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## 論文内容要旨

### Introduction

With the development of material science in the past several decades, the surface or interface properties between various matters have provided a very important direction in advanced material field, which has attracted much attention. For satisfying various industrial or environmental requirements, an empirical characterization of materials interactions at the surface/interface has been carried out, particularly, in practical production processes. So far, many people have investigated single-component functional and structure materials, however, they are insufficient to fulfill the demand of industrial development and human life. Hybrid, composite, and block-element materials are becoming popular research fields, and the researchers expect to take advantages of two or more than two component materials for creating high-level advanced materials, which can meet the requirements for resolving energy, environmental and economic problems. Controlling material surfaces or interfaces has been recognized as a more effective approach to prepare functional materials compared with modifying surface chemical elements or changing a surface structure. This dissertation is focused on a combination of amphiphilic fluorinated polymers with various interfaces involving air-water and oil-water interfaces. The nanostructure formation ability of amphiphilic fluorinated polymers was investigated in detail.

### Amphiphilic Fluorinated Polymers

Amphiphilic polymers have water-loving and oil-loving properties in itself, which make it possible to self-assemble into various texture structures. The key points for creating texture structures are elucidation of how non-covalent (secondary) interactions take place when molecules are placed at a certain environment, in my case, interface. It has already been reported that amphiphilic poly(*N*-alkylacrylamide)s and copolymers with various functional groups in side chains,

e.g., aromatic hydrocarbons, redox active groups, photoreactive groups, pH-sensitive groups, organometallic complexes, nonlinear groups, took a stable monolayer formation at the air-water interface. Highly ordered and densely packed polymer nanosheets were fabricated on the water surface supported by a two-dimensional hydrogen bonding network between polymer chains through amide groups.<sup>2</sup> Compared with hydrocarbons, fluorocarbons have lower intermolecular interactions, therefore, it is well known that fluorocompounds have quite low surface tension. If fluorocompounds are assembled with a well-defined nanostructure, more interesting surface properties will bring about, which are promising for advanced materials applications. To demonstrate nanostructure control of fluorinated polymers, the author selected poly(*N*-1*H*, 1*H*-pentadecafluorooctyl methacrylamide) (pC<sub>7</sub>F<sub>15</sub>MAA, Fig. 1),<sup>1</sup> which has hydrophobic –CO-NH- groups and hydrophobic fluorocarbon groups; those groups provide with amphiphilic properties, which enable to self-assemble into nano-scale or micro-scale structures utilizing very limiting space at the interface.

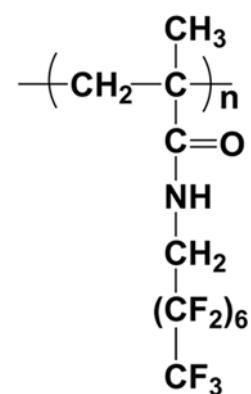


Figure 1 Chemical structure of pC<sub>7</sub>F<sub>15</sub>MAA.

## Fluorinated polymer nanosheets for photopatterning applications

The pC<sub>7</sub>F<sub>15</sub>MAA nanosheets were fabricated using the Langmuir-Blodgett method at the air-water interface. They were deposited on solid substrates by vertical dipping. The monolayer thickness was determined using surface plasmon resonance spectroscopy: 1.3 nm/monolayer. Subsequently, the surface wettability of polymer nanosheet was measured by Sessile drop method. The surface had fairly great contact angle (118°) and low critical surface free energy (8.5 mN/m), implying a highly oriented layer structure of pC<sub>7</sub>F<sub>15</sub>MAA in polymer nanosheets. Then the photopattern formation ability of pC<sub>7</sub>F<sub>15</sub>MAA nanosheets were investigated.

Deep-UV irradiation in air at room temperature resulted in positive-tone photopatterns with non-development process (Fig. 2(b)). AFM images proved that pC<sub>7</sub>F<sub>15</sub>MAA nanosheets were removed completely from the substrate (Fig 2(c)). In terms of surface wettability, the water contact angle decreased gradually from 118° to 10°, which provided an enormous

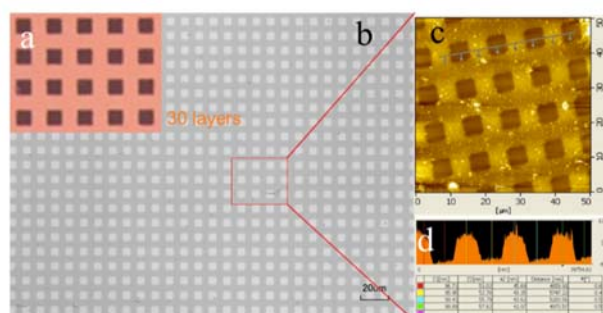


Figure 2 (a) Grid photomask; (b) 5 μm grid photopattern of 30 layers pC<sub>7</sub>F<sub>15</sub>MAA nanosheets; (c) AFM image of grid photopattern; (d) Cross-section image of grid photopattern.

