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
著者(和文)	程一丹
Author(English)	Yidan Cheng
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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

School of Materials and Chemical Technology CHENG Yidan

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 $[(\pi\text{-allyl})NiOCOCF_3]_2$ 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.

List of Publications

Chapter 2 Section 1

“Creation of Polymeric Nanostructures by Living Coordination Block Copolymerization of Allene Derivatives with Fluoroalkyl Substituents under Polymerization-induced Self-assembly Conditions and Their Application to Superhydrophobic Surfaces”

Yidan Cheng, Takeshi Wakiya, Shinsuke Inagi, Toshikazu Takata, Ikuyoshi Tomita, *Polym. Chem*., **2021**, *12*, 6771-6779.

Chapter 2 Section 2

“Preparation of Superhydrophobic Coatings by Reorganization of Micellar Structures”

Yidan Cheng, Takeshi Wakiya, Shinsuke Inagi, Toshikazu Takata, Ikuyoshi Tomita*, In preparation*

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"

Yidan Cheng, Takeshi Wakiya, Shinsuke Inagi, Toshikazu Takata, Ikuyoshi Tomita*, In preparation*

List of Presentations

Presentations of International Conferences

1. Yidan Cheng, Naoki Shida, Shinsuke Inagi, Takeshi Wakiya, Ikuyoshi Tomita, Creation of Superhydrophobic surface using polymeric nanostructures prepared by the living copolymerization of allene derivatives under polymerization-induced self-assembly conditions, International Chemical Congress of Pacific Basin Societies (Pacifichem 2021, Dec. 2021).
2. Yidan Cheng, Takeshi Wakiya, Shinsuke Inagi, Ikuyoshi Tomita, Creation of Superhydrophobic Surface Using Polymeric Nanostructures Prepared by the Living Coordination Block Copolymerization of Allene Derivatives Under Polymerization-induced Self-assembly Conditions, The 48th World Polymer Congress IUPAC-MACRO2020+, May 2021.
3. Yidan Cheng, Takeshi Wakiya, Shinsuke Inagi, Ikuyoshi Tomita, Superhydrophobic surface nanomaterials via π-Allylnickel-catalyzed living coordination block copolymerization of allene derivatives under polymerization-induced self-assembly conditions, ACS National Meeting Spring 2021, Apr. 2021.
4. Yidan Cheng, Hiroki Nishiyama, Shinsuke Inagi, Takeshi Wakiya, Ikuyoshi Tomita, Approach to Superhydrophobic Polymeric Nanostructures Based on Living Coordination Block Copolymerization of Allene Derivatives, 11th Workshop on Organic Chemistry for Junior Chemists (WOCJC-11), June 2019.

Presentations of Domestic Conferences

1. Yidan Cheng, Takeshi Wakiya, Shinsuke Inagi, Ikuyoshi Tomita, Synthesis of Superhydrophobic Cross-linked Nanostructured Materials by Living Coordination Block Copolymerization of Fluoroalkyl-substituted Allene with Hydrophobic Bisallene via Polymerization-induced Self-assembly Process, 4th G'L'owing Polymer Symposium in KANTO, July 2021.

2. Yidan Cheng, Takeshi Wakiya, Shinsuke Inagi, Ikuyoshi Tomita, Creation of Crystalline Polymeric Nanoplatelets by pi-Allylnickel-catalyzed Living Coordination Polymerization of Allene Derivatives via Polymerization-induced Crystallization-driven Self-assembly Process, 第 70 回高分子学会年次大会, May 2021.

3. Yidan Cheng, Takeshi Wakiya, Shinsuke Inagi, Ikuyoshi Tomita, Synthesis of Superhydrophobic Cross-linked Nanostructured Materials by the Living Coordination Block Copolymerization of Fluorous Allenes with Hydrophobic Allenes via Polymerization-induced Self-assembly Process, 第 70 回高分子学会年次大会, May 2021.

4. Yidan Cheng, Takeshi Wakiya, Shinsuke Inagi, Ikuyoshi Tomita, Synthesis of Superhydrophobic Nanomaterials by the Living Coordination Block Copolymerization of Fluorous Allenes with Hydrophobic Allenes via Polymerization-induced Self-assembly and Their Applications to Optically Transparent Surface Coatings, 第 69 回高分子討論会, Sep. 2020.

5. Yidan Cheng, Takeshi Wakiya, Hiroki Nishiyama, Shinsuke Inagi, Ikuyoshi Tomita. Synthesis of Superhydrophobic Nanomaterials by the Living Coordination Block Copolymerization of Fluorous Allenes with Hydrophobic Allenes via Polymerization-induced Self-assembly and Their Applications to Optically Transparent Surface Coating, 第 69 回高分子学会年次大会, May 2020.

6. 程 一丹, 西山 寛樹, 稲木 信介, 脇屋 武司, 冨田 育義. アレン類のリビ

ング配位共重合に基づく超撥水性高分子ナノ構造体の創製，第 69 回ネットワークポリマー講演討論会, Oct. 2019.

7. Yidan Cheng, Takeshi Wakiya, Hiroki Nishiyama, Shinsuke Inagi, Yoshitaka Kitamoto, Ikuyoshi Tomita, アレン類のリビング配位共重合に基づく超撥水性高分子ナノ構造体の創製，第 68 回高分子討論会, Sept. 2019.

8. Yidan Cheng, Yoshiyuki Oguchi, Takashi Wakiya, Hiroki Nishiyama, Shinsuke Inagi, Ikuyoshi Tomita, Synthesis of Hydrophobic Polymer Micelles Based on Living Coordination Block Copolymerization of Fluoroalkyl-Substituted Allene Derivatives, 第 8 回 CSJ 化学フェスタ 2018, Oct. 2018.