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（博士課程）
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論 文 要 旨

THESIS SUMMARY

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要旨（英文 800 語程度）
Thesis Summary（approx.800 English Words ）

This dissertation titled "High-χ Parameter Diblock Copolymers with Fluorinated Side Chains for Next Generation Lithography" focused on the molecular designs on novel high χ parameter block copolymers (BCPs) with semi-fluorinated liquid crystalline or amorphous side chains and essential efforts to satisfy the requirements in thin film for next-generation lithographic application.

Chapter 1 "General Introduction" firstly introduces block copolymers (BCPs) self-assembly theory. Owing to the advantage of high-χ parameter from BCPs with fluorinated side chains, the relevant works were further reviewed. The guideline for BCPs domain orientation control in thin film via tuning interface and the general BCP lithographic technology were also outlined.

Chapter 2 "The Role of Liquid Crystalline Side Chains for Long-range Ordering in the Block Copolymer Thin Films" focused on side chain liquid crystalline (SCLC) fluorinated functionalities capable of forming minimal spacing and controlling the orientation of the BCP domains in thin film. By introducing 1H,1H,2H,2H-perfluorodecanethiol onto a precursor polymer to obtain a novel BCP PS-*b*-P8FMA with C_8F_{17}-containing LC side chains, a high χ parameter (χ =0.244 at 25 °C) and strong LC side chain ordering enabled the formation of BCP domains in 6.3-36.3 nm scale. A co-existed 3.6 nm periodicity from smectic phase of SCLC was also verified. The quantitative analysis on images obtained from atomic force microscopy (AFM) of the thin films revealed the formation of fingerprint patterns with increased correlation length when the LC ordering began to dominate the hierarchical self-assembly.

Chapter 3 "Study on Effects of Semifluorinated Side Chains with Varied Lengths on Self-assembly Morphology of Diblock Copolymer" further investigated the hierarchical self-assembly morphology with a minimal spacing in thin film. Because of the confinement from smectic LC structures, anisotropic hexagonally packed PS cylinder domains with an averaged periodicity of 11.5 nm were characterized. Owing to the anisotropic array, two striations of distinctive dimensions (a_1=10.9 nm and a_2=12.7 nm) from side view of the array were observed. To better investigate the role of LC structures in this hierarchical self-assembly system, the effects of side chain length were investigated by introducing semi-fluorinated side chains of varied

lengths (CF_3, C_4F_9, C_6F_{13} and C_8H_{17}) into a fixed precursor BCP. The morphology studies on BCPs of varied fluorinated side chains revealed the significant role of LC side chain ordering on this anisotropy in hierarchy self-assembly morphology.

Owing to the observed anisotropic array in Chapter 3, the potential for tailoring domain size and domain orientation was indicated. Therefore, in the following Chapter 4 "Adjusting Thin Film Domain Spacings of Side-Chain Liquid Crystalline Semi-fluorinated Block Copolymers with Elliptical Cylinders with Anisotropic Hexagonal Packing", a facile approach of PS-*b*-P8FMA domain orientation control in thin film was demonstrated by tuning the composition of the copolymers of the bottom surface layer (BSL). Random copolymers poly(methyl methacrylate-*random*-2,2,2-trifluoroethyl methacrylate-*random*-methacrylic acid)s were used as BSLs in the study. Perpendicularly oriented PS domains in anisotropic hexagonally packed array were obtained by using a non-preferential neutral BSL. Besides, as the composition of BSL is tuned from PS-preferential to P8FMA-preferential, a dimension transition of striation pattern from d_1 (d_1=11.9 nm) to a wider d_2 (d_2=13.9 nm) is revealed, in which two distinctive dimensions of patterns are in response to non-tilted and tiled PS cylinders in parallel orientation to the substrate. Therefore, both type and dimension of long-ranged patterns could be easily tailored in thin films partially owing to the anisotropic feature of packing array. The thin film study in Chapter 4 using BCPs of varied side chain lengths also revealed the essential role of intensive LC ordering for successful orientation control on BCP domain in long-range orders.

Chapter 5 "A High-χ Silicon-backbone in Combination with Fluorinated Side Chains Block Copolymer of Ultra-fast Thermal Annealing for Forming Perpendicular Pattern" introduced perfluoroalkyl side chains into silicon-backbone BCP because of the well-known advantages of inorganic silicon-based hybrid BCPs, including high χ parameter and enormous etching contrast. A high χ parameter diblock polymer PS-*b*-PSi8F was synthesized by post-polymerization functionalization of its precursor polystyrene-*block*-poly(methyl vinyl siloxane) (PS-*b*-PMVS) with 1H,1H,2H,2H-perfluorodecanethiol via a thiol-ene reaction. The χ parameter was increased after the incorporation of super-hydrophobic of fluorinated side chain and the χ value at 160 °C was estimated to be 0.095 and 0.179 for precursor PS-*b*-PMVS and PS-*b*-PSi8F, respectively. This in turn resulted in enhanced segregation strength and thus self-assembled domains in minimal 10 nm-scale spacing were formed. The observed self-assembled morphologies were later found mutually consistent with the modified self-consistent field theory (SCFT) prediction. To overcome the preferential segregation due to the surface energy difference, the PS-*b*-PSi8F thin film was sandwiched between both neutral top and bottom interfaces, where the top coat involved a polarity switch and the bottom coat involved a cross-linking process. Perpendicular orientation of lamellae was successfully achieved in thin film and a pattern consisted of silicon oxide was subsequently obtained after removing organic components via oxygen plasma etching.

Chapter 6 "Downsizing the Thin Film Domain of Poly-(styrene-*block*-methyl methacrylate) by Introducing Fluorine to Randomly Pre-polymerized Functional Units" focused on chemically modified poly(styrene-*block*-methyl methacrylate) (PS-*b*-PMMA), which is the most widely studied BCP for lithography due to its ability to form perpendicularly oriented features when simply heated on an energetically non-preferential substrate. However, the desired smallest attainable pattern size prepared from PS-*b*-PMMA is limited to a full pitch of 24 nm, because of the weak segregation between segments. To address the problem, the randomly polymerized moieties were first incorporated into the PMMA-block inside PS-*b*-PMMA and later quantitative 2,2,2-trifluoroethanethiol was introduced into these randomly distributed pre-reserved reactive sites. By introducing 20 mol % of 2,2,2-trifluoroethanethiol into the PMMA block, the effective χ parameter was increased by near 60 %, resulting BCPs capable of forming sub-15 nm domain spacing. The existed neutralized interfacial conditions for PS-*b*-PMMA was still efficient for the newly synthesized BCPs, and super long-ranged 15 nm-lamellae can be oriented vertically with short thermal annealing time, owing to the combination between enhanced χ parameter and balanced surface free energies.

Chapter 7 "General Conclusion" summarizes the results presented in this dissertation. The usage of fluorinated side chains, regardless of being short ones as random units or being pendent rods along the integrated block, is proven highly effective for enhancing segregation intensity and pushing forward the smallest line-width limit in BCPs lithographic applications, such as nano-fabrication and organic electronics.