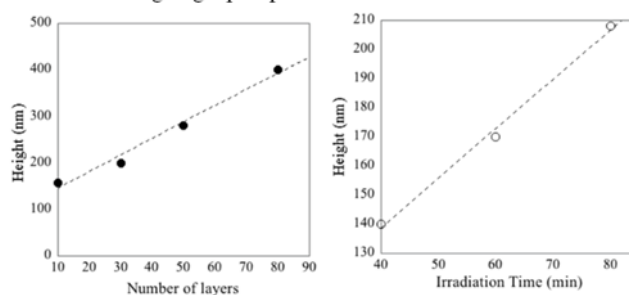


Figure 3 (a) Height of ink pattern as a function of the number of pC<sub>7</sub>F<sub>15</sub>MAA nanosheets layers; (b) Height of ink pattern as a function of irradiation time.

wettability contrast on the photopatterned surface. Using the salient benefit of photopatterned pC<sub>7</sub>F<sub>15</sub>MAA nanosheets, aqueous Ag ink patterns were yielded. The structure-property relationship of the film thickness of pC<sub>7</sub>F<sub>15</sub>MAA nanosheets, water contact angle, and Ag ink thickness was discussed (Fig. 3).

## Preparation of amphiphilic fluorinated polymer nanoparticles film and application for dissolved oxygen sensor

This chapter carries an enormously enhanced dissolved oxygen sensor system consisting of amphiphilic acrylamide-based polymers: poly(*N*-(1*H*, 1*H*-pentadecafluorooctyl) methacrylamide) (pC<sub>7</sub>F<sub>15</sub>MAA) and poly(*N*-dodecylacrylamide-*co*-5-[4-(2-methacryloyloxyethoxycarbonyl)phenyl]-10,15,20-triphenylporphinato platinum(II)) (p(DDA/PtTPP)).<sup>2</sup> The film was prepared by casting a mixed solution of pC<sub>7</sub>F<sub>15</sub>MAA and p(DDA/PtTPP) with AK225 and acetic acid onto a solid substrate. The film has a porous structure made of nanoparticle

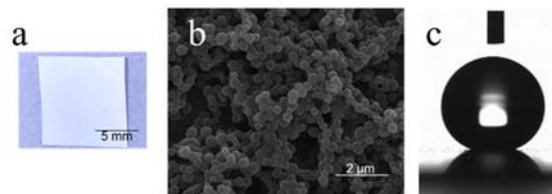


Figure 4 (a) pC<sub>7</sub>F<sub>15</sub>MAA/p(DDA/PtTPP) film; (b) SEM image of pC<sub>7</sub>F<sub>15</sub>MAA/p(DDA/PtTPP) film; (c) Static water contact angle.

assemblies with diameters of several hundreds of nanometers (Fig. 4). The nanoparticle formation ability ensures both superhydrophobicity with a water contact angle greater than 160° (Fig. 4(b)) and gas permeability so that molecular oxygen can enter the film from water. The film shows exceptional performance as the oxygen sensitivity reaches 126 (the intensity ratio at two different oxygen concentrations ( $I_{40}/I_0$ ); 40 and 0 (mgL<sup>-1</sup>) correspond to dissolved oxygen concentration) (Fig. 5). Understanding and controlling porous nanostructures will provide opportunities for making selective penetration/separation of molecules occurred at the superhydrophobic surface.

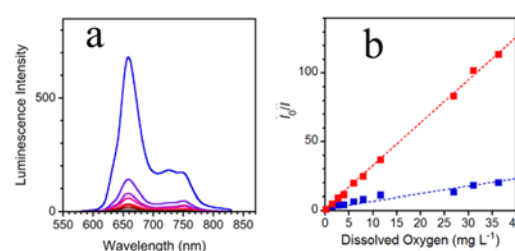


Figure 5. (a) Luminescence spectra of a porous pC<sub>7</sub>F<sub>15</sub>MAA/p(DDA/PtTPP) film in water as a function of oxygen concentration in the range from 0.1 (mg/L) (top) to 40 (mg/L) (bottom). (b) Stern-Volmer plots for the porous film (red) and the cast film (blue).

