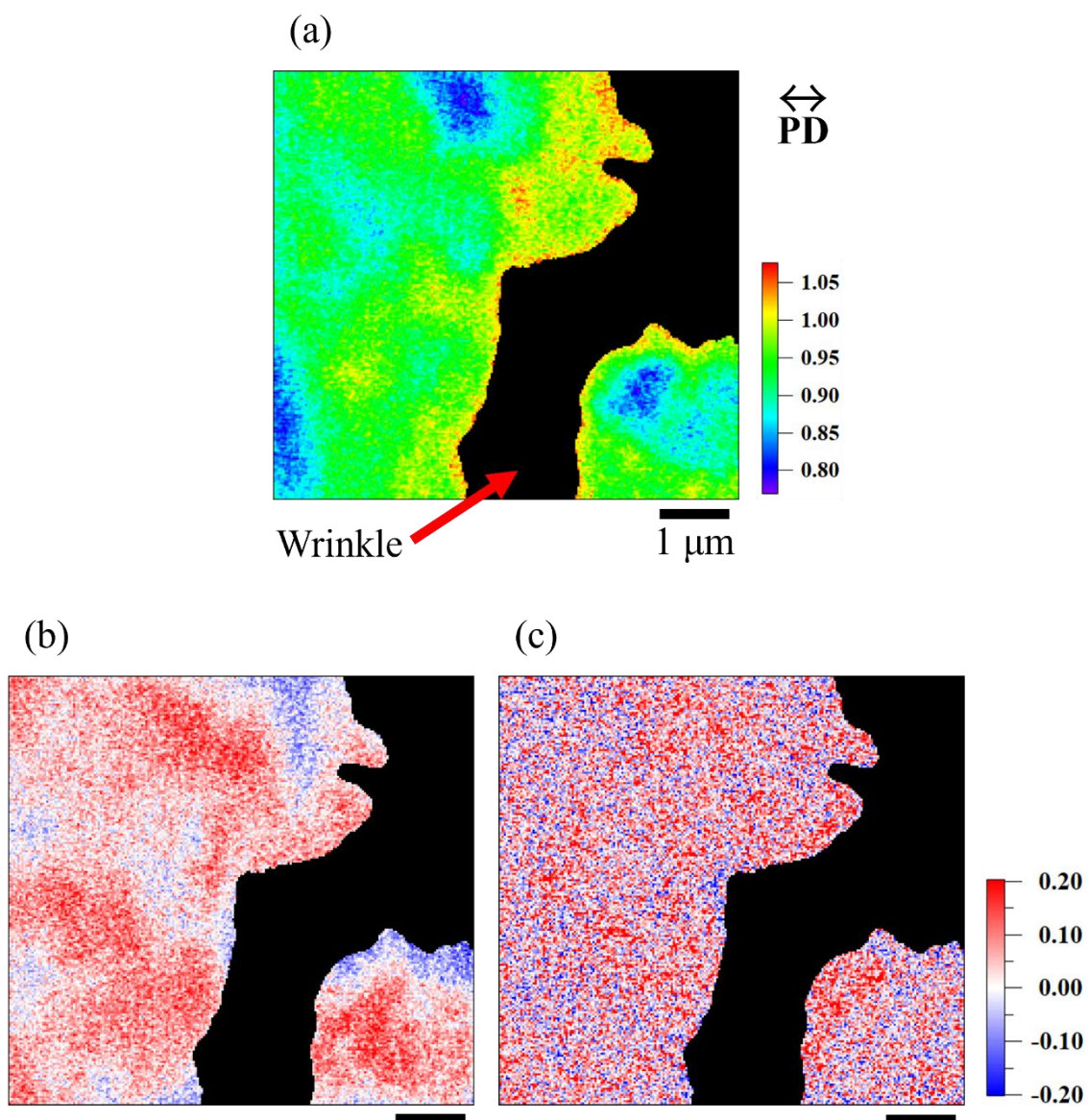


Figure 2.7. (a) Local density (ρ) and $\langle P_2 \rangle$ maps for (b) C–H bonds and (c) C–C bonds in the radial banded region indicated in Figure 2.5. In these maps, the wrinkled area pointed by the red arrow in (a) was excluded from the orientation analysis to ensure data reliability.

Figure 2.7 shows the high-resolution maps of the banded structure along the radial direction, corresponding to the region 2 indicated in Figure 2.5. In these maps, the radial growth direction of the fibrils was aligned with the vertical axis of the image. Figure 2.7a displays the local density distribution, while Figures 2.7b and 2.7c show the $\langle P_2 \rangle$ mappings for the C–H and C–C bonds, respectively. To ensure the reliability of the orientation analysis, the wrinkled area, which is pointed out by the red arrow in the density map, was excluded from the 2D orientation maps. The $\langle P_2 \rangle$ map for the C–H bonds exhibits a clear periodic contrast along this vertical growth direction.

Figure 2.8 shows the histograms of local density, ρ , and orientation order parameters, $\langle P_2 \rangle$, obtained from the center region (Figure 2.6) and the banded structure (Figure 2.7). The ρ distribution in the center region was shifted toward higher values compared to that in the banded structure. This shift can be attributed to the presence of crystal nuclei without a significant amorphous phase. In contrast, the relatively lower density in the banded structure was likely due to fibril branching and the development of inter-lamellar amorphous regions introduced during radial growth.

Regarding the orientation order parameters for C–H bonds, the distribution in the center region is narrower and centered closer to zero compared to the banded structure, suggesting a more developed orientation in the latter. However, unexpectedly, the most negative $\langle P_2 \rangle$ value in the banded structure was slightly higher than that in the central region. Importantly, the near-zero spatial average of $\langle P_2 \rangle$ across the nucleus is not due to a lack of molecular order, but rather due to the cancellation of orientation vectors from the differently directed bundles within the sheaf-like structure. According to Figure 2.5b, where the C–H bond orientation contrast is enhanced along the growth direction, it was expected that an improved orientation would result in both an increase

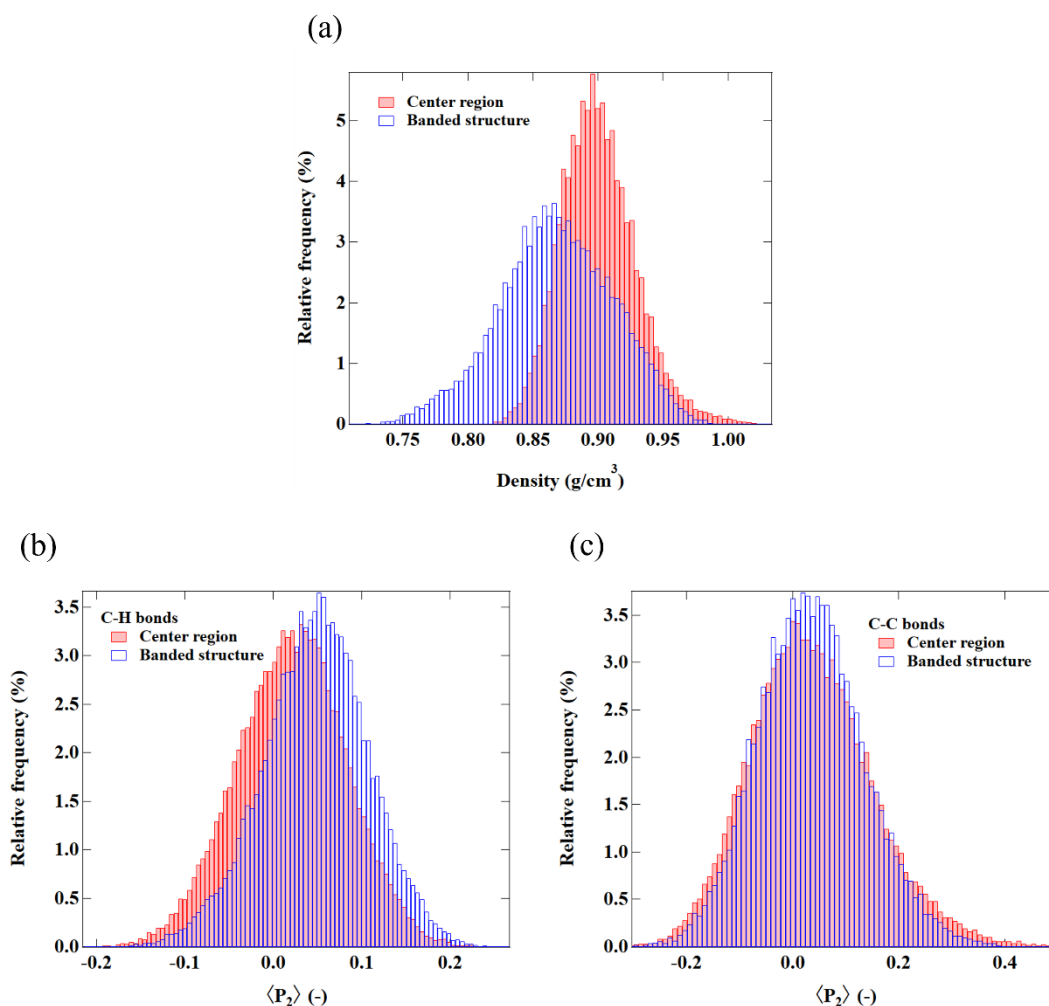


Figure 2.8. Histograms of (a) local density and orientation order parameters for (b) C–H bonds and (c) C–C bonds. The red and blue histograms are constructed based on the center region and the banded structure, respectively.

in the maximum $\langle P_2 \rangle$ and a decrease in the more negative $\langle P_2 \rangle$. This discrepancy from the prediction may reflect local structural inhomogeneity within the specific region analyzed in Figure 2.7.

In contrast, the $\langle P_2 \rangle$ distribution for C–C bonds is approximately similar in both regions, indicating a comparable degree of main-chain orientation regardless of the specific morphology within the spherulite.

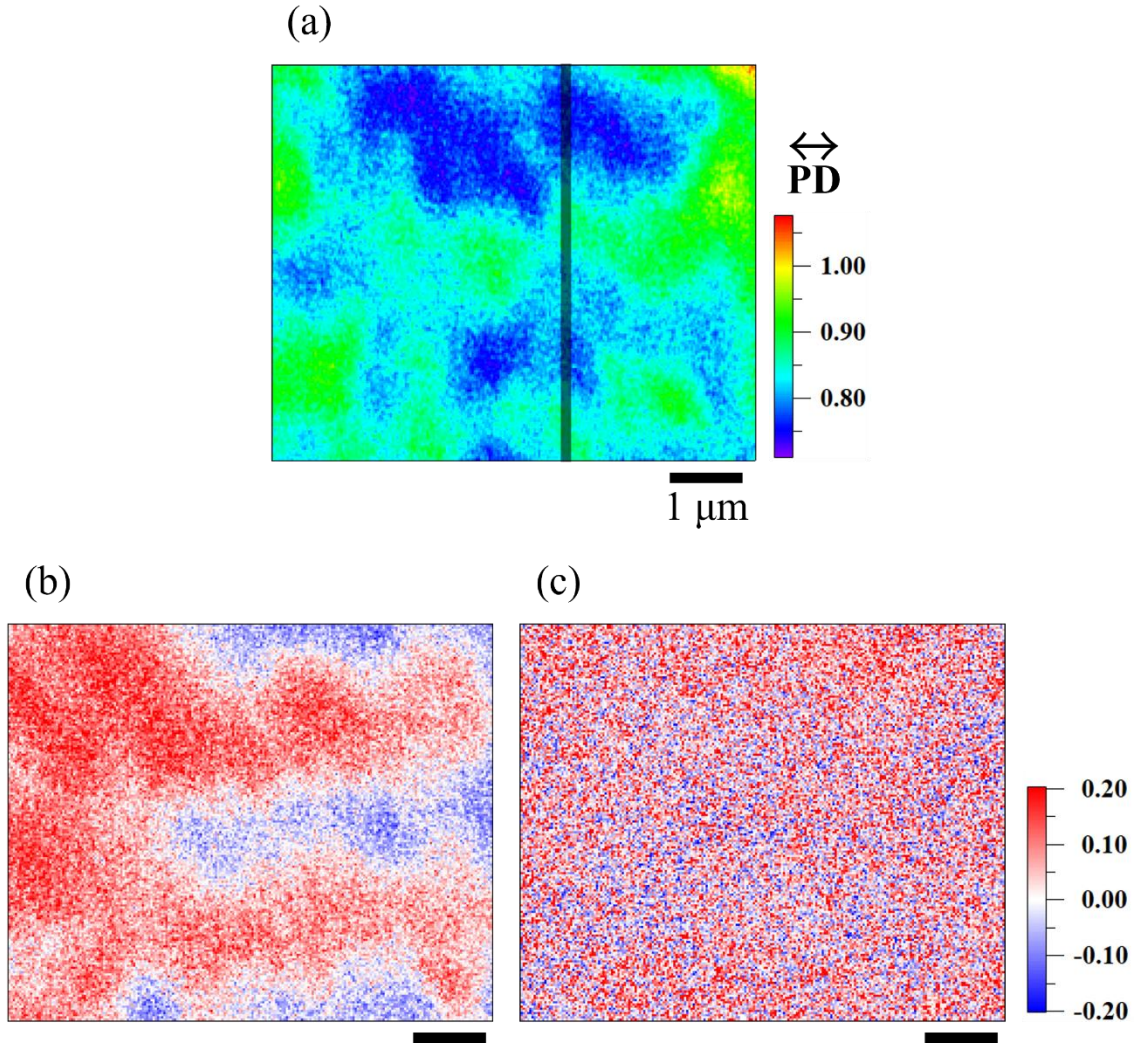


Figure 2.9. (a) Local density (ρ) map and $\langle P_2 \rangle$ map for (b) C–H bonds and (c) C–C bonds in a banded region of another spherulite. The vertical direction in the images corresponds to the radial direction of the spherulite. The black semi-transparent line indicates the regions from which the line profile was extracted.

To quantify structural parameters such as the band period and the distance between the fibril bundles, and to identify the factors governing the density distribution and the specific $\langle P_2 \rangle$ contrast of C–H and C–C bonds, a banded region without wrinkles was observed and analyzed in another spherulite different from the one in Figure 2.5. Figure 2.9 shows the 2D ρ map and the corresponding 2D $\langle P_2 \rangle$ maps for C–H and C–C bonds obtained from the additional observation. The ρ map and the $\langle P_2 \rangle$ map for C–H

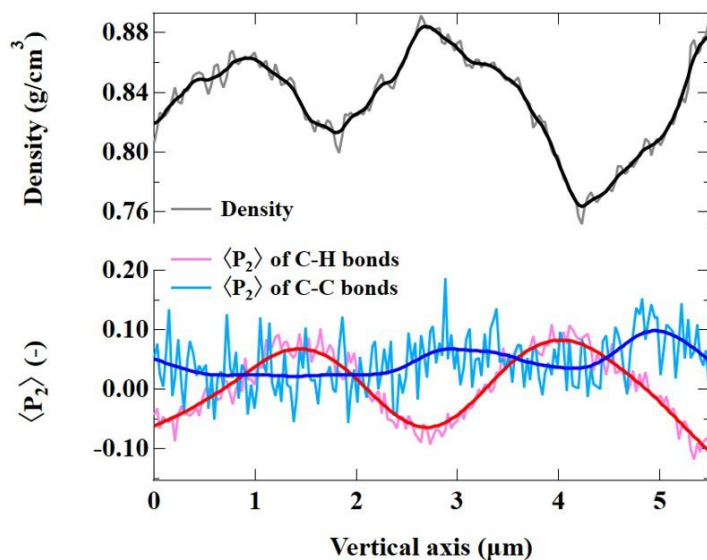


Figure 2.10. Line profiles of characteristic parameters in the vertical direction relative to the observed area.

bonds reflected not only the band periodicity parallel to the fibril growth direction but also the clear vertical spacing between fibril bundles. Furthermore, the $\langle P_2 \rangle$ map corresponding to C–C bonds was obtained, which slightly reflected the parallel band periodicity with a minimum value close to zero and a maximum value of approximately 0.1. The average and distribution of ρ and $\langle P_2 \rangle$ for C–H and C–C bonds were consistent with those observed in the region as shown in Figure 2.7. The black semi-transparent line shown in Figure 2.9a corresponds to the regions where line profile was obtained. The resulting vertical line profile is shown in Figure 2.10.

According to the line profiles obtained along the vertical direction (the fibril growth direction) in Figure 2.10, the fluctuations in ρ and $\langle P_2 \rangle$ of C–C bonds followed a similar periodicity. However, these variations were phase-shifted by a half-period relative to the fluctuation of the $\langle P_2 \rangle$ for C–H bonds. This phase shift is consistent with the results of previous studies showing that the horizontal orientation of C–C bonds and the horizontal orientation of C–H bonds alternate along the radial direction of the spherulite.

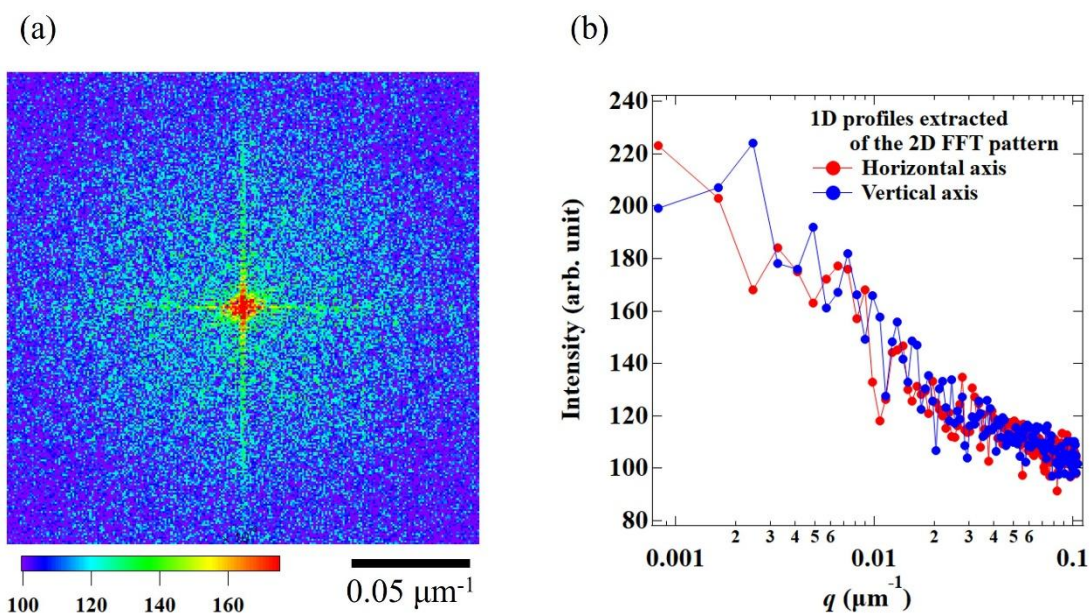


Figure 2.11. (a) Fourier-transformed image of $\langle P_2 \rangle$ map for C–H bonds and (b) 1D profiles horizontal and vertical axes. The vertical axis corresponds to the fibril growth direction.

In addition, to quantitatively and objectively evaluate the band period and the distance between the fibril bundles within the banded structure, a 2D Fourier transform was performed on the $\langle P_2 \rangle$ map of C–H bonds, which exhibits the most pronounced periodic contrast. In the Fourier-transformed image, the vertical and horizontal axes correspond to the periodicities along the fibril growth direction (band period) and the direction perpendicular to it (inter-fibrillar distance), respectively. The 1D profiles were extracted by sector-averaging along these two directions with an angular width of 5° centered at the origin of the Fourier-transformed image.

Figure 2.11 shows the Fourier-transformed image and 1D profiles parallel and perpendicular to the fibril growth direction. Regarding the features of the 1D profiles, the vertical axis exhibited distinct higher-order peaks, whereas the horizontal axis showed clear peaks only up to the second order. This difference in peak visibility

suggests that the periodic banded structure is formed with high spatial regularity along the fibril growth direction. In contrast, the spacing between fibril bundles appears to be less uniform, likely due to local fluctuations in the growth direction or the occurrence of fibril branching, which introduces structural heterogeneity in the direction perpendicular to the growth axis. This structural heterogeneity is consistent with the mass fractal dimension, 2.39, derived from the USAXS analysis.

The fractal nature indicates that the fibril bundles are loosely and probabilistically packed with significant amorphous regions between them, rather than being arranged in an ideally ordered packing. Such disordered packing leads to the rapid attenuation of higher-order peaks in the horizontal profile.

Based on the q -values of the primary peaks in the 1D profiles for each direction, the average band period and the average inter-fibrillar distance were estimated to be 2.56 μm and 1.92 μm , respectively. The correlation length ($\xi = 2.05 \mu\text{m}$) obtained from the extinction direction in Hv SALS scattering corresponds more closely to the average inter-fibrillar distance. This indicates that, regarding the characteristic structural length perpendicular to the growth axis, SALS captured a statistical average of the macroscopic region, while STXM directly visualized the fibril packing.

2.3.2.3 Structural Origins of Density and Orientation Contrast

The line profile analysis revealed a significant phase relationship between the structural parameters where the fluctuations in local density and the orientation order parameter of C–C bonds were synchronized, whereas the orientation order parameter of C–H bonds exhibited a clear phase shift of a half-period (π). This specific correlation can be theoretically explained by the geometric alignment of the polyethylene

orthorhombic unit cell undergoing periodic twisting around the b -axis growth direction, which is aligned vertically in the mapping as shown in Figure 2.12.

In the orthorhombic unit cell, the chemical bonds are arranged in an orthogonal relationship where the C–C bonds are parallel to the c -axis and the transition dipole moment (TDM) of the C–H bonds lies within the a - b plane. Based on the observation in this study that the C–H bonds exhibit a distinct orientation perpendicular to the spherulite growth direction, it is considered that the TDM of the C–H bonds lies within the a - b plane with the primary component aligned along the a -axis. This interpretation is supported by the fact that the C–H bonds directed toward the a -axis are more nearly parallel to the a -axis than those directed toward the b -axis are to the b -axis, which is consistent with a previous NEXAFS study on PE spherulites.

As the lamellae grow and twist around the b -axis, the projections of the a -axis and c -axis onto the observation plane oscillate periodically. The regions of maximum local density correspond to the edge-on orientation where the lamellar crystals stand perpendicular to the observation plane. In this state, the c -axis is oriented horizontally within the image plane, leading to the detection of a strong horizontal orientation of C–C bonds. Simultaneously, the a -axis points toward the observer along the Z -axis, meaning the a -component of the C–H TDM is not detected in the 2D projection. The remaining component aligned with the b -axis results in the observation of a vertical orientation for C–H bonds. Furthermore, the edge-on arrangement results in the maximum thickness of crystalline stacking along the X-ray path, which leads to the observed peak in local density.

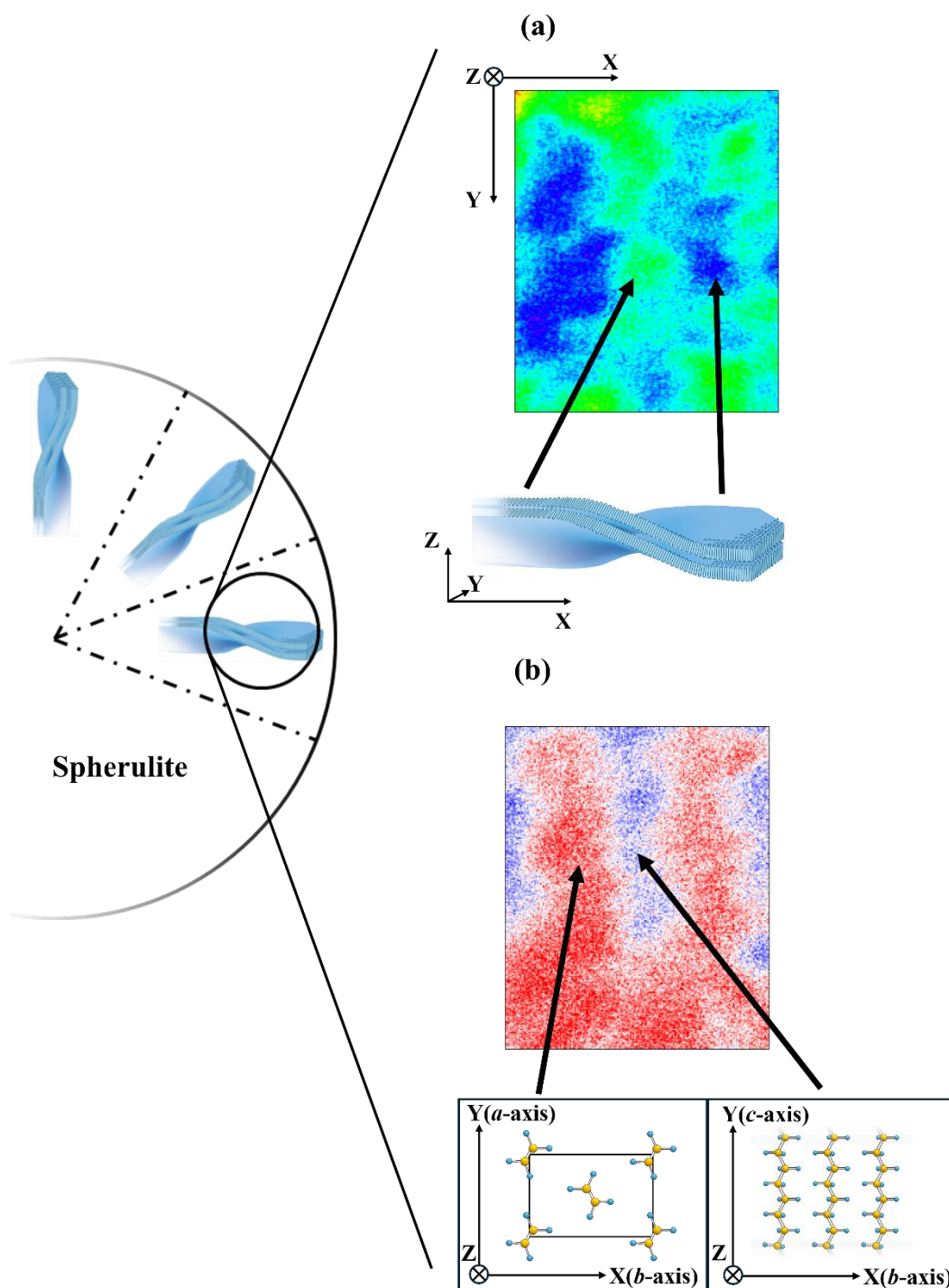


Figure 2.12. Geometric model of lamellar twisting and the resulting (a) local density fluctuation and (b) molecular orientations in the LLDPE spherulite.

Conversely, the regions of minimum local density correspond to the face-on orientation where the lamellar crystals lie parallel to the observation plane. In this arrangement, the c -axis points toward the observer, and because its projection onto the observation plane is minimized, the C–C bonds appear non-oriented or show a minimum orientation order parameter. Meanwhile, the a -axis is oriented horizontally within the image plane. Since the primary TDM component of the C–H bonds is aligned along the a -axis, this horizontal arrangement allows the orientation to be clearly detected as a strong horizontal signal. The face-on arrangement also results in the minimum thickness of crystalline stacking, leading to a valley in the local density profile.

This geometric model demonstrates that the observed 180-degree phase shift of C–H orientation relative to density and C–C orientation is a direct consequence of the orthogonality of the polyethylene unit cell.

The relatively weak density contrast observed in the banded structure within the STXM mappings is consistent with the lack of a well-defined SAXS peak for the lamellar long period. This suggests that while the molecular orientation exhibits clear periodicity due to the systematic twisting of the unit cells, the stacking regularity of the lamellae is locally disordered, which suppresses the development of sharp density fluctuations. Furthermore, the fact that the lateral inter-fibrillar regions were clearly visualized in the STXM analysis, allowing for the determination of a characteristic inter-fibrillar distance, is attributed to the loose packing of the fibrils. This structural interpretation is quantitatively supported by the mass fractal dimension of 2.39 obtained from USAXS analysis.

These results provide evidence that the hierarchical structure of LLDPE spherulites is characterized by a coexistence of a high degree of orientation order arising from lamellar twisting and a density-based packing that remains irregular and fractal in nature. The consistency between the real-space imaging by STXM and the reciprocal-space data from SAXS, USAXS, and light scattering confirms that the macroscopic morphology of the spherulite is fundamentally governed by this interplay between periodic lamellar twisting and micrometer heterogeneity characterized by fibril bundles grown within spherulites.

2.4 Conclusion

This study established a quantitative framework for characterizing the hierarchical structure of LLDPE spherulites by integrating dual-polarization STXM with multi-scale scattering techniques. By acquiring images at both horizontal and vertical X-ray polarizations using STXM, I decoupled local density (ρ) from the orientation order parameter ($\langle P_2 \rangle$) at sub-micrometer scales.

The STXM analysis revealed a distinct 180-degree phase shift between the periodic fluctuations of C–H bond orientation and those of local density and C–C bond orientation. This spatial correlation was consistently explained by a geometric model of the orthorhombic unit cell undergoing periodic twisting around the *b*-axis growth direction. Specifically, "edge-on" orientations correspond to density maxima and C–C bond alignment, while "face-on" orientations result in density minima and dominant C–H bond signals.

Furthermore, the integration of STXM, USAXS, and SALS data confirmed that while molecular orientation is highly ordered due to systematic lamellar twisting, the physical packing of fibrils remains loose, following a mass-fractal dimension of 2.39. These findings revealed that this highly ordered crystallographic twisting coexists with a branched and loose packing of fibrils. This research provides a methodology for the pixel-wise quantification of molecular order by STXM, bridging the gap between local chemical bonding and macroscopic hierarchical morphologies in crystalline polymers.

Reference

1. Keller, A. *Philosophical Magazine* **1957**, 2, 1171–1175.
2. Keller, A. *Prog. Phys.* **1968**, 31, 623–704.
3. Keith, H. D.; Padden, F. J. *J. Appl. Phys.* **1963**, 34, 2409–2421.
4. Bunn, C. W. *Trans. Faraday Soc.* **1939**, 35, 482–491.
5. Keith, H. D.; Padden, F. J. *J. Polym. Sci.* **1959**, 39, 123–138.
6. Lotz, B.; Cheng, S. Z. D. *Polymer* **2005**, 46, 577–610.
7. Strobl, G. R.; Schneider, M. *J. Polym. Sci., Polym. Phys.* **1980**, 18, 1343–1359.
8. Strobl, G. R.; Schneider, M. J.; Voigtmartin, I. G. *J. Polym. Sci., Polym. Phys.* **1980**, 18, 1361–1381.
9. Owen, A.; Bergmann, A. *Polymer Int.* **2004**, 53 (1), 12–14.
10. Takenaka, M.; Shimizu, H.; Nishitsuji, S. *Phys. Rev. E* **2007**, 75, 061802.
11. Stein, R. S.; Rhodes, M. B. *J. Appl. Phys.* **1960**, 31 (11), 1873–1884.
12. Samuels, R. J. *J. polym. sci., A-2: Polymer physic* **1971**, 9 (12), 2165–2246.
13. Yoon, D. Y.; Stein, R. S. *J. Polym. Sci., Polym. Phys. Ed.* **1974**, 12 (4), 735–761.
14. Hashimoto, T., *Principles and Applications of X-ray, Light and Neutron Scattering*; Springer Nature Singapore Pte Ltd.: Singapore, 2022.
15. Schönherr, H.; Snétivy, D.; Vancso, G. J., *Polymer Bulletin* **1993**, 30, 567–574.
16. Ferreiro, V.; Depecker, C.; Laureyns, J.; Coulon, G. *Polymer* **2004**, 45 (17), 6013–6026.
17. Wang, Y.; Zou, Y.; Araki, T.; Lüning, J.; Kilcoyne, A. L. D.; Sokolov, J.; Ade, H.; Rafailovich, M. *Macromolecules* **2010**, 43 (19), 8153–8161

18. Kilcoyne, A.L.D.; Tyliczszak, T.; Steele, W.F.; Fakra S.; Hitchcock, P; Franck K.; Anderson, E.; Harteneck, B.; Rightor, E. G.; Mitchell, G. E.; Hitchcock, A. P.; Yang, L.; Warwick, T.; Ade, H. *J. Synchrotron Rad.* **2003**, *10*, 125–136.
19. Ohigashi, T.; Arai, H.; Araki, T.; Kondo, N.; Shigemasa, E.; Ito, A.; Kosugi, N.; Katoh, M. *J. Phys.: Conf. Ser.* **2013**, *463*, 012006.
20. Takeichi, Y.; Inami, N.; Suga, H.; Ono K.; Takahashi Y. *Chem. Lett.* **2014**, *43*, 373–375.
21. Fu, J.; Urquhart, S. G. *J. Phys. Chem. A* **2005**, *109*, 11724–11732.
22. Fu, J.; Urquhart, S. G. *Langmuir* **2007**, *23*, 2615–2622.
23. Masunaga, H.; Ogawa, H.; Takano, T.; Sasaki, S.; Goto, S.; Tanaka, T.; Seike, T.; Takahashi, S.; Takeshita, K.; Nariyama, N.; Ohashi, H.; Ohata, T.; Furukawa, Y.; Matsushita, T.; Ishizawa, Y.; Yagi, N.; Takata, M.; Kitamura, H.; Sakurai, K.; Tashiro, K.; Takahara, A.; Amamiya, Y.; Horie, K.; Takenaka, M.; Kanaya, T.; Jinnai, H.; Okuda, H.; Akiba, I.; Takahashi, I.; Yamamoto, K.; Hikosaka, M.; Sakurai, S.; Shinohara, Y.; Okada, A.; Sugihara, Y. *Polym. J.* **2011**, *43*, 471–477.
24. Mandelkern, L.; Alamo, R. G., *Physical Properties of Polymers Handbook*; American Institute of Physics: Woodbury, NY, 1996.
25. Crist, B.; Mirabella, F. M. *J. Polym. Sci. Part B: Polym. Phys.* **1999**, *37* (21), 3131–3140.
26. Furuya, T.; Kojima, H.; Koji, Nishida, K.; Fukutani, Y.; Mutaguchi, A.; Koga, T. *J. Fiber Sci. Technol.* **2023**, *79* (2), 32–46.
27. Dhez, O.; Ade, H.; Urquhart, S.G. *J. Electron Spectrosc. Relat. Phenom.* **2003**, *128*, 85–96.

28. Debye, P.; Bueche, A. M. *J. Appl. Phys.* **1949**, *20* (6), 518–525.
29. Hernández Cruz, D.; Rousseau, M. E.; West, M. M.; Pézolet, M.; Hitchcock, A. P. *Biomacromolecules* **2006**, *7*, 836–843.

Chapter 3

STXM Studies on the Changes in the Spatial Distribution of Density and Chain Orientation of LLDPE with Strain

3.1. Introduction

Crystalline polymers such as polyethylene (PE) form hierarchical structures over the long length scale from 0.1nm to over 1 μ m. The regularly folded polymer chains form the crystal lattice structure, and the alternating layering of crystalline and amorphous phases forms the lamellae. Additionally, the fibril structure is formed by the growth of the lamellae, and the filling of the fibrils forms the spherulites.¹

Since PE exhibits excellent mechanical properties, many researchers have investigated the hierarchical structures of PE and the correlation between its mechanical properties and the structures.^{2,3} One of the essential features in the mechanical properties of PE is the yield behavior in the stress-strain (S-S) curve. The yield point is a crucial factor influencing the strength and durability of crystalline polymers. It is necessary to clarify the correlation between the yield behaviors and the changes in the hierarchical structure to control the mechanical properties of crystalline polymers.

In the case of high-density polyethylene (HDPE) with a single yield point in the S-S curve, several researchers have investigated the structural changes around the yield point using small- and wide-angle X-ray scattering (SAXS and WAXS,

respectively), as explored as follows.⁴⁻⁷ Before the yield point, the long spacing of lamellar structures increases along the stretching direction. Near the yield point, the formation of monoclinic phases is observed by time-resolved WAXS, indicating an onset of fine slip. Fine slip is a type of intralamellar slip that promotes the chains in crystalline parts to become parallel to the direction of stretching and is relevant to homogeneous shearing of the crystal blocks, leading to the transformation of stable phases into metastable or monoclinic phases. Monoclinic transitions occur in the (110) lattice planes in orthorhombic crystals due to cooperative shifting of molecular chains.⁸ In the strain softening region after the yield point, four-point patterns reflecting the chevron-type morphology of the lamellae are observed by SAXS and WAXS, indicating the occurrence of coarse slip. Coarse slip is another type of intralamellar slip, which involves fragmentation of the lamellae. In addition, the orientation of crystals changes significantly in the strain softening region.

Recently, the ultra-small-angle X-ray scattering (USAXS) technique has been developed to enable *in-situ* submicron-scale observations,⁹ as a result, it has become possible to investigate the changes in the hierarchical structure of PE under uniaxial stretching using USAXS, as well as SAXS and WAXS, extending the investigation to the 100 nm order. The density fluctuations at the initial state originate from the growth of the fibril structures during crystallization. The lamellar structures grow from crystal nuclei by repeatedly branching out, gradually filling the space as they expand. The branch structures form the density fluctuations or the spatial inhomogeneity of crystallinity, reflecting the power-law behavior in USAXS profiles. The density fluctuations induce the spatial inhomogeneity of the stress fields in the samples.

In previous studies,^{10, 11} butterfly patterns were observed under uniaxial tensile testing with USAXS, indicating that HDPE is deformed heterogeneously depending on a spatial fluctuation of the crystallinity. The butterfly patterns have been found in gels under uniaxial elongational deformation and semi-dilute solutions of polymers under simple shear.¹²⁻¹⁴ The butterfly pattern reflects the spatial inhomogeneity of density or concentration induced by strain. The increase in scattering intensity along the stretch direction is due to the strong correlation between density or concentration fluctuations that appear along the stretch direction. These stretch-induced density or concentration fluctuations are caused by the spatial inhomogeneity of mechanical properties. Doi and Onuki, and Furukawa and Tanaka theoretically proved that density fluctuation increases with the gradient of the stress field under deformation.^{15, 16} The spatial heterogeneity of the crystallinity observed by USAXS leads to spatial inhomogeneity in the stress field under uniaxial stretching, resulting in inhomogeneous deformation that induces spatial inhomogeneity of the density.

