Title	Nanoscale Film Morphologies of Topological Polymers [an abstract of entire text]
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Citation	北海道大学. 博士(工学) 甲第14025号
Issue Date	2020-03-25
Doc URL	http://hdl.handle.net/2115/80559
Type	theses (doctoral - abstract of entire text)
Note	この博士論文全文の閲覧方法については、以下のサイトをご参照ください。
Note(URL)	https://www.lib.hokudai.ac.jp/dissertations/copy-guides/
File Information	Brian_Jiwon_Ree_summary.pdf

博士論文の要約

Ree Brian Jiwon

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. Particularly, 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 comprehending the topological influences on polymer self-assembly characteristics and morphological properties. To accurately and precisely characterize the morphological features of topological polymers based on quantitative structural parameters and statistical evaluation, synchrotron X-ray scattering technique present advantages over microscopy. Specifically, synchrotron grazing incidence X-ray scattering method on polymer thin films was utilized to investigate the topology-morphology correlation on fundamental basis accompanied by novel modeling methods: three layer model and two phase cylinder model. The modeling analysis obtained detailed structural parameters, and achieved to provide detailed discussions and specific insights regarding 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*-PCL_{9k}), star shape (*st*-PCL_{9k}), cyclic shape (*cy*-PCL_{6k}), and two types of linear shape (*l*-PCL_{3k}-A and *l*-PCL_{3k} -B) through quantitative analysis of synchrotron grazing incidence X-ray scattering. All topological PCLs 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 between the morphological impact brought by movable and fixed rotaxane wheels. Particularly, the mobile rotaxane wheel tends to be populated in the interfacial and amorphous layers. In contrast, the fixed rotaxane wheel tends to be localized in the interfacial layer due to its immobility positioned 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 to polystyrene (*rot*-PS-M and *rot*-PS-F) by synchrotron GIXS: PVL-*rot*-PS-M and PVL-*rot*-PS-F. The quantitative analysis found that the movable rotaxane wheel significantly enhances the mobilities of both PVL axle and PS block. This consequently results in enhancing the phase-separation between PVL and PS, as well as the crystallization of PVL axle. With higher chain mobilities, PVL-*rot*-PS-M outperforms regarding the formation of phase-separated PVL/PS lamellar structure as well as in the crystallization of PVL axle chain when compared to PVL-*rot*-PS-F and diblock copolymer counterpart. All morphological features, in addition 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 examines 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 the immiscibility between PDGE and PTEGGE blocks, all copolymers form phase-separated nanostructures inside nanoscale films. However, the nanostructure type is highly dependent on the topology of the copolymer (linear, cyclic, or tadpole). For 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 copolymers, the domain spacing reductions are comparable to those predicted and reported. Furthermore, the cyclic and tadpole-shaped block copolymers form well-defined domain structures with unidirectional orientation. 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 structural parameters, lamellar orientation, and lamellar ordering depending upon the molecular topologies. In particular, all nanostructures exhibit sub-10 nm domain spacings, which are remarkably shorter than their 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 technique. All cage copolymers exhibit phase-separated nanostructures. Their morphological types and structural parameters are varied depending on the block arrangement within the three-armed cage topologies. 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. All results and insights regarding topology-morphology correlation were successfully obtained through the novel model analysis method (three layer model and two phase cylinder model) of synchrotron GIXS data developed for this dissertation. Throughout the previous chapters, the novel model analysis method has successfully demonstrated the delivery of statistical and quantitative structural parameters correlated to 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.