## Amphiphilic fluorinated polymer nanoparticle formations using immiscible solvents

In this chapter, the nanostructure formation ability of amphiphilic polymer pC<sub>7</sub>F<sub>15</sub>MAA was demonstrated through self-assembly at the interface of immiscible solvents. By mixing pC<sub>7</sub>F<sub>15</sub>MAA with AK-225 and water, apparently uniphase dispersion was obtained (Fig. 6(a)), implying that pC<sub>7</sub>F<sub>15</sub>MAA took a micelle formation. SEM measurements revealed that nanoparticle (< 50 nm) (Fig. 6)

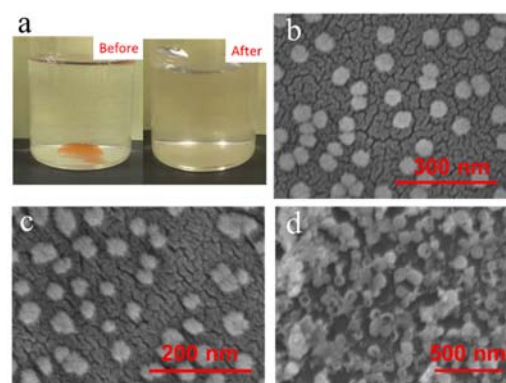


Figure 6 pC<sub>7</sub>F<sub>15</sub>MAA solution in immiscible solvents before and after stirring(a); SEM images of pC<sub>7</sub>F<sub>15</sub>MAA nanoparticles (b); after 3 months (c) and (d).

formations were possible by spreading the dispersion on the substrate. The micelle formation mechanism was examined by varying several parameters in micelle preparation conditions. Then oxygen-sensitive platinum porphyrin (PtOEP) was embedded in the nanoparticle to demonstrate the dissolved oxygen sensor performance. The nanoparticle showed so-called Soret and Q bands at 380 nm and at 540 nm, respectively (Fig. 7(a)). The nanoparticle "nanosensor" exhibited strong luminescence at 645 nm, which decreased greatly when the dissolved oxygen concentration was increased (Fig. 7(b)). As shown in Fig. 7(c) the luminescence sensitivity reached 42 in the range of 0–40 mg/L. The system had a response time of 10–15 s when switching from deoxygenated condition to oxygenated condition (Fig. 7(d)), which is faster response time compared with that of the dissolved oxygen sensor system discussed in the preceding chapter.

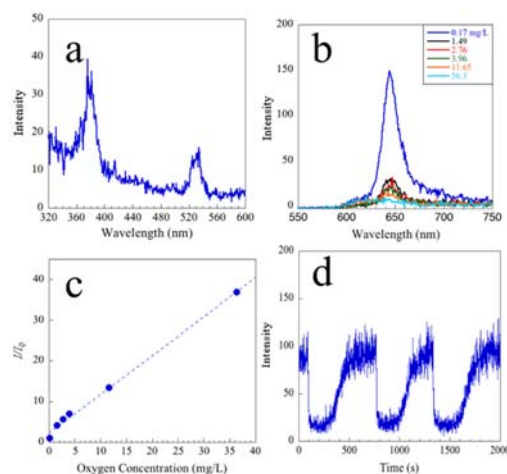


Figure 7 (a) Excitation spectra of PtOEP encapsulated  $pC_7F_{15}MAA$  nanoparticles in water; (b) Luminescence spectra of  $pC_7F_{15}MAA/PtOEP$  nanoparticles as a function of dissolved oxygen concentration; (c) Stern-Volmer plots; (d) Time course of PtOEP luminescence intensity.

## Summary

The fluorinated amphiphilic polymer was fabricated to create various micro or nanotextured structures using liquid-liquid surface or interface. The present research results show the potential of nanostructured amphiphilic fluorinated polymer, and the author believe that these nanostructured fluorinated polymer will be applied for printing and optical sensor field. Moreover, research results have a great impact in various fields using amphiphilic fluorinated materials, which can lead to more effective advanced materials for devoting thin film technology, surface chemistry, sensor, biomedical and bio-imaging field etc.

## Reference

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2. Gao, Y.; Chen T.; Yamamoto, S.; Miyashita, T.; Mitsuishi, M. *ACS Appl. Mater. Interfaces* **2015**, *7*, 3468-3472.