Studies conducted by the research group of Takenaka *et al.* with USAXS, SAXS, and WAXS reveal that the spatial inhomogeneity of polymer chain orientation is induced, as well as density fluctuations on the submicron scale under stretching HDPE.^{10,11} However, scattering methods provide only average information within the irradiated volume (typically μm to mm), making it impossible to investigate local orientation fluctuations on the sub-micrometer scale. To investigate the correlation between the orientation of polymer chains and density fluctuations, I employed scanning transmission X-ray microscopy (STXM).¹⁷

In stretched HDPE at the yield point where the butterfly pattern was observed by USAXS, STXM showed the spatial inhomogeneities of submicron-scale C–C bond

orientations, including not only the orientation of crystal lattice structures and lamellar structures but also the orientation of polymer chains in the amorphous phases.¹⁷ Additionally, 2D images reflecting sub-micrometer-scale density fluctuations were obtained, revealing that polymer chains are more highly aligned along the stretching direction in low-density regions than in high-density regions. Thus, the correlation between spatial heterogeneities in orientation and the fluctuation of crystallinity in stretched HDPE was clarified using STXM.

In this study, I focus on the yield behaviors between two yield points in linear low-density polyethylene (LLDPE). Some kinds of LLDPE have been reported to exhibit two yield points during uniaxial elongation. The changes in lamellar and lattice structures during the deformation of LLDPE, exhibiting two yield points, have been investigated using the X-ray scattering method.^{4, 5, 7, 21–23} Researchers concluded that the first yield point (1YP) originates from fine slip and the second point (2YP) from coarse slip. A previous study using USAXS¹¹ explored that the structural change on the submicron scales also affected the yield behaviors of the LLDPE that showed two yield points. Similar to the case of HDPE, butterfly patterns were observed in USAXS between the 1YP and the 2YP, and the scattering intensity along the stretching direction was enhanced. However, previous studies have primarily focused on average structural changes using X-ray scattering, and the spatial heterogeneity of deformation and orientation has remained largely unexplored.

Thus, I aim to clarify how spatial distributions of density and C–C bond orientations evolve on the submicron scales in LLDPE exhibiting two yield points. By combining STXM with *in-situ* X-ray scattering, local variations in density and chain orientation across different strain regimes were visualized and quantified. This

integrated approach provides new insight into the hierarchical deformation mechanisms in crystalline polymers, particularly the role of crystallinity-dependent mechanical melting and orientation dynamics.

3.2. Experimental Section

3.2.1. Sample Preparation

LLDPE (0.937 g/cm³, 4-methyl pentene-1 content) with a polystyrene-equivalent weight-average molecular weight (M_w) of 2.1×10^5 and a molecular weight distribution (M_w/M_n) of 5.33, as determined by gel permeation chromatography (GPC), was used in this study.

LLDPE sheets were prepared using two press machines (MINI TEST PRESS-10, Toyo Seiki Seisaku-sho, Ltd.) according to the following procedure. Firstly, one press machine was set to 180 °C, which is above the melting point of LLDPE, and the LLDPE pellets were pressurized in a 2 mm-thick mold for 10 minutes to ensure complete melting. The melt was then immediately transferred to another press machine set at 25°C and quenched to produce a 2 mm-thick press sheet. Finally, dumbbell specimens with a center width of 2 mm were punched from the sheet.

3.2.2. *In-Situ* X-ray Scattering Measurements

In-situ X-ray scattering was conducted while stretching dumbbell specimens at 1 mm/min at room temperature, using a custom-made tensile testing machine designed to measure stress-strain (S–S) curves and X-ray scattering simultaneously. Figure 3.1 shows the S–S curve obtained during the measurement. Simultaneous SAXS and

WAXS measurements were performed with an incident wavelength of 0.1 nm and an attenuator of a 60 μm -thick Mo plate in the second hutch of beamline BL03XU at SPring-8 (Hyogo, Japan).²⁴ The beam size at the sample position was 100 μm (horizontal) $\times$ 100 μm (vertical). For the SAXS/WAXS measurements, the camera length, exposure time, and detectors were set to 2.34 m/103 mm, 400 ms/400 ms, and PILATUS-1M (Dectris Ltd.)/ SOPHIAS (Rigaku Corp.), respectively. The WAXS detector was positioned at an inclined angle to avoid interference with the SAXS detector.²⁴ USAXS measurements were performed on the same beamline as the SAXS/WAXS measurements. The incident wavelength was 0.2 nm, and a 100 μm -thick Al plate was used as an attenuator. The beam size at the sample position was 160 μm (horizontal) $\times$ 80 μm (vertical). The camera length, exposure time, and detectors were set to 7.80 m, 850 ms, and PILATUS-1M, respectively. In the subsequent data analysis, the 2D scattering images were corrected for sample absorption, and background scattering from the air and instrument was subtracted.

3.2.3. STXM Observation

STXM is an X-ray microscopy technique in which synchrotron radiation X-rays are focused onto a sample using a Fresnel zone plate. The transmitted X-ray intensity (I) at the focal position is mechanically raster-scanned to obtain a spatial image of the intensity distribution.¹⁸⁻²⁰ By acquiring the incident X-ray (I_0), the optical density (OD) is obtained by the following equation.

$$OD = -\ln \frac{I}{I_0} \quad (3.1)$$

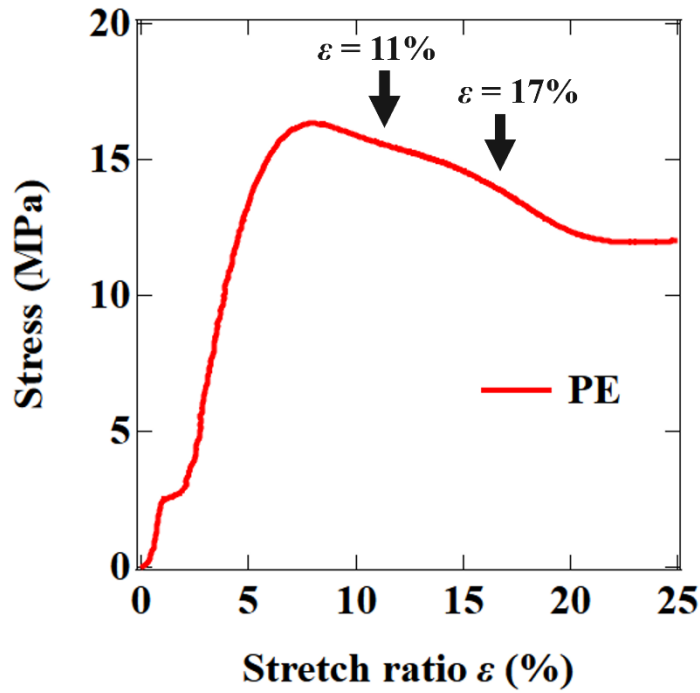


Figure 3.1. S–S curve during *in-situ* X-ray scattering measurements under uniaxial stretching.

Since STXM provides images of transmitted X-rays at several different energies, 2D images are acquired at various energies near the X-ray absorption edge of the atom of interest, and the near-edge X-ray absorption fine structure (NEXAFS) spectrum of the atom is obtained from the value of the *OD* at each pixel of the 2D images. Peaks corresponding to chemical bonds appear in the NEXAFS spectrum, which depends on the angle between the transition dipole moment (TDM) of the chemical bond and the direction of polarization of the X-ray (electric field).

I observed the LLDPE ultrathin sections of each stretch ratio by STXM. The ultrathin sections were prepared as follows: Firstly, uniaxial stretching at 1 mm/min was performed on the dumbbell specimens at room temperature by a homemade tensile testing machine. The specimens were stretched to reach the stretch ratio $\epsilon = 11\%$, where an abnormal butterfly pattern was clearly observed in *in-situ* USAXS measurements,

and at $\varepsilon = 17\%$ (corresponding to the second yield point, 2YP) as shown in Figure 3.1.

The stretch ratio ε is defined as

$$\varepsilon = \frac{L - L_0}{L_0} \quad (3.2)$$

where L_0 and L are the lengths of the sample before and after applying strain, respectively. Each specimen was held for 30 minutes at the specified ε to reach a stable state. Subsequently, ultrathin sections were prepared from the center of the stretched area using a cryo-microtome (EM UC7, Leica Microsystems). To prevent structural changes during the sectioning process, the specimens were cut below the glass transition temperature of LLDPE. An ultrathin section of the unstretched state ($\varepsilon = 0\%$) was also prepared as a reference.

STXM measurements were performed at BL-19A at the Photon Factory of the High Energy Accelerator Research Organization (KEK-PF: Tsukuba, Japan).²⁰ X-rays were incident in the direction perpendicular to the surface of the ultrathin sections. The energy range of incident X-rays in this study is 280-320 eV, which includes the range around the absorption energy of the carbon K-edge (about 285 eV). The exposure time was 2 ms. I observed the same locations in the ultrathin section at each stretch ratio ε by setting the direction of polarization of the X-rays parallel and perpendicular to the stretch direction, respectively, without rotating the specimens. Images for NEXAFS spectra were acquired with a spatial resolution of 100 nm, while those for orientation analysis were obtained at a resolution of 50 nm. All images used for orientation analysis were corrected for sample drift.

3.3. Results and Discussion

3.3.1. X-ray Scattering Measurements

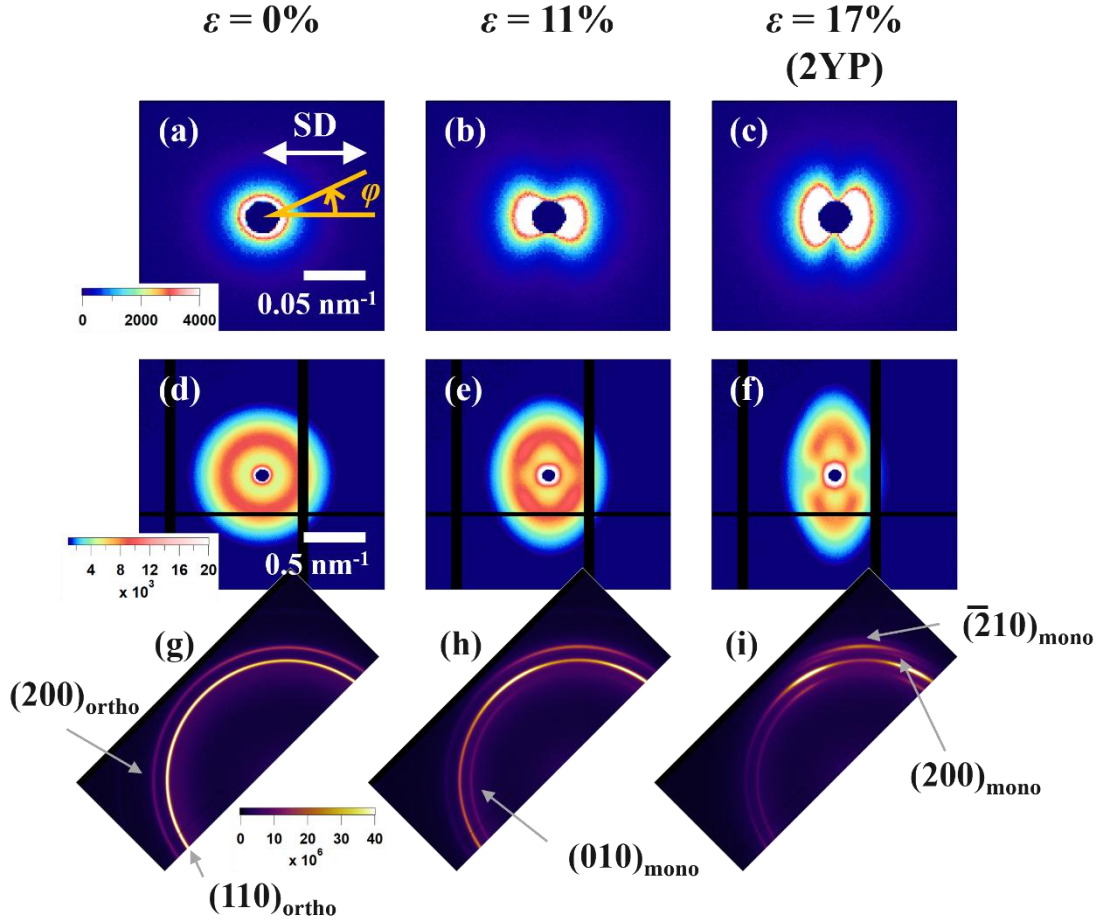


Figure 3.2. (a–c) USAXS, (d–f) SAXS, (g–i) WAXS 2D patterns of the LLDPE with strain. The arrow in part (a) corresponds to the stretch direction (SD).

Figure 3.2 shows the changes in USAXS/SAXS/WAXS 2D patterns with strain. Figure 3.3 shows the combined USAXS and SAXS 1D profiles along the directions parallel and perpendicular to the stretching axis. The magnitude of the scattering vector, q , is defined as

$$q = \frac{4\pi}{\lambda} \sin\left(\frac{\theta}{2}\right) \quad (3.3)$$

where λ and θ are the wavelength of the incident X-rays and the scattering angles,

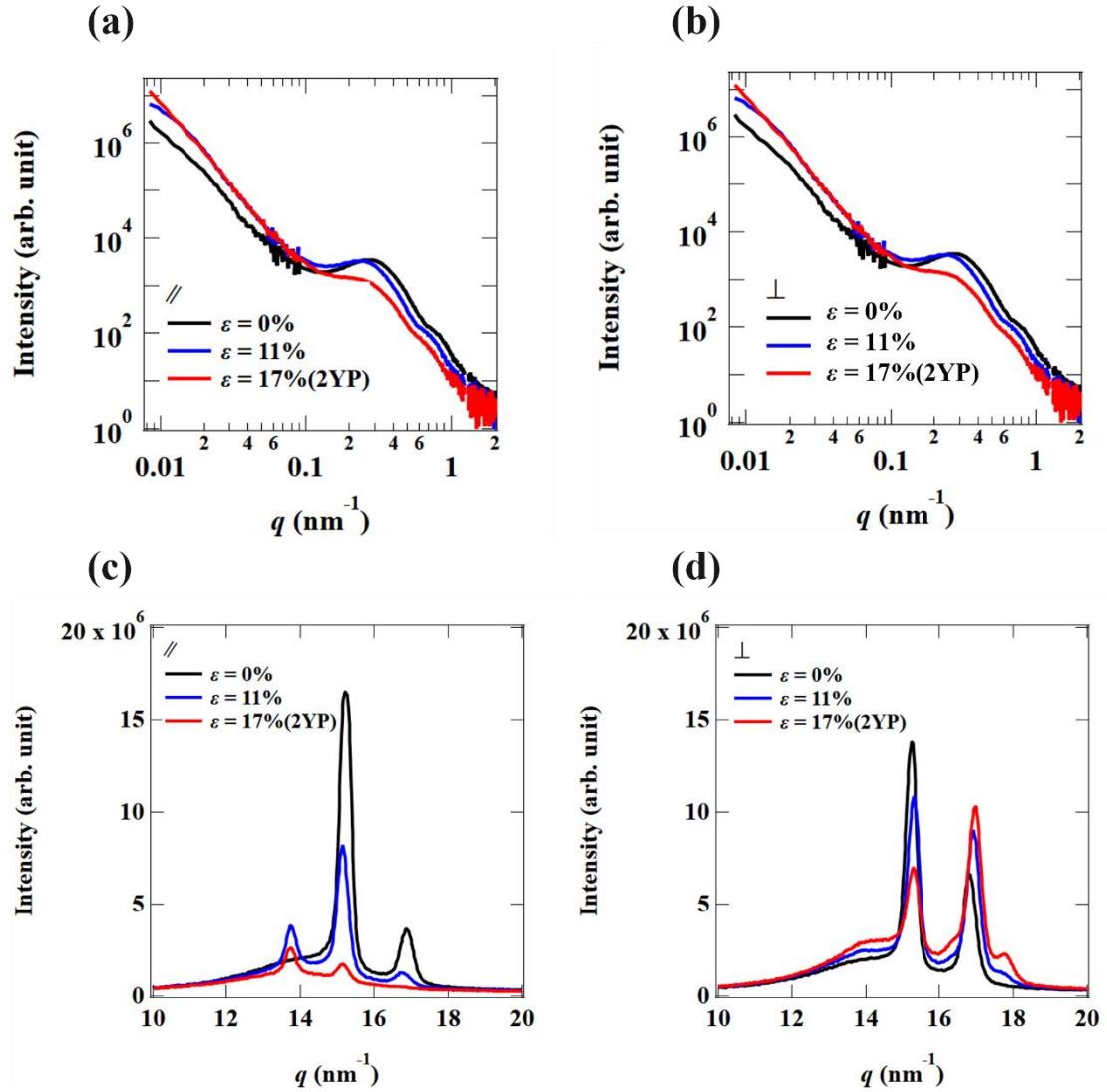


Figure 3.3. (a, b) Combined USAXS and SAXS, (c, d) WAXS 1D profiles parallel and perpendicular to the stretching directions, respectively.

respectively. The parallel intensity profiles $I_{\parallel}(q)$ were obtained from the USAXS and SAXS 2D patterns by averaging sectors within $\pm 2.5^\circ$ from the stretching direction ($\varphi = 0^\circ$), while the perpendicular profiles $I_{\perp}(q)$ were obtained from $\varphi = 90^\circ$. The definition of the azimuthal angle φ is shown in Figure 3.2a. Detailed analyses of the patterns were shown previously.¹¹

To characterize the anisotropy of the lamellar structures, the azimuthal crystal thickness $l_c(\varphi)$ and d-spacing $l_d(\varphi)$ were estimated from the correlation function, as

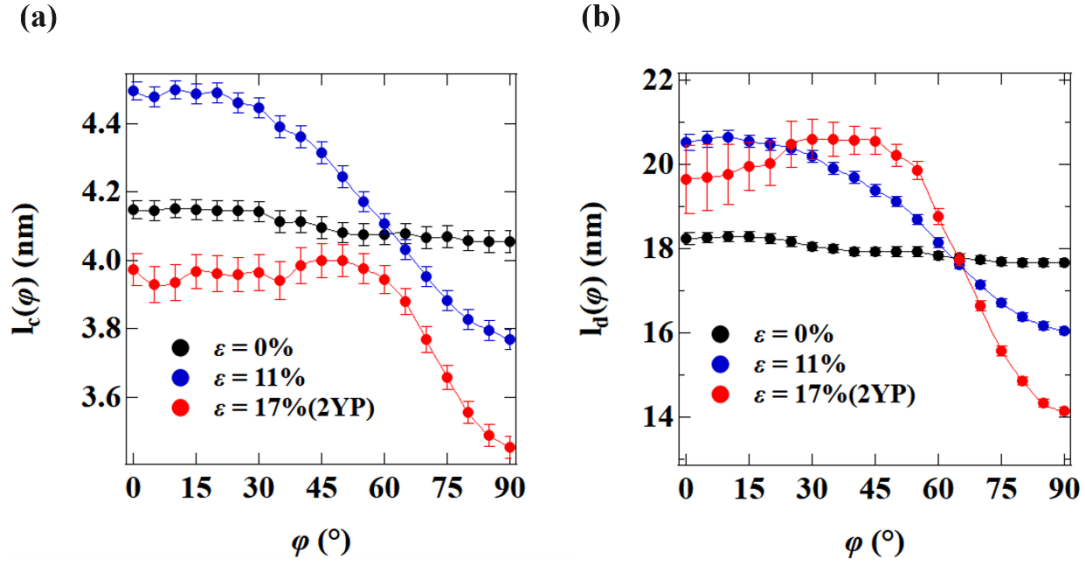


Figure 3.4. ϕ dependence of (a) the $l_c(\phi)$ and (b) $l_d(\phi)$ at each stretch ratio.

shown in Figure 3.4. The correlation functions were calculated from the SAXS profiles sector-averaged every 5° from $\phi = 0^\circ$ to 90° .^{25, 26} The value of $l_c(\phi)$ reached its maximum at $\phi = 0^\circ$ for $\varepsilon = 11\%$ and at $\phi = 0-45^\circ$ for $\varepsilon = 17\%$, reflecting the elongation of crystal layers within the lamellae at $\varepsilon = 11\%$ and the thinning of crystals due to mechanical melting during deformation at $\varepsilon = 17\%$. On the other hand, $l_d(\phi)$ reached its maximum at $\phi = 0^\circ$ for $\varepsilon = 11\%$ and at $\phi = 30-45^\circ$ for $\varepsilon = 17\%$, reflecting the elongation of lamellar structures at $\varepsilon = 11\%$ and the development of the chevron structure. The chevron-type morphology characterized by four-patterns in the SAXS (Figure 3.2e and f) is developed by the fragmentation and rotation of the lamellae.^{5, 21, 23}

To quantitatively evaluate the sub-micrometer-scale density fluctuations at each stretch ratio, the USAXS invariants, Q , were calculated using the following equation:

$$Q = 4\pi \int_{\phi=0}^{\phi=\frac{\pi}{2}} \int_{q=0.008 \text{ nm}^{-1}}^{q=0.063 \text{ nm}^{-1}} q I(q, \phi) \sin \phi dq d\phi \quad (3.4)$$

The values of $Q(\varepsilon)$ for each stretch ratio are listed in Table 3.1. The value of $Q(\varepsilon)$ increased up to 2YP, indicating that drawing induced sub-micrometer-scale density

Table 3.1. $Q(\varepsilon)$ at Each Stretch Ratio.

Stretch ratio	$\varepsilon = 0\%$	$\varepsilon = 11\%$	$\varepsilon = 17\%(2YP)$
$Q(\varepsilon)$	1.26×10^5	2.24×10^5	3.50×10^5

fluctuations between $\varepsilon = 11\%$ and $\varepsilon = 17\%$.

Furthermore, the Hermans orientation factor (f_H) of the c -axis (polymer chain) was calculated to evaluate the C–C bond orientation of LLDPE from the WAXS 1D profiles. Here, the c -axis is parallel to the polymer chains in the crystal structure.²⁷ The orientation factor is defined as

$$f_H = \frac{3\langle \cos^2 \phi_i \rangle - 1}{2} \quad (3.5)$$

$$\langle \cos^2 \phi_i \rangle = \frac{\int_0^\pi I(\phi_i) \cos^2 \phi_i \sin \phi_i d\phi_i}{\int_0^\pi I(\phi_i) \sin \phi_i d\phi_i} \quad (3.6)$$

where ϕ_i is the angle between the unit within a crystal of interest (e.g., c -axis) and the stretching direction. The c -axis orientation information for each component was obtained using Wilchinsky's method:^{28–30}

$$\langle \cos^2 \phi_{c-axis,ortho} \rangle = 1 - 0.565 \langle \cos^2 \phi_{(200),ortho} \rangle - 1.435 \langle \cos^2 \phi_{(110),ortho} \rangle \quad (3.7)$$

$$\langle \cos^2 \phi_{c-axis,mono} \rangle = 1 - 0.896 \langle \cos^2 \phi_{(010),mono} \rangle - 1.104 \langle \cos^2 \phi_{(200),mono} \rangle \quad (3.8)$$

$$\begin{cases} f_{H,ortho} = \frac{3\langle \cos^2 \phi_{c-axis,ortho} \rangle - 1}{2} \\ f_{H,mono} = \frac{3\langle \cos^2 \phi_{c-axis,mono} \rangle - 1}{2} \\ f_{H,amo} = \frac{3\langle \cos^2 \phi_{amo} \rangle - 1}{2} \end{cases} \quad (3.9)$$

The values of f_H for each component were integrated into an average $\langle f_H \rangle$ using the following equations:

$$\langle f_H \rangle = \frac{W_{ortho}}{W_{ortho} + W_{mono} + W_{amo}} f_{H,ortho} + \frac{W_{mono}}{W_{ortho} + W_{mono} + W_{amo}} f_{H,mono} + \frac{W_{amo}}{W_{ortho} + W_{mono} + W_{amo}} f_{H,amo} \quad (3.10)$$

$$W_{ortho} = 4\pi \int_0^{\frac{\pi}{2}} (q_{(200),ortho} I_{(200),ortho} w_{(200),ortho} \sin \varphi + q_{(110),ortho} I_{(110),ortho} w_{(110),ortho} \sin \varphi) d\varphi \quad (3.11)$$

$$W_{mono} = 4\pi \int_0^{\frac{\pi}{2}} (q_{(001),mono} I_{(001),mono} w_{(001),mono} \sin \varphi + q_{(200),mono} I_{(200),mono} w_{(200),mono} \sin \varphi + q_{(\bar{2}10),mono} I_{(\bar{2}10),mono} w_{(\bar{2}10),mono} \sin \varphi) d\varphi \quad (3.12)$$

$$W_{amo} = 4\pi \int_0^{\frac{\pi}{2}} q_{amo} I_{amo} w_{amo} \sin \varphi d\varphi \quad (3.13)$$

where q , I , and w are, respectively, the position, intensity, and width of each peak on the profiles. To calculate the WAXS 1D profiles, sectors were averaged every 5° between the meridian (stretching direction) and the equatorial direction from the WAXS 2D patterns. In addition, these parameters were obtained by deconvolution of the profiles into peaks originating from the crystalline and amorphous phases using a combination of Gaussian functions and a constant background.

Assuming that the scattering intensity distribution is symmetrical along the stretching axis, the crystallinity (X_c) of LLDPE during stretching is estimated by

$$X_c = \frac{W_{ortho} + W_{mono}}{W_{ortho} + W_{mono} + W_{amo}} \quad (3.14)$$

Subsequently, f_H of each component was integrated into the average $\langle f_H \rangle$.

When polymer chains are perfectly aligned along the stretching direction, $\langle f_H \rangle = 1$, whereas $\langle f_H \rangle = -1/2$ for chains aligned perpendicular. For random orientation, $\langle f_H \rangle = 0$. The value of $\langle f_H \rangle$ increased with strain, showing that the polymer chains gradually oriented along the stretching direction regardless of the phase component.

Finally, the crystallinity was evaluated from the WAXS data. The parameters obtained from WAXS are listed in Table 3.2. The crystallinity decreased under stretching, indicating that the strain induced mechanical melting of the crystals.

It was found that the anisotropy of the crystalline structures increased with strain, while the crystallinity decreased.

Table 3.2. $\langle f_H \rangle$ and Crystallinity at Each Stretch Ratio.

Stretch ratio	$\varepsilon = 0\%$	$\varepsilon = 11\%$	$\varepsilon = 17\%(2YP)$
$\langle f_H \rangle$	-3.92×10^{-4}	0.108	0.269
Crystallinity (%)	49.47	44.26	39.44

3.3.2. STXM Measurements

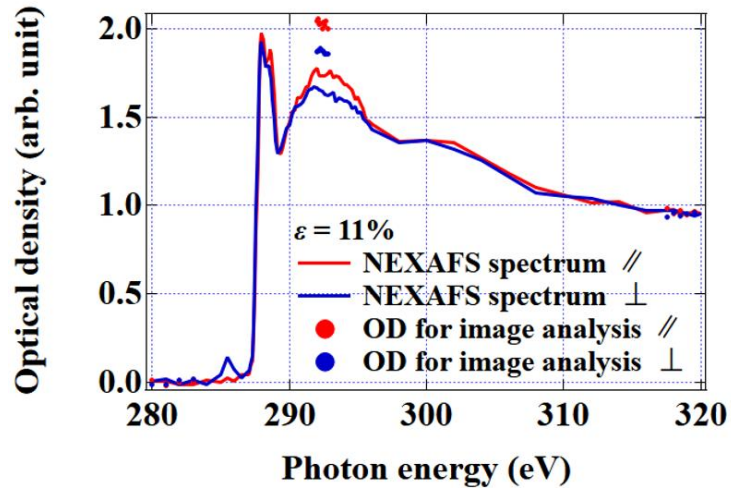


Figure 3.5. NEXAFS spectra at $\varepsilon = 11\%$. The Red and blue spectra were obtained by polarized X-rays parallel and perpendicular to the stretching direction, respectively.

Figure 3.5 shows the NEXAFS spectra from LLDPE at $\varepsilon = 11\%$. The red and blue indicate the data acquired with polarized X-rays parallel and perpendicular to the stretch direction, respectively. The solid lines are the space-averaged NEXAFS spectra from 280 to 320 eV, while the dots were obtained by measurements for image analysis.

The peaks near 292 eV correspond to C-1s $\rightarrow \sigma^*_{\text{C-C}}$ resonances.³¹ Anisotropy was found in the spectra of the stretched LLDPE samples.

The optical density (OD) is expressed by the following relationship:^{31, 32}

$$OD = \mu \rho t \quad (3.15)$$

where μ is the mass absorption coefficient, ρ is the density, and t is the sample thickness.

The OD of the chemical bond resonance is proportional to the square of $\cos \theta$ with θ being the angle between the electric field vector of incident X-rays (E) and the direction of transition dipole moment (TDM, μ_{if})³³, such as

$$OD \propto |E\mu_{if}|^2 \propto \cos^2 \theta. \quad (3.16)$$

Consequently, a higher degree of orientation of C–C bonds parallel to the stretching direction results in a larger OD at 292 eV obtained by linear polarized X-ray parallel to the stretching direction. On the other hand, the OD from 315 eV to 320 eV is far enough from the carbon K edge (~ 284 eV) so that it is not affected by the orientation of the chemical bonds but depends solely on the density and the thickness of the sample.

The average density of LLDPE at each stretch ratio was calculated from the crystallinity obtained by WAXS (Table 3.2), based on the theoretical densities of the crystalline and amorphous phases. The theoretical densities of the crystalline and amorphous phases are 1.00 g/cm³ and 0.855 g/cm³, respectively. Additionally, the μ of LLDPE at 318 ± 2 eV was determined to be 3.45×10^4 cm²/g based on the X-ray attenuation length obtained from the Center for X-ray Optics (CXRO) database.

Considering that the sample thickness at each strain is constant in the observed region, the sample thickness can be estimated from the average density, the value of μ , and the average value of OD in the 2D map at 318 ± 2 eV. The thicknesses at $\varepsilon = 0\%$, 11% and 17% were estimated to be 298, 321, and 310 nm, respectively. In addition, the OD

images at 318 ± 2 eV were converted to local density, ρ , mappings using the mass absorption coefficient and the estimated sample thickness. Figure 3.6 shows the change in the ρ images at 318 ± 2 eV with strain and the histograms for the ρ .

To evaluate the change in the distribution of ρ from $\varepsilon = 0\%$ to $\varepsilon = 17\%$, a ρ histogram was generated for each stretch ratio, as shown in Figure 3.7, and the root-mean-square deviation (RMSD) of the values in the ρ image was calculated, as listed in Table 3.3.

Table 3.3. RMSD at Each Stretch Ratio

Stretch ratio	$\varepsilon = 0\%$	$\varepsilon = 11\%$	$\varepsilon = 17\%(2YP)$
RMSD	4.46×10^{-2}	4.61×10^{-2}	5.51×10^{-2}

The distribution of the ρ observed by STXM increases with strain, agreeing with the increase in the intensity of USAXS with strain. Therefore, the density fluctuations were enhanced by strain. It should be noted that I confirmed that the observed region represents the global necking region. It was explored that the distribution of the ρ in a larger area (several tens of μm or more) agrees with that shown in Figure 3.6, indicating that the observed area is representative of the global necking region. The 2D images of the orientation for the C–C bond were obtained as follows. The orientation order parameter $\langle P_2 \rangle$ was calculated using:³⁴

$$\langle P_2 \rangle = \frac{OD_{C-C,\parallel} - OD_{C-C,\perp}}{OD_{C-C,\parallel} + 2OD_{C-C,\perp}} \quad (3.16)$$

where $OD_{C-C,\parallel}$ and $OD_{C-C,\perp}$ are, respectively, the values of OD due to C–C bonds parallel and perpendicular to the strain direction. These values were obtained by subtracting the background (the OD image at 318 ± 2 eV) from the images near 292 eV.

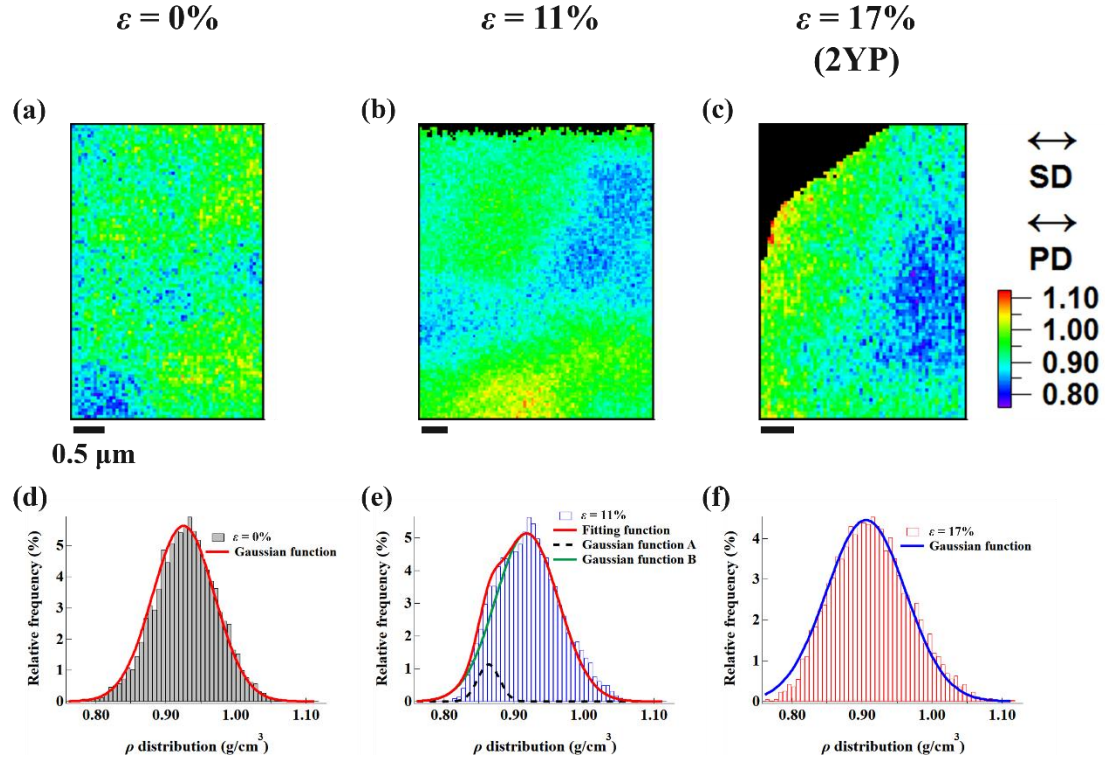


Figure 3.6. (a–c) ρ images at 318 ± 2 eV with strain and (d–f) histograms for ρ images. The polarized direction (PD) of incident X-rays and the stretch direction (SD) are horizontal on the page.

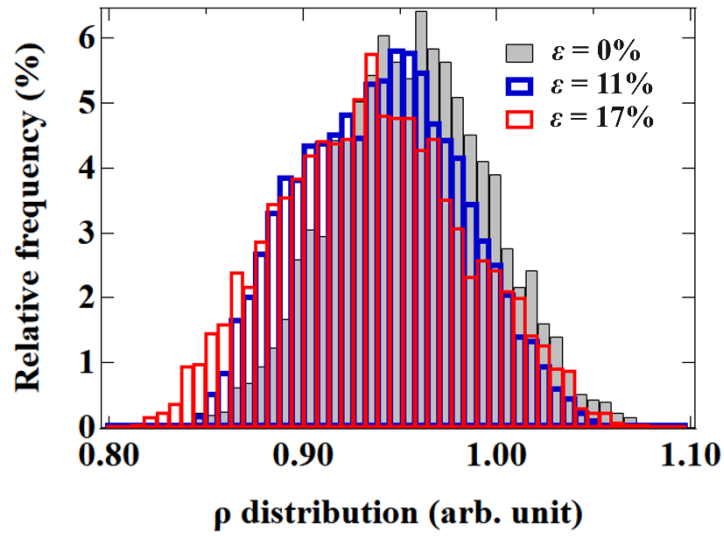


Figure 3.7. ρ histogram at each stretch ratio

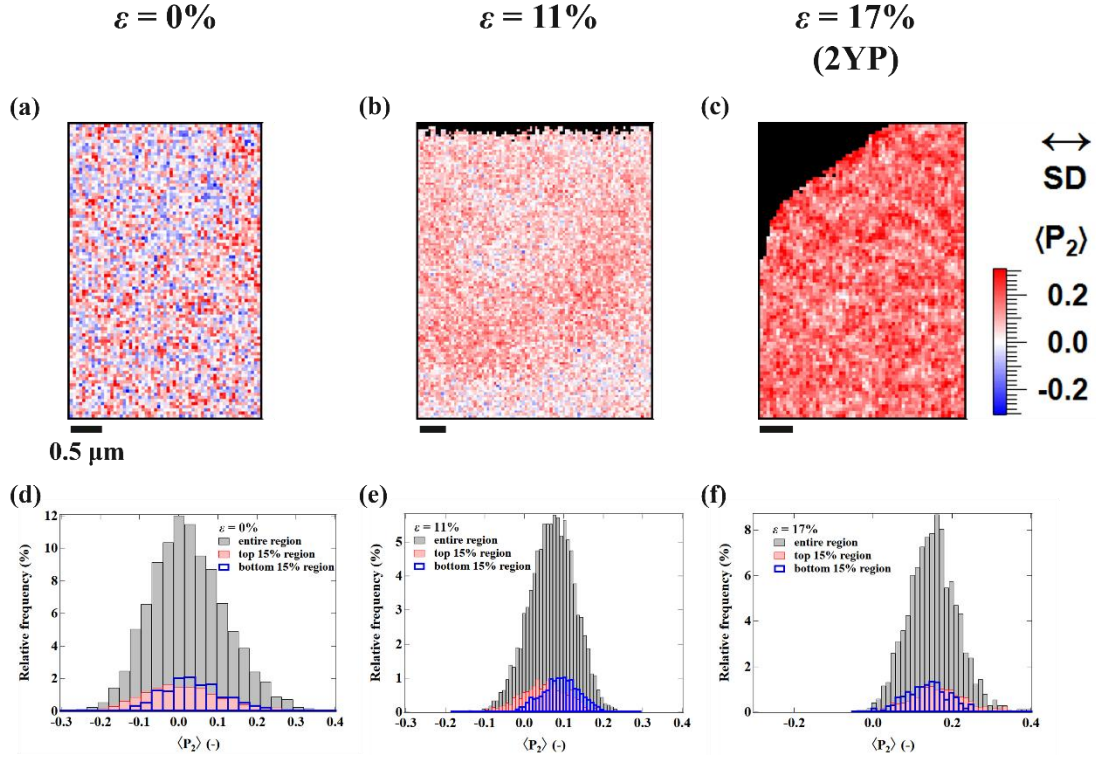


Figure 3.8. (a–c) $\langle P_2 \rangle$ images with strain and (d–f) histograms for $\langle P_2 \rangle$ images. The stretch direction (SD) is horizontal on the page.

