論文 / 著書情報
Article / Book Information

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種別(和文)	要約
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（博士課程）
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論 文 要 約

THESIS SUMMARY

系・コース： Department of, Graduate major in	材料 系 材料 コース	申請学位（専攻分野）： Academic Degree Requested	博士 Doctor of （ 工学 ）
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要旨（英文 800 語程度）

Thesis Summary（approx.800 English Words ）

This dissertation titled "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. In doing so, the self-assembly behavior can be tailored as desired.

Chapter 1 "General Introduction" presents a general introduction to the self-assembly behavior of block copolymers (BCPs) and the methods to control the self-assembling structures. This chapter specifically reviews advancements in post-functionalization method, highlighting the benefits and challenges of the method. In this chapter, the main focus and objectives of this study are clarified, along with the methodology employed to achieve these aims. Additionally, the chapter details the molecular design and synthesis methods used in this thesis.

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 random phase application method (RPA), using data from small angle X-ray scattering (SAXS). By introducing hydrophobic alkyl groups or hydrophilic hydroxyl and carboxyl groups through 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 includes 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 hydroxyl groups. For this purpose, polystyrene (PS) and a more hydrophobic block poly(methyl vinyl siloxane) (PMVS) are selected in the molecular design. Poly(styrene-*b*-methyl vinyl siloxane) (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 RPA method and the Hansen solubility parameters (HSP) are determined using multi-solvent method. Both the χ_{eff} parameters and HSP distance (*Ra*) initially decrease and then increase with the rising incorporation rate of hydroxyl groups. This finding is attributed to the introduction of hydroxyl 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 hydroxyl group content, morphology control is achieved resulting in structures such as lamellae, hexagonally packed cylinders and specially gyroids which is challenging to be obtained 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 Chapter 2 and 3, as well as literatures 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, hydroxyl, and carboxyl 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 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. While the introduction of functional groups may introduce challenges in the traditional process operation If successful, this research could lead to applications in microfabrication and organic electronics by combining the process optimization with precise control of self-assembling structures using the methods presented in this dissertation.

備考 ： 論文要旨は、和文 2000 字と英文 300 語を 1 部ずつ提出するか、もしくは英文 800 語を 1 部提出してください。

Note : Thesis Summary should be submitted in either a copy of 2000 Japanese Characters and 300 Words (English) or 1copy of 800 Words (English).

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