# 論文審査結果の要旨

フッ素系材料は多くの分野で実用的に応用されている材料である。その化学安定性や低分極率など非常に特徴的な性質を有する。しかしながら、一般的にフッ素系材料をナノメートルスケールで構造制御することは困難である。本論文は、フッ化炭素鎖を有する両親媒性高分子と界面場を組み合わせることにより、フッ素系高分子材料のナノ構造制御を検討した研究の成果をまとめたものであり、全編5章より構成されている。

第1章は緒言であり、本研究の背景と目的について述べている。

第2章では poly(*N*-1H,1H-pentadecafluorooctyl methacrylamide) (pC<sub>7</sub>F<sub>15</sub>MAA)が水面上で安定な単分子膜状態をとり固体基板上に高分子ナノシートとして転写できることを利用して表面濡れ性および照射による微細描画特性について検討を行っている。pC<sub>7</sub>F<sub>15</sub>MAA の表面自由エネルギーが 9.77mN/m と非常に低表面自由エネルギーであること、この値の大部分が分散項により占められること、室温大気下紫外光照射により平滑性を保持したまま 118°の水の接触角を有する pC<sub>7</sub>F<sub>15</sub>MAA ナノシートから 10°の親水表面へと表面濡れ性を大幅に変化できること、フォトマスクを介した光照射によりフォトマスクと同じサイズの微細描画ができ、ナノメートルスケールの膜厚制御とともに水溶性銀インクのパターンを作製できることを明らかにしている。

第3章では、pC<sub>7</sub>F<sub>15</sub>MAA を2種類の相溶性溶媒(AK-225 と酢酸)に溶解し固体基板上にキャスト・溶媒蒸発することで、数百ナノメートルの直径を有する高分子ナノ粒子薄膜を見出している。pC<sub>7</sub>F<sub>15</sub>MAA ナノ粒子薄膜の作製条件を検討し、溶媒混合比や濃度がナノ粒子薄膜の品質に大きな影響を及ぼすことを明らかにしている。水の接触角 160°を越える超撥水表面を有し、X線光電子分光法によりナノ粒子表面が CF<sub>3</sub> や CF<sub>2</sub> で覆われていることを確認している。さらにこの超撥水表面を利用して、発光型溶存酸素センサー薄膜へと応用し溶存酸素濃度に対する感度  $I_0/I_{40}=126$  とこれまでに見られない非常に高感度な溶存酸素センサーの構築に成功している。

第4章では、非相溶性溶媒(AK-225 と水)中において pC<sub>7</sub>F<sub>15</sub>MAA がミセルを形成することを利用して平均直径 50 nm のナノ粒子が作製できることを見出している。X線光電子分光法によりナノ粒子表面が極性基で覆われていることが明らかにされている。これは第3章の結果とまったく異なるものであり、二種類の溶媒が作り出す界面環境によって粒子外側あるいは内側へと自在に低表面エネルギーを有するフッ化炭素基の分子配向を制御できることを意味している。AK-225 と水中で形成される pC<sub>7</sub>F<sub>15</sub>MAA ミセルが直径 280 nm の大きさを有すること、臨界ミセル濃度がモノマー換算で 0.02mol/L と求められ、低分子フッ素系表面活性剤と同等であることに着目し、pC<sub>7</sub>F<sub>15</sub>MAA ナノ粒子が一つのミセルから形成されることを突き止めている。ナノ粒子内部が非水系であることから、疎水性ポルフィリン白金錯体を取り込み、発光型ナノ粒子溶存酸素センサーとしての応用を試みている。

第5章は本論文の総括である。

以上要するに本論文は、Langmuir-Blodgett 法に見られる気水界面や相溶性、非相溶性溶媒の液液界面とフッ素系両親媒性高分子を組み合わせることで、界面での分子配向を利用したナノ構造制御技術に展開できることを見出し、二次元平面に構造制御された高分子ナノシートにおいては表面濡れ性制御による銀インクの三次元構造制御を実証し、きたる印刷技術に基づくエレクトロニクス分野への研究展開が期待される。液液界面を利用したナノ粒子薄膜や水分散系ナノ粒子形成においては、フッ素系高分子材料の三次元的ナノ構造制御を実現し、本論文で紹介された方法論がフッ素系高分子材料のさらなる発展に貢献できる可能性を明示し、高分子化学及び材料化学の発展に寄与するところが少なくない。

よって、本論文は博士(工学)の学位論文として合格と認める。