The value of $\langle P_2 \rangle$ is 1 for perfect parallel alignment of the C–C bonds in the stretching direction, while the value is -0.5 for perfect perpendicular alignment. $\langle P_2 \rangle = 0$ corresponds to randomly oriented C–C bonds..

Figure 3.8 shows the change in $\langle P_2 \rangle$ images with strain and the histograms of $\langle P_2 \rangle$ in all, the top and the bottom 15% values of *OD* regions at 318 ± 2 eV. The image shows the anisotropy of the C–C bonds parallel to the direction of stretching.

Table 3.4 shows the average values of $\langle P_2 \rangle$ for the entire area, as well as the top and bottom 15% *OD* regions at 318 ± 2 eV. Each $\langle P_2 \rangle$ value increased with strain, which is attributed to the alignment of crystalline structures and polymer chains in amorphous regions.

Table 3.4. $\langle P_2 \rangle$ at Each Stretch Ratio.

Stretch ratio	$\varepsilon = 0\%$	$\varepsilon = 11\%$	$\varepsilon = 17\%(2YP)$
Entire $\langle P_2 \rangle$	2.52×10^{-2}	6.99×10^{-2}	0.162
Low ρ region	4.01×10^{-2}	9.06×10^{-2}	0.151
High ρ region	1.62×10^{-2}	4.97×10^{-2}	0.174

3.3.3. Hierarchical Structure at Each Stretch Ratio

In the following, the above observations were analyzed to clarify the characteristics of the hierarchical structure at each stretch ratio.

The USAXS/SAXS/WAXS 2D patterns for unstretched sample were isotropic, as shown in Figure 3.2a, d, and g. The azimuthal crystal thickness $l_c(\varphi)$ and d-spacing $l_d(\varphi)$ of the lamellar structures at $\varepsilon = 0\%$ were about 4.13 nm and 18.1 nm at each azimuthal angle, respectively. The Hermans orientation function $\langle f_H \rangle$ at $\varepsilon = 0\%$ was -3.92×10^{-4} , showing the random orientation of structures. As shown in Figure 3.6d, the density distribution follows a unimodal distribution. Besides, the $\langle P_2 \rangle$ histograms for the top and bottom 15% *OD* regions are both centered at zero and are identical (Figure 3.8d), indicating that the orientation of the crystalline structures is isotropic, similar to that of the amorphous region.

I observed a four-point pattern in the SAXS 2D pattern for the specimen stretched at $\varepsilon = 11\%$ (Figure 3.2e). This pattern originates from a chevron-type morphology formed through the fragmentation and rotation of the lamellar structure. As shown in Figure 3.4, the crystal thickness and d-spacing at $\varepsilon = 11\%$ show a clear φ dependence. The more the lamellar structures are oriented parallel to the stretching direction, the larger the crystal thickness and d-spacing between the lamellae. Considering the four-point pattern observed in SAXS and the φ dependence of crystal

thickness, the fragmentation occurred in lamellae with relatively thin crystal layers.

The WAXS 2D pattern (Figure 3.2h) shows the split peak of the (110)_{ortho} plane and the peaks originating from the monoclinic crystal at $\varepsilon = 11\%$.⁸ The fragmentation of crystals and orthorhombic-to-monoclinic transition occurred at $\varepsilon = 11\%$.¹¹ The obtained Hermans orientation factor at $\varepsilon = 11\%$ was $\langle f_H \rangle = 0.108$, revealing that the *c*-axes of crystals and polymer chains were oriented in the stretching direction compared to the unstretched state. The crystallinity evaluated by WAXS decreased compared to $\varepsilon = 0\%$, indicating that the mechanical melting occurred.

An abnormal butterfly pattern was observed in the USAXS data (Figure 3.2b), reflecting that an enhancement of spatial density fluctuations and inhomogeneous deformation occurred on the sub-micrometer scale.

The density distribution obtained by STXM (Figure 3.6e) consists of bimodal distributions. This reflects a stretch-induced density fluctuation, in which the difference between the original densities in the low-density and high-density regions increases due to stretching. This difference arises because mechanical melting occurred in some crystals, causing them to become amorphous, while there were many crystals in which mechanical melting did not occur. As shown in Figure 3.8e, the $\langle P_2 \rangle$ values in the high-density region (top 15% of *OD* values) and the low-density region (bottom 15% of *OD* values) are different from each other. The $\langle P_2 \rangle$ values in the low-density region are distributed with a center of 9.06×10^{-2} , whereas the $\langle P_2 \rangle$ values in the high-density region are distributed with a center of 4.97×10^{-2} . The difference in $\langle P_2 \rangle$ values indicates inhomogeneous deformation in different density regions on the sub-micrometer scale, which is consistent with the butterfly pattern observed in USAXS.

The STXM observation at $\varepsilon = 11\%$ reveals that in low-density or low-crystallinity regions, C–C bonds are slightly oriented parallel to the direction of stretching as the material is stretched, while in high-density regions, C–C bonds are not so oriented.

As shown in Figure 3.2f, the SAXS pattern for $\varepsilon = 17\%$ is a clear four-point pattern, indicating that the fragmentation and rotation in the lamellae were developed after $\varepsilon = 11\%$. The d-spacing at $\varphi = 30\text{--}45^\circ$ is the largest and is similar to the maximum value for $\varepsilon = 11\%$ according to Figure 3.4. In addition, the crystal thickness at $\varphi = 0\text{--}45^\circ$ decreased to 3.96 nm with strain. The decline in the crystal thickness is related to mechanical melting. Considering that the d-spacing at $\varphi = 30\text{--}45^\circ$ corresponds to the chevron-type morphology after the fragmentation, the mechanical melting occurred in the crystals of the lamellae oriented parallel to the stretch direction and then fragmentation occurred when the crystal thickness reached a critical value and the amorphous layers extended sufficiently.

In the WAXS 2D pattern (Figure 3.2i), the split peaks of the $(110)_{\text{ortho}}$ plane were clearly observed, and peaks originating from the monoclinic crystal were more clearly observed than at $\varepsilon = 11\%$. The value of $\langle f_H \rangle = 0.272$ for $\varepsilon = 17\%$ reflects that the c -axis of the crystal and the amorphous polymer chain were oriented in the stretching direction more than that for $\varepsilon = 11\%$. The crystallinity decreased even more under stretching, which is consistent with the decrease in crystal thickness.

The abnormal butterfly pattern in USAXS (Figure 3.2c) indicates that crystals and polymer chains were deformed non-uniformly on the sub-micrometer scales, similar to the behavior at $\varepsilon = 11\%$. At this strain, the density distribution returns to a broad unimodal-like distribution as shown in Figure 3.7. This shows that mechanical melting

progressed from $\varepsilon = 11\%$ to $\varepsilon = 17\%$, mainly in the high-density region. The values of $\langle P_2 \rangle$ in the low-density and high-density regions are almost equal and are distributed with centers of 0.151 and 0.174, respectively, as shown in Figure 3.8f.

These facts observed by STXM reveal that mainly in the high-density region, the C-C bonds become oriented parallel to the stretching direction as much as the C-C bonds in the low-density region, while mechanical melting occurred after $\varepsilon = 11\%$.

3.4. Changes in the Hierarchical Structure under Stretching

Schematic illustrations of the changes in the hierarchical structure of LLDPE were constructed based on the X-ray scattering and STXM results, as shown in Figure 3.9. The low-density and high-density regions mentioned in the STXM results reflect low-crystallinity and high-crystallinity areas, such as between fibrils in PE and fibrils, respectively.

In the unstretched state, polymer chains and the c -axis of crystals are randomly oriented in a wide field of view, and the density follows a normal distribution.

At $\varepsilon = 11\%$, SAXS and WAXS results show that mechanical melting and fragmentation are occurring in the crystal. Besides, based on $\langle P_2 \rangle$ values in the STXM image, PE is well stretched in the low crystallinity area compared to in the high crystallinity area. At this stretch ratio, mechanical melting occurs mainly in the low crystallinity area where deformation is larger. Thus, mechanical melting and fragmentation are induced in the lamellae, which are oriented along the stretch direction and have thin crystal layers in this area. In this way, a decrease in density occurs in the low crystallinity area. In the high crystallinity area, crystals are retained despite

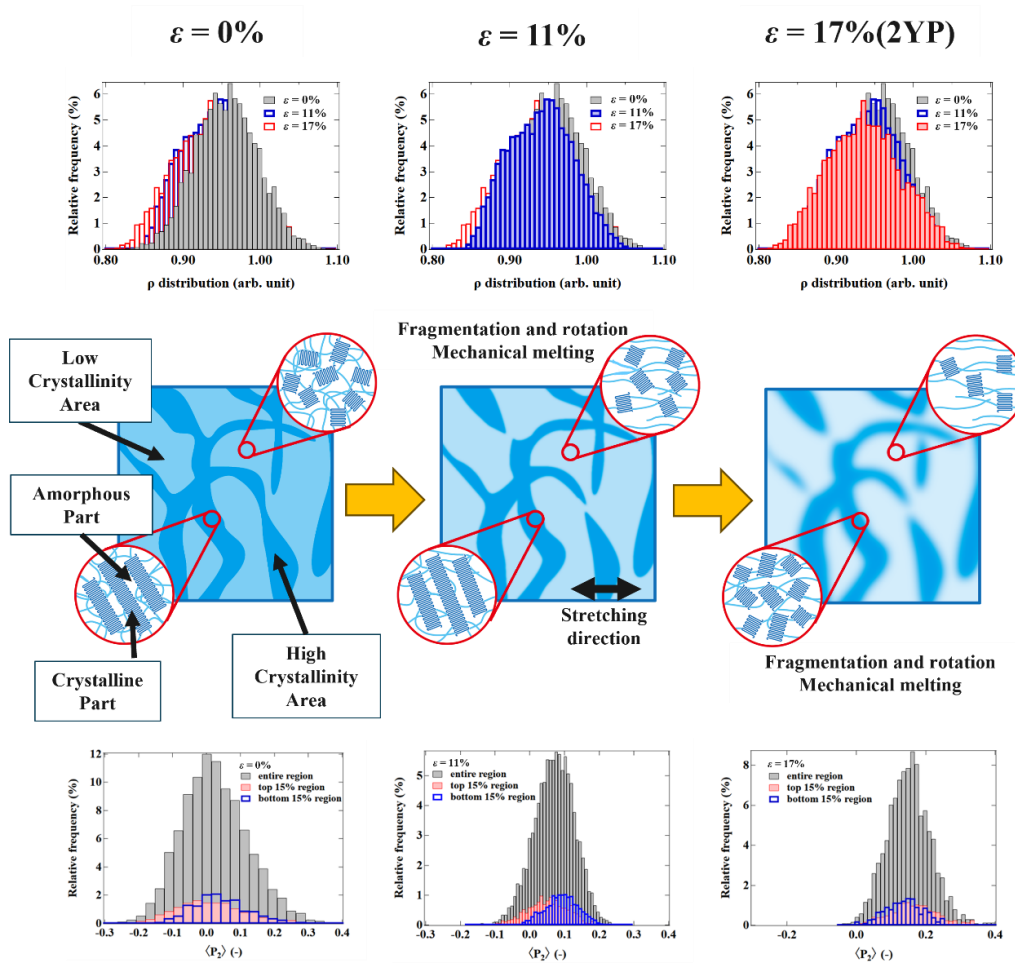


Figure 3.9. Schematic illustrations of the changes in the hierarchical structures under stretching.

stretching, so mechanical melting does not occur as much, and the c -axis of the crystal is less oriented parallel to the direction of stretching. The difference in the way crystals change in these areas causes spatial stretch-induced density fluctuations on the submicron scales and inhomogeneity of chain orientation. This density fluctuation is enhanced by mechanical melting of the crystals and agrees with the USAXS 2D pattern.

After $\varepsilon = 11\%$, crystals held in the high crystallinity area undergo mechanical melting and fragmentation, resulting in a wide density distribution like a unimodal distribution. At $\varepsilon = 17\%$, the c -axis of these fragmented crystals is rotated parallel to the stretching direction as much as amorphous chains in the low crystallinity area, as shown

in Figure 3.8f. This indicates that stress causes fragmentation of crystals rather than orienting polymer chains with possible entanglement, and then the fragmented crystals are rotated and oriented more easily than the chains. Therefore, there is no significant difference in the distribution of $\langle P_2 \rangle$ in each crystallinity area, but the deformation in each area is different until $\varepsilon = 17\%$, that is, non-uniform deformation occurs as shown in Figure 3.2i. Mechanical melting and fragmentation of the crystals reduce the density in the high crystallinity area, but the density fluctuations increase at $\varepsilon = 17\%$. This is consistent with the results of the USAXS 2D result.

3.5. Conclusion

In this study, USAXS, SAXS, and WAXS measurements, as well as STXM measurements, were performed on LLDPE samples with different stretch ratios. In addition, the results of each measurement were combined to assess the spatial distribution of density and polymer chain orientation at sub-micrometer scales. At $\varepsilon = 11\%$, , an abnormal butterfly pattern characterizing stretch-induced density fluctuations was observed via USAXS, along with an inhomogeneous distribution of density and orientation of the internal structure in real space revealed by STXM.

Furthermore, the results at $\varepsilon = 17\%$ indicate that mechanical melting and fragmentation lead to a broad unimodal density distribution with increasing density fluctuations from $\varepsilon = 11\%$ to $\varepsilon = 17\%$, while the difference in the orientation of the crystals and polymer chains causes unequal deformation. The obtained data demonstrate that, from the first to the second yield point, LLDPE deforms in a crystallinity-dependent, spatially heterogeneous manner at sub-micrometer scales.

References

1. Strobl, G. *The Physics of Polymers: Concepts for Understanding Their Structures and Behavior*; Springer: Berlin, Heidelberg, 2007.
2. Galeski, A. *Prog. Polym. Sci.* **2003**, 28 (12), 1643–1699
3. Xu, S.; Zhou, J.; Pan, P. *Prog. Polym. Sci.* **2023**, 140, 101676
4. Brooks, N. W. J.; Unwin, A. P.; Duckett, R. A.; Ward, I. M. *J. Macromol. Sci., Part B: Phys.* **1995**, 34, 29–54.
5. Butler, M. F.; Donald, A. M.; Ryan, A. J. *Polymer* **1997**, 38, 5521–5538.
6. Butler, M. F.; Donald, A. M.; Ryan, A. J. *Polymer* **1998**, 39, 39–52.
7. Hiss, R.; Hobeika, S.; Lynn, C.; Strobl, G. *Macromolecules* **1999**, 32, 4390–4403.
8. Takahashi, Y.; Ishida, T.; Furusaka, M. *J. Polym. Sci., Part B: Polym. Phys.* **1988**, 26, 2267–2277.
9. Yagi, N.; Inoue, K. *J. Appl. Crystallogr.* 2003, 36, 783–786.
10. Takenaka, M.; Shimizu, H.; Nishitsuji, S. *Phys. Rev. E* **2007**, 75, 061802.
11. Kishimoto M.; Mita K; Ogawa H.; Takenaka M. *Macromolecules* **2020**, 53, 9097–9107.
12. Bastide, J.; Leibler, L.; Prost, J. *Macromolecules* **1990**, 23, 1821– 1825.
13. Mendes E.; Oeser R.; Hayes C.; Boue F.; Bastide J. *Macromolecules* **1996**, 29, 5574–5584.
14. Hashimoto, T.; Fujioka K. *J. Phys. Soc. Jpn.* **1991**, 60, 356–359.
15. Doi, M.; Onuki, A. *J. Phys. II* **1992**, 2, 1631–1656.
16. Furukawa, A.; Tanaka, H. *Nat. Mater.* **2009**, 8, 601–609.

17. Arakawa, M.; Kishimoto, M.; Nakanishi, Y.; Takenaka, M. *Polym J.* **2022**, *54*, 243–248.
18. Kilcoyne, A.L.D.; Tyliszczak, T.; Steele, W.F.; Fakra S.; Hitchcock, P; Franck K.; Anderson, E.; Harteneck, B.; Rightor, E. G.; Mitchell, G. E.; Hitchcok, A. P.; Yang, L.; Warwick, T.; Ade, H. *J. Synchrotron Rad.* **2003**, *10*, 125–136.
19. Ohigashi, T.; Arai, H.; Araki, T.; Kondo, N.; Shigemasa, E.; Ito, A.; Kosugi, N.; Katoh, M. *J. Phys.: Conf. Ser.* **2013**, *463*, 012006.
20. Takeichi, Y.; Inami, N.; Suga, H.; Ono K.; Takahashi Y. *Chem. Lett.* **2014**, *43*, 373–375.
21. Gerasimov, V. I.; Genin, Y. V.; Tsvankin, D. Y. *J. Polym. Sci., Polym. Phys. Ed.* **1974**, *12*, 2035–2046.
22. Lucas, J. C.; Failla, M. D.; Smith, F. L.; Mandelkern, L.; Peacock, A. J. *Polym. Eng. Sci.* **1995**, *35*, 1117–1123.
23. Gaucher-Miri, V.; Séguéla, R. *Macromolecules* **1997**, *30*, 1158–1167.
24. Masunaga, H.; Ogawa, H.; Takano, T.; Sasaki, S.; Goto, S.; Tanaka, T.; Seike, T.; Takahashi, S.; Takeshita, K.; Nariyama, N.; Ohashi, H.; Ohata, T.; Furukawa, Y.; Matsushita, T.; Ishizawa, Y.; Yagi, N.; Takata, M.; Kitamura, H.; Sakurai, K.; Tashiro, K.; Takahara, A.; Amamiya, Y.; Horie, K.; Takenaka, M.; Kanaya, T.; Jinnai, H.; Okuda, H.; Akiba, I.; Takahashi, I.; Yamamoto, K.; Hikosaka, M.; Sakurai, S.; Shinohara, Y.; Okada, A.; Sugihara, Y. *Polym. J.* **2011**, *43*, 471–477.
25. Strobl, G. R.; Schneider, M. *J. Polym. Sci., Polym. Phys.* **1980**, *18*, 1343–1359.
26. Strobl, G. R.; Schneider, M. J.; Voigtmartin, I. G. *J. Polym. Sci., Polym. Phys.* **1980**, *18*, 1361–1381.

27. Flory P. J.; Yoon D. Y. *Nature* **1978**, 272, 226–229.
28. Wilchinsky, Z. W. *J. Appl. Phys.* **1959**, 30, 792.
29. Wilchinsky, Z. W. *J. Appl. Phys.* **1960**, 31, 1969–1972.
30. Schrauwen, B. A. G.; Breemen, L. C. A. v.; Spoelstra, A. B.; Govaert, L. E.; Peters, G. W. M.; Meijer, H. E. H. *Macromolecules* **2004**, 37, 8618–8633.
31. Dhez, O.; Ade, H.; Urquhart, S.G. *J. Electron Spectrosc. Relat. Phenom.* **2003**, 128, 85–96.
32. Fu, J.; Urquhart, S. G. *Langmuir* **2007**, 23, 2615–2622.
33. Fu, J.; Urquhart, S. G. *J. Phys. Chem. A* **2005**, 109, 11724–11732.
34. Hernández Cruz, D.; Rousseau, M.-E.; West, M. M.; Pézolet, M.; Hitchcock, A. P. *Biomacromolecules* **2006**, 7, 836–843.

Chapter 4

Differences in Hierarchical Structural Changes between Unoriented P(3HB) and P(3HB-*co*-3HH) under Stretching

4.1 Introduction

Plastics have been used in numerous products because of their usability and processability. However, owing to their durability and stability, it is difficult to decompose plastic products in nature, and environmental pollution caused by plastic waste is a problem that needs urgent solution. There is also the problem of depletion of petroleum resources used for plastics and the CO₂ emissions released during manufacturing. To overcome these problems, research on environmentally friendly polymers has been promoted in recent years. Poly[(R)-3-hydroxybutyrate] [P(3HB)] is a biodegradable polyester produced by microorganisms and is promising as an environmentally friendly polymer. Many researchers have studied P(3HB) for practical applications.¹⁻⁶

P(3HB) has a fracture strength comparable to that of polypropylene. However, its fracture elongation is usually less than 5%.^{1,3} Moreover, secondary crystallization occurs at room temperature, resulting in the enhancement of brittleness.⁷⁻⁹

To improve the brittleness of P(3HB), copolymerization with a second monomer to reduce the crystallinity has been proposed.^{3, 10} The introduction of 3-hydroxyhexanoate (3HH), an amorphous component monomer unit, is accomplished by microbial synthesis from palm oil. The produced random copolymer P(3HB-*co*-3HH) exhibits a crystallinity lower than P(3HB), and the ductility is improved.

P(3HB) is a crystalline polymer that forms a hierarchical structure similar to that of common polyolefins. The hierarchical structure is classified into four levels: crystal structures where molecular chains are folded regularly, lamella structures where amorphous and crystalline phases are alternately stacked, fibril structures developed by the growth of lamellae, and spherulite structures formed by the filling of fibrils.

Many researchers have investigated the correlation between the internal structure and physical properties of oriented P(3HB) and its copolymers, and the structural changes during uniaxial stretching. However, there are only a few cases in which the structural changes during uniaxial stretching of unoriented samples have been investigated and the correlations with physical properties have been clarified. Moreover, the changes in the hierarchical structures on the sub-micrometer scale have not been investigated, although the structures on the sub-micrometric scale strongly correlate to the mechanical properties described below.

The structures of crystalline polymers have been widely studied by small- and wide-angle X-ray scattering (SAXS and WAXS, respectively). When a crystalline polymer is uniaxially stretched, the strain–stress (S–S) curve reflects the strength and ductility of the material, and the yield behavior on the S–S curve reflects the change in

internal structure. Therefore, changes in lamellar and crystalline structures under uniaxial drawing have been investigated by *in-situ* SAXS and WAXS.^{11–13}

The recent development of ultra-small-angle scattering (USAXS) has also enabled the study of the correlation between structure and physical properties on the submicrometric scale, on the order of 100 nm. USAXS observation of the crystalline polymer polyethylene provides information on the fibril structures, which are larger than the lamellar structures.

In a previous study conducted by the research group of Takenaka et al. using USAXS, an "abnormal" butterfly pattern was observed, in which the scattering intensity parallel to the direction of elongation increases near the yield point during uniaxial tensile testing of polyethylene.^{14, 15} The abnormal butterfly pattern has been observed in swollen gels,¹⁶ slide-ring gels under uniaxial drawing,¹⁷ and stretched mixtures of short and long polystyrene homopolymers.¹⁸ The increase in scattering intensity along the deformation direction indicates an enhancement of density or concentration fluctuations induced along the same direction during stretching.

The stretch-induced density or concentration fluctuations are driven by spatial inhomogeneity of deformation resulting from the difference in deformation amounts between regions with disparate mechanical properties. Doi and Onuki,¹⁹ Furukawa and Tanaka²⁰ and Kurotani and Tanaka²¹ proved theoretically that shear-induced enhancement in density fluctuations results from the gradient of the stress field caused by the spatial asymmetry of mechanical properties associated with the density field. Thus, the abnormal butterfly pattern observed during the drawing of polyethylene reflects the difference in deformation between fibril regions with high crystallinity and

non-fibril regions with low crystallinity, as crystalline polymers have spatially heterogeneous stress fields associated with crystallinity fluctuations.

In this study, the structural changes of unoriented P(3HB) and P(3HB-*co*-3HH) under uniaxial stretching were investigated in a time-resolved manner over a wide q -range by USAXS, SAXS and WAXS. By comparing the two, I clarify how the introduction of the copolymer P(3HH) affected the changes in hierarchical structures of P(3HB) and P(3HB-*co*-3HH) under uniaxial stretching and clarify the origin of the improvement of the mechanical properties.

4.2 Experimental Section

4.2.1 Sample Preparation

P(3HB) and P(3HB-*co*-11mol%-3HH) samples provided by the Iwata laboratory, the University of Tokyo, were used in this study.

Sheets of each material were prepared according to the following procedure. First, the material was pressurized in a 0.5 mm-thick mold for 10 min to melt it using a press machine set at 180 °C. The melt was then immediately transferred to a vacuum oven set at 60 °C and quenched for over 2 h to produce a 0.5 mm-thick pressed sheet. Finally, dumbbell specimens with a center width of 3.2 mm were punched from the prepared sheets.

4.2.2 *In-Situ* X-ray Scattering Measurements

In-situ X-ray scattering (USAXS/SAXS/WAXS) measurements during uniaxial stretching were performed in the second hutch of beamline BL03XU at SPring-8, Hyogo, Japan.²² Using a custom-made tensile testing machine designed to measure stress–strain curves and X-ray scattering simultaneously, the dumbbell specimens were stretched at a rate of 1 mm/min at room temperature.

USAXS measurements were conducted with an X-ray exposure time of 400 ms. The incident X-ray wavelength, the specimen-to-detector length, and the beam size at the center of the specimens were 2.0 Å, 7.84 m, and 160 µm (horizontal) × 80 µm (vertical), respectively. A PILATUS-1M detector (Dectris Ltd) was employed for data collection. In addition, 100 µm-thick and 200 µm-thick Al plates were used as attenuators for P(3HB) and P(3HB-co-11mol%-3HH), respectively.

Simultaneous SAXS and WAXS measurements were performed with exposure times of 400 ms for P(3HB) and 800 ms for P(3HB-co-11mol%-3HH). The incident X-ray wavelength was 1.0 Å, and the beam size at the center of the specimens was 300 µm (horizontal) × 300 µm (vertical). A 10 µm-thick Au plate was used as the attenuator. The camera lengths were set to 2.35 m for SAXS and 105 mm for WAXS, and a PILATUS detector was utilized for these measurements.

The 2D scattering images were corrected for X-ray transmittance, and air and background scattering were subtracted for further analysis. The USAXS data for P(3HB-co-11mol%-3HH) were obtained by accumulating two consecutive datasets to form a single representative dataset.

4.3 Result and Discussion

4.3.1 S-S Curves

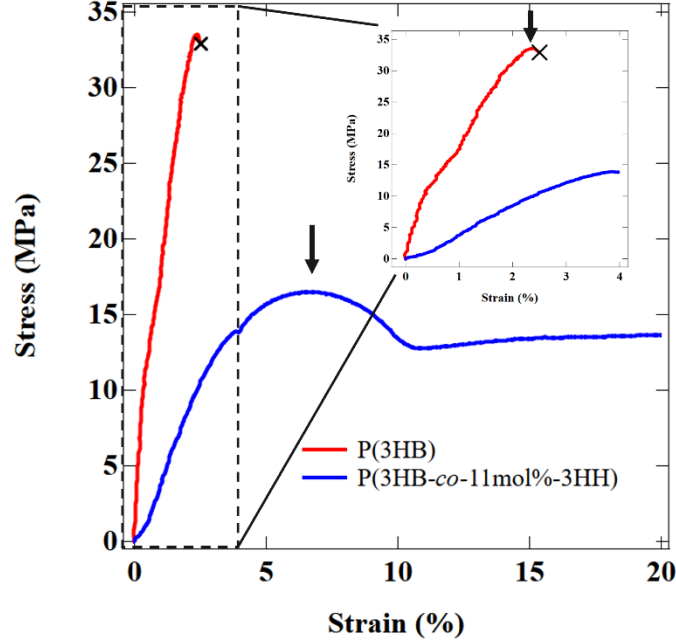


Figure 4.1. S–S curves of the P(3HB) and P(3HB-co-11mol%-3HH). Arrows indicate the respective yield points and crosses indicate the respective elongations at break.

Fig. 4.1 shows S–S curves obtained during the simultaneous SAXS and WAXS measurements. The stress is the engineering stress and the strain ε is defined by the following equation:

$$\varepsilon = \frac{L - L_0}{L_0} \quad (4.1)$$

Here, L_0 and L are the chuck distances before and after stretching, respectively.

The yield points for P(3HB) and P(3HB-co-11mol%-3HH) were observed at $\varepsilon = 2.38$ and 6.74%, respectively. Although Young's modulus of the copolymer was lower than that of the homopolymer, the introduction of the amorphous monomer units improved the breaking elongation as shown in Fig. 4.1.

4.3.2 Comparison of the Hierarchical Structures of Unstretched P(3HB) and P(3HB-*co*-11mol%-3HH)

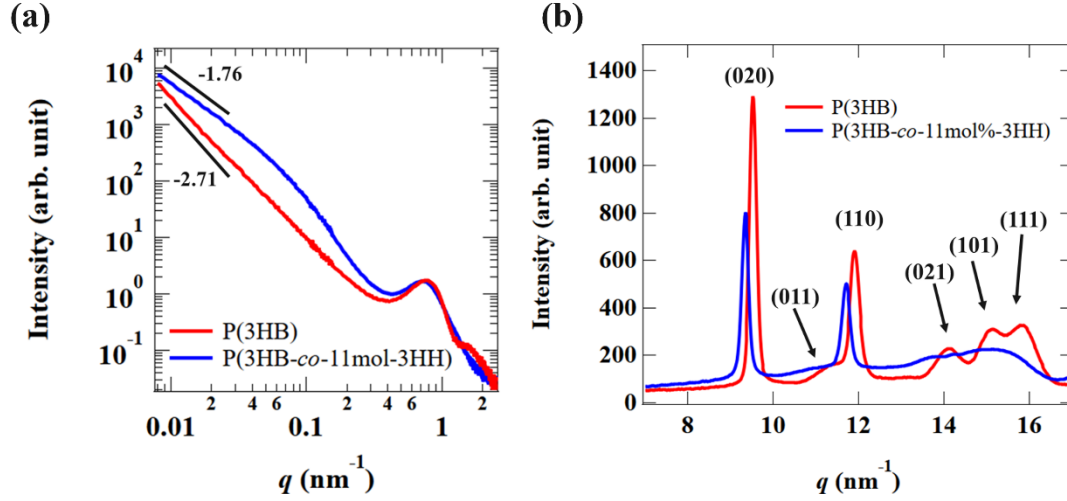


Figure 4.2. (a) Combined USAXS/SAXS 1D profiles and (b) WAXS profiles of the P(3HB) and P(3HB-*co*-11mol%-3HH) before stretching ($\varepsilon = 0\%$).

Figure 4.2 presents the scattering intensity $I(q)$ of USAXS, SAXS and WAXS for P(3HB) and P(3HB-*co*-11mol%-3HH) before stretching. Here, q is the magnitude of the scattering vector $\mathbf{q}$ and given by $q = (4\pi/\lambda) \sin(\theta/2)$ where λ and θ are the wavelength of the incident X-rays and the scattering angle, respectively. Note that the USAXS, SAXS and WAXS 2D patterns (Figures 4.3a, g and m for unstretched P(3HB) and Figure 4.8a, g and m for unstretched P(3HB-*co*-11mol%-3HH)) were isotropic. The WAXS peaks of the copolymer were located at lower q values than those of the homopolymer because the crystal structure was changed slightly by introducing amorphous component monomer units, as reported by Doi *et al.*,²³ indicating that the addition of the comonomer prevents the chain from folding neatly. Moreover, the homopolymer profile clearly showed higher-order peaks, whereas the copolymer profile was less distinct, indicating the lack of long-range order of the crystal structure of the copolymer.

Power-law behaviors for both P(3HB) and the copolymer were observed in the range of $0.008 \text{ nm}^{-1} < q < 0.02 \text{ nm}^{-1}$, as shown in Figure 4.2a, with exponents of $I(q) \propto q^{-2.71}$ and $I(q) \propto q^{-1.76}$, respectively. Figure 4.2a demonstrates that the USAXS intensity of the copolymer was higher than that of the homopolymer in the unstretched state. This result indicates that the density fluctuations of the copolymer on the submicrometre scale were more pronounced.

At $q > 0.02 \text{ nm}^{-1}$, the scattering intensity reflects the lamellar structures. A higher-order peak was seen in the scattered intensity of P(3HB), whereas the scattering intensity of P(3HB-*co*-11mol%-3HH) did not show the higher-order peak, suggesting that the regularity of the stacking of the homopolymer was higher than that of the copolymer. To characterize the lamellar structures, we calculated correlation functions from the scattering profiles for both specimens.^{24, 25} The d-spacing (d_l) and crystal thickness (d_c) of each specimen were estimated as listed in Table 4.1 by comparing the crystallinity obtained from WAXS, discussed below, with the ratio of the thickness to the d-spacing. The d-spacing in the copolymer was larger than that of the homopolymer and the crystal thickness was smaller. The reduction of crystal thickness in the copolymer was attributed to the suppression of crystallization of P(3HB) by the introduction of amorphous component monomer units.

Table 4.1. Characteristic Parameters Before Stretching ($\varepsilon = 0\%$).

name	d_l (nm)	d_c (nm)	X_c (%)
P(3HB)	7.36	5.39	61.70
P(3HB- <i>co</i> -11mol%-3HH)	7.50	2.14	22.82

Finally, the crystallinity of each sample was determined by fitting the 1D WAXS profile using Gaussian functions and a constant background to model the crystalline peaks and the amorphous halo. The resulting parameters are listed in Table 4.1. The crystallinity of the copolymer was lower than that of the homopolymer, a trend that is consistent with the SAXS analysis.

In summary, P(3HB) had high crystallinity, and the spherulites exhibited a high regularity of lamellar stacking. On the other hand, P(3HB-co-11mol%-3HH) had low crystallinity, and fibrils with a lower regularity of lamellar stacking filled the spherulites.

4.3.3 Changes in the Hierarchical Structure under Stretching P(3HB)

Figure 4.3 shows the changes in the USAXS, SAXS and WAXS 2D patterns with strain for the P(3HB) homopolymer, and Figure 4.4 shows the combined USAXS and SAXS 1D profiles along the directions parallel (denoted as $I_{\parallel}(q)$) and perpendicular (denoted as $I_{\perp}(q)$) to the stretching direction. The $I_{\parallel}(q)$ and $I_{\perp}(q)$ profiles were obtained from the USAXS and SAXS 2D patterns by averaging the sector within $\pm 2.5^{\circ}$ from the stretching direction ($\mu = 0^{\circ}$) and its vertical ($\mu = 90^{\circ}$), respectively. Azimuthal angle μ is defined as shown in Figure 4.3.

Near the yield point (YP), inhomogeneous deformation was observed on the submicrometre scale in P(3HB). After $\varepsilon = 1.8\%$, $I_{\parallel}(q)$ increased significantly in the USAXS region, as shown in Fig. 4.4, and the abnormal butterfly patterns became clearly visible in Figure 4.3. These patterns in USAXS represent heterogeneous deformations on the submicrometric scale under uniaxial stretching, where density

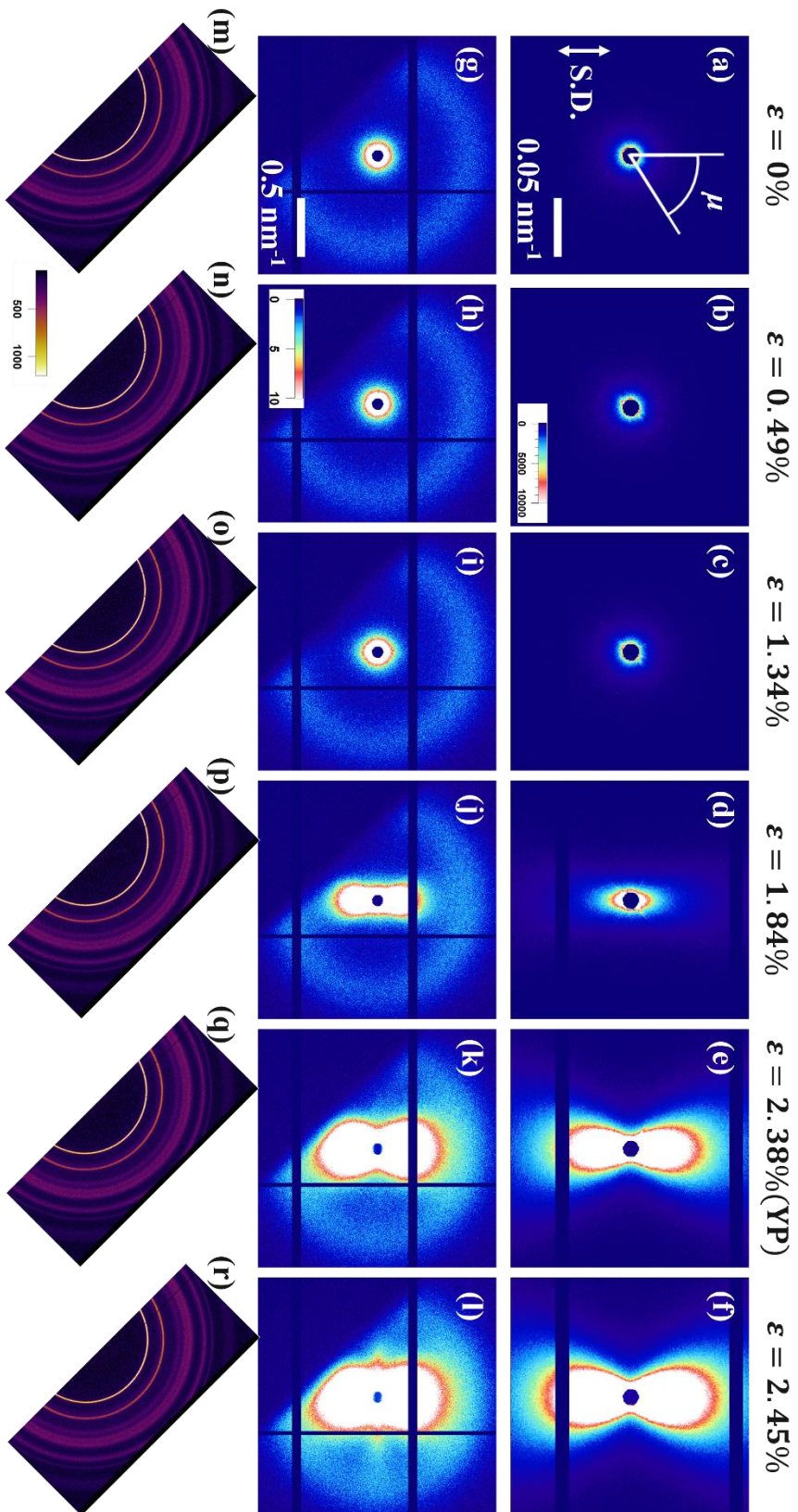


Figure 4.3. (a–f) USAXS, (g–l) SAXS, and (m–r) WAXS 2D patterns of P(3HB) with strain. The stretching direction (S.D.) is parallel along the arrow in (a).

