論文 / 著書情報
Article / Book Information

題目(和文)	重合誘起自己組織化プロセスにおけるアレン誘導体のリビング配位ブロック共重合によるフルオラスセグメントを有する高分子ナノ構造体の創製と超撥水性コーティングへの応用
Title(English)	Creation of Polymer Nanostructured Materials Having Fluorous Segments by Living Coordination Block Copolymerization of Allene Derivatives Under Polymerization-induced Self-assembly Process and Their Applications to Superhydrophobic Coatings
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学位種別(和文)	博士論文
Category(English)	Doctoral Thesis
種別(和文)	論文要旨
Type(English)	Summary

（博士課程）
Doctoral Program

論 文 要 旨

THESIS SUMMARY

系・コース： Department of, Graduate major in	応用化学　系 応用化学　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 thesis entitled "Creation of Polymer Nanostructured Materials Having Fluorous Segments by Living Coordination Block Copolymerization of Allene Derivatives Under Polymerization-induced Self-assembly Process and Their Applications to Superhydrophobic Coatings" has dealt with the production of polymeric nanostructures of linear block copolymers and core-cross-linked star polymers by the π-allylnickel-catalyzed precision living coordination block copolymerization of allene derivatives in a fluorous media. Applications of the nanostructured materials thus obtained through the polymerization-induced self-assembly process to superhydrophobic coatings are also described.

In Chapter 1, "General Introduction", the research backgrounds of superhydrophobicity, living polymerizations, their applications to polymerization-induced self-assembly processes, and π-allylnickel catalyzed living coordination polymerization of allene derivatives, and the objectives and significant points of the studies in this thesis are described.

In Chapter 2, "Creation of Nanostructured Materials by Living Coordination Block Copolymerization and Their Applications to Superhydrophobic Coatings", the synthesis of block copolymers by the π-allylnickel-catalyzed living coordination block copolymerization of a fluoroalkyl-substituted allene and a hydrophobic allene under the polymerization-induced self-assembly process and applications of the nanostructured materials thus obtained to the superhydrophobic coatings are described. In Section 1, the block copolymerization of a fluoroalkyl-substituted allene, 1-(1*H*,1*H*,2*H*,2*H*-heptadecafluorodecyoxy)-2,3-butadiene, and a hydrophobic allene, phenoxyallene, was carried out by [(π-allyl)$NiOCOCF_3$]$_2$ in a fluorous solvent, 1,1,1,2,2,3,4,5,5,5-decafluoro-3-methoxy-4-(trifluoromethyl)pentane, to produce nanostructured polymeric materials possessing fluorous corona through the polymerization-induced self-assembly (PISA) process. It was found that the nanostructures of the resulting polymeric micelles are dependent upon the feed ratio of the fluoroalkyl-substituted allene and phenoxyallene, where the structures altered from spherical micelles to the networked micelles by reducing the length of the fluoroalkyl-containing (*i.e.*, the solvophilic) segments as supported by the transmission electron microscope (TEM) observations. The dip-coating of the glass substrate was carried out by the use of the micellar solutions of the block copolymers in the fluorous solvent, from which the optically transparent superhydrophobic surface with the highest visible light transmittance over 80%, the static contact angle of the water droplet over 150°, and the sliding angle below 5° was effectively obtained under the appropriate conditions.

In Section 2, a coagulation/redispersion process of the polymeric nanostructured materials was carried out to facilitate the chance for the superhydrophobic coatings using the polymeric nanostructures that originally

possessed insufficient superhydrophobic properties. The as-prepared polymeric nanostructured materials were coagulated with a poor solvent and the solid fractions thus produced were redispersed in the fluorous media, from which the larger scale nanostructures were found to be produced from the original small nanostructures presumably by assembling the as-prepared nanostructures. Based on this facile coagulation/redispersion technique to generate larger structures from the original nanostructures such as spherical micelles, the possibility to attain the superhydrophobic coatings was expanded from versatile nanostructured samples.

In Chapter 3, “Synthesis of Core-cross-linked Star Polymers by Living Coordination Copolymerization Through Polymerization-induced Self-assembly Process and Their Applications to Superhydrophobic and Slippery Liquid-infused Porous Surfaces”, core-cross-linked star polymers (CCSPs) possessing fluorinated outer segments were prepared by the π-allylnickel-catalyzed living coordination block copolymerization of a perfluoroalkyl-substituted allene, 1-(1*H*,1*H*,2*H*,2*H*-heptadecafluorodecyoxy)-2,3-butadiene, and a hydrophobic bisallene, 1,4-bis(propa-1,2-dien-1-yloxy)benzene, in a fluorous solvent, 1,1,1,2,2,3,4,5,5,5-decafluoro-3-methoxy-4-(trifluoromethyl)pentane. The nanostructured materials consisting of the CCSPs were obtained via the polymerization-induced self-assembly (PISA) process. It was found that the nanostructures thus prepared varied from sphere-like to network by the decrease of the relative feed ratio of the perfluoroalkyl-substituted allene to the bisallene, as supported by the transmission electronic microscopy (TEM) measurements. The superhydrophobic coatings were attained by the facile spray-coatings of the CCSPs having network nanostructures onto glass substrates. The superhydrophobic coatings thus prepared proved to exhibit excellent heat and solvent-vapor resistant properties with respect to the surface coatings using core-non-cross-linked nanostructured materials. Large static contact angles of a water droplet (~160°) and small sliding angles (<5°) indicated the excellent superhydrophobicity of the resulting coatings. The porous surface morphology of the superhydrophobic coatings promised access to the slippery liquid-infused porous surface (SLIPS) by absorbing a fluorous PFPE oil, Galden® HT 230, as a lubricant liquid, simply by immersing the coated substrates. The SLIPS thus prepared exhibited unique hydrophobic and oleophobic properties, where both water and dichloromethane showed low sliding angles of the liquid droplets.

In Chapter 4, “Summary”, the works presented in this thesis are summarized and future perspectives related to the present studies are described.

As stated above, this thesis has accomplished new methods to produce artificial polymeric superhydrophobic coatings by the use of nanostructured materials produced by the living block copolymerization under the polymerization-induced self-assembly process. The results obtained in this thesis provide useful findings to the fields of both polymer synthetic chemistry and industrial applications. Therefore, this thesis is worth doctor of engineering.