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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. A systematic interpretation based on the number of chains, the number of chain ends, and the number of chain junctions for all types of topologies could be effective for understanding the polymer topology influences upon self-assembly characteristics and morphological properties. For accurate and precise morphological characterization of topological polymers with quantitative structural parameters and statistical evaluation, synchrotron X-ray scattering technique present advantages over microscopy. To achieve a fundamental comprehension of topology-morphology correlation, synchrotron grazing incidence X-ray scattering (GIXS) data of polymer thin films were analyzed by novel modeling methods: three layer model and two phase cylinder model. Model analysis achieved detailed discussions and provide specific insights the correlation of polymer topology and polymer morphology in nanoscale films for following case studies: a set of topologically complex poly(ε-caprolactone) homopolymers, a set of rotaxane containing poly(δ-valerolactone) homopolymers, a set of pseudo miktoarm block copolymers based on poly(δ-valerolactone)s macromolecular rotaxane linked to polystyrene, a set of cyclic and tadpole block copolyethers, a set of multicyclic and caged block copolyethers.

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.

Chapter 9 summarizes the results. Chapter 2 and 3 demonstrate the impact of polymer topology in semi-crystalline homopolymers PCL and PVL, in which the sterics originating from the bulkiness of connection joints or rotaxane wheels impact the crystallization processes and influence the overall nanoscale film morphologies. Chapter 4 demonstrates that pseudo-miktoarm topology is capable of improving the nanoscale film morphology more than conventional linear topology. Chapter 5 reveal that the cyclic and tadpole topologies offer block copolymers to self-assembled into well-defined, orientation-controlled, and cylinder or lamellar based nanostructures with significantly reduced domain spacings than linear topology. Chapter 6 exhibits bicyclic topology offers self-assembly behavior enabling the formation of well-defined cylinder or lamellar based nanostructures with approximately 10 nm domain spacings. Chapter 7 demonstrates tricyclic topology as highly efficient polymeric platform for developing high performance nanolithographic materials based on sub 10 nm domain spacing. Chapter 8 shows the cage topology is also capable of enabling approximately 10 nm domain spacings in phase separated structures. All results and insights regarding topology-morphology correlation were successfully obtained through the utilization of novel model analysis method (three layer model and two phase cylinder model) of synchrotron GIXS data. Throughout the dissertation, the novel model analysis method has demonstrated the delivery of statistical and quantitative information regarding the extent of polymer topology's impact upon morphological behavior of various polymers in nanoscale film. Such analysis method presents a potential as an effective tool to aid in the future development of topological polymers for nanotechnology applications.