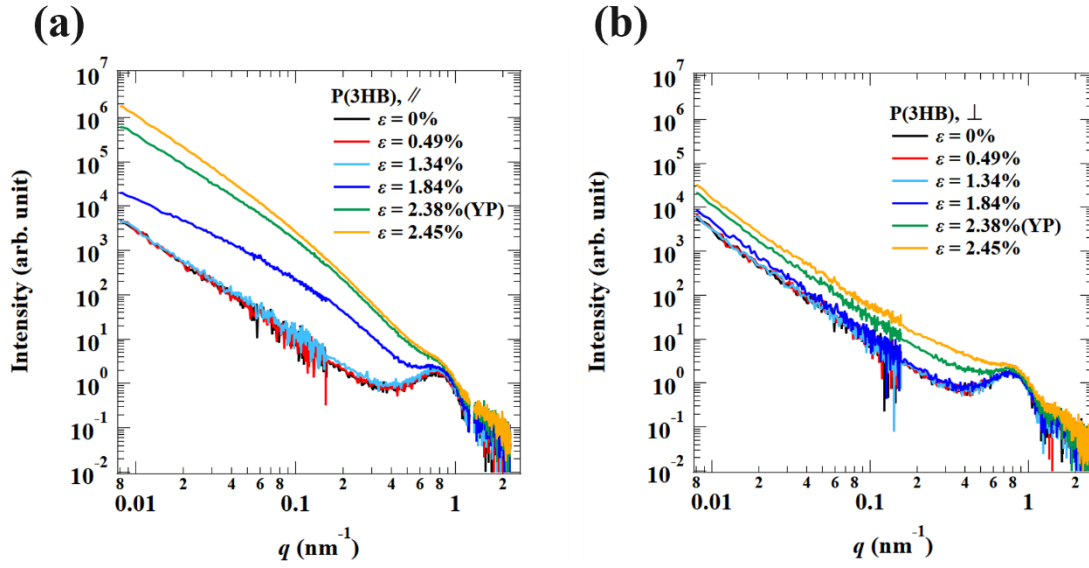


Figure 4.4. Combined USAXS and SAXS profiles for the P(3HB). The profiles in (a) and (b) correspond to $I_{\parallel}(q)$ and $I_{\perp}(q)$, respectively.

fluctuations are induced. Kishimoto *et al.* previously reported similar abnormal butterfly patterns in polyethylene during uniaxial stretching.¹⁵ As suggested in that study, the spatial inhomogeneity of the stress field arising from the inhomogeneity of the crystallinity causes strain-induced density fluctuations. Theoretical work by Furukawa, Tanaka and Kurotani has indicated that such spatial inhomogeneity in the stress field enhances concentration or density fluctuations during deformation.^{20, 21}

As shown in Figure 4.3, SAXS scattering patterns resembling the abnormal butterfly patterns in USAXS were also observed near the yield point. The peaks from the lamellar structures were overlapped by these patterns, indicating that heterogeneous deformation also occurred on length scales slightly larger than the lamellae.

After the yield point, weak streak scattering perpendicular to the stretching direction appeared, and a slight enhancement in $I_{\perp}(q)$ was observed in Figures 4.31 and 4.4b. This streak scattering reflects the formation of string-like nanovoids aligned

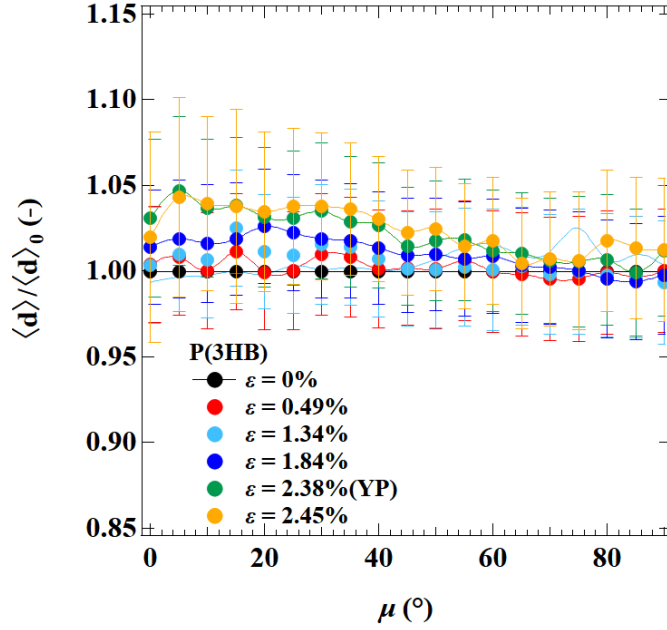


Figure 4.5. μ dependence of $\langle d \rangle / \langle d \rangle_0$ for the P(3HB) with strain.

with the strain direction. The voids originate from the density fluctuations enhanced by stretching.

To investigate the changes in lamellar structure in greater detail, correlation functions were calculated from the SAXS 1D profiles, which were obtained by averaging sectors in 2D patterns at every 5° from $\mu = 0^\circ$ to 90° .²⁴⁻²⁶ The average d-spacing, $\langle d \rangle$, was estimated from these correlation functions, and the ratio $\langle d \rangle / \langle d \rangle_0$ was calculated for each μ , as shown in Figure 4.5. The results indicate that as the stretch ratio increases, $\langle d \rangle / \langle d \rangle_0$ along $\mu = 0^\circ$ tends to increase.

Furthermore, the WAXS 1D profiles were analysed to calculate the Hermans orientation factor (f_H) for the a -, b - and c -axis (polymer chain) of the crystal. These 1D profiles were obtained by sector-averaging every 5° from $\mu = 0^\circ$ to 90° from the 2D patterns. The orientation factor is defined as:

$$f_H = \frac{3\langle \cos^2 \phi_i \rangle - 1}{2} \quad (4.2)$$

where ϕ_i is the angle between the unit within a crystal of interest (e.g., c -axis) and the stretching direction. Assuming rotational symmetry around the stretching direction, $\langle \cos^2 \phi_i \rangle$ is expressed as:

$$\langle \cos^2 \phi_i \rangle = \frac{\int_0^{\pi/2} I(\phi_i) \cos^2 \phi_i \sin \phi_i d\phi_i}{\int_0^{\pi/2} I(\phi_i) \sin \phi_i d\phi_i} \quad (4.3)$$

where $I(\phi_i)$ is the pole concentration corresponding to the relative amount of crystalline material having plane normals in the direction of ϕ_i . The orientation factors for the a -, b - and c -axes (f_a, f_b, f_c) were obtained, and the orientation of polymer chains in the amorphous phase (f_{amo}) was estimated using Wilchinsky's method:^{27, 28}

$$\langle \cos^2 \phi_{b-axis} \rangle = \langle \cos^2 \phi_{(020)ortho} \rangle \quad (4.5)$$

$$\langle \cos^2 \phi_{c-axis} \rangle = 1 - 0.810 \langle \cos^2 \phi_{(020)ortho} \rangle - 1.190 \langle \cos^2 \phi_{(110)ortho} \rangle \quad (4.6)$$

$$\langle \cos^2 \phi_{a-axis} \rangle + \langle \cos^2 \phi_{b-axis} \rangle + \langle \cos^2 \phi_{c-axis} \rangle = 1 \quad (4.7)$$

$$f_a = \frac{3\langle \cos^2 \phi_{a-axis} \rangle - 1}{2}, f_b = \frac{3\langle \cos^2 \phi_{b-axis} \rangle - 1}{2}, f_c = \frac{3\langle \cos^2 \phi_{c-axis} \rangle - 1}{2} \quad (4.8)$$

$$f_{H,amo} = \frac{3\langle \cos^2 \phi_{amo} \rangle - 1}{2} \quad (4.9)$$

The value of f_H is 1 for perfect parallel alignment of interest, whereas the value is -0.5 for perfect perpendicular alignment. $f_H = 0$ represents random orientation or orientation along the magic angle ($\phi_i = 54.7^\circ$).

The ε dependences of f_a , f_b , f_c and f_{amo} for the homopolymer are shown in Figure 4.6. These results reveal that the c -axis of the crystal was aligned perpendicularly to the stretching direction, while the a - and b -axes were oriented parallel. Additionally, the polymer chains in the amorphous phases were oriented slightly along the stretching direction.

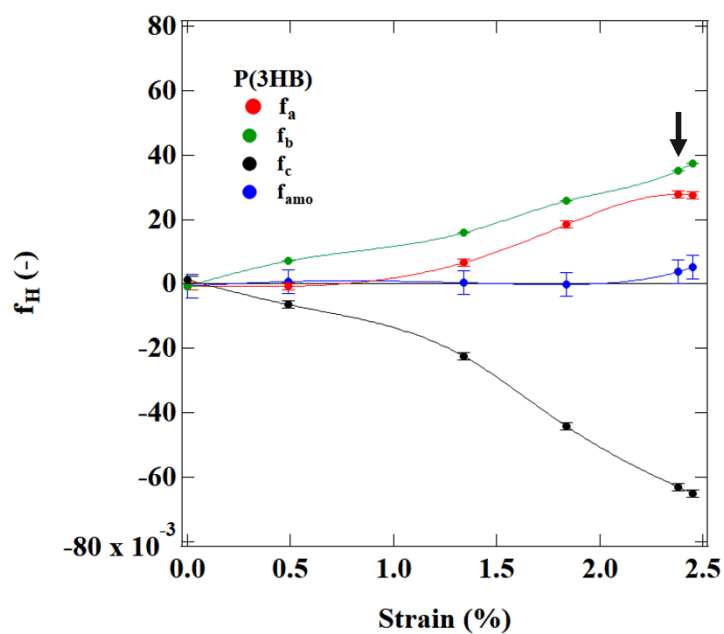


Figure 4.6. Changes in f_H for P(3HB) with strain. Arrow indicates the yield point.

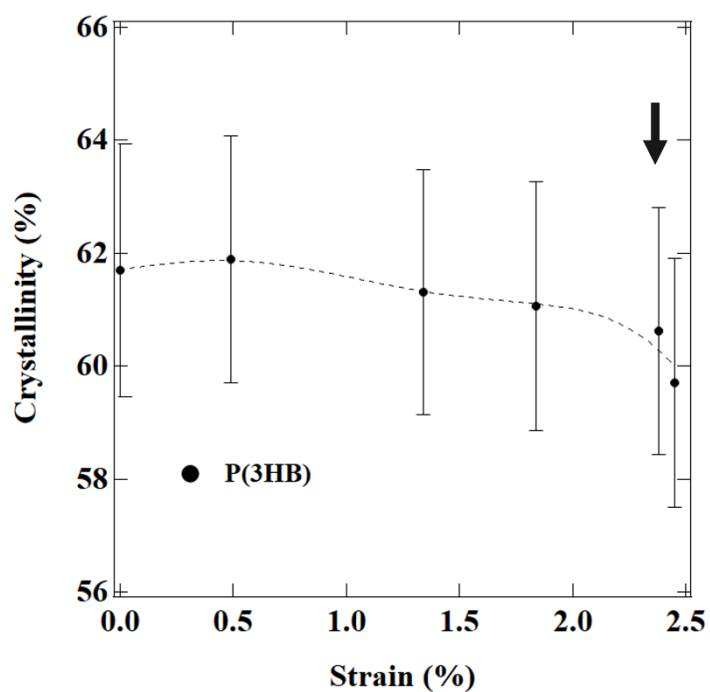


Figure 4.7. Crystallinity of the P(3HB) at each ratio. Arrow indicates the yield point.

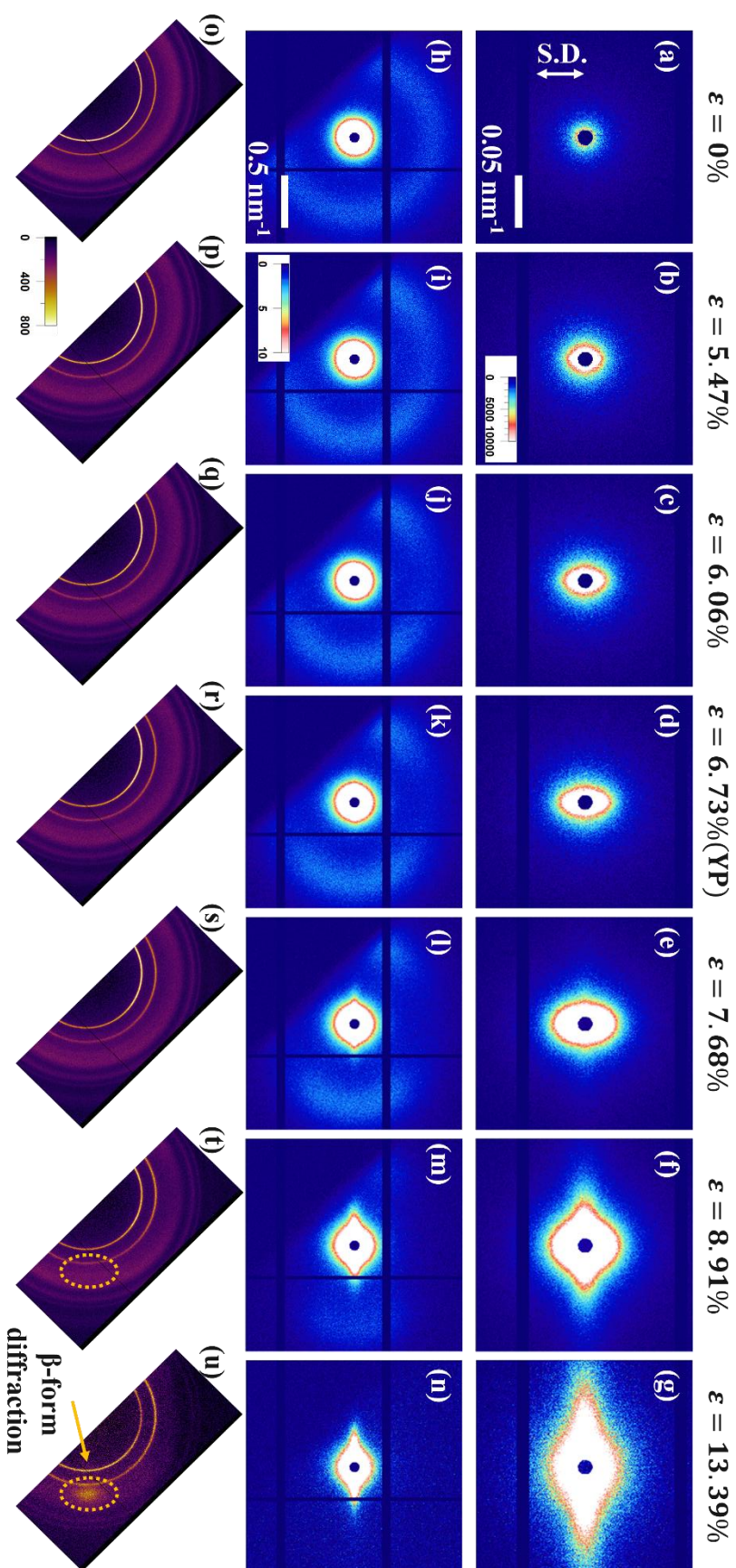


Figure 4.8. (a–g) USAXS, (h–n) SAXS, and (o–u) WAXS 2D patterns of the P(3HB-co-11mol%-3HH) with strain. The stretching direction (S.D.) is parallel along the arrow in (a).

The crystallinity of the homopolymer at each stretch ratio was also estimated from the peak separation of the WAXS 1D profiles using Gaussian functions and a constant background (Figure 4.7). The crystallinity decreased during stretching and significantly declined after the yield point. Considering the collapse of the lamellar structure parallel to the stretching direction with strain, the change in crystallinity indicates that mechanical melting occurred via coarse slip in the lamellae after the yield point, as observed in polyethylene.^{11, 15, 29} Coarse slip represents the fragmentation of the crystalline parts in the lamellae into smaller blocks, leading to lamellar disintegration.

4.3.4 Changes in the Hierarchical Structure under Stretching

P(3HB-*co*-11mol%-3HH)

Figure 4.8 shows the changes in the USAXS, SAXS, and WAXS 2D patterns with strain for the P(3HB-*co*-11mol%-3HH), and Figure 4.9 shows the combined USAXS and SAXS 1D profiles. Similar to the case of P(3HB), $I_{\parallel}(q)$ increased in the USAXS region. However, no clear abnormal butterfly pattern was observed in the USAXS in P(3HB-*co*-11mol%-3HH). This is attributed to the fact that the spatial inhomogeneity of the stress field is lower than that of the homopolymer. As shown in the WAXS profiles at $\varepsilon = 0\%$ in Figure 4.2b, the long-range order of the crystal structure of the copolymer was poorer than that of the homopolymer. Due to the poor long-range order in the copolymer, the stress of the higher-crystallinity region or the fibrils for the copolymer was lower than that for the homopolymer. Thus, the inhomogeneity of the stress field for the copolymer was lower than that for the homopolymer.

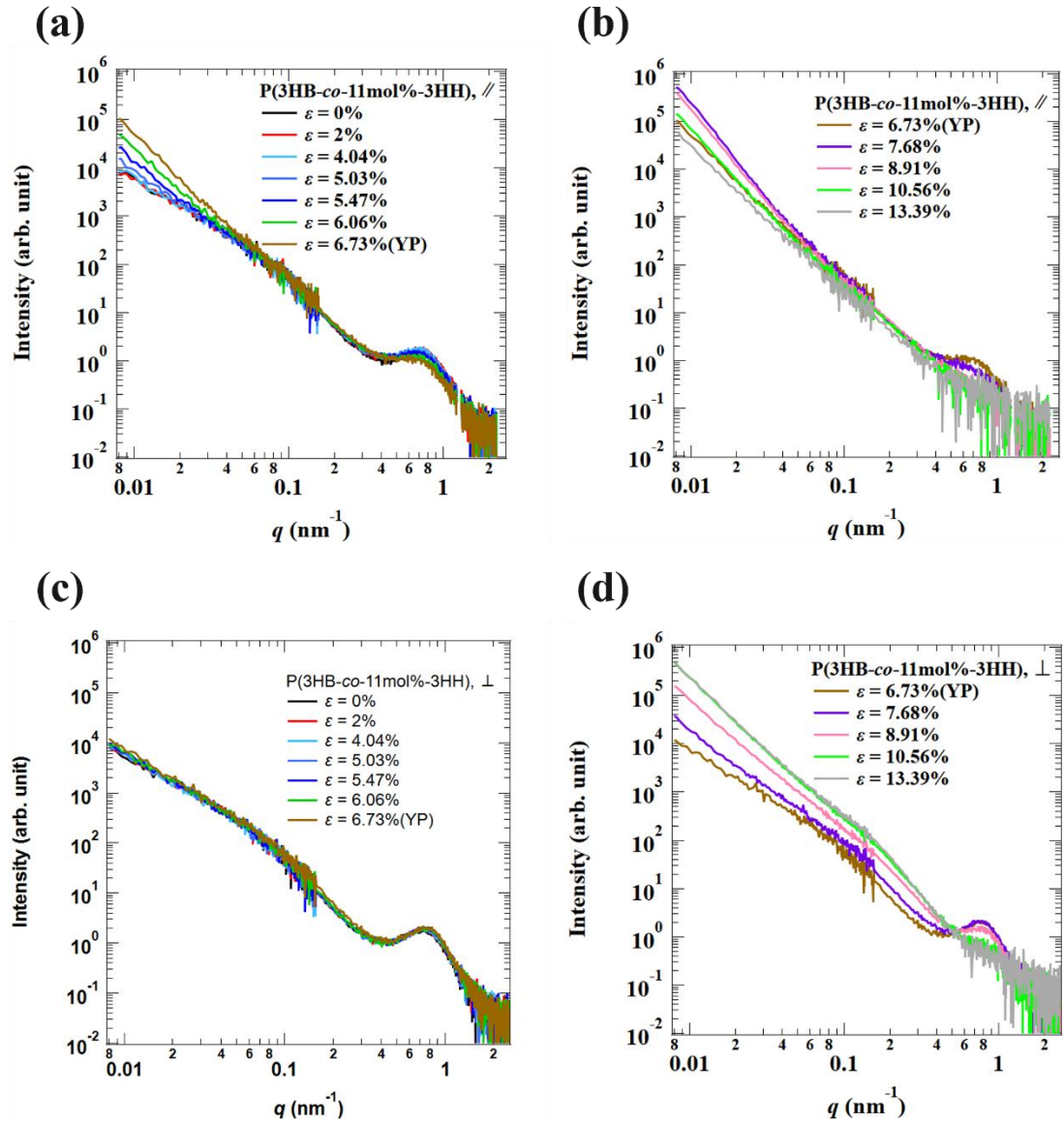


Figure 4.9. Combined USAXS and SAXS profiles for the P(3HB-*co*-11mol%-3HH). The profiles in (a, b) and (c,d) correspond to $I_{\parallel}(q)$ and $I_{\perp}(q)$, respectively.

The change in μ dependence of the $\langle d \rangle / \langle d \rangle_0$ with strain and the ε dependences of orientation factors and crystallinity for the copolymer were calculated, as shown in Figures 4.10, 4.11, and 4.12, respectively. The changes in the parameters with strain reveal that the changes in the hierarchical structures with stretching are divided into region I ($0\% \leq \varepsilon \leq 6.73\%$ (the yield point)) and region II ($7.68\% \leq \varepsilon$).

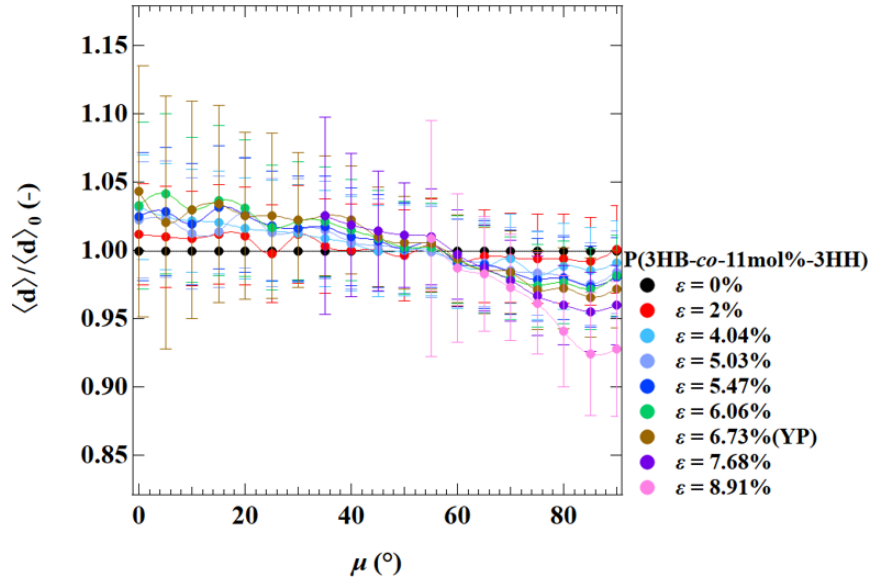


Figure 4.10. (a) μ dependence of the $\langle d \rangle / \langle d \rangle_0$ for the P(3HB-co-11mol%-3HH) with strain and (b) its error bars.

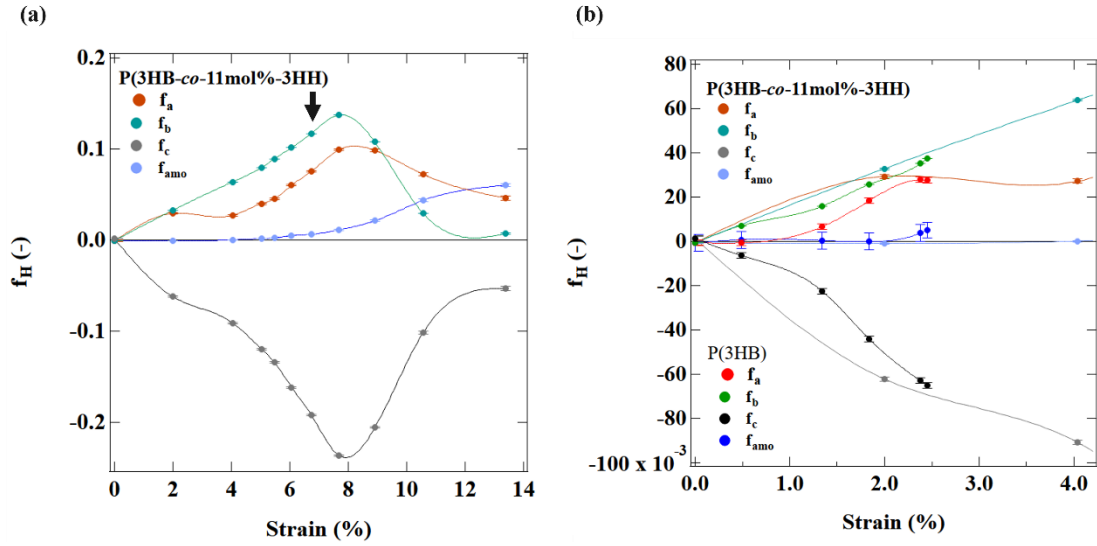


Figure 4.11. (a) Changes of f_H for the P(3HB-co-11mol%-3HH) with strain and (b) Comparison of f_H for the P(3HB) and the P(3HB-co-11mol%-3HH). Arrow in (a) indicates the yield point of the P(3HB-co-11mol%-3HH).

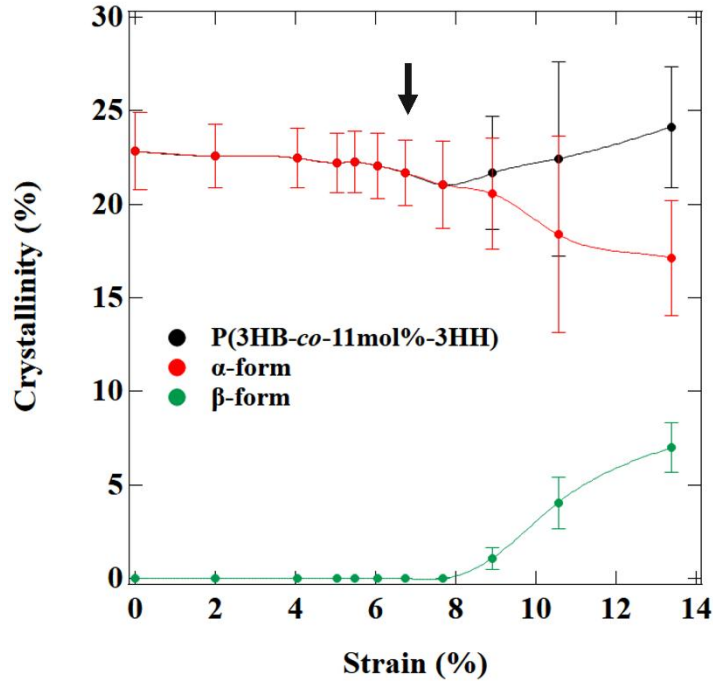


Figure 4.12. Crystallinity of the P(3HB-*co*-11mol%-3HH) at each ratio. The black plot shows the transition of crystallinity of the entire P(3HB-*co*-11mol%-3HH) with strain, the red of α -forms and the green of β -forms. Arrow indicates the yield point.

4.3.5. Hierarchical Structure in Each Region

In the following, the above observations were analysed to clarify the characteristics of the hierarchical structure in region I ($0\% \leq \varepsilon \leq 6.73\%$ (the yield point)) and region II ($7.68\% \leq \varepsilon$).

In Region I, Clear abnormal butterfly patterns for the copolymer were not observed in USAXS near the yield point, unlike the case of the homopolymer, as shown in Figure 4.8. The enhancement in $I_{\parallel}(q)$ was less than that of the homopolymer. This indicates that the reduction in the stability of the crystals by introducing the amorphous component monomer unit suppressed spatial heterogeneity of the stress field between fibrillar and non-fibrillar regions more than in the homopolymer, improving the deformation heterogeneity on the submicrometric scale.

As shown in Figure 4.8, the disappearance of the SAXS peaks along $\mu = 0^\circ$ was observed after $\varepsilon = 5.03\%$, indicating that the stacking of lamellae along the stretching direction was deformed by coarse slip, as seen in polyethylene.^{11, 15, 29}

According to the result from the correlation functions, the average of the d-spacing in the lamellar structures, $\langle d \rangle / \langle d \rangle_0$, at $\mu = 90^\circ$ decreased as the copolymer was elongated. In addition, $\langle d \rangle / \langle d \rangle_0$ at $\mu = 0^\circ$ increased from $\varepsilon = 0\%$ to $\varepsilon = 4.04\%$ but did not change much after $\varepsilon = 5.03\%$ from the value at $\varepsilon = 4.04\%$. This indicates that the copolymer elongated in the direction parallel to the stretching direction and contracted in the perpendicular direction in accordance with the stretching ratio until $\varepsilon = 4.04\%$. By contrast, after $\varepsilon = 5.03\%$, a slight coarse slip occurred in the stacked lamellae, resulting in little change in $\langle d \rangle / \langle d \rangle_0$ along the strain direction.

As shown in Figure 4.11b, the ε dependences of f_a , f_b , f_c , and f_{amo} for the copolymer were in good agreement with the f_H changes for the homopolymer up to rupture. This indicates that the introduction of P(3HH) does not affect the degree of orientation of the polymer chains and P(3HB) crystals under stretching. The effect of copolymerization is mainly in the suppression of crystallization and the dispersion of stress due to the hierarchical structure formed with the suppression. After $\varepsilon = 4.04\%$, the c -axis of the crystals was oriented even closer to perpendicular to the stretching direction, and the a -axis, b -axis, and amorphous polymer chains were oriented even closer to parallel, as shown in Figure 4.11a.

The change in the crystallinity of α -forms, as shown in Figure 4.12, was different after $\varepsilon = 6.73\%$, indicating that the rate of decrease in the crystallinity of α -forms became larger after $\varepsilon = 6.73\%$ and that mechanical melting occurs mainly after the yield point.

In region II, streak scattering perpendicular to the stretching direction was observed by USAXS and SAXS measurements, as shown in Figure 4.8. The appearance of streaks indicates that voids extended in the stretching direction were formed on length scales on the order of 10 nm to the submicrometric.

Regarding the Hermans orientation factor, the values of f_a , f_b , and f_c shifted closer to 0 under stretching, while the value of f_{amo} increased. After $\varepsilon = 8.91\%$, the crystals appeared to be randomly oriented, but this reflected the information from the crystals where mechanical melting had not occurred.

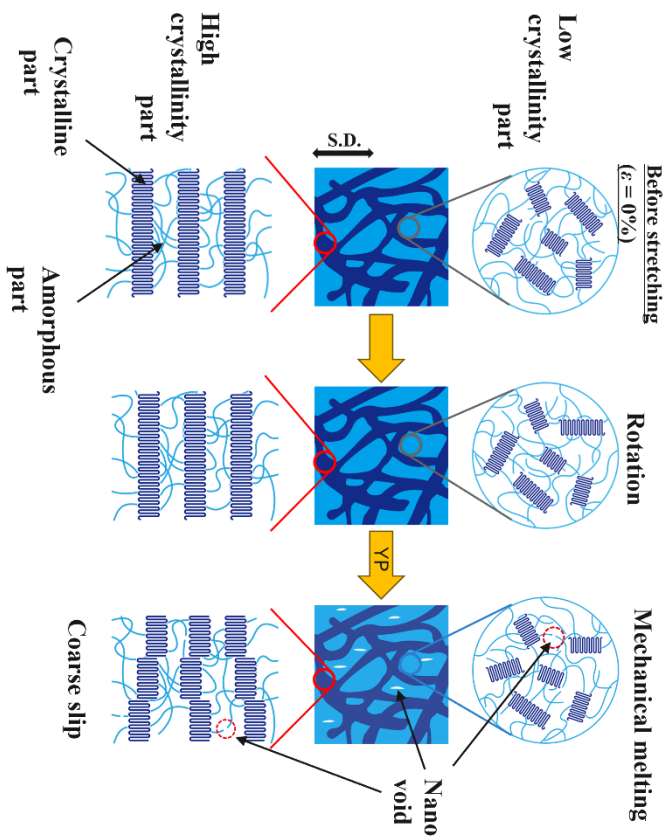
An extra diffraction peak from the β -form was observed in the direction perpendicular to the drawing direction after $\varepsilon = 8.91\%$, as shown in Figures 4.8t and 4.8u. Orts *et al.* observed the formation of the β -phase in WAXD patterns when they stretched non-oriented poly(3-hydroxybutyrate-co-3-hydroxyvalerate).² The β -form crystal is obtained by applying stress to some parts of the α -form lamellae and the amorphous components connected to these parts.^{2, 4, 5, 6, 30} Therefore, the WAXS results indicate that the molecular chains were pulled out from the (020) plane of the α -form crystals oriented along the stretching direction after $\varepsilon = 8.91\%$, and then the pulled chains transformed into the β -form.

4.3.6 Changes in the Hierarchical Structure and Difference between P(3HB) and P(3HB-co-11mol%-3HH) under stretching

Figure 4.13 shows illustrations of the changes in the hierarchical structure during stretching. P(3HB) consisted of thick crystals in lamellae and spherulite structures with high regularity, resulting in high crystallinity. In contrast, in P(3HB-co-11mol%-3HH), lamellae consisting of thin crystals were formed and the crystallinity was lower.

The strong inhomogeneity characterized by the abnormal butterfly patterns was observed in the homopolymer near the yield point, and it ruptured soon after the creation of nanovoids. On the other hand, the copolymer continued to deform beyond the elongation at which the homopolymer broke. This difference is attributed to the stability of crystal structures under strain relevant to the long-range order. The spatial heterogeneity of the stress field was lower in the copolymer, and inhomogeneous deformation was less likely to occur. The reason for the significant improvement in the ductility of the copolymer is mainly the dispersion of stress due to the introduction of P(3HH).

(a) P(3HB)



(b) P(3HB-co-11 mol%-3HH)

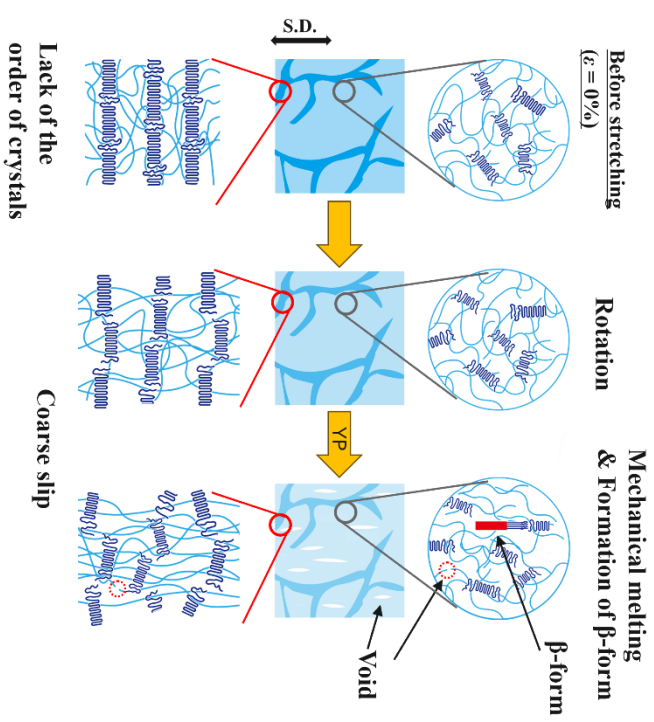


Figure 4.13. Schematic illustrations of the changes in the hierarchical structure of (a) P(3HB) and (b) P(3HB-co-11 mol%-3HH) during stretching

4.4 Conclusion

In this study, the structural changes of P(3HB) and P(3HB-*co*-11mol%-3HH) were investigated on various scales during uniaxial stretching by *in-situ* USAXS, SAXS, and WAXS. The P(3HB) homopolymer was highly crystallized and consisted of thick crystals with high regularity. The introduction of 3HH units suppressed crystallization and formed thinner crystals with reduced long-range order.

Abnormal butterfly patterns, which characterize the heterogeneity of deformation on the submicrometric scale, were weaker for the copolymer. This is due to the stress dispersion caused by the hierarchical structure formed with the suppression of crystallization. The mechanism of β -phase formation through mechanical melting while stretching unoriented P(3HB-*co*-11mol%-3HH) was also clarified. This study highlights that the effect of copolymerization is primarily the suppression of crystallization and the associated stress dispersion.

References

- 1 Anderson, A. J.; Dawes, E. A. *Microbiol. Rev.* **1990**, *54*, 450–472.
- 2 Orts, W. J.; Marchessault, R. H.; Bluhm, T. L.; Hamer, G. K. *Macromolecules* **1990**, *23*, 5368–5370.
- 3 Sudesh, K.; Abe, H.; Doi, Y. *Prog. Polym. Sci.* **2000**, *25*, 1503–1555.
- 4 Iwata, T. *Macromol. Biosci.* **2005**, *5*, 689–701.
- 5 Iwata, T.; Fujita, M.; Aoyagi, Y.; Doi, Y.; Fujisawa, T. *Biomacromolecules* **2005**, *6*, 1803–1809.
- 6 Kabe, T.; Tanaka, T.; Marubayashi, H.; Hikima, T.; Takata, M.; Iwata, T. *Polymer* **2006**, *93*, 181–188.
- 7 de Koning, G. J. M.; Lemstra, P. J. *Polymer* **1992**, *33*, 3292–3294.
- 8 de Koning, G. J. M.; Lemstra, P. J. *Polymer* **1993**, *34*, 4089–4094.
- 9 Biddlestone, F.; Harris, A.; Hay, J. N.; Hammond, T. *Polym. Int.* **1996**, *39*, 221–229.
- 10 Liebergesell, M.; Mayer, F.; Steinbüchel, A. *Appl. Microbiol. Biotechnol.* **1993**, *40*, 292–300.
- 11 Butler, M. F.; Donald, A. M.; Ryan, A. J. *Polymer* **1997**, *38*, 5521–5538.
- 12 Sakurai, T.; Nozue, Y.; Kasahara, T.; Mizunuma, K.; Yamaguchi, N.; Tashiro, K.; Amemiya, Y., *Polymer* **2005**, *46*, 8846–8858.
- 13 Guo, H.; Wang, J.; Zhou, C.; Zhang, W.; Wang, Z.; Xu, B.; Li, J.; Shang, Y.; Christiansen, J. C.; Yu, D.; Wu, Z.; Jiang, S. *Polymer* **2015**, *70*, 109–117.

