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論文審査の要旨（2000 字程度）

This dissertation, “Tailoring Self-Assembling Structures of Block Copolymers via Side-Chain Post-Functionalization with Thiol-Ene Reaction,” focuses on the development of a new molecular design that allows for the modification of the effective Flory–Huggins interaction parameters (χ_{eff}) of diblock copolymers.

Chapter 1, “General Introduction,” outlines the background and state of the art of polymer science and provides context for the results of block copolymers (BCPs) presented herein.

Chapter 2, “Synthesis and Self-Assembling Structure Control of PS-*b*-PAGE,” discusses the synthesis and morphological study of diblock copolymers where the interaction parameters are modified by introducing functional groups with different hydrophilicity into side-chains. In the molecular design, a hydrophobic block, polystyrene, and a slightly more hydrophilic block, poly(allyl glycidyl ether), are selected. Poly(styrene-*b*-allyl glycidyl ether) (PS-*b*-PAGE) is synthesized through the living anionic polymerization of PS, followed by the living anionic ring-opening polymerization of PAGE. This process results in well-characterized BCPs containing allyl groups, which are then modified by thiol-ene reaction. The χ_{eff} parameters of BCPs before and after the post-functionalization are determined using the random phase application method (RPA), using data from small angle X-ray scattering (SAXS). By introducing hydrophobic alkyl groups or hydrophilic hydroxy and carboxy groups through a thiol-ene reaction, the χ_{eff} parameters between the hydrophobic PS and hydrophilic PAGE blocks can either decrease or increase. This modification leads to changes in the self-assembled structures, which include disorder, lamellae, and hexagonally packed cylinders, depending on the χ_{eff} parameters.

Chapter 3, “Synthesis and Self-Assembling Structure Control of PS-*b*-PMVS,” aims to control the χ_{eff} value solely by varying the degree of modification of hydroxy groups. For this purpose, polystyrene (PS) and a more hydrophobic block polymethylvinylsiloxane (PMVS) are selected in the molecular design. Poly(styrene-*b*-methylvinylsiloxane) (PS-*b*-PMVS) is synthesized via living anionic polymerization, resulting in well-characterized diblock copolymers containing a reactive PMVS which is then modified by thiol-ene reaction. The χ_{eff} parameters are determined using the RPA method, and the Hansen solubility parameters (HSP) are determined using the multi-solvent method. Both the χ_{eff} parameters and HSP distance (*Ra*) initially decrease and then increase with the rising incorporation rate of hydroxy groups. This finding is attributed to the introduction of hydroxy groups, which increases the polarity and hydrophilicity of PMVS. At low introduction ratios, the slight increase in polarity and hydrophilicity of the hydrophobic block PMVS reduces the χ_{eff} and *Ra*. However, at higher introduction ratios, the substantial increase in polarity and hydrophilicity raises the χ_{eff} and *Ra*. By tuning hydroxy group content, morphology control is achieved, resulting in structures such as lamellae, hexagonally packed cylinders, and especially gyroids, which are challenging to obtain using traditional linear BCPs.

Chapter 4, “Prediction of Self-Assembling Structures for Side-Chain Post-Functionalized BCPs,” develops prediction models for the side-chain modified BCPs to predict the self-assembling structures using machine learning (ML) techniques. With this objective, data from a series of side-chain modified BCP from Chapters 2 and 3, as well as literature, are selected. In constructing ML models, HSP serves as the input data instead of χ_{eff}, which is challenging to determine. To extensively discuss the correlation between HSP and χ_{eff} for side-chain modified BCPs, a series of PAGE homopolymers are synthesized via living ring-opening polymerization and post-functionalized with alkyl, hydroxy, and carboxy groups using thiol-ene reaction. The strong correlation between HSP distance (*Ra*) and χ_{eff} indicates the feasibility of using HSP to predict χ_{eff}. In machine learning, the best-performing model, using a random forest algorithm, achieves a prediction accuracy of 0.87, significantly higher than the baseline of 0.56 obtained using traditional self-consistent field theory. These results indicate that, even with a small dataset, the ML model developed in this study is effective for predicting the self-assembling structure for side-chain functionalized BCPs.

Chapter 5, “General Conclusion,” summarizes the results presented in this dissertation and discusses the future prospects of the research presented here. This work could be extended by transferring the post-functionalization methodology to the creation of functional BCP materials. 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 this dissertation is of sufficient value as a doctoral thesis.