論文 / 著書情報
Article / Book Information

題目(和文)	
Title(English)	Formation of Double Gyroid and Patchy Particle Nanostructures through the Self-Assembly of Diblock Copolymers
著者(和文)	童亮
Author(English)	Liang Tong
出典(和文)	学位:博士(工学), 学位授与機関:東京工業大学, 報告番号:甲第11782号, 授与年月日:2022年3月26日, 学位の種別:課程博士, 審査員:早川 晃鏡,扇澤 敏明,松本 英俊,戸木田 雅利,道信 剛志
Citation(English)	Degree:Doctor (Engineering), Conferring organization: Tokyo Institute of Technology, Report number:甲第11782号, Conferred date:2022/3/26, Degree Type:Course doctor, Examiner:,,,,
学位種別(和文)	博士論文
Category(English)	Doctoral Thesis
種別(和文)	審査の要旨
Type(English)	Exam Summary

（博士課程）

論文審査の要旨及び審査員

報告番号	甲第　　号		学位申請者氏名	童　亮	
論文審査 審査員		氏　名	職　名		氏　名	職　名
	主査	早川　晃鏡	教授	審査員	道信　剛志	准教授
	審査員	扇澤　敏明	教授			
		松本　英俊	教授			
		戸木田　雅利	教授			

論文審査の要旨（2000 字程度）

This dissertation, titled "Formation of Double Gyroid and Patchy Particle Nanostructures through the Self-Assembly of Diblock Copolymers", aims to fabricate next-generation materials containing highly ordered double gyroid and patchy particle nanostructures by self-assembly using block polymers. This article is composed of the following five chapters.

Chapter 1, "Introduction", presents the topic on the formation of triply periodic minimal surface structure and non-spherical particle nanostructures by self-assembly of block polymers. Moreover, an extensive summary of the methods used to prepare such triply periodic minimal surface structure and non-spherical particles is reported. The novel properties and future application potential that these structures may support are discussed, thus outlining the purpose of this research.

Chapter 2 is "Synthesis and Characterization of Diblock Copolymers Containing Fluorinated Methacrylate". This chapter describes the synthesis of fluorine-containing methacrylate monomers and polymers used in this study. Methacrylate monomers with different numbers of fluorine (PxFEMA) are polymerized by using macro chain-transfer agents on poly(2-vinyl pyridine)s (P2VPs), and the properties of the resulting polymers are analyzed. Next, the synthesized polymers are made into thin films by spin-coating and placed in an electron scanning microscope for electron irradiation. We find that the PxFEMA films, which gradually decompose and form depressions with increasing irradiation time, while the P2VP films show almost no deformation under the electron irradiation. This indicates that the PxFEMA polymer has the property of being highly decomposable under electron irradiation. Besides, the diblock copolymer P2VP-b-PxFEMA is synthesized, and the volume fraction of P2VP is controlled to be in the range of 61%-65%. It is found that microphase separation of the two segments is enhanced with the increase of the fluorine group in the PxFEMA block. The decomposition of one of the segments under electron irradiation with the enhancement of the microphase separation strength properties will result in porous materials and poly(2-vinyl pyridine)-*block*-poly(2,2,2-trifluoroethyl methacrylate) (P2VP-*b*-PTFEMA), which has three fluorine groups, is worthy of further study.

Chapter 3 is "Long-range Ordered Double Gyroid Structures via Solution Casting from Poly(2-vinyl pyridine)-*block*-poly(2,2,2-trifluoroethyl methacrylate)". A more detailed study for the P2VP-*b*-PTFEMA block copolymer in Chapter 2 is presented, especially focusing the formation of a double gyroid structure. The difference in the swelling rate of the solvent on the two segments of the diblock copolymer in the solution casting method is used to change the volume fraction of the blocks to obtain a non-thermodynamically stable microphase-separated structure. In turn, various volume fractions can be simulated using the diblock copolymer throughout the drying process for screening a range of volume fractions. The self-assembly of P2VP-*b*-PTFEMAs with different mass composition ratios by solution casting method result in lamellae, cylinders, and even rare double gyroid structures. The effects of the molecular weight and mass composition of the prepared P2VP-*b*-PTFEMAs on the formation of microphase-separated structures are investigated. Based on small-angle X-ray scattering, transmission electron microscope, SEM analysis, and the establishment of 3D models for comparison, it is found that the structural planes of the obtained 3D samples of $P2VP_{83}$-*b*-$PTFEMA_{46}$ films are corresponding to the typical (211), (110), and (111) planes of the Ia3d space symmetry. Thereby, it is confirmed that the double gyroid structure formed by simple solution casting using the difference in the swelling rate of chloroform in the two segments of the diblock copolymer is highly reliable and reproducible.

Chapter 4 is "Creation of Golf Ball-like Particles Using Diblock Copolymers via 3D Confined Self-Assembly". P2VP-*b*-PTFEMAs are subjected to 3D confinement self-assembly method "self-organized precipitation (SORP)" to form emulsified droplets, which finally precipitate to form particles. SORP method explores a combination of five suitable solvents multiplied by four non-solvent. In one of the SORP methods, a mixed solvent combination of acetone-water forms spherical structures of P2VP-*b*-PTFEMAs with a particle size of about 150 nm. After 90 °C 24 hours of annealing under evacuation, uniform concave pores are obtained on the surface with a morphology very similar to that of the golf ball surface structure. The pore size is found to be positively correlated with the presentation of PTFEMA molecular chains. The annealing temperatures are compared and analyzed with the solution casting method in Chapter 3 and the melting method after direct heating. The effect of solvent on the formation of nanostructures in different self-assemblies is also elaborated. Finally, another annealing method, microwave annealing, was used to obtain spheres with smooth surfaces and small spheres inside, indicating that the internal microphase-separated structure is well-formed inside the particles after annealing.

Chapter 5, "Conclusion and Prospects", summarizes and reviews the results of this study, and a commentary on the future pathways available for the field of the fabrication of double gyroid and patchy particle nanostructures is discussed. 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.

注意：「論文審査の要旨及び審査員」は、東工大リサーチリポジトリ（T2R2）にてインターネット公表されますので、公表可能な範囲の内容で作成してください。