- 14 Takenaka, M.; Shimizu, H.; Nishitsuji, S. *Phys. Rev. E* **2007**, *75*, 061802.
- 15 Kishimoto, M.; Mita, K.; Ogawa, H.; Takenaka, M. *Macromolecules* **2020**, *53*, 9097–9107.
- 16 Bastide, J.; Leibler, L.; Prost, J. *Macromolecules* **1990**, *23*, 1821–1825.
- 17 Karino, T.; Okumura, Y.; Zhao, C.; Kataoka, T.; Ito, K.; Shibayama, M. *Macromolecules* **2005**, *38*, 6161– 6167.
- 18 Hayes, C.; Bokobza, L.; Boué, F.; Mendes, E.; Monnerie, L. *Macromolecules* **1996**, *29*, 5036– 5041.
- 19 Doi, M.; Onuki, A. *J. Phys. II* **1992**, *2*, 1631–1656.
- 20 Furukawa, A.; Tanaka, H. *Nat. Mater.* **2009**, *8*, 601–609.
- 21 Kurotani, Y.; Tanaka, H. *Commun. Mat.* **2022**, *3* (67), 1–11.
- 22 Masunaga, H.; Ogawa, H.; Takano, T.; Sasaki, S.; Goto, S.; Tanaka, T.; Seike, T.; Takahashi, S.; Takeshita, K.; Nariyama, N.; Ohashi, H.; Ohata, T.; Furukawa, Y.; Matsushita, T.; Ishizawa, Y.; Yagi, N.; Takata, M.; Kitamura, H.; Sakurai, K.; Tashiro, K.; Takahara, A.; Amamiya, Y.; Horie, K.; Takenaka, M.; Kanaya, T.; Jinnai, H.; Okuda, H.; Akiba, I.; Takahashi, I.; Yamamoto, K.; Hikosaka, M.; Sakurai, S.; Shinohara, Y.; Okada, A.; Sugihara, Y. *Polym. J.* **2011**, *43*, 471–477.
- 23 Doi, Y.; Kitamura, S.; Abe, H. *Macromolecules* **1995**, *28*, 4822– 4828.
- 24 Strobl, G. R.; Schneider, M. *J. Polym. Sci., Polym. Phys.* **1980**, *18*, 1343–1359.
- 25 Strobl, G. R.; Schneider, M. J.; Voigtmartin, I. G. *J. Polym. Sci., Polym. Phys.* **1980**, *18*, 1361–1381.

- 26 Hashimoto, T., *Principles and Applications of X-ray, Light and Neutron Scattering*; Springer Nature Singapore Pte Ltd.: Singapore, 2022.
- 27 Wilchinsky, Z. W. *J. Appl. Phys.* **1959**, *30*, 792.
- 28 Wilchinsky, Z. W. *J. Appl. Phys.* **1960**, *31*, 1969–1972.
- 29 Gerasimov, V. I.; Genin, Y. V.; Tsvankin, D. Y. *J. Polym. Sci., Polym. Phys. Ed.* **1974**, *12*, 2035–2046.
- 30 Phongtamrug, S.; Tashiro, K. *Macromolecules* **2019**, *52*, 2995–3009.

Chapter 5

Enhancement of the Density Fluctuations of Polyamide-6 with Strain below Glass Transition Temperature

5.1 Introduction

Polyamide 6 (PA6) is one of the most widely utilized engineering thermoplastics due to its excellent mechanical properties, such as high tensile strength and toughness, as well as its superior resistance to wear and chemicals. Consequently, it finds extensive applications in various industrial fields, including automotive components, electrical infrastructure components, and packaging films.¹ The polymorphism of PA6, generally consisting of α and γ forms, is governed by crystallization conditions, particularly the crystallization temperature (T_c) and thermomechanical history.²⁻⁵ The difference between α -forms and γ -forms lies in the chain conformation and the mode of interchain hydrogen bonds.

The α -crystal is the thermodynamically stable phase consisting of fully extended polymer chains in a planar zigzag conformation.⁶⁻⁸ In this structure, hydrogen bonds are formed between the N-H and C=O groups of adjacent antiparallel chains. The α -form is characterized by a monoclinic unit cell with parameters, $a = 0.956$ nm, b (chain axis) = 1.724 nm, $c = 0.801$ nm, and $\beta = 67.5^\circ$.⁶ On the other hand, the γ -crystal that typically forms during rapid cooling is a metastable phase compared to α -crystal. It is

characterized by a twisted chain conformation where hydrogen bonds are composed between adjacent parallel chains. Similar to the α -form, the γ -form is monoclinic but possesses different unit cell parameters, $a = 0.933$ nm, b (chain axis) = 1.688 nm, $c = 0.478$ nm, and $\beta = 121^\circ$.⁸

The α -, γ -crystals and amorphous phase form lamellar structures with alternating layers of crystalline and amorphous phase.⁹ Crystalline polymer generally consists of spherulites filled with branching structures which are formed by the growth of lamellae. Previous studies have investigated the structures of compression-molded PA6, composites containing fillers such as clay,^{10, 11} and fibers.^{12, 13} In particular, wide-angle X-ray scattering (WAXS) and small-angle X-ray scattering (SAXS) have been extensively utilized to examine the temperature dependence of crystallization and phase transitions,^{4, 7, 8, 14} as well as the structural evolution during stretching,^{13, 15–18} focusing on the crystal lattice and lamellar scales. A crystal-crystal transformation from the α -phase to γ -phase and a twinning mechanism of α -crystals have been reported as the strain-induced structural changes in PA6.^{17, 18} While SAXS and WAXS techniques have successfully elucidated these changes at the crystal lattices and lamellar structures, the structural development on the fibril scales during deformation remains less understood.

In recent years, ultra-small-angle X-ray scattering (USAXS) has developed as a powerful tool to bridge this gap, investigation of hierarchical structure up to the submicrometric scales. In the undeformed state of crystalline polymers such as polyethylene (PE)¹⁹ and poly(3-hydroxybutyrate) (P(3HB)),²⁰ USAXS measurements provide insights into the density fluctuations or spatial inhomogeneity of crystallinity corresponding to fibrils and inter-fibrillar regions within the spherulite. From this scattering behavior, the mass-fractal dimension can be evaluated to determine the

degree of fibril filling within the spherulites.

Furthermore, during the tensile deformation of these polymers, several studies have reported the observation of an “abnormal” butterfly pattern, characterized by an increase in scattered intensity in the direction parallel to the stretching direction.^{19, 21-24} This pattern has been observed in swollen gel under elongation using small-angle neutron scattering²⁵ and the rubber filled with inorganic particles under uniaxial stretching using USAXS,^{26, 27} as well as in dilute polystyrene solutions and mixtures of two oligomers under shear using light scattering.²⁷ The butterfly pattern reflects strain-induced density or concentration fluctuations arising from spatial inhomogeneities in deformation due to mechanical heterogeneity. Simulation calculations have demonstrated that a scattered butterfly pattern, reflecting the non-uniform deformation of a swelling gel under uniaxial stretching, is observed.^{28, 29} In addition, theoretical studies have proven that the enhancement of density fluctuations under shear originates from stress gradients caused by the spatial inhomogeneity of mechanical properties coupled with the density field.³¹⁻³³

The butterfly patterns observed in stretched PE and P(3HB) also reflect an enhancement in density fluctuations on the sub-micron scales. This indicates that the material undergoes heterogeneous deformation involving spatial inhomogeneity of crystallinity, arising from the variation in deformability between fibrils and inter-fibrillar regions. Notably, these phenomena were observed during stretching at temperatures above their glass transition temperature (T_g), where the amorphous chains possess sufficient mobility.

However, it remains unclear whether similar strain-induced density fluctuations occur in polymers deformed below their T_g , where the amorphous chains are in a glassy

state. PA6, with a T_g typically around 50 °C,⁹ serves as an ideal model system to investigate this behavior at room temperature. Although the crystal-crystal transitions in PA6 below T_g have been discussed, the correlation between these crystalline changes and larger-scale density fluctuations has not been explored.

In this study, I investigated the hierarchical structural evolution of PA6 during uniaxial stretching at room temperature (below T_g) using *in-situ* USAXS, SAXS, and WAXS measurements. This setup allowed me to monitor the deformation mechanisms across scales ranging from several nanometers to the sub-micron level. I report, for the first time in PA6, the observation of abnormal butterfly patterns in the USAXS region during deformation below T_g . This finding suggests that stretch-induced density fluctuations and heterogeneous deformation mechanisms are significant even in the glassy state, providing new insights into the yielding and plastic deformation behavior of crystalline polymers.

5.2 Experimental Section

5.2.1 Sample Preparation

Sheets were prepared from PA6(Sigma-Aldrich, 1.084 g/mL at 25 °C) using two press machines (a custom-made model and IMC-180C, Imoto Machinery Co., Ltd.) in the following steps. Firstly, I dried PA6 pellets in a vacuum oven at 80 °C for 12 h. Secondly, one press machine was set to 260 °C, above the melting point of the PA6, and we pressurized the PA6 pellets in a 2 mm thick mold for 15 minutes to melt them. The melt was then immediately transferred to the other press machine and quenched to produce a 2 mm-thick press sheet. The press sheets were crystallized at 100 °C and

180 °C, respectively. Finally, dumbbell specimens with a center width of 2 mm were punched from each sheet.

5.2.2 *In-Situ* X-ray Scattering Measurements

In-situ X-ray scattering measurements were performed while stretching dumbbell specimens at 1 mm/min at room temperature below the glass transition temperature of PA6 by a custom-made tensile testing machine designed to measure the strain-stress (S–S) curves and X-ray scattering simultaneously. I confirmed that the X-ray beam always irradiated the center of the specimens under uniaxial stretching with a camera. The time-resolved SAXS/WAXS and USAXS experiments were performed in the second hutch of beamline BL03XU at SPring-8, Hyogo, Japan.³⁴

The SAXS and WAXS measurements were performed simultaneously with the WAXS detector tilted to avoid interference with the SAXS detector. The beam size at the sample position was 300 μm (horizontal) $\times$ 300 μm (vertical) in all X-ray scattering measurements. The camera length, exposure time, and detectors were set to 2.34 m/102 mm, 800 ms/800 ms, and PILATUS-1M (Dectris Ltd.)/ SOPHIAS (Rigaku Corp.) for SAXS/WAXS, respectively. For USAXS, the camera length, exposure time, and detectors were set to 7.88 m, 400 ms, and PILATUS-1M, respectively. The incident wavelengths for SAXS/WAXS and USAXS were 1.0 Å and 2.0 Å, respectively. Besides, a 40 μm thick Mo plate was used in the SAXS/WAXS, and a 100 μm thick Al plate was used in the USAXS. For the data analysis, I corrected the 2D scattering intensities for air and background scattering and then I divided the intensities by the thickness of the specimens. The thickness during stretching was calculated based on the thickness before stretching and the Lambert–Beer’s law.

5.2.3 Differential Scanning Calorimetry (DSC) measurements

Thermal analysis was performed on a DSC (PerkinElmer, Inc) calibrated with indium. The about 20 mg samples were scanned at a heating rate of 10 °C/min. The crystallinity of each sample was calculated from the enthalpy of the melting endotherm using the melting enthalpy of 100% crystallized PA6 $\Delta H_m^0 = 230$ J/g whatever the crystalline form.^{18, 35} Before the thermal characterizations, all samples were dried at room temperature under vacuum for a day.

5.3 Results and Discussion

5.3.1 S-S Curves

Figure 5.1 shows the S–S curves obtained during the USAXS measurements. The stress is the engineering stress. Overall stress was higher for PA6 at $T_c = 180$ °C than that at $T_c = 100$ °C during the stretching process to rupture. In specimen at each T_c , I observed two YPs. The 1YP and 2YP for PA6 at $T_c = 180$ °C are $\varepsilon = 4.23\%$ and $\varepsilon = 8.74\%$, respectively, while those for PA6 at $T_c = 100$ °C are $\varepsilon = 4.48\%$ and $\varepsilon = 8.69\%$, respectively. As shown in Figure 5.1, the break strain of PA6 at $T_c = 100$ °C was slightly smaller than that of PA6 at $T_c = 180$ °C.

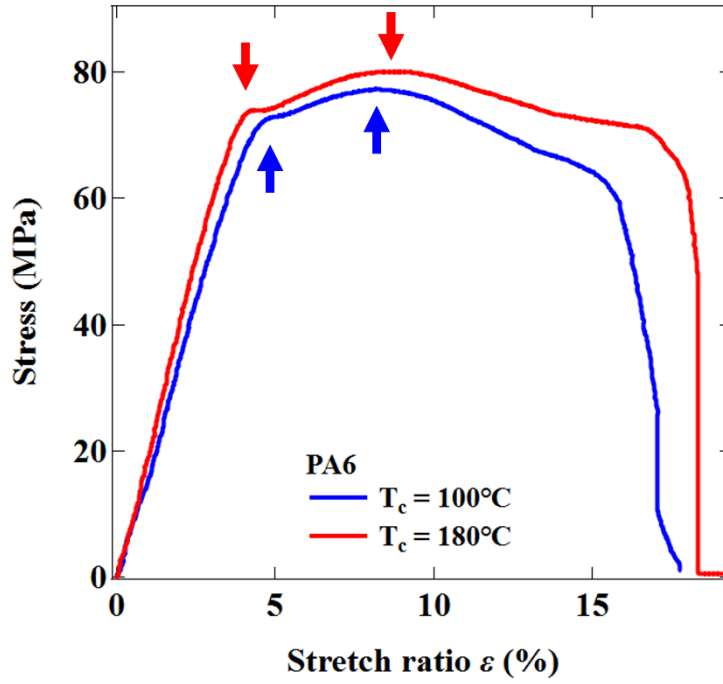


Figure 5.1. S–S curves of the PA6 at $T_c = 100^\circ\text{C}$ and $T_c = 180^\circ\text{C}$. The arrows indicate the YPs.

5.3.2 Analysis of Hierarchical Structures before Strain

Scattering 1D profiles, $I(q)$, were obtained by averaging the 2D patterns circularly. Figure 5.2a shows the combined USAXS and SAXS profiles and Figure 5.2a shows WAXS profiles for both specimens before stretching. Here, q is the magnitude of the scattering vector, q , defined as $q = (4\pi/\lambda)\sin(\theta/2)$, where λ and θ are the wavelength of the incident X-rays and the scattering angles, respectively. Besides, the WAXS profiles in this study were derived by subtracting the baseline intensity from the measured intensity profiles.

The 2D USAXS and SAXS patterns before stretching ($\varepsilon = 0\%$) for PA6 at $T_c = 180^\circ\text{C}$ (Figure 5.6 a,i, respectively) and $T_c = 100^\circ\text{C}$ (Figure 5.13 a, i, respectively) were isotropic. Figure 5.6q and 5.13q show the 2D WAXS patterns for PA6 at $T_c = 180^\circ\text{C}$ and $T_c = 100^\circ\text{C}$, respectively. The 2D WAXS pattern for PA6 at $T_c = 180^\circ\text{C}$ was

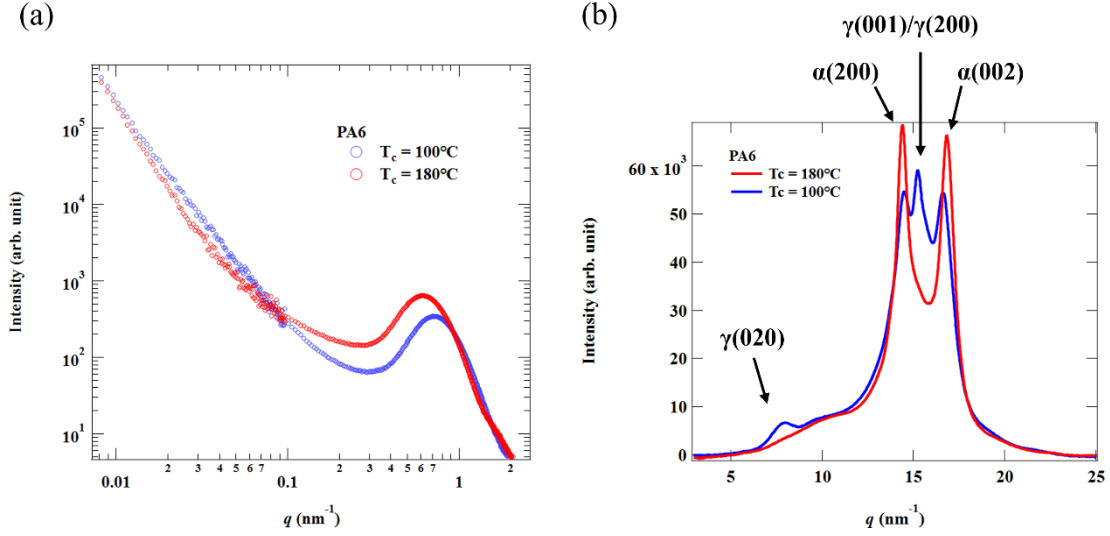


Figure 5.2. (a) Combined USAXS/SAXS profiles and (b) WAXS profiles of the PA6 at $T_c = 100^\circ\text{C}$ and $T_c = 180^\circ\text{C}$ before stretching ($\varepsilon = 0\%$).

also isotropic, but that for PA6 at $T_c = 100^\circ\text{C}$ was marginally anisotropic, indicating that the orientation of the structure on the $\text{\AA}$ scales was slightly induced in the preparation processes.

The images of PA6 spherulites observed by polarized light microscopy are shown in Figure 5.3. The radius of the spherulite was about $120 \mu\text{m}$ and $100 \mu\text{m}$ for $T_c = 180^\circ\text{C}$ and $T_c = 100^\circ\text{C}$, respectively. The difference between the polarized light microscopic images of Figure 5.3a and b is the irregular extinction regions that radiate from the center. There are more irregular extinction regions at $T_c = 100^\circ\text{C}$ than those at $T_c = 180^\circ\text{C}$, indicating more branching of the fibrils at $T_c = 100^\circ\text{C}$.

The power-law exponents of the 1D profiles for both specimens are between -3 and -4 in the region of $q < 0.02 \text{ nm}^{-1}$, indicating the surface fractal dimension.^{19, 36} Based on the spherulite size, it is indicated that the surface fractal dimensions at $q < 0.02 \text{ nm}^{-1}$ originate from the interfaces between the spherulites. To analyze the hierarchical structure, I derived the characteristic parameters from the following

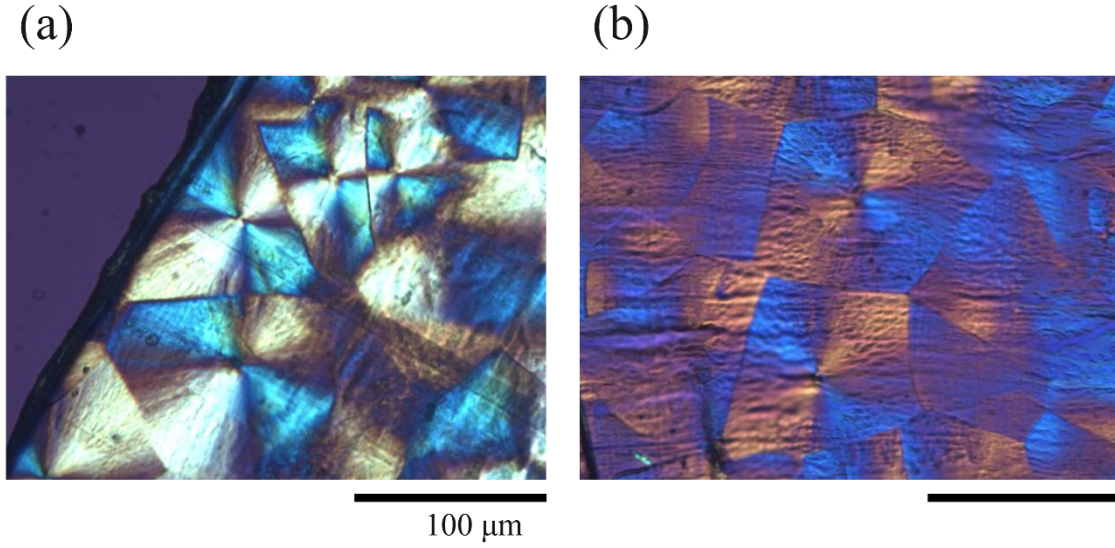


Figure 5.3. The spherulites observed by polarized light microscopy for PA6 at (a) $T_c = 100\text{ }^{\circ}\text{C}$ and (b) $T_c = 180\text{ }^{\circ}\text{C}$.

theoretical scattering curve equation. This theoretical equation is based on the unified Guinier/power-law approach,³⁷ with the addition of a Gauss function (a peak position q_m , a value associated with peak width σ) representing the peak derived from the lamellar structures at approximately $q = 0.6\text{ nm}^{-1}$.

$$\begin{aligned}
 I_{theor}(q) = & \underbrace{G_1 \exp\left(-\frac{q^2 R_{g3}^2}{3}\right)}_{(1)} q^{-p_4} + \underbrace{G_2 \exp\left(-\frac{q^2 R_{g3}^2}{3}\right)}_{(2)} \\
 & + \underbrace{B_3 \left[\text{Erf}\left(\frac{q R_{g3}}{\sqrt{6}}\right)\right]^{3p_3} q^{-p_3} \exp\left(-\frac{q^2 R_{g2}^2}{3}\right)}_{(3)} + \underbrace{G_4 \exp\left(-\frac{q^2 R_{g2}^2}{3}\right)}_{(4)} \\
 & + \underbrace{B_5 \left[\text{Erf}\left(\frac{q R_{g2}}{\sqrt{6}}\right)\right]^{3p_2} q^{-p_2} \exp\left(-\frac{q^2 R_{g1}^2}{3}\right)}_{(5)} + \underbrace{G_6 \exp\left(-\frac{q^2 R_{g1}^2}{3}\right)}_{(6)} \\
 & + \underbrace{B_7 \left[\text{Erf}\left(\frac{q R_{g1}}{\sqrt{6}}\right)\right]^{3p_1} q^{-p_1}}_{(7)} + \underbrace{A \exp\left(-\frac{(\log(q) - \log(q_m))^2}{\sigma^2}\right)}_{(8)} \quad (5.1)
 \end{aligned}$$

$$\text{Erf}(x) = \int_0^x \exp(-t^2) dt \quad (5.2)$$

Here, $G_1, G_2, B_3, G_4, B_5, G_6, B_7$ and A are constant of proportionality and the number (1) to (7) assigned for the seven elemental scattering functions in Equation (5.1) correspond to the solid or broken line in Figure 5.4a and b. Besides, $q_3 = R_{g3}^{-1}$, $q_2 = R_{g2}^{-1}$, and $q_1 = R_{g1}^{-1}$ are wavenumbers characterizing the boundaries of each hierarchy, respectively, and p_4, p_3, p_2 , and p_1 are power-law exponents characterizing each hierarchy, respectively. Equation (5.1) contains information of the interfaces between the spherulites at $q > q_3$, fibrils at $q_3 > q > q_2$, shape of lamellae at $q_2 > q > q_1$ and surface of crystal lamella at $q_3 > q$, respectively. In the region of $q_2 > q$, I performed the analysis by fixing $p_2 = 2$ and $p_1 = 4$, the Porod's law based on the shape and surface of the lamella. The obtained parameters are listed in Table 5.1.

The theoretical elemental scattering function (2), (4) and (6) follow the Guinier law and R_{g3}, R_{g2} and R_{g1} are the radius gyrations corresponding to each hierarchical structure. On the assumption that the shape of fibrils is a long cylinder, $R_{g3}^2 = \left(\frac{R^2}{2} + \frac{H^2}{3}\right)$, $R_{g2}^2 = \frac{R^2}{2}$ where R and H are the radius and half height of a long cylinder.³⁶ Therefore, the radius and height of fibrils are estimated to be 17.0 nm and 408 nm at $T_c = 180^\circ\text{C}$ and 14.0 nm and 333 nm at $T_c = 100^\circ\text{C}$. In the region of $q_3 > q > q_2$, the power-law behavior at $T_c = 180^\circ\text{C}$ and $T_c = 100^\circ\text{C}$ expressed by $I(q) \sim q^{-2.29}$ and $I(q) \sim q^{-2.83}$, respectively. Those power-law exponents are the mass-fractal dimensions originating from fibril structures.

Table 5.1. Characteristic Parameters obtained from the unified

Guinier/power-law approach

T_c (°C)	p_4 (-)	p_3 (-)	R_{g3} (nm)	R_{g2} (nm)	R_{g1} (nm)	q_m (nm ⁻¹)
180	3.53	2.29	118.5	12.0	2.52	0.616
100	3.21	2.83	96.7	9.89	1.97	0.719

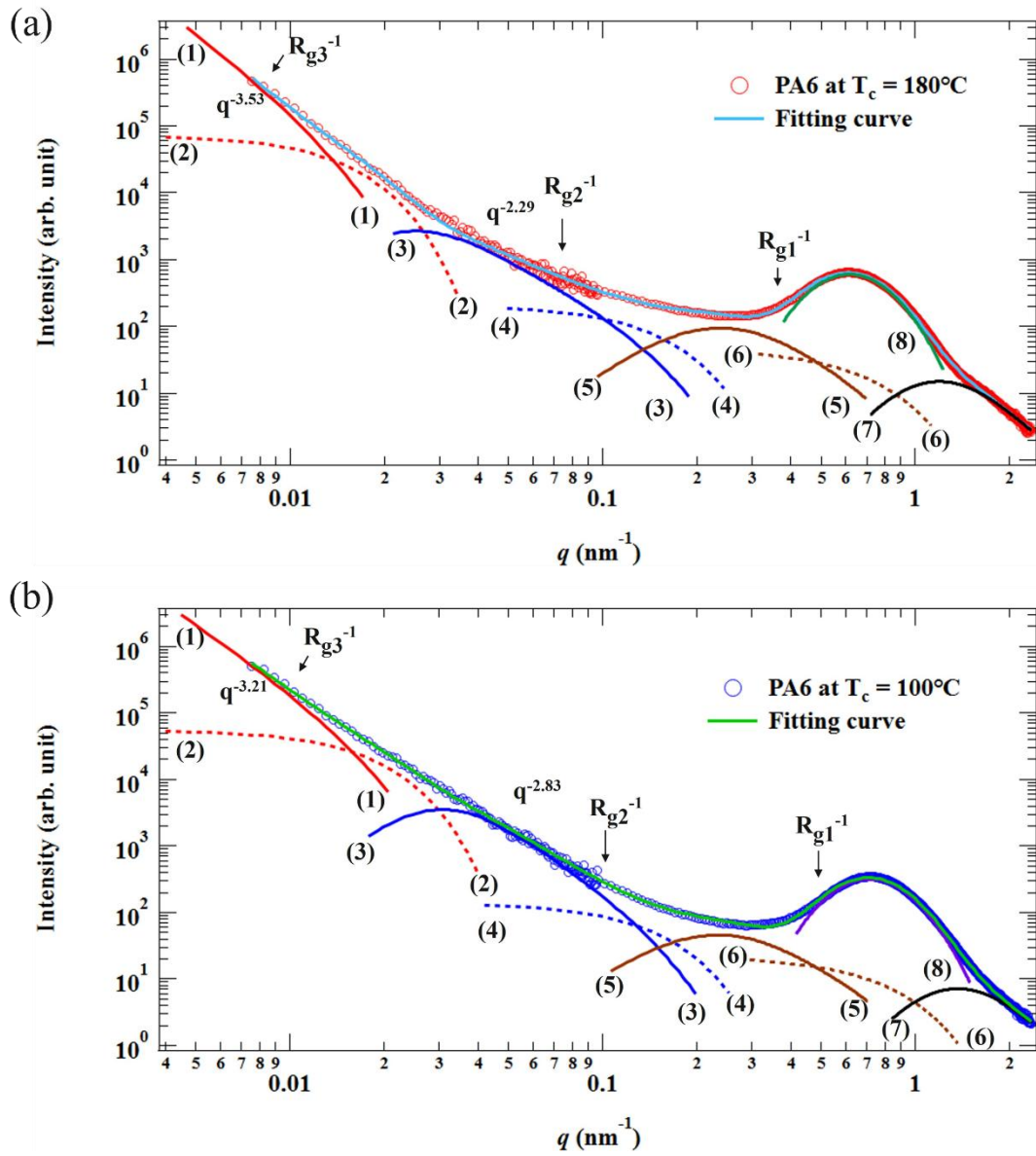


Figure 5.4. Combined USAXS/SAXS profiles of the PA6 at (a) $T_c = 180^\circ\text{C}$ and (b) $T_c = 100^\circ\text{C}$ before stretching ($\varepsilon = 0\%$).

To estimate the long period (l_p), crystal thickness (l_c) and amorphous thickness (l_a) of lamellae, one dimensional correlation functions $K(z)$ were calculated from the scattering profiles for both specimens.^{38, 39}

$$K(z) = \frac{\int_{0.065 \text{ nm}^{-1}}^{2.00 \text{ nm}^{-1}} q^2 I(q) \cos qz \, dq}{\int_{0.065 \text{ nm}^{-1}}^{1.50 \text{ nm}^{-1}} q^2 I(q) \, dq} \quad (5.3)$$

The characteristic parameters estimated from one dimensional correlation functions are listed in Table 5.2. According to Babinet reciprocity theorem, it is not easy to determine which characteristic parameter derived from the linear part at about $z = 0$ in the $K(z)$ corresponds to l_a or l_c . Although the DSC results showed the crystallinity at $T_c = 180^\circ\text{C}$ and $T_c = 100^\circ\text{C}$ were 45.23% and 46.06%, respectively, in this study, l_a and l_c were determined so that the linear crystallinity was higher than the crystallinity obtained from DSC because the crystallinity in the lamellar structures within fibrils should be higher than that of the entire sample.

Table 5.2. Characteristic parameters estimated from the one-dimensional correlation functions

T_c ($^\circ\text{C}$)	l_p (nm)	l_a (nm)	l_c (nm)
180	8.44	2.38	6.06
100	7.33	2.18	5.15

Finally, I confirmed the crystallinity of each sample by fitting the WAXS 1D profile with Gaussian functions to separate crystalline peaks and amorphous halo. The peak separation results are shown in Figure 5.5a and b, respectively. As shown in Figure 5.5b, the peaks originating from the γ -form crystal appeared only in the WAXS profile of PA6 at $T_c = 100^\circ\text{C}$. In the profile for both specimens, I found the gentle peak at

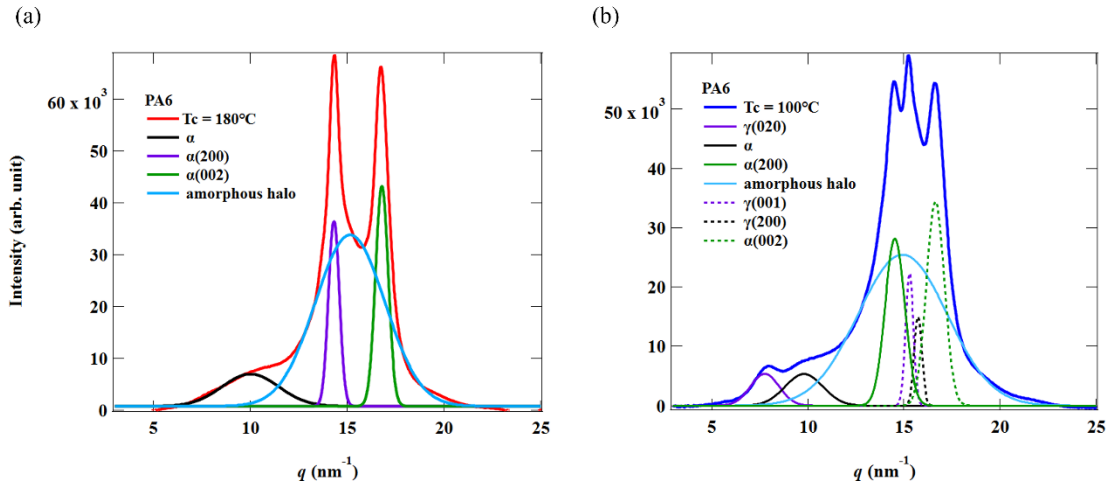


Figure 5.5. 1D WAXS profile with crystalline peaks and amorphous halo at (a) $T_c = 180\text{ }^{\circ}\text{C}$ and (b) $T_c = 100\text{ }^{\circ}\text{C}$.

10 nm^{-1} . This peak is expected to be derived from the α -crystal since it also appeared in the WAXS profile of PA6 at $T_c = 180\text{ }^{\circ}\text{C}$. In this work, the peak at 10 nm^{-1} is assumed to be $\alpha(020)$. Based on the position and area of the separated peaks, the crystallinity at $T_c = 180\text{ }^{\circ}\text{C}$ and $T_c = 100\text{ }^{\circ}\text{C}$ were calculated to be 34.34% and 43.24%, respectively. Since the crystallinity estimated from WAXS was discrepant with the results obtained from DSC, it was multiplied by a factor to match the DSC results in subsequent analyses.

The DSC results showed that the crystallinity of both specimens were almost equivalent. However, their hierarchical structures were dramatically different, as the above multifaceted analysis revealed. In PA6 at $T_c = 180\text{ }^{\circ}\text{C}$, the spherulites with a radius of about $120\text{ }\mu\text{m}$ were formed. The mass fractal dimension, 2.29, of the fibrils is consistent with the scarcity of irregular extinction regions along the radial direction in the polarized light microscope image, indicating a low branching frequency of fibrils filled within the spherulite, in other words, wide non-fibrillar regions between the fibrils. Due to the high crystallization temperature, thick and long fibrils and lamellae with large l_p and l_c , consisting only of stable α -crystals, were formed compared to PA6

at $T_c = 100\text{ }^{\circ}\text{C}$. In contrast, the spherulite size at $T_c = 100\text{ }^{\circ}\text{C}$ was relatively small, about $100\text{ }\mu\text{m}$, because the nucleation frequency was higher compared to PA6 at $T_c = 180\text{ }^{\circ}\text{C}$. This accelerated nucleation is associated with an increased branching frequency of fibrils, which is reflected in the high mass fractal dimension, 2.83. This high dimensionality indicates that the spherulites are densely filled with branched fibrillar networks. This dense packing and high branching frequency lead to fluctuations in orientation of fibrils, which appears as the irregular extinction regions observed by the polarized light microscope. Furthermore, thinner fibrils and lamellae with smaller l_p and l_c , composed of a mixture of α - and unstable γ -crystals, were formed.

5.3.3 Case of PA6 at $T_c = 180\text{ }^{\circ}\text{C}$

In this chapter, I focus on the hierarchical structural developments during the stretching process of a specimen made at $T_c = 180\text{ }^{\circ}\text{C}$ and formed only of stable α -crystals. Figure 5.6 shows the changes in USAXS/SAXS/WAXS 2D patterns with strain. The stretching process can be divided into the following three regions according to the structural development events. The region before 1YP is described as Region I, the region from 1YP to 2YP as Region II, and the region after 2YP as Region III.

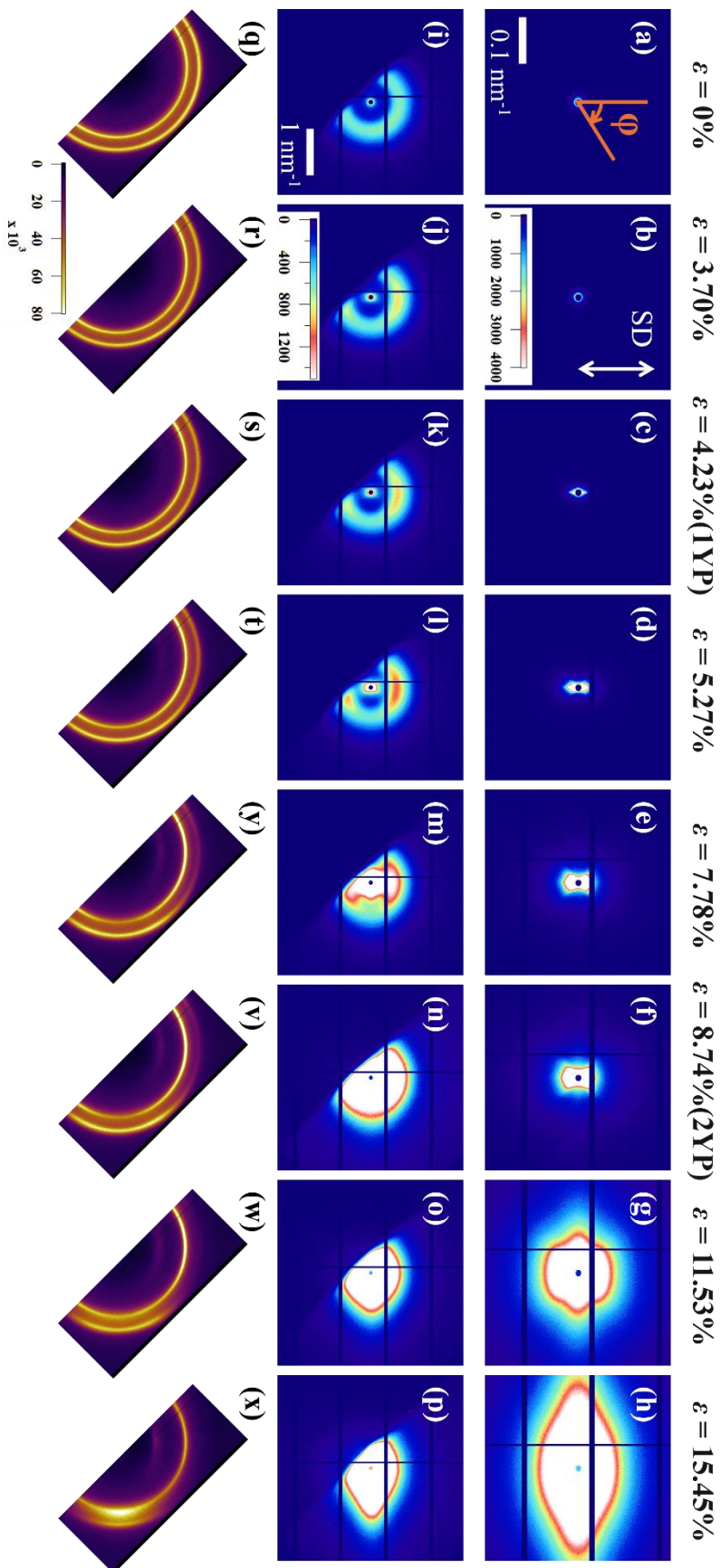


Figure 5.6. (a–h) USAXS, (i–p) SAXS, and (q–x) WAXS 2D patterns of the PA6 at $T_c = 180^\circ\text{C}$ with strain. The arrow in part (b) corresponds to the stretching direction.

