Amphiphilic Fluorinated Polymer Nanoparticle Film
Formation and Dissolved Oxygen Sensing Application

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Abstract. Fluorinated polymer nanoparticle films were prepared by dissolving amphiphilic fluorinated polymer, poly(N-1H,1H-pentadecafluoroctylmethacrylamide) (pC7F15MAA) in two miscible solvents (AK-225 and acetic acid). A superhydrophobic and porous film was obtained by dropcasting the solution on substrates. With higher ratios of AK-225 to acetic acid, pC7F15MAA was densified around acetic acid droplets, leading to the formation of pC7F15MAA nanoparticles. The condition of the nanoparticle film preparation was investigated by varying the mixing ratio or total concentration. A highly sensitive dissolved oxygen sensor system was successfully prepared utilizing a smart surface of superhydrophobic and porous pC7F15MAA nanoparticle film. The sensitivity showed \( I_0/I_{40} = 126 \) in the range of dissolved oxygen concentration of 0 ~ 40 mg L\(^{-1}\). The oxygen sensitivity was compared with that of previous reports.

1. Introduction
In the past decades, polymer nanoparticles have attracted much attention in polymer science.\[1-3\] The field of polymer nanoparticles is expanding and playing an important role in fundamental and practical research areas, ranging from sensors, electronics, photonics, conducting materials, medicine, biotechnology, pollution control, to environmental technology. Among several types of polymer nanoparticles, prepolymer nanoparticles have been intensively investigated.

Recently we demonstrated porous nanoparticle film preparation using amphiphilic fluorinated polymers.\[4\] We introduced an enormously enhanced dissolved oxygen sensor system consisting of amphiphilic acrylamide-based polymers: poly(N-1H, 1H-pentadecafluoroctylmethacrylamide) (pC7F15MAA) and poly(N-dodecylacrylamide-co-5-[4-(2-methacryloyloxyethoxycarbonyl)phenyl]-10,15,20-tri phenylporphinato platinum(II)) (p(DDA/PtTPP)) (Figure 1). The nanoparticle formation ability ensures both superhydrophobicity with a water contact angle larger than 160\(^\circ\) and gas permeability so that molecular oxygen can enter the film from water. The film was prepared by casting a mixed solution of pC7F15MAA and p(DDA/PtTPP) with AK225 and acetic acid onto a solid substrate. The film has a porous structure made of nanoparticle assemblies with diameters of several hundreds of nanometers. The film shows exceptional performance as the oxygen sensitivity reaches 126 (the intensity ratio at two different oxygen concentrations (I_0/I_{40}); 40 and 0 (mg L\(^{-1}\)) correspond to dissolved oxygen concentration). Herein the nanoparticle film formation was investigated by varying the mixing ratio and concentration of the mixed solution. The dissolved oxygen sensitivity is also discussed by comparing the result with those of previous reports.
2. Experimental Section

2.1. Materials

1H,1H-Pentadecafluorooctylamine was purchased from SynQuest Labs., Inc. Methacryloyl chloride was purchased from Wako Pure Chemical Industries, Ltd. AK-225 (a mixture of CF₂CF₂CHCl₂ and CClF₂CF₂CHClF) was purchased from Asahi Glass Co., Ltd. Hexane, dodecane, and tetradecane were purchased from Kanto Chemical Co., Inc. n-Octane was purchased from Tokyo Chemical Industry Co., Ltd. Decane was purchased from Wako Pure Chemical Industries, Ltd. All chemicals were used without purification.

Amphiphilic fluorinated polymer of poly(N-1H, 1H-pentadecafluorooctylmethacrylamide) (pC7F15MAA, Figure 1) was prepared by free radical polymerization in AK-225. The polymer was reprecipitated in the excess amount of chloroform three times. Amphiphilic Pt-labeled porphyrin copolymer (p(DDA/PtTPP)) was prepared by free radical polymerization in toluene as described in a previous report.[5] The amount of PtTPP was determined by 6 mol% using UV spectroscopy, assuming that the mole extinction coefficient of PtTPP at 402 nm is 3.08×10⁵ M⁻¹cm⁻¹.[6]

2.2. Preparation of pC7F15MAA nanoparticle film

For preparing a porous film consisting of pC7F15MAA nanoparticle assemblies, we used two types of solvents; AK-225 and acetic acid. AK-225 serves as a good solvent while acetic acid serves as a poor solvent. A mixed solution of pC7F15MAA and p(DDA/PtTPP) (95:5 w/w) in AK-225 and acetic acid was casted on solid substrates such as silicon wafer and glass substrate at room temperature. The cast film was kept at room temperature for at least one day to remove solvents.

2.3. Luminescence measurement

Luminescence spectra were measured using a fluorospectrophotometer (F-4500, Hitachi Ltd.). The sensing system was put in a quartz cell filled with water. The luminescence spectra were measured by varying a mixing ratio of argon and oxygen through a portable gas mixture device (PMG-1, Kofloc). The dissolved oxygen concentration was controlled by bubbling the water at a certain oxygen concentration for 10 min. The dissolved oxygen concentration was monitored using a dissolved

![Figure 1. Chemical structures of pC7F15MAA and p(DDA/PtTPP).](image)
oxygen meter (SG6, Mettler-Toledo International Inc). The measurement was carried out at room temperature.

