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論文審査の要旨（2000 字程度）

This dissertation titled “High-χ Parameter Diblock Copolymers with Fluorinated Side Chains for Next Generation Lithography” focuses 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, such as BCP domain orientation control in thin film states.

Chapter 1 “General Introduction” outlines the background and state of the art of the field of polymer science and provides context for the results presented herein.

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

Chapter 3 “Study on Effects of Semi-fluorinated Side Chains with Varied Lengths on Self-assembly Morphology of Diblock Copolymer” discusses the hierarchical self-assembly morphology with a minimum spacing in the thin film. Because of the confinement from smectic LC structures, anisotropic hexagonally packed PS cylinder domains with an averaged periodicity of 11.5 nm are characterized and two striations of distinctive dimensions of 10.9 and 12.7 nm from the side view of the array are observed. The morphology studies on BCPs of varied fluorinated side chains reveal the significant role of LC side chain ordering on this anisotropy in the hierarchical self-assembled morphology.

Chapter 4 “Adjusting Thin Film Domain Spacings of Side-Chain Liquid Crystalline Semi-fluorinated Block Copolymers with Elliptical Cylinders with Anisotropic Hexagonal Packing” discusses a facile approach of PS-*b*-P8FMA domain orientation control in the thin film demonstrated by tuning the composition of the copolymers of the bottom surface layer (BSL). Perpendicularly oriented PS domains in the anisotropic hexagonally packed array are 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 narrower d1 (d1=11.9 nm) to a wider d2 (d2=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 types and dimensions of long-ranged patterns can be easily tailored in thin films partially owing to the anisotropic feature of packing array.

Chapter 5 “A High-χ Silicon-backbone in Combination with Fluorinated Side Chains Block Copolymer of Ultra-fast Thermal Annealing for Forming Perpendicular Pattern” discusses the development of siloxane-backbone BCP with a perfluoroalkyl side chain. A high χ parameter diblock polymer, namely PS-*b*-PSi8F, is 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 is increased after the incorporation of super-hydrophobic of the fluorinated side chain and the χ value at 160 °C is estimated to be 0.095 and 0.179 for precursor PS-*b*-PMVS and PS-*b*-PSi8F, respectively. The observed self-assembled morphologies are 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 is sandwiched between both neutral top and bottom interfaces where the top-coat involves a polarity switch and the bottom-coat involves a cross-linking process. Perpendicular orientation of lamellae is successfully achieved in the thin film and a pattern consisted of silicon oxide is 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” discusses the improvement of poly(styrene-*block*-methyl methacrylate) (PS-*b*-PMMA) that is the most widely studied BCP for lithography. By incorporating the randomly polymerized poly(glycidyl methacrylate) (PGMA) into the PMMA block moieties of the PS-*b*-PMMA, introducing a quantitative reaction of 2,2,2-trifluoroethanethiol is carried out 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 is increased by near 60 %, resulting in BCPs capable of forming sub-15 nm domain spacing. The existed neutralized interfacial conditions for PS-*b*-PMMA are 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 conclusions”, summarizes the results obtained in this study. In short, this dissertation examines in detail the development of BCP materials from molecular design, synthesis to control of the nanostructures in the thin films for next generation lithography, and clarifies the suitable primary and higher-order structures of the BCPs. It gives the knowledge for wide-ranging development and has a great contribution to not only academics but engineering and industry. Therefore, it is recognized that it is of sufficient value as a doctoral thesis.