5.3.3.1 USAXS and SAXS Analysis

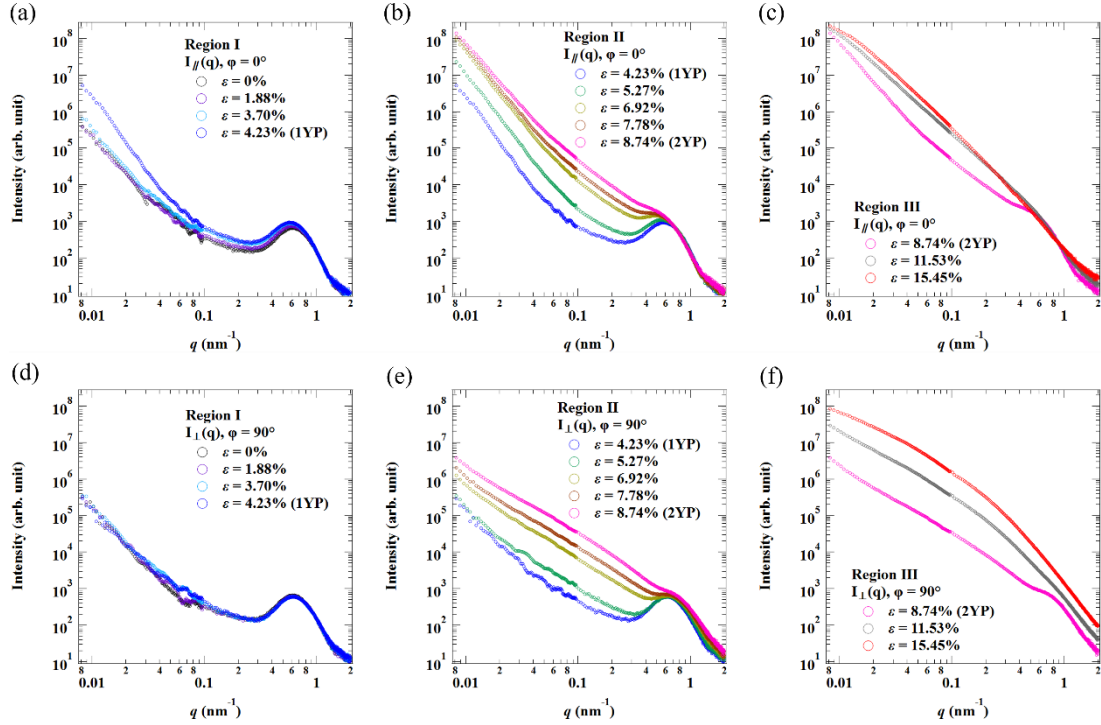


Figure 5.7. Combined USAXS and SAXS profiles at $T_c = 180^\circ\text{C}$ in (a, d) Region I, (b, e) Region II, (c, f) Region III. The profiles in (a–f) correspond to the scattering intensities meridional and equatorial directions, respectively.

Figure 5.7 shows the combined USAXS and SAXS 1D profiles along the directions parallel and perpendicular to the stretching axis. The meridional profiles $I_{\parallel}(q)$ were obtained from the USAXS and SAXS 2D patterns by averaging sectors within $\pm 2.5^\circ$ from the stretching direction ($\varphi = 0^\circ$), while the equatorial profiles $I_{\perp}(q)$ were obtained from $\varphi = 90^\circ$. The definition of the azimuthal angle φ is shown in Figure 5.6a.

Firstly, there were little changes in $I_{\parallel}(q)$ and $I_{\perp}(q)$ before $\varepsilon = 4.23\%$ in Region I, while the scattering intensity in $I_{\parallel}(q)$ for $\varepsilon = 4.23\%$ increased in the low q -region. The enhancement in $I_{\parallel}(q)$ at $\varepsilon = 4.23\%$ shows that abnormal butterfly patterns began to be observed by USAXS, indicating the internal structures began to deform homogeneously

under uniaxial stretching. These butterfly patterns are attributed to the mechanical heterogeneity between the high-crystallinity fibrils and the low-crystallinity inter-fibrillar regions. The patterns reflect stretch-induced density fluctuations originating from the spatial inhomogeneity of crystallinity, indicating a difference in deformability between the fibrillar and inter-fibrillar parts. In Region II, $I_{\parallel}(q)$ further increased and the peaks approximately at $q = 0.7 \text{ nm}^{-1}$ shifted toward the low q -region.

Simultaneously, $I_{\perp}(q)$ in $q < 0.3 \text{ nm}^{-1}$ also enhanced and the peaks of the long period for the lamellae shifted to the high q -region. The increase in $I_{\perp}(q)$ reflects the emerge of voids via cavitation, which is consistent with the streaks observed in USAXS and SAXS 2D patterns in the equatorial directions. Therefore, the butterfly patterns in Figure 5.7e and f are hexagonal-like, which is different from the patterns observed when polyethylene is stretched. Finally, as shown in Figures 5.6g, h, o and p, the scattering intensities in the low q -region were stronger and the peaks reflecting the long period of the layered structure disappeared. This suggests further formation of voids or expansion of void size in region III.

To investigate the behavior of the lamellar structure, correlation functions were calculated from the combined USAXS and SAXS profiles at each azimuthal angle in Regions I and II. After $\varepsilon = 6.92\%$, the fitted Debye-Bueche function was subtracted from the scattering profile in the small-angle region before obtaining the correlation functions to reduce the scattering intensity contribution of the butterfly pattern. Debye-Bueche function is defined as⁴⁰

$$I(q) = \frac{I(0)}{[1 + (q\xi)^2]^2} \quad (5.4)$$

where ξ and $I(0)$ are the correlation length of the inhomogeneous structure and $I(q)$ at $q = 0$, respectively.

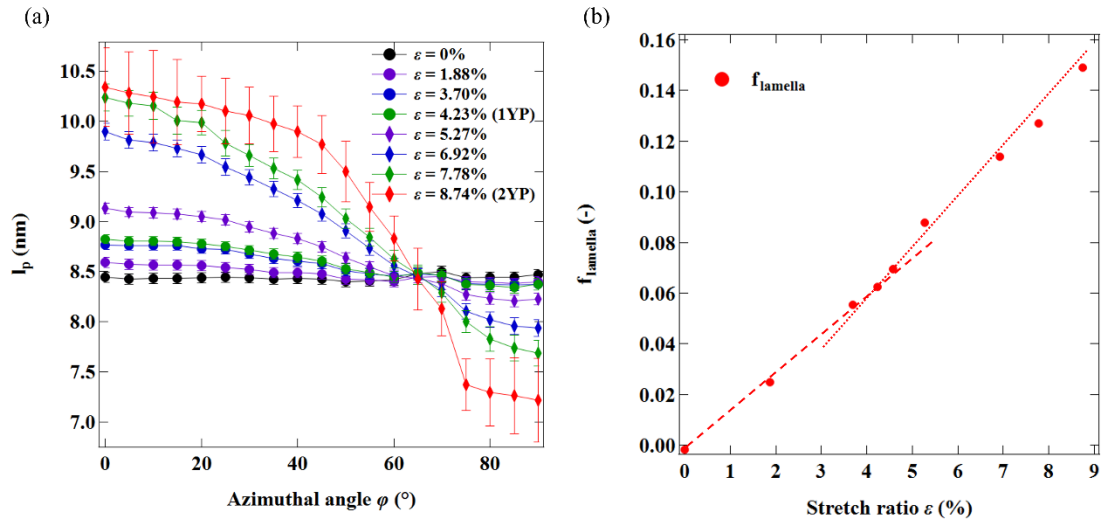


Figure 5.8. (a) Azimuthal dependence of l_p with strain and (b) stretch ratio dependence of $f_{lamella}$ for $T_c = 180$ °C.

Figure 5.8a shows the azimuthal profiles for l_p at different stretch ratios. The azimuthal dependence of l_p is consistent with the shift of the peak position corresponding to the long period of lamellae in Figure 5.7. Regarding the azimuthal dependence of l_p during the stretching process, l_p reached its maximum at $\varphi = 0^\circ$. This reflects the extension of the lamellar structure caused by interlamellar separation within fibrils oriented perpendicular to the stretching direction in the spherulitic structure. Conversely, l_p reached its minimum at $\varphi = 90^\circ$, which is attributed to the contraction perpendicular to the stretching direction resulting from the Poisson effect.^{41, 42} The rate of change in l_p increased after 1YP, showing that the internal structure was more easily deformed. It is worth noting that l_p for $\varepsilon = 8.74\%$ increased significantly at $\varphi = 35^\circ$. The elongation of lamellar structures at $\varphi = 35^\circ$ indicates the existence of shear band in PA6 under uniaxial stretching. The shear band is a narrow region where deformation at a specific angle occurs in a concentrated manner, as observed when polymers are

stretched below the glass transition temperature. The Hermans orientation factors of lamellar structures, $f_{H, \text{lamella}}$, were estimated from the intensity at $q=2\pi/l_p$, I_{lamella} , in SAXS 1D profiles according to following equations.^{36, 43, 44}

$$f_{H, \text{lamella}} = \frac{3\langle \cos^2 \varphi_{\text{lamella}} \rangle - 1}{2} \quad (5.5)$$

$$\langle \cos^2 \varphi_{\text{lamella}} \rangle = \frac{\int_0^{\pi/2} I_{\text{lamella}} \cos^2 \varphi \sin \varphi d\varphi}{\int_0^{\pi/2} I_{\text{lamella}} \sin \varphi d\varphi} \quad (5.6)$$

If the lamellar structures are perfectly oriented parallel to the stretching direction, Hermans orientation factor, $f_{H, \text{lamella}}$ is 1.0, whereas a perpendicular orientation results in $f_{H, \text{lamella}}$ of -0.5. For a random orientation of lamella, the value of $f_{H, \text{lamella}}$ is 0. Figure 5.8b shows the transition of f_{lamella} under stretching. Even in Region I, which is the initial stage of the stretching process, the lamellae are oriented along the direction of stretching, which corresponds to the deformation-induced changes in alignment of the fibrils extending radially from the center of spherulites. The rate of increase in f_{lamella} was slightly greater after 1 YP, in agreement with the tendency in l_p .

5.3.3.2 WAXS Analysis

Figure 5.9 shows WAXS 1D profiles at typical stretch ratios. The position of each peak showed a tendency to shift toward the low q -region in the meridional direction and toward the high q -region in the equatorial direction with stretching. To investigate the behavior of crystals, I fitted the WAXS 1D profile in each azimuthal direction at each stretch ratio with Gaussian functions to separate crystalline peaks and amorphous halo.

The azimuthal peak intensities with strain are shown in Figure 5.10. When polymeric materials are stretched, as shown in Figure 5.10a, the molecular chain axis of

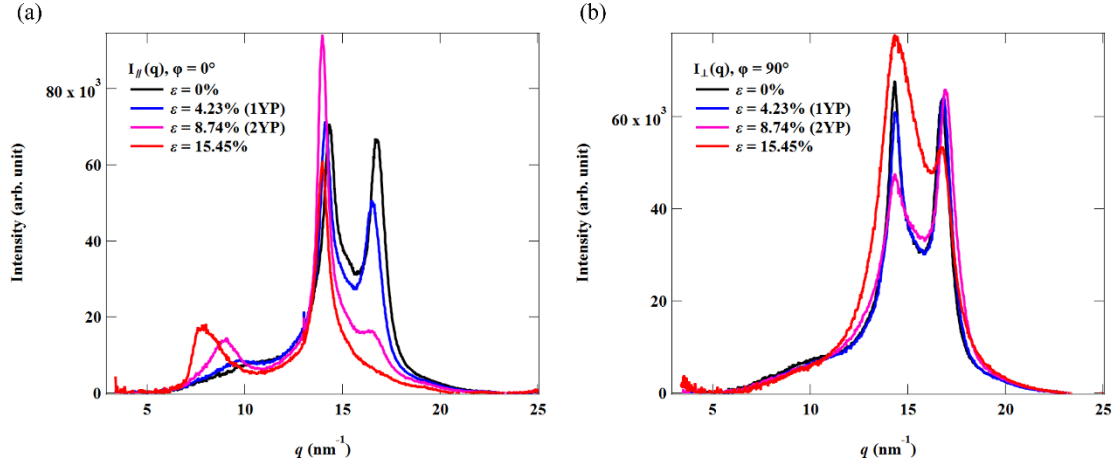


Figure 5.9. WAXS profiles at $T_c = 180\text{ }^{\circ}\text{C}$ correspond to the scattering intensities (a) meridional and (b) equatorial directions at typical stretch ratios.

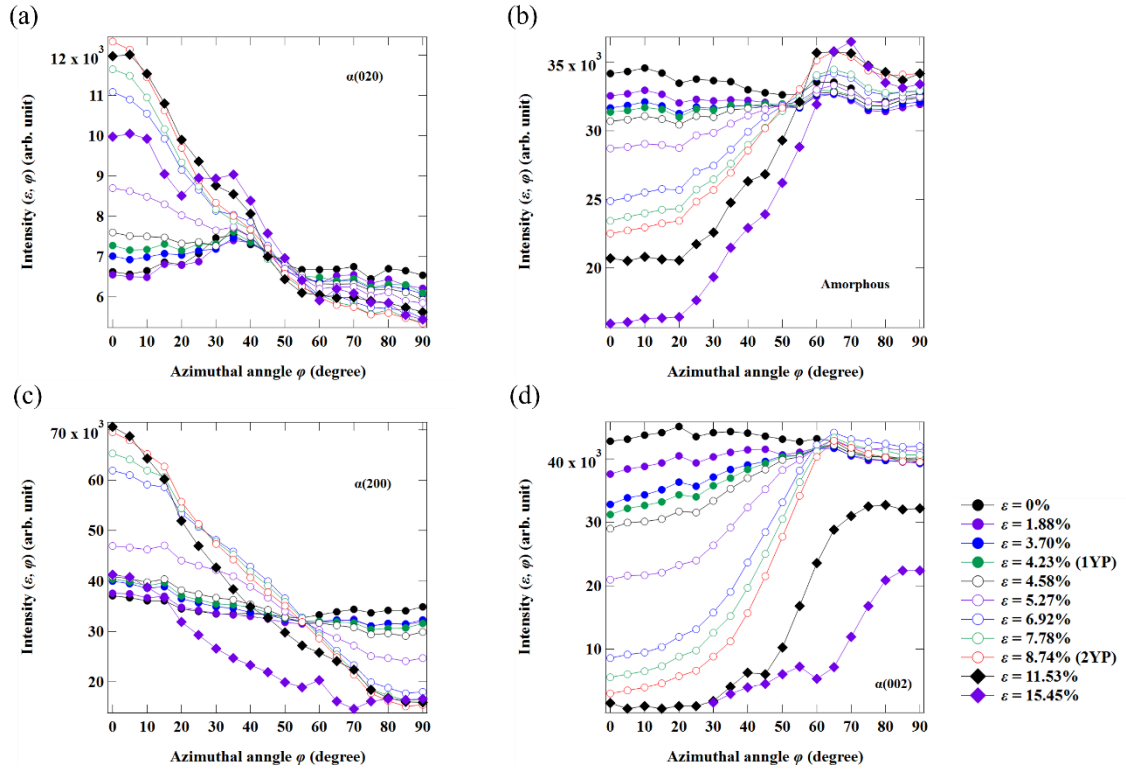


Figure 5.10. Azimuthal intensity at $T_c = 180\text{ }^{\circ}\text{C}$ of (a) $\alpha(020)$, (b) amorphous halo, (c) $\alpha(200)$ and (d) $\alpha(002)$.

the crystals is aligned in the stretching direction, therefore, the peak intensity of $\alpha(020)$ is maximum at $\varphi = 0^\circ$. In conjunction with this orientation, the intensity of the peaks reflecting the orientation of the other crystal axes is expected to reach a maximum at $\varphi = 90^\circ$. However, the azimuthal intensity of $\alpha(200)$ reached a maximum at $\varphi = 0^\circ$ with strain.

This tendency occurs at low strains in PA6, suggesting that a twinning mechanism has occurred in α -crystals.¹⁸ This mechanism leads to reorientations of the $\alpha(200)$ and $\alpha(002)$ planes with respect to the drawing axis. Therefore, the azimuthal intensities of $\alpha(200)$ and $\alpha(002)$ reflected not only pure crystal orientation but also reorientation by twinning mechanism.

As shown in Figure 5.10b, maximum azimuthal intensity of amorphous halo was at $\varphi = 60^\circ$, indicating the presence of shear bands as well as the change in long periods of the lamellar structures.

In Region III, strong peak at $q = 14.6 \text{ nm}^{-1}$ in the equatorial direction and weak peak at $q = 7.8 \text{ nm}^{-1}$ in the meridional direction emerged in WAXS 1D profiles as shown in Figure 5.11. These peaks are derived from β -crystals and obtained by subtracting the WAXS profiles at 2YP from those in Region III.⁹ The β -form is a mesophase with a pseudohexagonal lattice structure where hydrogen bonds are randomly located around the chain axis.⁴⁵

Figure 5.12a shows the changes in crystallinity and Hermans orientation factors for polymer chains in α -forms and amorphous phases at $T_c = 180^\circ\text{C}$ under strain. These orientation factors were calculated by the same manner as that for lamellar structures. These trends corresponded to Regions I, II and III. With reference to the crystallinity, there was static in region I. Subsequently, in region II, the fraction of α - crystals

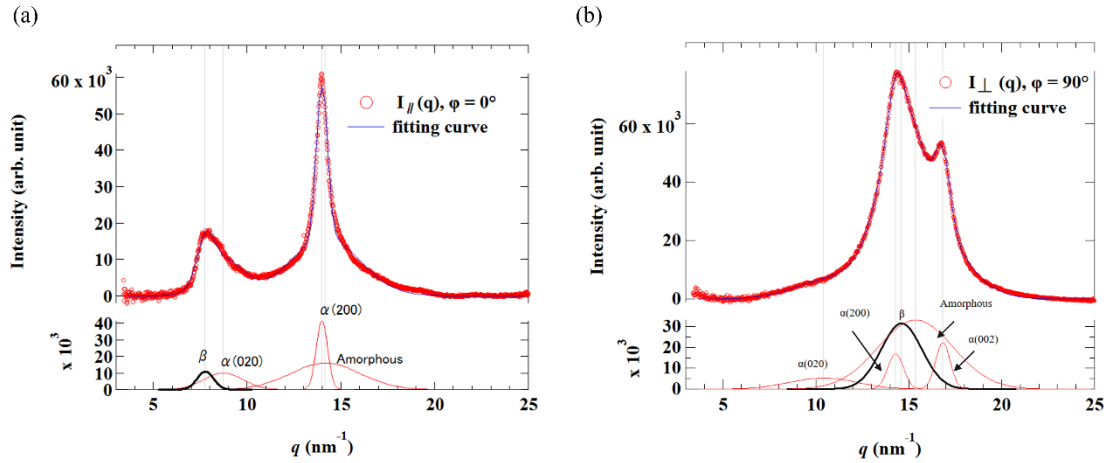


Figure 5.11. Peaks of β -crystals and other components in WAXS profiles at $\varepsilon = 15.45\%$ in (a) meridional and (b) equatorial directions.

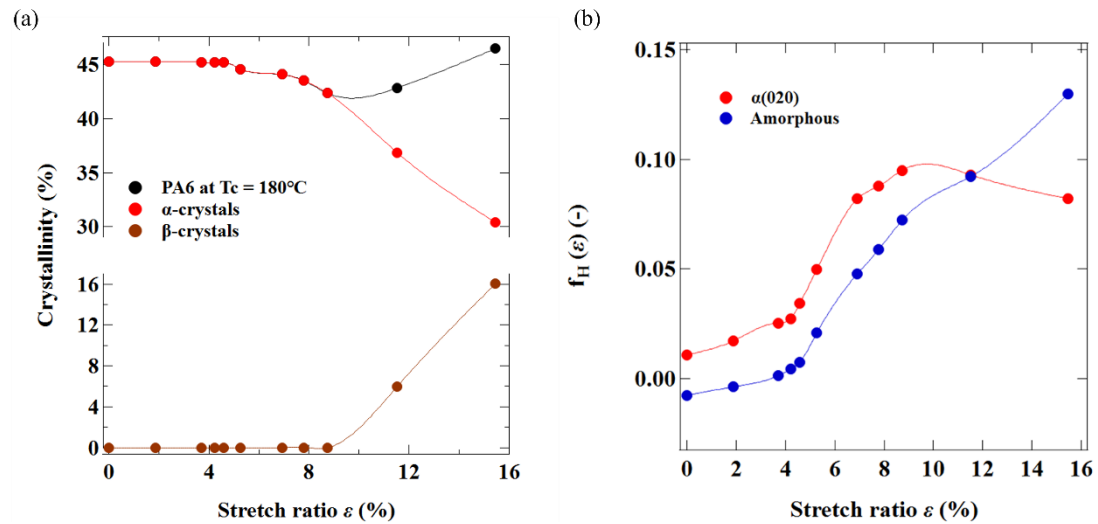


Figure 5.12. Changes in (a) crystallinity at $T_c = 180^\circ\text{C}$ (composed of α - and β -crystals) and orientation factors of molecular axis of α -crystals and molecular chains in amorphous phase.

began to decrease slightly by stretch-induced mechanical melting. Eventually, the fraction of α -crystals decreased significantly, and β -crystals were formed in region III, resulting that the crystallinity of the overall sample increased. The proportion of β -crystals formed is higher than that of α -crystals reduced, suggesting that β -crystals are formed by molecular chains in the amorphous phase oriented in the stretching direction

rather than directly from α -crystals.

The orientation factors of molecular axis of α -crystals, $f_{H,\alpha(020)}$, and molecular chain in amorphous phase, $f_{H,amo}$ showed the same tendency in Region I and II. Firstly, $f_{H,\alpha(020)}$ and $f_{H,amo}$ increased slightly from their initial values in Region I. Secondly, $f_{H,\alpha(020)}$ and $f_{H,amo}$ showed substantial increases with the increase in $f_{H,\alpha(020)}$ being slightly greater than that in $f_{H,amo}$. The behavior of $f_{H,\alpha(020)}$ corresponds to the trend $f_{H,lamella}$ for the lamella within fibrils. The difference in orientation factors between α -crystals and the amorphous phase reflects the distinct deformation mechanisms of each phase. The superior orientation of α -crystals is primarily attributed to the occurrence of coarse slip near the yield points. This slip-induced rotation of the crystal lattice actively promotes the alignment of the molecular chain axis toward the stretching direction. This mechanism is consistent with the WAXS results in stretched PE, where crystal slip facilitates a higher degree of orientation than that of the amorphous chains during stretching.²²

Regarding the amorphous phase, the relatively lower orientation may also be influenced by structural constraints in a glassy state. It is possible that the glassy amorphous phase in the non-fibrillar regions is accommodated on the fibrillar scale through the heterogeneous deformation, while the orientation of molecular chains remains restricted at this stage. Such factors could contribute to the poorer orientation of the amorphous network between fibrils. Therefore, the observed gap between $f_{H,\alpha(020)}$ and $f_{H,amo}$ is likely driven by the active rotation of crystals via coarse slip, further emphasized by the potential mobility restrictions within the amorphous phase in a glassy state.

Eventually, in Region III, $f_{H,\alpha(020)}$ did not change greatly while $f_{H,amo}$ continued to

increase. The behavior of α -crystals in Region III indicates that stress was dispersed by the formation of β -crystals or by mechanical melting of oriented α -crystals, resulting in the inability of lamellar structures within fibrils to further align with strain. In contrast, the growth of $f_{H,amo}$ is unaffected by the behavior of the fibrils, indicating that the molecular chains became capable of following the deformation and oriented preferentially in the stretching direction.

5.3.4 Case of PA6 at $T_c = 100\text{ }^\circ\text{C}$

In this chapter, hierarchical structures with strain in PA6 at $T_c = 100\text{ }^\circ\text{C}$, consisting of α -crystals and unstable γ -crystals are focused. Figure 5.13 shows the developments in USAXS/SAXS/WAXS 2D patterns with strain.

5.3.4.1 USAXS and SAXS Analysis

Figure 5.14 shows the combined USAXS and SAXS 1D profiles along the meridional and equatorial directions. The azimuthal dependence of the profiles with strain was generally in agreement with that at $T_c = 180\text{ }^\circ\text{C}$. The only difference was that $I_\perp(q)$ increased slightly from $\varepsilon = 3.60\%$ compared to that before the extension. This means that the formation of voids occurred at stretch ratios prior to 1YP.

Figure 5.15 shows the change in long periods of lamellar structures at each azimuthal angle with strain and the stretch ratio dependence of $f_{lamella}$. The lamellae elongated to a maximum at $\varphi = 0^\circ$ while drawing, and the degree of elongation did not increase at a specific angle, such as l_p for $\varepsilon = 8.74\%$ at $T_c = 180\text{ }^\circ\text{C}$. This difference indicates that shear bands were less likely to form at $T_c = 100\text{ }^\circ\text{C}$.

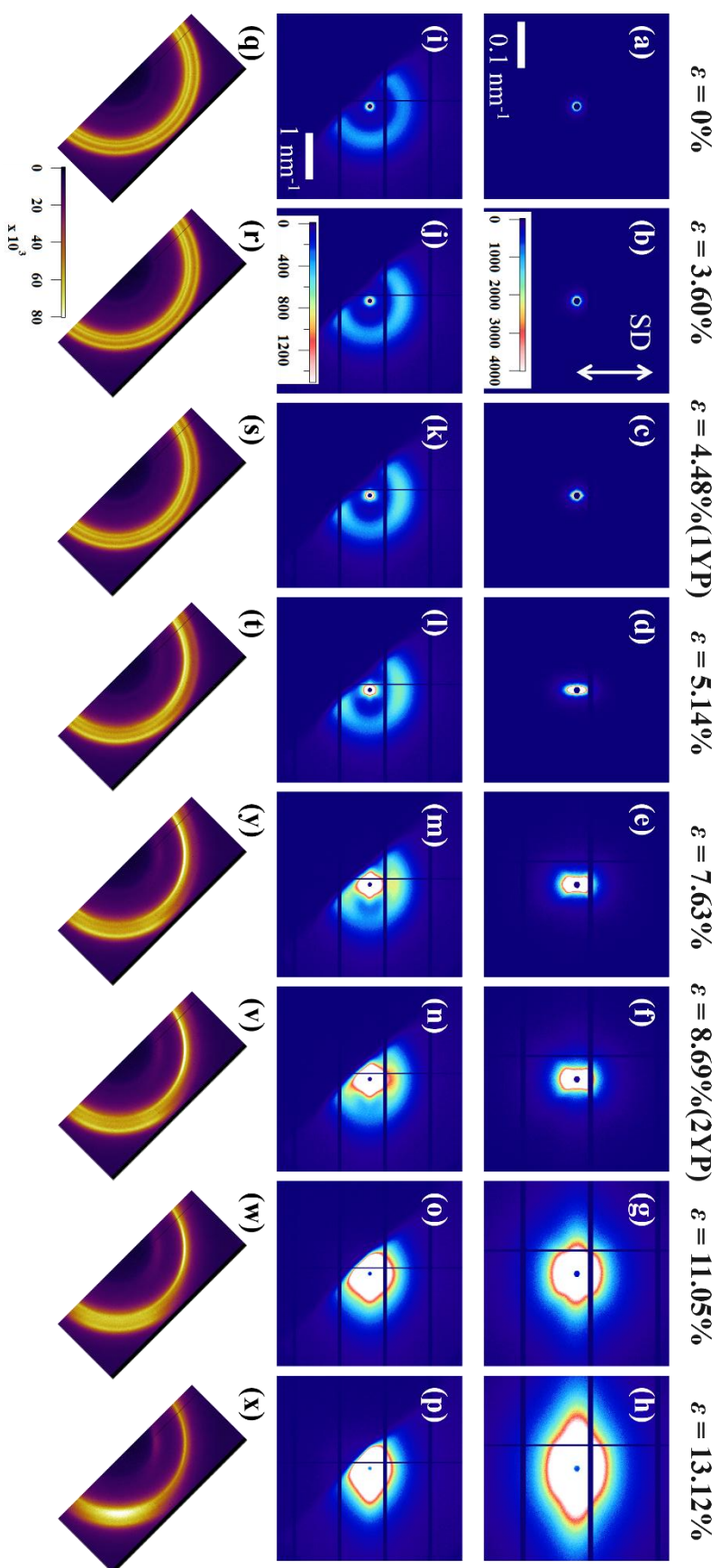


Figure 5.13. (a–h) USAXS, (i–p) SAXS, and (q–x) WAXS 2D patterns of the PA6 at $T_c = 100^\circ\text{C}$ with strain. The arrow in part (b) corresponds to the stretching direction.

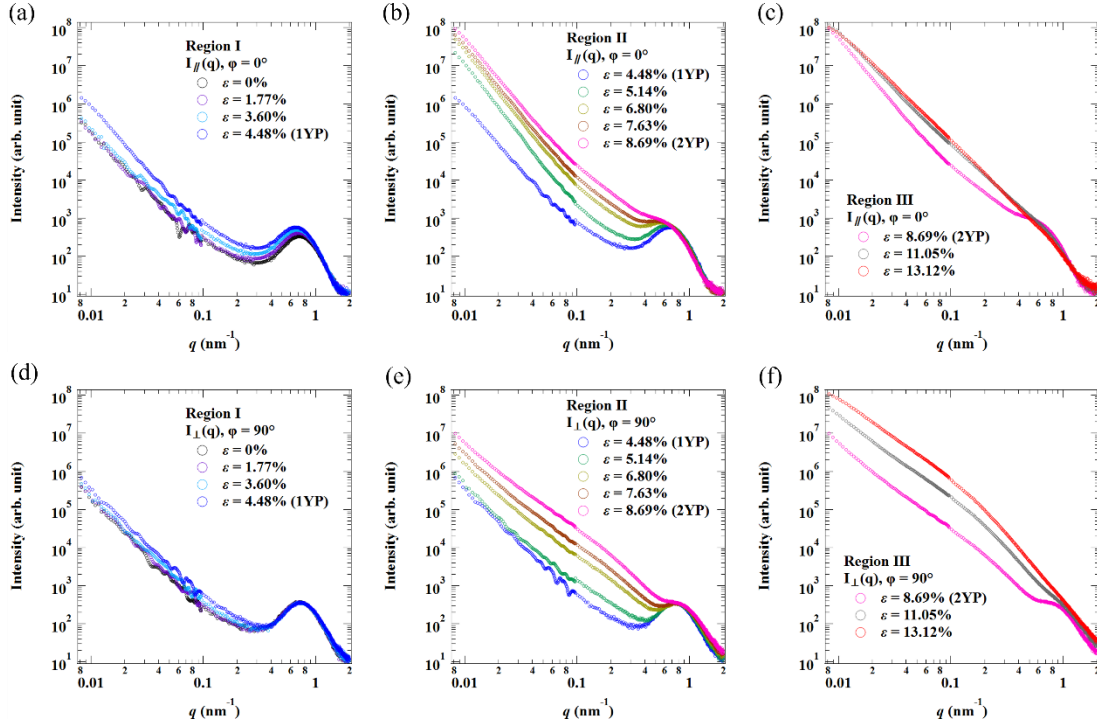


Figure 5.14. Combined USAXS and SAXS profiles at $T_c = 100\text{ }^{\circ}\text{C}$ in (a, d) Region I, (b, e) Region II, (c, f) Region III. The profiles in (a–f) correspond to the scattering intensities meridional and equatorial directions, respectively.

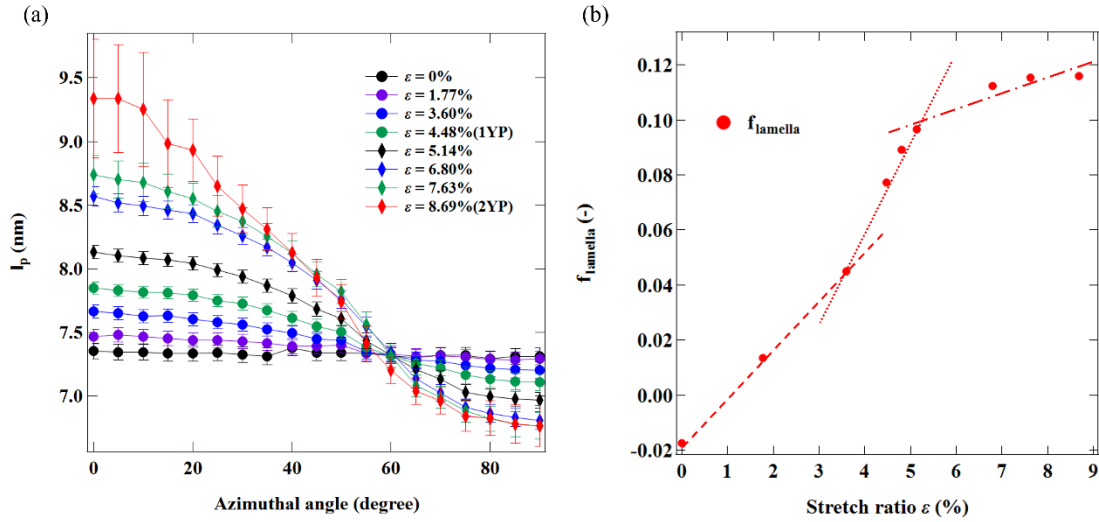


Figure 5.15. (a) Azimuthal dependence of I_p with strain and (b) stretch ratio dependence of f_{lamella} for $T_c = 100\text{ }^{\circ}\text{C}$

The difference in the orientation of the lamellar structure with stretching between $T_c = 100\text{ }^{\circ}\text{C}$ and $T_c = 180\text{ }^{\circ}\text{C}$ was significant. In PA6 at $T_c = 100\text{ }^{\circ}\text{C}$, the rate of increase in f_{lamella} was greater from $\varepsilon = 3.60\%$, which is before 1YP, whereas the values of f_{lamella} moderately changed in the middle of 1YP and 2YP. The tendency of f_{lamella} at around $\varepsilon = 3.60\%$ indicates that cavitation occurred between fibrils facilitated the deformation of non-fibrillar regions and the subsequent realignment of fibrils, resulting in the growth of f_{lamella} . On the other hand, at 2YP, mechanical melting occurred in the lamellae oriented in the direction of stretching, resulting in apparently poor development of orientations of the lamellae.

5.3.4.2 WAXS Analysis

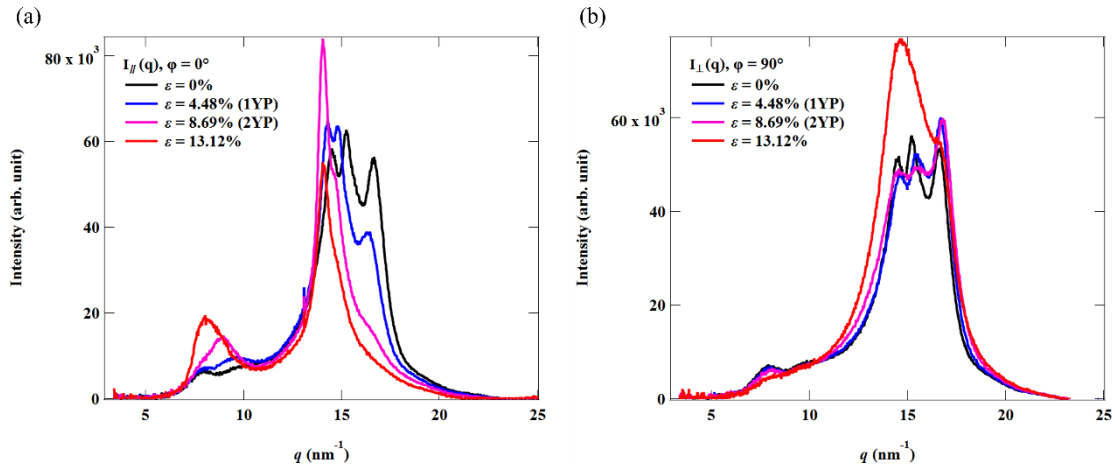


Figure 5.16. WAXS profiles of the PA6 at $T_c = 100\text{ }^{\circ}\text{C}$ correspond to the scattering intensities (a) meridional and (b) equatorial directions at typical stretch ratios.

Figure 5.16 shows WAXS 1D profiles at typical stretch ratios. The trends of the shift in peak position and formation of β -crystals with stretching were the same as those at $T_c = 180\text{ }^{\circ}\text{C}$.

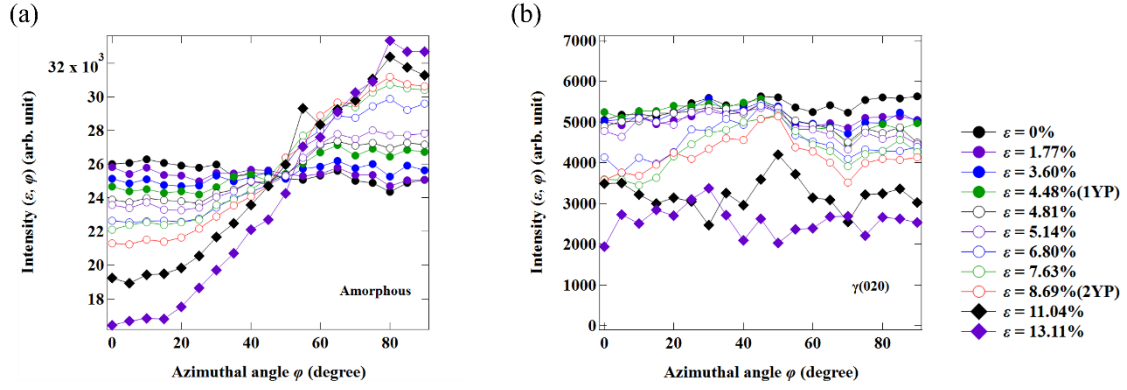


Figure 5.17. Azimuthal intensity at $T_c = 100^\circ\text{C}$ of (a) amorphous halo and (b) $\gamma(020)$.

