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Author(s)	Ree, Brian Jiwon
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博士の専攻分野の名称 博士（工学） 氏名 REE BRIAN JIWON

	主査	教授	渡慶次 学
	副査	教授	佐藤 敏文
審査担当者	副査	教授	佐田 和己
	副査	准教授	田島 健次
	副査	准教授	山本 拓矢

学 位 論 文 題 名

Nanoscale Film Morphologies of Topological Polymers
(トポロジカルポリマーが形成するナノスケール薄膜のモルフォロジーに関する研究)

Polymer topology describes the shape and spatial features of the polymer's main chain. In particular, all nonlinear topological polymers are characterized by their different physical properties such as self-assembly behavior. This phenomenon occurs from the unique spatial features impacting the chain conformation and the physical properties. Currently, there are many reports demonstrating novel synthetic strategies for a wide range of topologically complex polymers. Due to the difficulty in synthesis, however, there is a lack of characterization studies, and the comprehension of how different topological features impact the overall polymer morphology and self-assembly remain unexplored. To resolve this issue, a thorough interpretation of topology-morphology correlation is necessary. For accurate and precise morphological characterization of topological polymers with quantitative structural parameters and statistical evaluation, synchrotron X-ray scattering technique present many advantages over microscopy. To establish a fundamental understanding of topology-morphology correlation, the author carried out quantitative analyses of synchrotron grazing incidence X-ray scattering (GIXS) data of polymer thin films through novel modeling methods: (1) three layer model and (2) two phase elliptical hexagonal cylinder model. These novel models achieved in providing detailed structural parameters of resulting polymer thin film morphology and key insights regarding the topology-morphology correlation.

Chapter 1 outlines the current state of research on topological polymers, background in the relationship between polymer topology and polymer self-assembly behavior, theoretical background regarding synchrotron X-ray scattering technique, theoretical details of the novel analytical models utilized in this dissertation, and the objective of the dissertation.

Chapter 2 discusses the nanoscale film morphologies of various poly(ϵ -caprolactone)s in cage shape (cg-PCL9k), star shape (st-PCL9k), cyclic shape (cy-PCL6k), and two types of linear shape (l-PCL3k-A and l-PCL3k-B) through quantitative analysis of synchrotron grazing incidence X-ray scattering. All PCL polymers always form lamellar structures based on orthorhombic crystal lattice in nanoscale films. However, the cage-shaped and cyclic polymers form a mixture of horizontal and vertical lamellar structures, whereas all other counterparts form only horizontal lamellar structures. The structural parameters, including overall crystallinity and orientational orthorhombic crystal domains, are further varied by the molecular topologies as well as the bulkiness of joints and end groups. This is the first investigation of thin film morphologies of topological PCLs.

Chapter 3 describes the phase transitions and nanoscale film morphologies of poly(δ -valerolactone) (PVL) axles bearing movable and fixed dibenzo-24-crown-8-ether wheels (rot-M and rot-F): PVL-rot-M and PVL-rot-F. The PVL axles exhibit a strong tendency to form horizontal lamellar structure. Overall, the structural parameters show the differences and influences of the movable and fixed rotaxane wheels. Particularly, the rot-M wheel tend to be populated in the interfacial and amorphous layers. In contrast, the rot-F wheel tend to be localized in the interfacial layer rather than the amorphous layer because of its immovability constrained at the polymer chain end. This is the first detailed investigation of thin film morphologies of PVL polyrotaxane system as well as the characterization of PVL crystal lattice structure in thin film.

Chapter 4 describes the nanoscale film morphologies of poly(δ -valerolactone) (PVL) axles bearing movable and ionically-fixed rotaxane wheels linked with polystyrene (rot-PS-M and rot-PS-F) by synchrotron GIXS: PVL-rot-PS-M and PVL-rot-PS-F. The quantitative analyses found that the movable rotaxane wheel could significantly enhance the mobilities of PVL axle and PS block, which are essential for their phase-separation and the PVL axle's crystallization. With higher chain mobilities due to the movable rotaxane wheel, PVL-rot-PS-M always reveals much better performance in the formation of phase-separated PVL/PS lamellar structure as well as in the crystallization of PVL axle chain, compared to PVL-rot-PS-F and counter diblock copolymer. All morphology details, as well as thermal stability and phase transition details are discussed with considering the natures of movable, ionically-fixed and covalent-bonded linkers between PVL and PS blocks. This is the first detailed investigation of phase-separated microstructures of PVL-PS polyrotaxane system in nanoscale films.