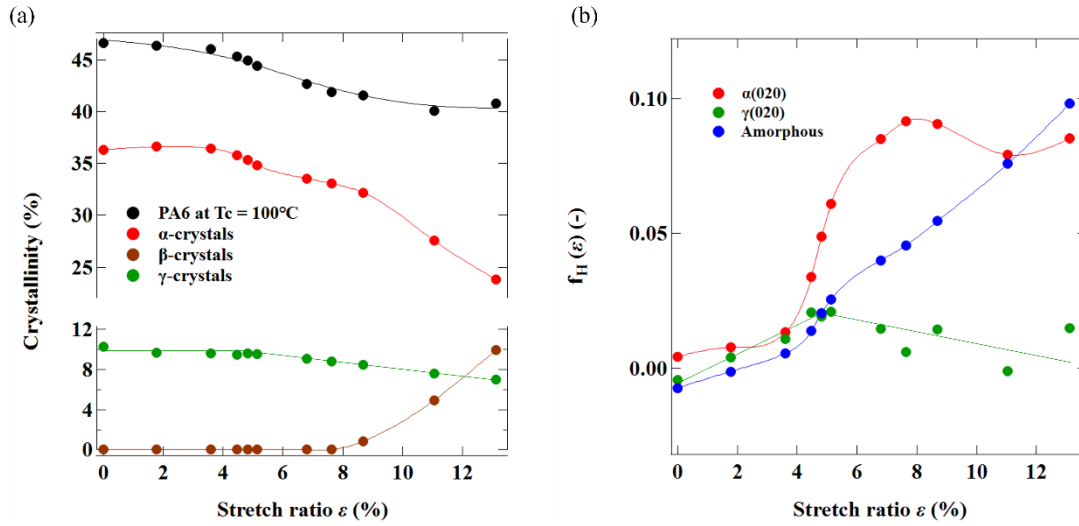


Figure 5.18. Changes in (a) crystallinity of PA6 at $T_c = 100^\circ\text{C}$ (composed of α -, β - and γ -crystals) and orientation factors of molecular axis of α -, γ -crystals and molecular chains in amorphous phase.

The azimuthal intensity of the α -crystal peak was also like that of $T_c = 180^\circ\text{C}$, showing that a twinning mechanism occurred in the α -crystal. In contrast, the azimuthal dependence of the amorphous halo is unique, exhibiting that the peak intensities were highest at $\phi = 0^\circ$ and lowest at $\phi = 90^\circ$ as shown in Figure 5.17a. The tendency of intensities of amorphous halo to enhance from $\phi = 0^\circ$ to $\phi = 90^\circ$ and the azimuthal dependence of I_p suggests the absence of shear bands in PA6 at $T_c = 100^\circ\text{C}$.

In addition, the difference from PA6 at $T_c = 180\text{ }^{\circ}\text{C}$ is that γ -crystals were contained at $T_c = 100\text{ }^{\circ}\text{C}$. The azimuthal intensity from the $\gamma(020)$ plane, which has little overlap with other peaks among the γ -crystal peaks, provides information on the changes in the γ -crystal caused by stretching. As shown in Figure 5.17b, the intensity of $\gamma(020)$ peak varied differently before $\varepsilon = 5.14\%$, from $\varepsilon = 5.14\%$ up to 2YP and after 2YP, respectively. Initially, this intensity decreased in the equatorial direction, subsequently decreasing in the meridian direction, and eventually declined uniformly across all azimuthal angles. This initial decrease indicates a slight orientation of the γ -crystals, although the subsequent decrease indicates either mechanical melting or γ - α transition occurred in the oriented γ -crystals.

Figure 5.18 presents the evolution of crystallinity and orientation as a function of strain at $T_c = 100\text{ }^{\circ}\text{C}$. Distinct behaviors were observed in Regions I, II, and III. In Region I, crystallinity remained constant. Subsequently, in Region II, the proportions of α - and γ -forms began to decrease slightly due to stress-induced melting. Notably, these rate of decrease was more pronounced than that observed at $T_c = 180\text{ }^{\circ}\text{C}$. This increased susceptibility to mechanical melting is attributed to the lower stability of crystals formed at $T_c = 100\text{ }^{\circ}\text{C}$ compared to those formed at $T_c = 180\text{ }^{\circ}\text{C}$. Although a γ - α transition likely occurred in this region, it was not discernible from the crystallinity because the quantity of mechanically melted α -crystals exceeded the amount of α -crystals generated from the γ -phase. In Region III, while the rate of γ -crystal reduction paralleled that of Region II, the α -crystal content decreased significantly. Similar to the behavior at $T_c = 180\text{ }^{\circ}\text{C}$, β -crystals formed at these strain levels; however, the substantial melting of α -crystals resulted in no apparent change in the total crystallinity of the sample. The fraction of formed β -crystals was equivalent to the combined

reduction of α - and γ -crystals.

The orientation factors, $f_{H,\alpha(020)}$ and $f_{H,amo}$, exhibited trends similar to those observed at $T_c = 180^\circ\text{C}$. In the initial stage of stretching, both factors increased slightly, followed by a dramatic increase in Region II. Finally, while $f_{H,\alpha(020)}$ leveled off, $f_{H,amo}$ continued to increase. Besides, the orientation factor of molecular axis of γ -crystals, $f_{H,\gamma(020)}$ increased modestly in Region I and subsequently decreased in Regions II and III. The decrease in $f_{H,\gamma(020)}$ is related to the mechanical melting or γ - α transition, indicating that these occur preferentially from oriented γ -crystals.

5.3.5 Changes in the Hierarchical Structures under Stretching

Schematic illustrations of the changes in the hierarchical structures in the PA6 at $T_c = 180^\circ\text{C}$ and $T_c = 100^\circ\text{C}$ were made based on the above discussion and are shown in Figure 5.19.

With respect to the hierarchical structures before stretch, due to the high crystallization temperature, PA6 at $T_c = 180^\circ\text{C}$ formed thick and long fibrils consisting only of stable α -crystals, and the low branching frequency resulted in wide non-fibrillar regions. In contrast, PA6 at $T_c = 100^\circ\text{C}$ formed relatively smaller spherulites due to the high nucleation frequency; however, they were filled with highly branched fibrils and contained unstable γ -crystals. Despite the significant differences in their initial morphologies, such as spherulite size, fibril branching density, and crystal stability, both samples exhibited a similar deformation mechanism.

At first, spherulites deformed along the drawing direction before 1YP, causing the lamellar structures located in the equatorial regions to orient towards the drawing direction. In PA6 at $T_c = 100^\circ\text{C}$, the formation of voids before 1YP is likely associated

with the morphology characterized by highly branched fibrils.

From 1YP to 2YP, USAXS revealed butterfly patterns attributed to stretch-induced density fluctuations, indicating that inhomogeneous deformation occurred due to differences in deformability between the fibrillar and non-fibrillar regions. In addition to the onset of void formation in the specimen at $T_c = 180\text{ }^{\circ}\text{C}$, both specimens exhibited significant orientation of molecular chains in the crystalline and amorphous phases, along with mechanical melting in the oriented crystals. Heterogeneous deformation stretched amorphous phase in a glassy state and induced poorer amorphous orientation, while the significant orientation and mechanical melting of crystals indicate that fibrils located in the equatorial regions fragmented, facilitating the alignment of crystals. At $T_c = 100\text{ }^{\circ}\text{C}$, not only did mechanical melting of γ -crystals or γ - α transition occur, but the decrease in crystallinity was also more pronounced compared to that at $T_c = 180\text{ }^{\circ}\text{C}$. This indicates that all crystals formed at $T_c = 100^{\circ}\text{C}$ possessed lower stability. The timing of void formation and crystal stability appear to play a crucial role in shear banding. At $T_c = 100\text{ }^{\circ}\text{C}$, the early onset of voids and stress dissipation via mechanical melting presumably suppressed the strain localization required for shear band formation.

Eventually, after 2YP, severe mechanical melting of the oriented α -crystals occurred, resulting in a significant decrease in their fraction. Simultaneously, β -crystals were generated from the highly oriented amorphous chains. Regarding the orientation behavior, distinct trends were observed: while the orientation of α -crystals leveled off, the glassy polymer chains in the amorphous phase continued to orient in the deformation direction.

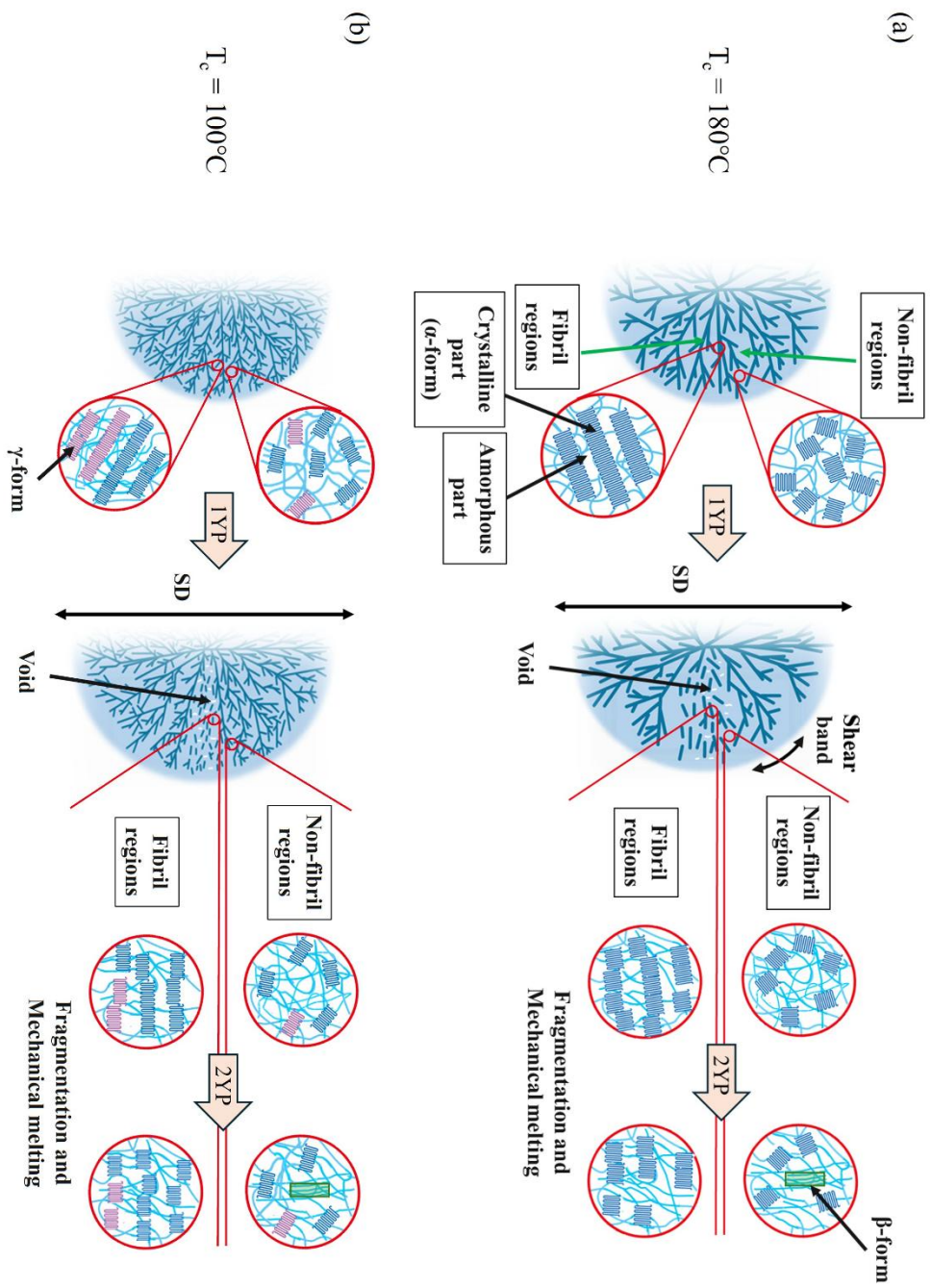


Figure 5.19. Schematic illustrations of the changes in the hierarchical structures in the PA6 at (a) $T_c = 180^\circ\text{C}$ and (b) $T_c = 100^\circ\text{C}$ during stretching.

5.4 Conclusion

In this study, I investigated the hierarchical structural evolution of PA6 crystallized at different temperatures ($T_c = 180\text{ }^{\circ}\text{C}$ and $100\text{ }^{\circ}\text{C}$) during uniaxial stretching at room temperature below T_g , utilizing *in-situ* USAXS, SAXS, and WAXS measurements.

My results confirmed, for the first time, the emergence of abnormal butterfly patterns in the USAXS region for PA6 deformed below T_g . This finding demonstrates that significant heterogeneous deformation involving stretch-induced density fluctuations occurs even when amorphous chains are in a frozen, glassy state. Crucially, the multiscale analysis revealed that the hierarchical structural development follows a consistent deformation pathway between the two specimens, despite their distinct initial morphologies. Both samples exhibited a three-stage deformation process as follows. In the initial stage, the spherulites and lamellae deform along the drawing direction. Subsequently, inhomogeneous deformation, which is characterized by density fluctuations arising from spatial inhomogeneity of crystallinity and mechanical melting of oriented crystals, occur. Finally, severe mechanical melting of the oriented α -crystals and the simultaneous generation of β -crystals from the highly oriented amorphous chains take place.

Within this deformation mechanism, the initial hierarchical structure served as a determinant for the local stress concentration and the onset of strain localization. Specifically, the high branching frequency and unstable crystals in the specimen at $T_c = 100\text{ }^{\circ}\text{C}$ induced early cavitation before 1YP due to stress concentration. This early onset of the void formation suppressed the formation of shear bands, which were clearly

observed in the specimen consisting of stable crystals at $T_c = 180\text{ }^{\circ}\text{C}$ where void formation was delayed.

In conclusion, this study establishes that the macroscopic deformation of PA6 below T_g is fundamentally governed by a common mechanism involving stretch-induced density fluctuations and crystal-amorphous phase transitions, while the initial morphology dictates the specific competition between cavitation and formation of shear bands. These insights highlight the critical role of density fluctuations and heterogeneous deformation even in the glassy state, thereby broadening the understanding of the mechanical response of the frozen amorphous phase.

References

1. Herzog, B.; Kohan, M. I.; Mestemacher, S. A.; Pagilagan, R. U.; Redmond, K.; Sarbandi, R., R. Polyamides. In *Ullmann's Encyclopedia of Industrial Chemistry*, 7th ed.; Wiley-VCH: Weinheim, 2013.
2. Roldan, L. G.; Kaufman, H. S. *J. Polym. Sci. Part B: Polym. Lett.* **1963**, *1* (11), 603–608.
3. Kyotani, M.; Mitsuhashi, S. *J. Polym. Sci., Part A-2: Polym. Phys.* **1972**, *10* (8), 1497–1508.
4. Parker, J. P.; Lindenmeyer, P. H. *J. Appl. Polym. Sci.* **1977**, *21* (3), 821–837.
5. Cavallo, D.; Gardella, L.; Alfonso, G. C.; Portale, G.; Balzano, L.; Androsch, R. *Colloid Polym. Sci.* **2011**, *289* (9), 1073–1079.
6. Holmes, D. R.; Bunn, C. W.; Smith, D. J. *J. Polym. Sci.* **1955**, *17* (84), 159–177.
7. Arimoto, H., *J. Polym. Sci., Part A*, **1964**, *2* (5), 2283–2295.
8. Arimoto, H.; Ishibashi, M.; Hirai, M.; Chatani, Y. *J. Polym. Sci., Part A* **1965**, *3* (1), 317–326.
9. Xu, J.-R.; Ren, X.-K.; Yang, T.; Jiang, X.-Q.; Chang, W.-Y.; Yang, Shuang.; Stroeks, A.; Chen, E.-Q. *Macromolecules* **2018**, *51* (1), 137–150.
10. Kojima, Y.; Matsuoka, T.; Takahashi, H.; Kurauchi, T. *J. Appl. Polym.* **1994**, *51* (4), 683–687.
11. Fornes, T. D.; Yoon, P. J.; Keskkula, H.; Paul, D. R., *Polymer* **2001**, *42*, 9929–9940.
12. Salem, D. R.; Moore, R. A. F.; Weigmann, H. -D. *J. Polym. Sci. Part B: Polym. Phys.* **1987**, *25* (3), 567–589.

13. Murthy, N. S.; Bray, R. G.; Correale, S. T.; Moore, R. A. F. *Polymer* **1995**, *36*, 3883–3873.
14. Gurato, G.; Fichera, A.; Grandi, F. Z.; Zannetti, R.; Canal, P. *Makromol. Chem.* **1974**, *175* (3), 953–975.
15. Samon, J. M.; Schultz, J. M.; Hsiao, B. S. *Polymer* **2000**, *41*, 2169–2182.
16. Dencheva, N.; Denchev, Z.; Oliveira, M. J.; Funari, S. S. *J. Appl. Polym. Sci.* **2006**, *103* (4), 2242–2252.
17. Guo, H.; Wang, J.; Zhou, C.; Zhang, W.; Wang, Z.; Xu, B.; Li, J.; Shang, Y.; de Claville Christiansen, J.; Yu, D.; Wu, Z.; Jiang, S. *Polymer* **2015**, *70*, 109–117.
18. Pepin, J.; Gaucher, V.; Rochas, C.; Lefebvre, J.-M. *Polymer* **2019**, *175*, 87–98.
19. Takenaka, M.; Shimizu, H.; Nishitsuji, S. *Phys. Rev. E* **2007**, *75*, 061802.
20. Owen, A.; Bergmann, A. *Polymer International* **2004**, *53* (1), 12–14.
21. Kishimoto M.; Mita K; Ogawa H.; Takenaka M. *Macromolecules* **2020**, *53*, 9097–9107.
22. Arakawa, M.; Kishimoto, M.; Nakanishi, Y.; Takenaka, M. *Polym J.* **2022**, *54*, 243–248.
23. Arakawa, M.; Kishimoto, M.; Uchida, K.; Nakanishi, Y.; Takenaka, M. *Macromolecules* **2026**, *59* (1), 369–378.
24. Arakawa, M.; Kabe, T.; Iwata, T.; Takenaka, M. *J. Appl. Crystallogr.* **2025**, *58* (3), 886–896.
25. Mendes, E.; Oeser, R.; Hayes, C.; Boue, F.; Bastide, J. *Macromolecules* **1996**, *29*, 5574–5584.

26. Shinohara, Y.; Kishimoto, H.; Inoue, K.; Suzuki, Y.; Takeuchi, A.; Uesugi, K.; Yagi, N.; Muraoka, K.; Mizoguchi, T.; Amemiya, Y. *J. Appl. Crystallogr.* **2007**, *40* (s1), s397–s401.
27. Takenaka, M., *Polym. J.* **2012**, *45* (1), 10–19.
28. Takenaka, M.; Miyazawa, M.; Nishitsuji, S.; Hashimoto, T. *J. Chem. Phys.*, **2004**, *121* (15), 7501-7504.
29. Bastide, J.; Leibler, L.; Prost, J. *Macromolecules* **1990**, *23*, 1821-1825.
30. Mendes, E., Jr.; Lindner, P.; Buzier, M.; Boue, F.; Bastide, J. *Phys. Rev. Lett.* **1991**, *66* (12), 1595-1598.
31. Doi, M.; Onuki, A. *J. Phys. II* **1992**, *2*, 1631–1656.
32. Furukawa, A.; Tanaka, H. *Nat. Mater.* **2009**, *8*, 601–609.
33. Kurotani, Y.; Tanaka, H. *Commun. Mat.* **2022**, *3* (67), 1–11.
34. Masunaga, H.; Ogawa, H.; Takano, T.; Sasaki, S.; Goto, S.; Tanaka, T.; Seike, T.; Takahashi, S.; Takeshita, K.; Nariyama, N.; Ohashi, H.; Ohata, T.; Furukawa, Y.; Matsushita, T.; Ishizawa, Y.; Yagi, N.; Takata, M.; Kitamura, H.; Sakurai, K.; Tashiro, K.; Takahara, A.; Amamiya, Y.; Horie, K.; Takenaka, M.; Kanaya, T.; Jinnai, H.; Okuda, H.; Akiba, I.; Takahashi, I.; Yamamoto, K.; Hikosaka, M.; Sakurai, S.; Shinohara, Y.; Okada, A.; Sugihara, Y. *Polym. J.* **2011**, *43*, 471–477.
35. Wunderlich, B. *Macromolecular Physics: Crystal Melting*, Vol. 3; Academic Press: New York, 1980.
36. Hashimoto, T., *Principles and Applications of X-ray, Light and Neutron Scattering*; Springer Nature Singapore Pte Ltd.: Singapore, 2022.

37. Beaucage, G. *J. Appl. Crystallogr.* **1995**, 28 (6), 717-728.
38. Strobl, G. R.; Schneider, M., *J. Polym. Sci., Polym. Phys.* **1980**, 18, 1343–1359.
39. Strobl, G. R.; Schneider, M. J.; Voigtmartin, I. G. *J. Polym. Sci., Polym. Phys.* **1980**, 18, 1361–1381.
40. Debye, P.; Bueche, A. M. *J. Appl. Phys.* **1949**, 20 (6), 518–525.
41. Xiong, B.; Lame, O.; Chenal, J.-M.; Rochas, C.; Seguela, R.; Vigier, G. *Polymer* **2014**, 55 (5), 1223–1227.
42. Damodaran, S.; Schuster, T.; Rode, K.; Sanoria, A.; Brüll, R.; Stöhr, N. *Polymer* **2015**, 60, 125–136.
43. Alexander, L. E., *X-ray Diffraction Methods in Polymer Science*; John Wiley and Sons Inc.: New York, 1969.
44. Wang, C.; Hashimoto, T.; Lu, C.-Y.; Lu, P.-H.; Tsai, C.-W. *Macromolecules* **2024**, 57 (24), 11586-11598.
45. Ziabicki, A. *Colloid Polym. Sci.* **1959**, 167 (2), 132–141.

Chapter 6

Spatial Heterogeneity of Density and Orientation in Stretched Polyamide-6 Revealed by STXM

6.1 Introduction

Polyamide 6 (PA6) is one of the crystalline polymers, consisting of hierarchical structures. The molecular structure of PA6 contains amide bonds, which result in the formation of strong hydrogen bonds between molecular chains.¹⁻³ Consequently, PA6 possesses a glass transition temperature (T_g) of approximately 50 °C,⁴ higher than room temperature.

To clarify the correlation between structural evolution and mechanical properties, many researchers have studied the PA6 during uniaxial stretching by small- and wide-angle X-ray scattering (SAXS and WAXS, respectively).⁵⁻⁹ In chapter 5, I found the abnormal butterfly pattern at the yield points by ultra-small-angle X-ray scattering (USAXS) while PA6 was stretched uniaxially under room temperature below the T_g .

The butterfly pattern is characterized by anisotropic scattering with enhancement of intensity parallel to the stretching direction, reflecting stretch-induced density fluctuations.¹⁰ Crystalline polymers inherently possess a spatial heterogeneity of crystallinity, generally composed of crystalline regions and amorphous regions on the fibrillar scales.¹¹ Theoretical studies by Doi and Onuki,¹² and Furukawa and Tanaka¹³

have established that under deformation of dynamically asymmetric systems, a coupling between density fluctuations and spatial inhomogeneities in the stress field (or elastic modulus) leads to an enhancement of density fluctuations driven by the stress gradient. In the case of crystalline polymers, the contrast in mechanical properties between the crystalline and amorphous phases leads to such spatial heterogeneity of stress field. Consequently, the butterfly pattern observed in crystalline polymers by USAXS arises from the density fluctuation on the fibril scales induced by stretching, which reflects the distinct variation of the deformability between the fibrils and inter-fibrillar regions.¹⁰

In previous studies, the butterfly patterns have been observed by USAXS during stretching polyethylene (PE)^{10, 14, 15} and poly(3-hydroxybutyrate) (P(3HB))¹¹ at room temperature above their T_g . By contrast, I observed the butterfly pattern in PA6 stretched at room temperature below its T_g by USAXS, indicating that the semi-crystalline hierarchical structures undergo non-uniform deformation even in a glassy state on the submicrometric scales. Based on the behavior of stretched PE discussed in Chapter 3, STXM observation for stretched PE expected that this non-uniformity in a stretched PE would arise because the low-crystallinity inter-fibrillar regions deform more extensively than the rigid fibrils on the submicrometric scales.

Consistent with the behavior observed in PE by *in-situ* X-ray scattering measurements under strain at room temperature,¹⁵ time-resolved SAXS and WAXS analyses during stretching PA6 at room temperature revealed that the α -crystals and lamellar structures in PA6 were more oriented along the stretching direction than the amorphous polymer chains, which is attributed to coarse slip near the yield point and low mobility of molecular chains in a glassy state. However, unlike elastic PE, PA6 at room temperature is in a glassy state, and therefore the spatial distribution of molecular

orientation under heterogeneous deformation may differ from that of PE. This spatial distribution, however, remains to be elucidated.

X-ray scattering techniques provide only statistically averaged information across the entire irradiation volume, resulting in an inability to obtain the local structural details essential for understanding inhomogeneity. Therefore, following the methodology established in Chapter 3, I employed Scanning Transmission X-ray Microscopy (STXM) to investigate the spatial correlation between local density and molecular orientation in real space. Considering that the polymer chains in the crystal lattice of PA6 adopt a planar zigzag conformation similar to PE,¹⁻³ it is anticipated that linear dichroism associated with C–C bond orientation will be observable by STXM.^{15,}¹⁶ In the Near-Edge X-ray Absorption Fine Structure (NEXAFS) spectra obtained using linearly polarized X-rays in STXM, this dichroism is expected to appear at the energy corresponding to the $C-1s \rightarrow \sigma^*_{C-C}$ resonances, similar to the case of stretched PE.

In this study, comprehensive USAXS/SAXS/WAXS and STXM measurements were conducted on PA6 samples in both the unstretched state and the state stretched below T_g to the strain at the second yield point, where the butterfly pattern was observed by USAXS.

Using STXM, I successfully visualized the real-space density distribution resulting from stretch-induced density fluctuations and mechanical melting in a glassy PA6, similar to the behavior observed in PE. Furthermore, the analysis revealed spatial heterogeneity in orientation that depends on the local distribution of crystallinity.

6.2 Experimental Section

6.2.1 Sample Preparation

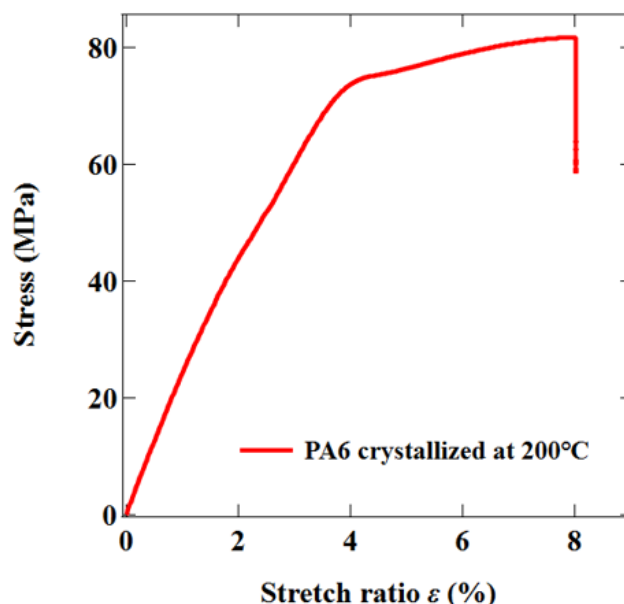


Figure 6.1. S-S curve of the PA6 crystallized at 200 °C.

PA6 pellets (Sigma-Aldrich; density: 1.084 g/mL at 25 °C) were dried in a vacuum oven at 80 °C for 12 h prior to processing. A 2-mm-thick sheet was prepared using two press machines (MINI TEST PRESS-10, Toyo Seiki Seisaku-sho, Ltd.). First, the pellets were hot-pressed in a mold at 260 °C (above the melting point of PA6) for 15 min. The molten sample was immediately transferred to the second press machine and quenched to form a solid sheet. The sheet was subsequently annealed at 200 °C to promote crystallization. Finally, dumbbell-shaped specimens with a center width of 2 mm were punched from the annealed sheet.

To investigate the structural characteristics at the second yield point, the specimens were stretched using a tensile tester (TENSILON, A&D Co., Ltd.). The specimens were extended to $\varepsilon = 8.03\%$, which corresponds to the second yield point,

and were held at this fixed strain for 30 minutes. Figure 6.1 shows the stress-strain (S–S) curve during sample preparation. The stress plot is the engineering stress.

6.2.2 X-ray Scattering Measurements

X-ray scattering measurements (USAXS, SAXS, and WAXS) were performed at the second hutch of beamline BL03XU at SPring-8 (Hyogo, Japan). A camera was used to ensure that the X-ray beam irradiated the center of the dumbbell-shaped specimens. For all measurements, the beam size at the sample position was 300 μm (horizontal) $\times$ 300 μm (vertical), and the exposure time was set to 800 ms. Simultaneous SAXS and WAXS measurements were conducted using an incident wavelength of 1.0 $\text{\AA}$. The camera lengths were 2.36 m for SAXS and 122 mm for WAXS. A PILATUS-1M (Dectris Ltd.) and a SOPHIAS (Rigaku Corp.) were used as detectors for SAXS and WAXS, respectively. The WAXS detector was tilted to intercept the SAXS signal. A 40 μm thick Mo plate was used as an attenuator. USAXS measurements were performed using an incident wavelength of 2.0 $\text{\AA}$ and a camera length of 7.62 m. A PILATUS-1M detector was used without an attenuator.

For data analysis, the 2D scattering intensities were corrected for background scattering by subtracting the data obtained without the specimen from the sample data, taking into account the X-ray transmittance measured by ion chambers installed upstream and downstream of the specimen. Finally, the corrected intensities were normalized by the specimen thickness.

6.2.3 STXM Measurements

Ultrathin sections were prepared from the center of PA6 dumbbell specimens using a cryo-microtome (EM UC7, Leica Microsystems). Specimens were prepared from two states: an unstretched sample and a sample stretched to $\varepsilon = 8.03\%$. To prevent structural relaxation or changes during preparation, the sectioning process was performed at a temperature below the glass transition temperature of PA6.

Scanning Transmission X-ray Microscopy (STXM) measurements were conducted at Beamline 19A (BL-19A) of the Photon Factory, High Energy Accelerator Research Organization (KEK-PF), Tsukuba, Japan.¹⁷ The X-rays were incident perpendicular to the surface of the ultrathin sections. The incident X-ray energy range was set to 280–320 eV to cover the Carbon K-edge absorption region (≈ 285 eV). The exposure time was 2 ms per pixel. To investigate the molecular orientation based on the linear dichroism of the chemical bonds, the same regions of interest on the ultrathin sections were observed with the linear polarization vector of the incident X-rays set parallel and perpendicular to the stretching direction, respectively. This was achieved by adjusting the X-ray polarization without rotating the specimens. Image sequences were acquired for NEXAFS analysis with a spatial resolution of 100 nm, and high-resolution images for orientation analysis were acquired with a spatial resolution of 50 nm.

The transmitted X-ray intensity (I) at the focal position was spatially mapped by raster scanning the sample. The optical density (OD) was calculated from the transmitted intensity (I) and the incident intensity (I_0) using the following equation:

$$OD = -\ln \frac{I}{I_0} \quad (6.1)$$

NEXAFS spectra were derived from the *OD* values at each pixel across the energy stack. The spectral peaks correspond to specific chemical bonds and are sensitive to the angle between the transition dipole moment (TDM) of the bond and the X-ray electric field vector. Prior to orientation analysis, image drifts were corrected.

6.2.4 Differential Scanning Calorimetry (DSC) Measurements

Thermal analysis was performed on a DSC (PerkinElmer, Inc) calibrated with indium. The about 19 mg samples were scanned at a heating rate of 10 °C/min. The crystallinity of each sample was calculated from the enthalpy of the melting endotherm using the melting enthalpy of 100% crystallized PA6 $\Delta H_m^0 = 230$ J/g regardless of the crystalline form.^{18, 19} Before the thermal characterizations, all samples were dried at room temperature under vacuum for a day.

6.3 Results and Discussion

6.3.1 Analysis by USAXS, SAXS and WAXS Measurements

Figure 6.2 shows the USAXS, SAXS, and WAXS 2D patterns for the unstretched sample and the sample stretched to $\varepsilon = 8.03\%$. The USAXS pattern before drawing was isotropic, whereas an anisotropic butterfly pattern was observed for the sample stretched to $\varepsilon = 8.03\%$. This butterfly pattern reflects stretch-induced density fluctuations on the fibril scale, indicating heterogeneous deformation between the fibrils and the inter-fibrillar regions. In Chapter 5, *in-situ* X-ray scattering measurements during deformation revealed streaks in the SAXS and USAXS patterns at the second yield point, which was attributed to scattering from voids. In contrast, no such streak

was observed in the patterns obtained after holding the sample at $\varepsilon = 8.03\%$ for 30 minutes, as shown in Figure 6.2d and e. This absence indicates that the voids generated upon reaching the second yield point closed due to stress relaxation during the 30-minute holding period. The SAXS pattern at $\varepsilon = 0\%$ had an isotropic ring originating from the long period of lamellar structures, while the SAXS pattern at $\varepsilon = 8.03\%$ had the ellipse with minor axis parallel to the direction of stretching. The anisotropy indicated that the elongation parallel to the stretch direction and contraction in the perpendicular direction.

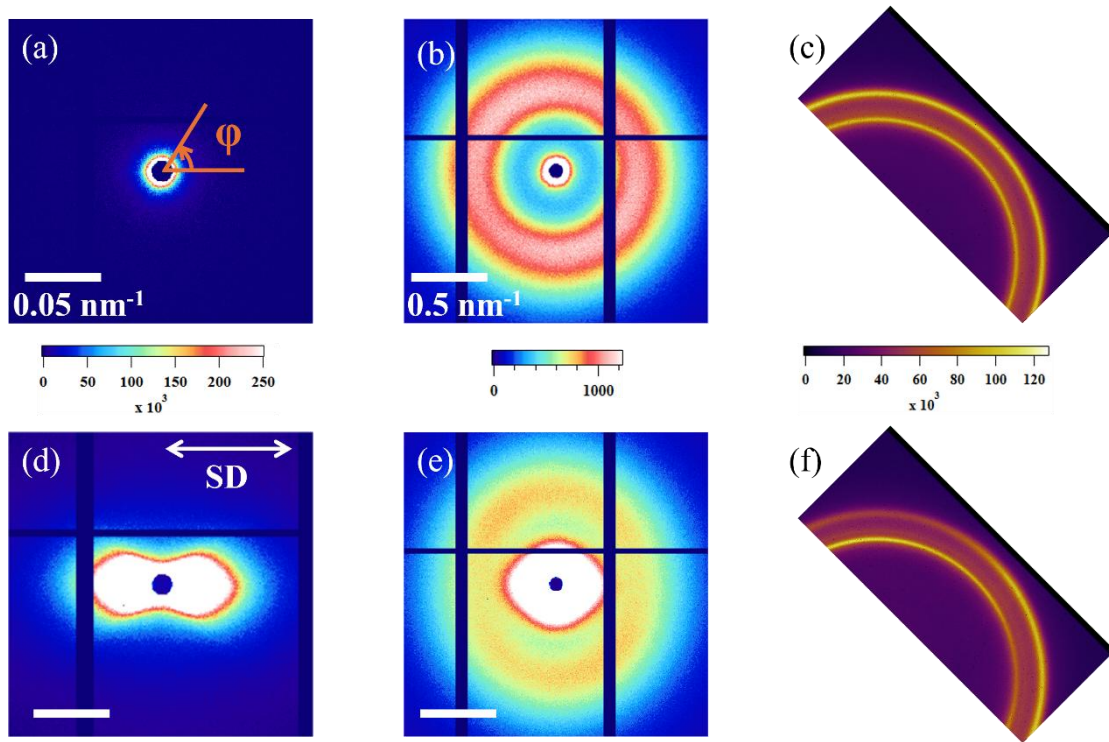


Figure 6.2. 2D scattering patterns of PA6 crystallized at 200 °C: (a) USAXS, (b) SAXS, and (c) WAXS patterns before stretching; (d) USAXS, (e) SAXS, and (f) WAXS patterns after stretching to $\varepsilon = 8.03\%$. The arrow in (d) denotes the stretching direction (SD).

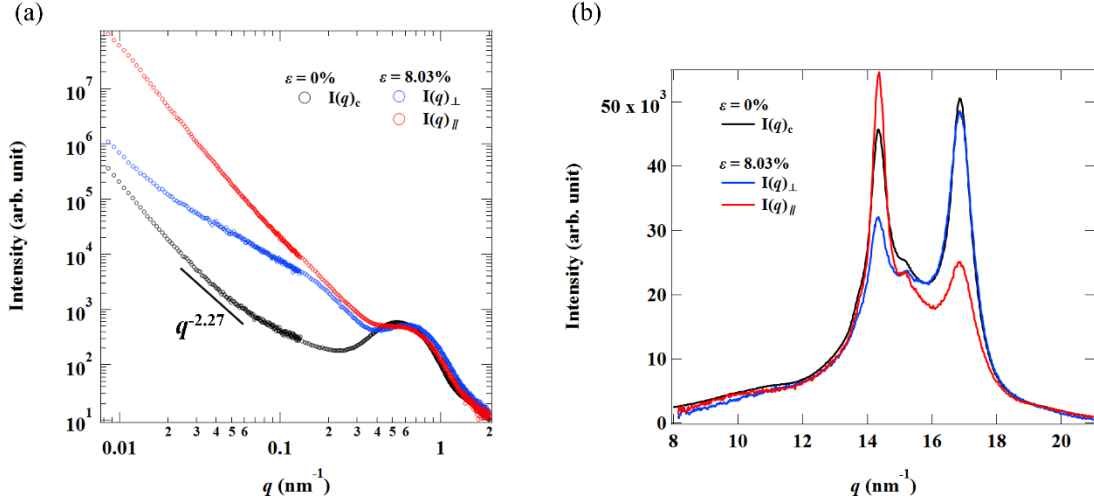


Figure 6.3. (a) Combined USAXS and SAXS profiles and (b) WAXS profiles. The black lines represent circularly averaged profiles before stretching. The blue and red lines represent sector-averaged profiles perpendicular and parallel to the stretching direction at $\varepsilon = 8.03\%$, respectively.

Figure 6.3 shows the combined USAXS and SAXS 1D profiles and WAXS 1D profiles for both specimens. The magnitude of the scattering vector, q , is defined by $q = (4\pi/\lambda)\sin(\theta/2)$, where λ and θ are the wavelength of the incident X-rays and the scattering angles, respectively. The profiles for the unstretched sample, $I(q)_c$, were averaged circularly. For the sample stretched at $\varepsilon = 8.03\%$, the parallel profiles $I_{\parallel}(q)$ were obtained by averaging sectors within $\pm 2.5^\circ$ from the stretching direction ($\varphi = 0^\circ$), while the perpendicular profiles $I_{\perp}(q)$ were obtained from $\varphi = 90^\circ$. The definition of the azimuthal angle φ is shown in Figure 6.2d. Detailed analyses of the patterns are shown in Chapter 5.

For the unstretched sample, the profile $I(q)_c$ exhibited power-law behavior satisfying $I(q)_c \sim q^{-2.27}$ on the fibril scale. This power-law exponent corresponds to the mass-fractal dimension of the fibril structures.^{10, 20, 21} Therefore, this value indicates that the spherulites crystallized at 200 °C were filled loosely with fibrils. To quantitatively

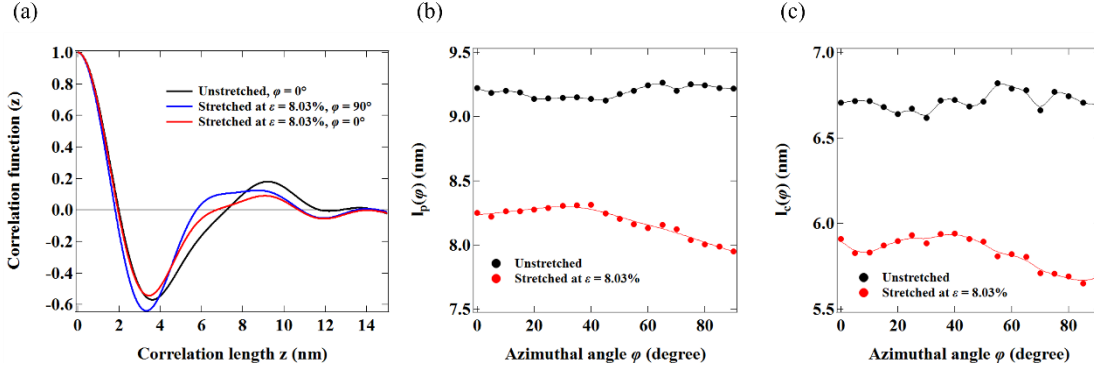


Figure 6.4. Correlation function for both samples and φ dependence of (a) long period $l_p(\varphi)$ and (b) crystal thickness $l_c(\varphi)$.

evaluate the density fluctuations associated with the fibrils and inter-fibrillar regions, the USAXS invariants, Q , are calculated with the following equation.²¹

$$Q = 4\pi \int_{\varphi=0}^{\varphi=\frac{\pi}{2}} \int_{q=0.031 \text{ nm}^{-1}}^{q=0.111 \text{ nm}^{-1}} qI(q, \varphi) \sin \varphi dq d\varphi \quad (6.2)$$

The Q values increased significantly from 56.99 (a.u.) at $\varepsilon = 0\%$ to 1894 (a.u.) at $\varepsilon = 8.03\%$. This increase confirms that the drawing process induced substantial density fluctuations.

To characterize the anisotropy of the lamellar structures, the azimuthal long period $l_p(\varphi)$ and crystal thickness $l_c(\varphi)$ were estimated from the one-dimensional electron density correlation functions.^{22, 23} The correlation functions were calculated from the SAXS profiles sector-averaged at every 5° from $\varphi = 0^\circ$ to 90° . As shown in Figure 6.4a, the correlation function for the unstretched sample exhibited a unimodal peak corresponding to the distribution of long periods. In contrast, the correlation function derived from the $I_\perp(q)$ for the sample at $\varepsilon = 8.03\%$ showed a bimodal peak. This indicates a coexistence of structures, where some lamellae remained undeformed while others contracted due to the Poisson effect.^{24, 25}

Both $l_p(\varphi)$ and $l_c(\varphi)$ were found to decrease compared to the unstretched state. These changes depend on the azimuthal angle. In the direction perpendicular to the stretching, these declines reflect the lateral contraction due to the Poisson effect, consistent with the *in-situ* X-ray scattering measurements during deformation described in Chapter 5. By contrast, the behavior along $\varphi = 0^\circ$ is governed by the stress relaxation process. Although the lamellar structure was initially elongated upon reaching the second yield point (as shown in Chapter 5), holding the sample at this strain for 30 minutes induced structural changes. The decrease in $l_c(\varphi)$ is attributed to mechanical melting occurring during this stress relaxation. Furthermore, the decrease in $l_p(\varphi)$ suggests that the taut tie molecules, which were highly stretched at the second yield point, relaxed during the holding period.

Table 6.1. Hermans orientation factors (f_H) and degrees of crystallinity for PA6 samples at $\varepsilon = 0\%$ and $\varepsilon = 8.03\%$.

Strain (ε)	f_H (Amorphous)	f_H (α -form)	Total Crystallinity (%)	α -form (%)	γ -form (%)
0%	1.11×10^{-4}	2.76×10^{-3}	52.2	51.2	0.96
8.03%	1.98×10^{-2}	3.01×10^{-2}	46.3	45.7	0.65

In WAXS 1D profiles, the small peak at $q = 15.06 \text{ nm}^{-1}$ originated from the γ -forms was observed, showing the PA6 crystallized at 200°C contained some γ -crystals. The proportion of γ -crystals was less than 1%, as will be discussed later. Furthermore, the Hermans orientation factor (f_H) of the polymer chain axis was calculated in the same manner as in Chapter 5 to evaluate the molecular orientation from the WAXS 1D profiles.^{21, 26, 27}

As listed in Table 6.1, the f_H value for the α -phase was slightly larger than that for the amorphous phase. Consistent with the discussion in Chapter 5, this gap is likely driven by the active rotation of α -crystals via coarse slip, coupled with the constraints of mobility in the glassy amorphous phase. Specifically, at the yield point, the amorphous phase between the fibrils appears to accommodate the heterogeneous deformation on the submicrometric scales, while the orientation of molecular chains is hindered at this stage. These factors collectively contribute to the poorer orientation of the amorphous network compared to the crystalline regions.

Finally, the change in crystallinity was evaluated from the WAXS data, calibrated using the DSC results as listed in Table 6.1. The crystallinity at $\varepsilon = 8.03\%$ decreased compared to the unstretched sample, indicating that strain-induced mechanical melting occurred even during the holding period. As indicated by the *in-situ* X-ray measurements discussed in Chapter 5, mechanical melting also leads to the fragmentation of long fibril structures into smaller crystalline blocks during this stress relaxation process.

Consequently, it was found that while the anisotropy of the crystalline structures increased with strain, the overall crystallinity decreased.

6.3.2 STXM Measurements

Figure 6.5 shows the NEXAFS spectra from PA6 at $\varepsilon = 8.03\%$. The red and blue lines indicate the spectra acquired with linearly polarized X-rays parallel and perpendicular to the stretching direction, respectively. The solid lines represent NEXAFS spectra scanned from 280 to 320 eV, while the dots correspond to the specific energy points selected for image analysis. The peak near 292 eV corresponds to C-1s $\rightarrow$

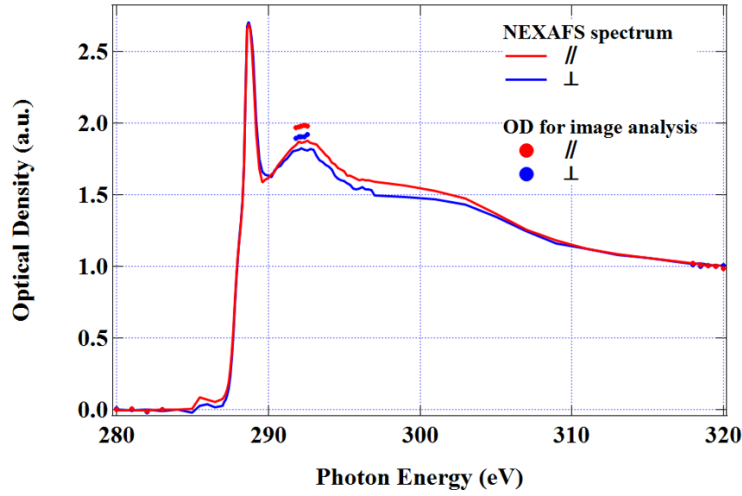


Figure 6.5. NEXAFS spectra at $\varepsilon = 8.03\%$. The Red and blue spectra were obtained by polarized X-rays parallel and perpendicular to the stretching direction, respectively.

σ^*_{C-C} resonances.²⁸ The optical density (OD) has the following relationship.^{28, 29}

$$OD = \mu \rho t \quad (6.3)$$

where μ is the mass absorption coefficient, ρ is the density, and t is the sample thickness.

OD of the chemical bond resonance is proportional to the square of $\cos \theta$, where θ is the angle between the electric field vector of incident X-rays (E) and the direction of transition dipole moment (TDM, μ_{if}),³⁰ such as

$$OD \propto |E \mu_{if}|^2 \propto \cos^2 \theta. \quad (6.4)$$

Therefore, the difference between the OD values obtained with polarizations parallel and perpendicular to the stretching direction reflects the molecular orientation within the stretched sample. As shown in Figure 6.5, the OD at 292 eV with parallel polarization was higher than that with perpendicular polarization. Since the TDM of the σ^*_{C-C} transition lies along the bond axis, this result indicates that the C–C bonds, in other words, the polymer chain backbones in PA6 are preferentially oriented along the stretching direction.

In contrast, the energy region from 318 eV to 320 eV is sufficiently far from the carbon K edge (≈ 285 eV). *OD* in this region is not affected by the orientation of the chemical bonds and depends solely on the density and the thickness of the sample. I calculated the average density of PA6 at each stretch ratio from the crystallinity listed in Table 6.1, based on the theoretical density of the crystalline and amorphous phases. The theoretical density of the α -, γ -crystals and amorphous phases is 1.23 g/cm³, 1.17 g/cm³ and 1.08 g/cm³, respectively.³¹

Additionally, I calculated the mass absorption coefficient (μ) of PA6 at 318 ± 2 eV at each stretch ratio, which is 2.62×10^4 cm²/g based on the X-ray attenuation length from the website of the Center for X-ray Optics (CXRO). Assuming that the sample thickness is uniform within the observed region for each strain state, the thickness was estimated using the calculated average density, the value of μ , and the average *OD* obtained from the 2D map at 319 ± 1 eV. The thicknesses at $\varepsilon = 0\%$ and 8.03% were estimated to be 359 and 401 nm, respectively. Finally, by applying these μ and thickness values to Equation 6.3, the *OD* images at 319 ± 1 eV were converted into local density (ρ) maps.

Figure 6.6 shows the evolution of the ρ maps and their histograms with strain. The contrasts in Figure 6.6a and b correspond with spatial density distribution between high-crystalline fibril region and low-crystalline inter-fibril region. The ρ histogram for the unstretched state exhibited a unimodal distribution, whereas that at $\varepsilon = 8.03\%$ showed a bimodal distribution. This trend is similar to that observed in stretched PE discussed in Chapter 3, indicating the development of stretch-induced density fluctuations.

Furthermore, to quantify the magnitude of the density fluctuations, the standard

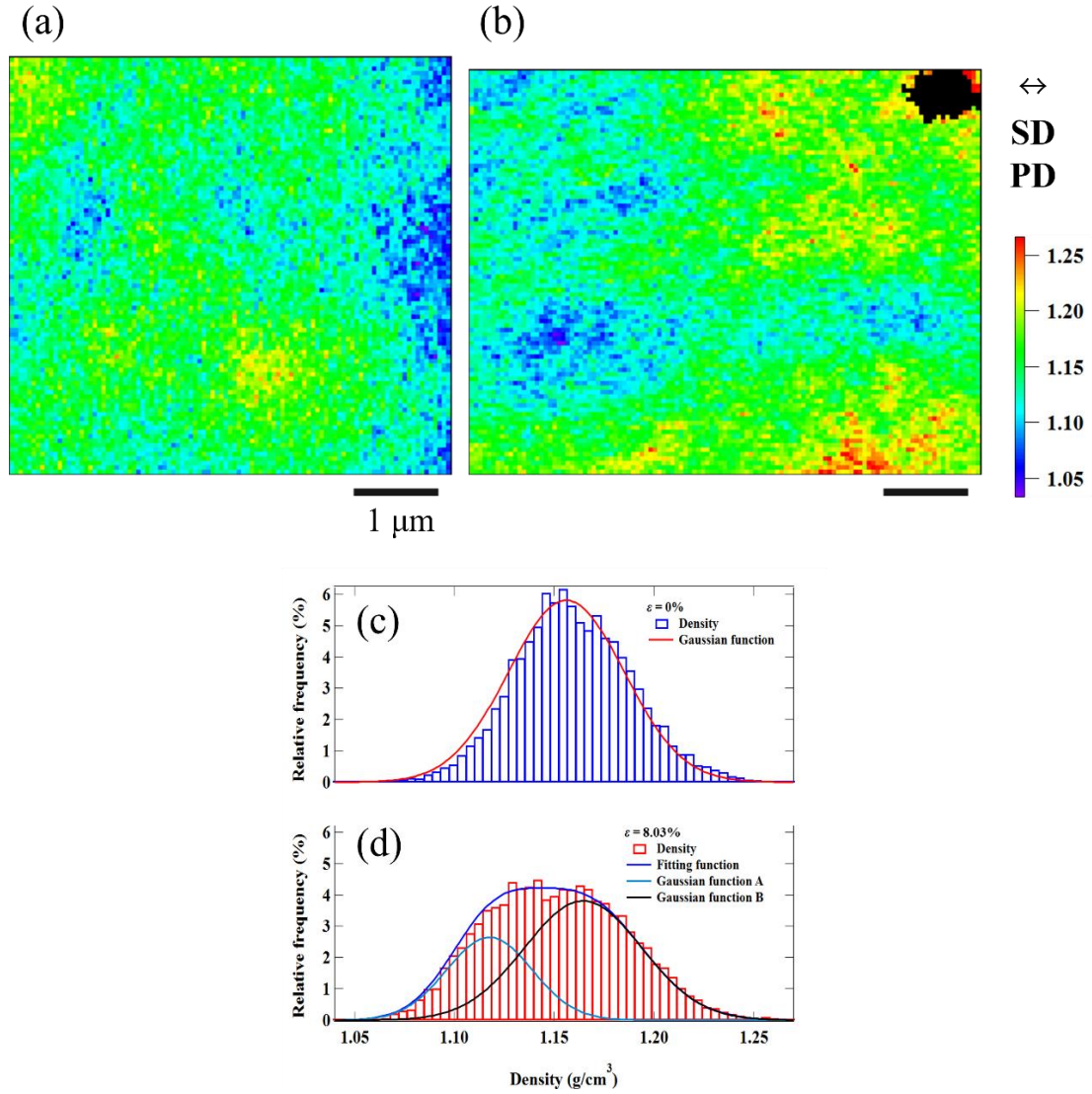


Figure 6.6. ρ maps and corresponding histograms for PA6 acquired at 319 ± 1 eV. (a, c) Unstretched sample ($\epsilon = 0\%$). (b, d) Sample stretched at $\epsilon = 8.03\%$. The polarization direction (PD) and stretching direction (SD) are horizontal on the page.

deviation of the pixel values in the ρ maps was calculated. The standard deviation increased from $2.93 \times 10^{-2} \text{ g/cm}^3$ at $\epsilon = 0\%$ to $3.52 \times 10^{-2} \text{ g/cm}^3$ at $\epsilon = 8.03\%$. This increase is consistent with the butterfly pattern observed by USAXS, which reflects the stretch-induced density fluctuation. Therefore, both the real-space (STXM) and reciprocal-space (USAXS) analyses consistently indicate the development of pronounced density fluctuations induced by strain.

The 2D maps of the orientation for the C–C bond were obtained as follows.

The orientation order parameter, $\langle P_2 \rangle$, was calculated by using the following equation.³²

$$\langle P_2 \rangle = \frac{OD_{C-C,\parallel} - OD_{C-C,\perp}}{OD_{C-C,\parallel} + 2OD_{C-C,\perp}} \quad (6.5)$$

where $OD_{C-C,\parallel}$ and $OD_{C-C,\perp}$ represent the optical densities attributed to the C–C bonds measured with polarizations parallel and perpendicular to the stretching direction, respectively. These values were obtained by subtracting the non-resonant background absorption associated with the values of the OD image at 319 ± 1 eV from the images acquired near the resonance peak at 292 eV. The value of $\langle P_2 \rangle$ is 1 for perfect parallel alignment of the C–C bonds in the stretching direction, while the value is -0.5 for perfect perpendicular alignment. $\langle P_2 \rangle = 0$ corresponds to the C–C bonds oriented randomly.

Figure 6.7 presents the $\langle P_2 \rangle$ maps and the corresponding histograms of $\langle P_2 \rangle$ calculated for the total values, the top 15% (high-density), and the bottom 15% (low-density) of the ρ regions at 319 ± 1 eV, both before and after stretching. These $\langle P_2 \rangle$ maps show the spatial orientation distribution of the C–C bonds. By constructing histograms for the upper and lower 15% of the ρ regions, it is possible to separately analyze the structural changes induced by stretching in the fibrils and inter-fibrillar regions, respectively. Table 6.2 summarizes the average $\langle P_2 \rangle$ values for the entire OD region, the high-, and the low-density regions.

In the unstretched state ($\varepsilon = 0\%$), the $\langle P_2 \rangle$ values were close to zero, whereas they exhibited a slight increase at $\varepsilon = 8.03\%$. Notably, the average $\langle P_2 \rangle$ value for the bottom 15% of the density distribution was comparable to the value of f_H of the amorphous phase determined from the WAXS 1D profile analysis. This confirms that the low-density regions in the ρ maps correspond to the non-fibrillar regions composed

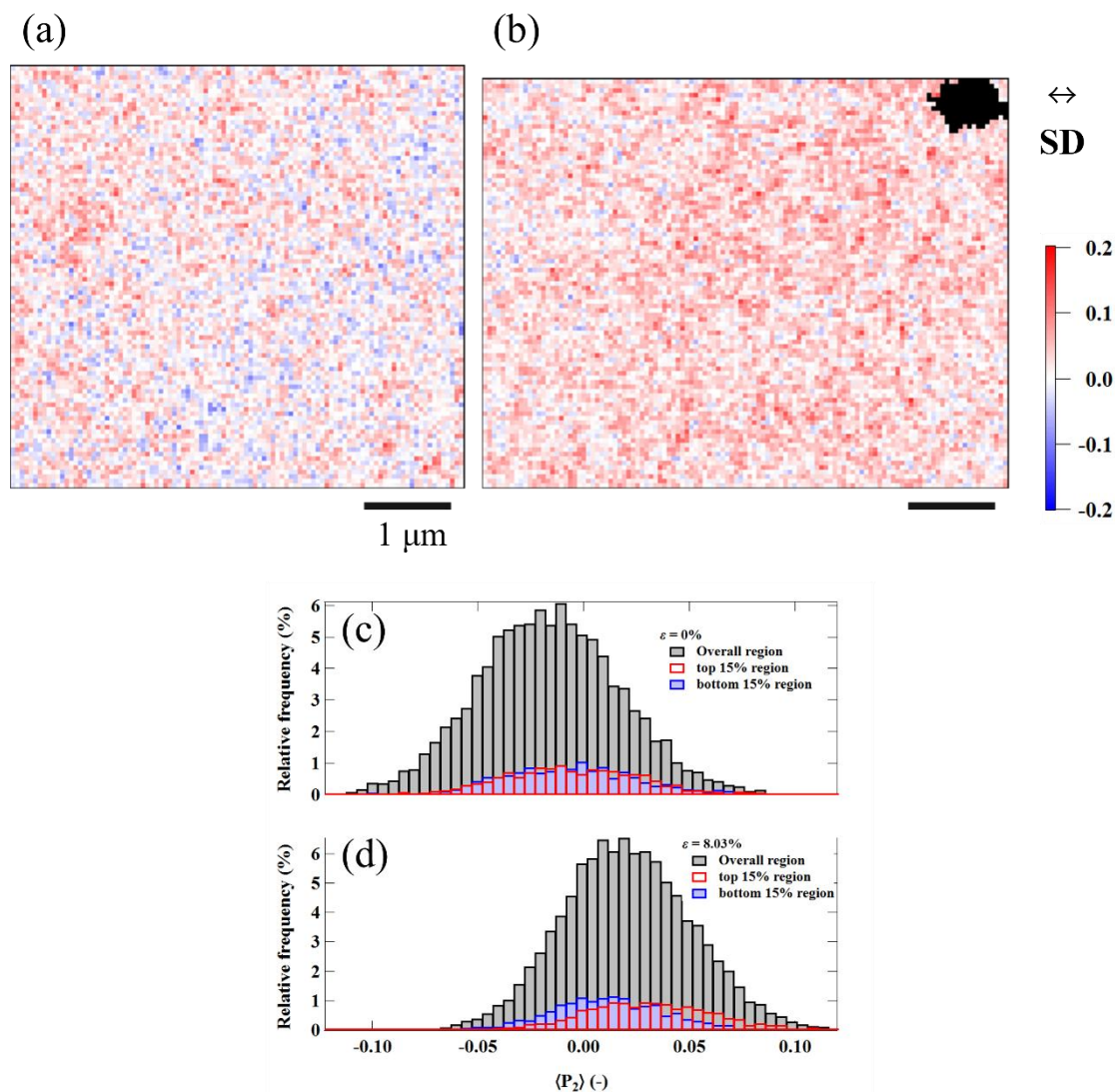


Figure 6.7. $\langle P_2 \rangle$ maps and corresponding histograms for PA6 in (a, c) unstretched state ($\varepsilon = 0\%$) and (b, d) state stretched at $\varepsilon = 8.03\%$, respectively. The stretching direction (SD) is horizontal on the page.

mainly of the amorphous phase. Besides, the average $\langle P_2 \rangle$ in the high-density region was slightly higher than that in the low-density region.

Significantly, the comparison between WAXS and STXM consistently indicates that the orientation of α -crystals is more pronounced than the amorphous orientation in the stretched state. This behavior differs clearly from that observed in PE during stretching above T_g ,^{15, 16} where allow more orientation of polymer chains

between fibrils than that in fibril regions. In PA6, the polymer chains in the glassy amorphous phase accommodate submicron-scale inhomogeneous deformation due to the stress induced by stretching, while its poor mobility results in limited orientation. Consequently, while density fluctuations on the fibril scale occur similarly in both polymers, the microscopic response is fundamentally different. In PA6, crystalline domains that undergo coarse slip and subsequent fragmentation associated with mechanical melting during stretching rotate and align more readily than the constrained amorphous network.

Table 6.2. $\langle P_2 \rangle$ for PA6 at Each Stretch Ratio.

Stretch ratio (ε)	Entire $\langle P_2 \rangle$	Low ρ region	High ρ region
0%	-6.23×10^{-3}	3.21×10^{-3}	5.23×10^{-3}
8.03%	3.06×10^{-2}	2.09×10^{-2}	4.03×10^{-2}

The combined analysis of X-ray scattering results and STXM measurements shows following conclusions about the structural evolutions. In the unstretched state, the spherulites packed loosely by fibril structures, as indicated by the mass-fractal dimension of 2.27. The overall structure exhibited random orientation, and the density distribution obtained from STXM was unimodal.

In contrast, at the second yield point, stretch-induced density fluctuations and orientational heterogeneity emerged due to stretching, resulting in a bimodal density distribution. These features are attributed to mechanical melting and heterogeneous deformation associated with the spatial distribution of crystallinity. In particular, this behavior of orientation differs from the heterogeneity observed in stretched PE, where deformation typically promotes significant orientation of the amorphous chains. In

glassy PA6, it was revealed that the amorphous phase accommodates heterogeneous deformation at the submicron scale, while microscopically exhibiting poor orientation. Consequently, the rotation and alignment of crystalline regions proceed more readily than the orientation of the amorphous network.

6.4 Conclusion

In this study, the spatial heterogeneity of chain orientation associated with strain-induced density fluctuations on the fibril scale in PA6 was clarified through a combined analysis using STXM and *in-situ* X-ray scattering (USAXS/SAXS/WAXS).

At the strain where the butterfly pattern was observed in USAXS, I successfully obtained real-space images of strain-induced density fluctuations using STXM. The spatially resolved analysis revealed that the orientational order in the high-density, crystalline regions was significantly more pronounced than in the low-density, amorphous regions.

The most significant insight arises from the obvious contrast with the behavior of PE. While both PA6 and PE exhibit similar macroscopic density fluctuations arising from heterogeneous deformation and mechanical melting, their microscopic responses are fundamentally different. In rubbery PE, the amorphous chains between fibrils undergo more considerable orientation on the submicron scales than polymer chains in fibril structures. Contrastingly, in glassy PA6, polymer chains deform in response to submicron-scale inhomogeneous strain in the inter-fibril regions, but the microscopic orientation is poorer than in the regions containing more crystal phase within the fibrils.

References

1. Holmes, D. R.; Bunn, C. W.; Smith, D. J. *J. Polym. Sci.* **1955**, *17* (84), 159–177.
2. Arimoto, H. *J. Polym. Sci., Part A*, **1964**, *2* (5), 2283–2295.
3. Arimoto, H.; Ishibashi, M.; Hirai, M.; Chatani, Y. *J. Polym. Sci., Part A* **1965**, *3* (1), 317–326.
4. Xu, J.-R.; Ren, X.-K.; Yang, T.; Jiang, X.-Q.; Chang, W.-Y.; Yang, Shuang.; Stroeks, A.; Chen, E.-Q. *Macromolecules* **2018**, *51* (1), 137–150.
5. Murthy, N. S.; Bray, R. G.; Correale, S. T.; Moore, R. A. F. *Polymer* **1995**, *36*, 3863–3873.
6. Samon, J. M.; Schultz, J. M.; Hsiao, B. S., *Polymer* **2000**, *41*, 2169–2182.
7. Dencheva, N.; Denchev, Z.; Oliveira, M. J.; Funari, S. S. *J. Appl. Polym. Sci.* **2006**, *103* (4), 2242–2252.
8. Guo, H.; Wang, J.; Zhou, C.; Zhang, W.; Wang, Z.; Xu, B.; Li, J.; Shang, Y.; de Claville Christiansen, J.; Yu, D.; Wu, Z.; Jiang, S. *Polymer* **2015**, *70*, 109–117.
9. Pepin, J.; Gaucher, V.; Rochas, C.; Lefebvre, J.-M. *Polymer* **2019**, *175*, 87–98.
10. Takenaka, M.; Shimizu, H.; Nishitsuji, S. *Phys. Rev. E* **2007**, *75*, 061802.
11. Arakawa, M.; Kabe, T.; Iwata, T.; Takenaka, M. *J. Appl. Crystallogr.* **2025**, *58* (3), 886–896.
12. Doi, M.; Onuki, A. *J. Phys. II* **1992**, *2*, 1631–1656.
13. Furukawa, A.; Tanaka, H. *Nat. Mater.* **2009**, *8*, 601–609.
14. Kishimoto M.; Mita K; Ogawa H.; Takenaka M. *Macromolecules* **2020**, *53*, 9097–9107.

15. Arakawa, M.; Kishimoto, M.; Uchida, K.; Nakanishi, Y.; Takenaka, M. *Macromolecules* **2026**, *59* (1), 369–378.
16. Arakawa, M.; Kishimoto, M.; Nakanishi, Y.; Takenaka, M. *Polym J.* **2022**, *54*, 243–248.
17. Takeichi, Y.; Inami, N.; Suga, H.; Ono K.; Takahashi Y. *Chem. Lett.* **2014**, *43*, 373–375.
18. Pepin, J.; Gaucher, V.; Rochas, C.; Lefebvre, J.-M. *Polymer* **2019**, *175*, 87-98.
19. Wunderlich, B. *Macromolecular Physics: Crystal Melting*; Academic Press: New York, **1980**; Vol. 3.
20. Owen, A.; Bergmann, A. *Polymer International* **2004**, *53* (1), 12-14.
21. Hashimoto, T., *Principles and Applications of X-ray, Light and Neutron Scattering*; Springer Nature Singapore Pte Ltd.: Singapore, 2022.
22. Strobl, G. R.; Schneider, M. *J. Polym. Sci., Polym. Phys.* **1980**, *18*, 1343–1359.
23. Strobl, G. R.; Schneider, M. J.; Voigtmartin, I. G. *J. Polym. Sci., Polym. Phys.* **1980**, *18*, 1361–1381.
24. Xiong, B.; Lame, O.; Chenal, J.-M.; Rochas, C.; Seguela, R.; Vigier, G. *Polymer* **2014**, *55* (5), 1223–1227.
25. Damodaran, S.; Schuster, T.; Rode, K.; Sanoria, A.; Brüll, R.; Stöhr, N. *Polymer* **2015**, *60*, 125–136.
26. Alexander, L. E., *X-ray Diffraction Methods in Polymer Science*; John Wiley and Sons Inc.: New York, 1969.
27. Wang, C.; Hashimoto, T.; Lu, C.-Y.; Lu, P.-H.; Tsai, C.-W. *Macromolecules* **2024**, *57* (24), 11586-11598.

28. Dhez, O.; Ade, H.; Urquhart, S.G. *J. Electron Spectrosc. Relat. Phenom.* **2003**, *128*, 85–96.
29. Fu, J.; Urquhart, S. G. *Langmuir* **2007**, *23*, 2615–2622.
30. Fu, J.; Urquhart, S. G. *J. Phys. Chem. A* **2005**, *109*, 11724–11732.
31. Roldan, L. G.; Kaufman, H. S. *J. Polym. Sci. Part B: Polym. Lett.* **1963**, *1* (11), 603–608.
32. Hernández Cruz, D.; Rousseau, M.-E.; West, M. M.; Pézolet, M.; Hitchcock, A. *P. Biomacromolecules* **2006**, *7*, 836–843.

Summary

This thesis includes the studies on the time evolution of hierarchical structures in crystalline polymers under deformation, utilizing a combination of real-space chemical imaging and reciprocal-space multiscale X-ray analysis. I summarize each chapter as follows.

In Chapter 1, I described the background, the motivation, and the outline of this thesis.

In Chapter 2, I developed a quantitative framework for STXM to characterize LLDPE spherulites, integrated with multi-scale scattering. By decoupling local density from the orientation order parameter at the sub-micrometer scale, I identified a distinct 180-degree phase shift between C–H bond orientation and fluctuations in density and C–C bond orientation by STXM. I consistently explained this spatial correlation using a geometric model of the orthorhombic unit cell twisting around the *b*-axis. My analysis confirmed that systematic lamellar twisting coexists with a mass-fractal fibril packing, providing a methodology for the pixel-wise quantification of molecular order via dual-polarization STXM.

In Chapter 3, I investigated the evolution of density and C–C bond orientation in LLDPE during uniaxial stretching, focusing on structural changes at the strains near two yield points. By combining STXM with *in-situ* X-ray scattering, I quantified crystallinity-dependent inhomogeneous deformation across different strain regimes. I found that molecular orientation develops preferentially in low-density regions, providing new insights into deformation dynamics at the sub-micrometer scale.

In Chapter 4, I studied the hierarchical structural changes in the biodegradable homopolymer P(3HB) and the copolymer P(3HB-*co*-3HH) to clarify the origin of

improved ductility. Using *in-situ* USAXS, SAXS, and WAXS, I found that the introduction of 3HH comonomer units suppresses long-range order and facilitates stress dispersion. This structural formation suppresses sub-micrometer inhomogeneous deformation, as evidenced by the weaker “abnormal” butterfly patterns in USAXS.

In Chapter 5, in order to investigate the universality of heterogeneous deformation, I observed the structural evolution of PA6 during stretching at room temperature below its T_g . I reported the observation of abnormal butterfly patterns in the USAXS region for a polymer in the glassy state. The results indicate that strain-induced density fluctuations occur even when amorphous chains are in a glassy state, and I clarified that the competition between cavitation and shear banding is governed by crystal stability and initial morphology.

In Chapter 6, in order to clarify the local inhomogeneity of chain orientation in polar crystalline polymers, I performed STXM observations on stretched PA6. I visualized the spatial fluctuations of density and C–C bond orientation. In glassy PA6, it was found that the orientation of amorphous chains between fibrils is restricted at the submicron scale, and crystalline domains within fibrils orient more readily than the amorphous network. This microscopic response indicates a fundamental difference in the deformation mechanisms between glassy PA6 and rubbery PE.

List of Publications

1. “Hierarchical Structure of LLDPE Spherulites Revealed through Integrated Molecular Orientation and Density Distribution Analysis via STXM, X-ray Scattering, and Light Scattering”
Arakawa, M.; Kishimoto, M.; Nakanishi, Y.; Ogawa, H.; Nishida, K.; Takenaka, M.
To be submitted.
(Chapter 2)
2. “STXM Studies on the Changes in the Spatial Distribution of Density and Chain Orientation of LLDPE with Strain”
Arakawa, M.; Kishimoto, M.; Uchida, K.; Nakanishi, Y.; Takenaka, M.
Macromolecules **2026**, 59 (1), 369–378.
(Chapter 3)
3. “Differences in Hierarchical Structural Changes between Unoriented P(3HB) and P(3HB-co-3HH) under Stretching”
Arakawa, M.; Kabe, T.; Iwata T.; Takenaka, M.
J. Appl. Cryst. **2025**, 58, 886–896
(Chapter 4)
4. “Enhancement of the Density Fluctuations of Polyamide-6 with Strain below Glass Transition Temperature”
Arakawa, M.; Wang, C.; Nakanishi, Y.; Ogawa, H.; Takenaka, M.
To be submitted.
(Chapter 5)
5. “Spatial Heterogeneity of Density and Orientation in Stretched Polyamide-6 Revealed by STXM”
Arakawa, M.; Nakanishi, Y.; Miyazaki, T.; Ogawa, H.; Takenaka, M.
To be submitted.
(Chapter 6)

Other Publications

6. “Spatial Inhomogeneity of Chain Orientation Associated with Strain-Induced Density Fluctuations in Polyethylene”
Arakawa, M.; Kishimoto, M.; Nakanishi, Y.; Mita, K.; Takenaka, M.
Polymer Journal **2022**, *54*, 243–248.
7. “Water-Assisted Microphase Separation of Cationic Random Copolymers into Sub-5 nm Lamellar Materials and Thin Films”
Imai, S.; Arakawa, M.; Nakanishi, Y.; Takenaka, M.; Aoki, H.; Ouchi, M.; Terashima, T.
Macromolecules **2022**, *55*, 20, 9113–9125.
8. “Neutron Reflectivity Study on the Adsorption Layer of Polyethylene Grown on Si Substrate”
Shimokita, K.; Yamamoto, K.; Miyata, N.; Shibata, M.; Nakanishi, Y.; Arakawa, M.; Takenaka, M.; Kida, T.; Tokumitsu, K.; Tanaka, R.; Shiono, T.; Yamada, M.; Seto, H.; Yamada, N. L.; Aoki, H.; Miyazaki, T.
Langmuir **2024**, *40*, 30, 15758–15766.
9. “Strain-induced density fluctuations in linear low-density polyethylene”
Kishimoto, M.; Mita, K.; Ogawa, H.; Shibasaki, K.; Arakawa, M.; Takenaka, M.
J. Appl. Cryst. **2025**, *58*, 879–885
10. “Modeling the extraction of bound rubber from silica-filled styrene-butadiene rubber with toluene”
Tamura, Y.; Arakawa, M.; Takenaka, M.; Nakanishi, Y.; Fujinami, S.; Shibata, M.; Yamamoto, K.; Miyata, N.; Yamada, M.; Seto, H.; Yamada, N. L.; Aoki H.; Miyazaki, T.
Polymer **2025**, *333*, 128662.
11. “Nondestructive Evaluation of the Spatial Distribution of Nanofillers and Network Structures in Buried Epoxy Resins under Adhesion Conditions”
Ogawa, H.; Tobita, N.; Ono, S.; Wang, P.; Kubozono, T.; Yoshihara, D.; Yamada, S.; Arakawa, M.; Yamamoto, S.; Tanaka, K.; Takenaka, M.
ACS Appl. Polym. Mater. **2025**, *7*, 15, 10051–10061.

Acknowledgments

The present thesis is based on the studies conducted at the Institute for Chemical Research (ICR), Kyoto University, Kyoto between 2020 and 2026. The studies carried out from 2023 to 2026 were supported by JSPS Grant-in-Aid for JSPS Fellows Grant Number JP 23KJ1338.

I would like to express my deepest gratitude to Prof. Mikihiro Takenaka for his constant guidance, encouragement, invaluable comments, and fruitful discussions throughout my graduate and undergraduate studies.

Prof. Tsuyoshi Koga and Prof. Yo Nakamura are especially acknowledged for their critical review of this thesis.

I would like to express my sincere thanks to Assoc. Prof. Hiroki Ogawa, Assist. Prof. Yohei Nakanishi, Assist. Prof. Kazuki Shibasaki and Dr. Koji Nishida for their helpful advice and encouragement, and I also thank all the members of Takenaka laboratory for their kind help.

I greatly thank Dr. Kiminori Uchida and Dr. Mizuki Kishimoto (Mitsui Chemicals, Inc.) for invaluable discussions and opportunities for the synchrotron radiation X-ray experiments. I am especially indebted to Dr. Kishimoto for his excellent supervision and support during his doctoral studies in Takenaka laboratory, which greatly enriched this research.

I wish to thank Prof. Tadahisa Iwata and Assist. Prof. Taizo Kabe (University of Tokyo, Tokyo) for sample provision and invaluable discussions.

I would like to thank Prof. Chi Wang (National Cheng Kung University, Tainan)

for his technical support in analysis, fruitful discussions, encouragement, and insightful advice.

I am sincerely grateful to Dr. Hiroyasu Masunaga (Japan Synchrotron Radiation Research Institute, JASRI) for his kind support in the USAXS, SAXS, and WAXS measurements at SPring-8 BL03XU; to Assist. Prof. Yasuo Takeichi, Assist. Prof. Shohei Yamashita and Assist. Prof. Daisuke Wakabayashi (KEK) for their kind support in the STXM observation.

The synchrotron radiation X-ray experiments included in this thesis are listed in the following table:

Proposal No.	Facility	Beamline No.	Corresponding Chapter
2020G091	Photon Factory	BL-19A	Chapter 3
2021G680	Photon Factory	BL-19A	Chapter 3
2022B7263	SPring-8	BL03XU	Chapter 4
2023A7214	SPring-8	BL03XU	Chapters 3 and 4
2023B7263	SPring-8	BL03XU	Chapters 3 and 4
2023G062	Photon Factory	BL-19A	Chapter 6
2023G170	Photon Factory	BL-19A	Chapters 2 and 6
2024A7214	SPring-8	BL03XU	Chapter 5
2024B7263	SPring-8	BL03XU	Chapters 2, 5 and 6
2025B7408	SPring-8	BL03XU	Chapter 2

Finally, I wish to express my heartfelt thanks to my family for their continuous support and encouragement.

March 2026

Masato Arakawa