Chapter 5 examine the nanoscale film morphologies of a series of cyclic and tadpole-shaped poly(n-decyl glycidyl ether-block-2-(2-(2-methoxyethoxy)ethoxy)ethyl glycidyl ether)s in equivalent volume fractions, including their linear counterpart: c-PDGE-b-PTEGGE, tp-A-PDGE-b-PTEGGE, tp-B-PDGE-b-PTEGGE, and l-PDGE-b-PTEGGE. Due to their immiscibility between PDGE and PTEGGE, all polymers form phase-separated nanostructures. However, the nanostructure type is highly dependent on topology type. For the cyclic topology, the domain spacing reduction is nearly double in comparison to the linear counterpart than those predicted and reported. Even for the tadpole-shaped copolymer films, the domain spacing reductions are comparable to those predicted and reported. Furthermore, the cyclic and tadpole-shaped block copolymers form well-defined and oriented domain structures. This is the first detailed structural characterization of block copolymers with cyclic and tadpole topologies in nanoscale films.

Chapter 6 describes the nanoscale film morphologies of a series of four different bicyclic block copolymers based on poly(n-decyl glycidyl ether) and poly(2-(2-(2-methoxyethoxy)ethoxy)ethyl glycidyl ether) blocks in equivalent volume fractions with respect to their bicyclic topologies: Bicycle-A, B, C, and D. The quantitative synchrotron GIXS characterization has found that all topological bicyclic copolymers form phase-separated nanostructures. The morphological types and structural parameters of the nanostructures are highly dependent on the molecular topologies. Bicycle-A favorably forms hexagonal cylindrical nanostructure while Bicycle-B, C, and D form lamellar nanostructures. Interestingly, all bicyclic copolymers demonstrate nanostructures with significantly reduced domain spacings compared to the linear counterpart. This is the first quantitative morphological investigation of bicyclic block copolymers in nanoscale films.

Chapter 7 discusses the nanoscale film morphologies of a series of tricyclic heteroblock copolymers based on poly(n-decyl glycidyl ether) and poly(2-(2-(2-methoxyethoxy)ethoxy)ethyl glycidyl ether) blocks in equivalent volume fractions: Tricycle-A, B, and C. The morphological features have been identified and parameterized via synchrotron GIXS analysis. All tricyclic copolymer films are amorphous but reveal phase-separated lamellar nanostructures. The nanostructure reveals variations in the dimensional parameters, orientation, and positional stability depending upon the molecular topologies. In particular, all nanostructures exhibit sub 10 nm domain spacings, which are remarkably smaller than that of the linear counterpart. This is the first quantitative morphological characterization of tricyclic block copolymers in nanoscale films.

Chapter 8 describes the nanoscale film morphology details of cage-shaped heteroblock copolymers in three different topologies (Cage-A, B, and C) have been investigated for the first time by using synchrotron GIXS. All cage copolymers exhibit phase-separated nanostructures. Their types and structural parameters are varied depending on the cage topologies. Very interestingly, all nanostructures show domain spacings approximately 10 nm. These domain spacings are only 25.5 to 45.2 % of that of the linear block copolymer counterpart. Overall, this study has demonstrated that the cage-shaped heteroblock copolymer approach is a very efficient route to produce nanostructure with significantly reduced domain spacing. This is the first detailed investigation of phase-separated nanostructures formed by cage block copolymers in nanoscale films.

In conclusion, the author has successfully developed two novel theoretical models (three layer model and two phase elliptical hexagonal cylinder model) that were capable of analyzing a wide range of GIXS data from nanoscale films of various topological homopolymers and copolymers. The author has also established an effective methodology in resolving the morphological features of topologically complex polymers and identifying the topology-morphology correlation, which is a great achievement benefitting topological polymer research. Such analysis method presents a great potential as an effective tool to aid in developing novel topological polymers for various applications. This dissertation can be recognized to be awarded a Ph.D. degree in engineering from Hokkaido University.