2.4. Lifetime measurement
Time-resolved luminescence lifetime measurements were done using a single photon counting system. The sample was put in an in-house temperature-controlled pressure chamber. A Q-switched Nd:YAG laser (5 ns pulse duration, 10 Hz and 355 nm) was used as an excitation source. Luminescence decay data were obtained using a streak camera system (C4334, Hamamatsu Photonics K.K.). The decay curves were fitted with single exponential function. For the lifetime measurements in water, we set the sample in a quartz cuvette filled with water. The measurements were conducted after bubbling the water at a certain oxygen concentration for at least 10 min.

3. Results and Discussion

3.1. Porous pC7F15MAA nanoparticle film preparation

3.1.1. Effect of the mixing ratio
We examined how the experimental condition affect the nanoparticle film formation. First a mixed solution of pC7F15MAA in acetic acid and AK-225 with different mixing ratios (6:1, 5:1, 4:1, 3:1, 2:1, 1:1, 1:3, 1:4, 1:5, 1:6 v/v) was casted on solid substrates such as silicon wafer and glass substrate at room temperature. The cast film was kept at room temperature for at least one day to remove solvents. SEM images show that porous nanoparticle films were observed for the mixing ratio of acetic acid : AK-225 = 1:3 (Figure 2). Nanoparticle assembly formation is uniform on the whole substrate surface. For the mixing ratio of 1:5, however, inhomogeneous nanoparticle film formation was observed (Figure 2(b)). Though nanoparticles were generated, they took no film formation; the substrate was exposed in part. By screening the mixing ratio, it was found that no porous nanoparticle film formation was observed for the mixing ratios 1:5, and 6:1 (Table 1). AK-225 is miscible with acetic acid. In the case of the higher mixing ratio of acetic acid (6:1), the effect of poor solvent on the solubility of pC7F15MAA is too strong. The pC7F15MAA cannot be dissolved in the mixed solvent immediately as AK-225 becomes vaporized. Regarding the nanoparticle size, the size became larger for 1:5 and 1:6 mixing ratios. In such situation, pC7F15MAA chains take more expanded conformations and undergo entanglements more easily as the solution is concentrated because of the solvent vaporization. Consequently pC7F15MAA nanoparticles with larger diameters (> 1μm) were generated and they took aggregates, resulting in inhomogeneous surface coating.

![Figure 2](image-url) SEM images of pC7F15MAA nanoparticle films with a mixing ratio V_{acetic acid}: V_{AK-225} = (a) 1:3 and (b) 1:5.
3.1.2. Effect of concentration
The effect of pC7F15MAA concentration was also examined with a constant volume ratio of 3:1. Figure 3 shows SEM images of pC7F15MAA nanoparticle films at concentrations of 0.25, 0.5, 0.75, and 1 wt%. Results show that a well-defined nanoparticle film was formed at a concentration of 0.5 wt% (Figure 3(b)). At lower concentration, pC7F15MAA nanoparticle films were covered by pC7F15MAA "sheet" (thin film) (Figure 3(a)). However, at high concentrations crack formation was observed in pC7F15MAA nanoparticle films (Figures 3(c) and 3(d)). Results imply that pC7F15MAA nanoparticle film formation is closely related to the solvent vaporization and that there is an optimized concentration: 0.5 wt%.

![Figure 3. SEM images of pC7F15MAA nanoparticle films with different concentrations; (a) 0.25 wt%, (b) 0.5 wt%, (c) 0.75 wt%, and (d) 1 wt%.](image)

3.1.3. Size distribution of pC7F15MAA nanoparticles
Figure 4 shows SEM images of pC7F15MAA nanoparticle films at the different mixing ratios of 5:1, 3:1, and 1:4. There is larger size distribution for 5:1 (Figure 4(a)). It becomes smaller as the AK-225 composition increases. For the mixing ratio 1:4 (Figure 4(c)), pC7F15MAA nanoparticles with the size ranging 400 - 700 nm were observed.

3.1.4. Surface wettability
The surface wettability pC7F15MAA nanoparticle films (acetic acid: AK-225 = 1:4) was examined using various solvents. Depending on the solvents, the films have different contact angles. Figure 5 shows contact angles of pC7F15MAA nanoparticle films. The water contact angle reaches more than 160°, indicating that the surface of pC7F15MAA nanoparticle films is superhydrophobic.

### Table 1. Film formation ability as a function of the mixing ratio.

| V\text{acetic acid} : V\text{AK-225} | 6:1 | 5:1 | 4:1 | 3:1 | 1:1 | 1:2 | 1:3 | 1:4 | 1:5 | 1:6 |
|---------------------------------------|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|
| Film quality                          | ×   | ○   | ○   | ○   | ○   | ○   | ○   | ○   | ×   | ×   |
|                                       | ○ good; × poor |
Figure 4. SEM images of pC7F15MAA nanoparticle films with different volume ratios: Acetic acid: AK-225 (v/v) = (a) 5:1, (b) 3:1, and (c) 1:4.

Figure 5. Surface wettability of pC7F15MAA nanoparticle films.

the surface of pC7F15MAA nanoparticle films shows quite low contact angle for methanol, ethanol, isopropyl alcohol, THF, ethyl acetate, and acetone. This indicates that pC7F15MAA nanoparticle film has high potential of solvent selective separation.

Next the critical surface free energy of pC7F15MAA nanoparticle film was investigated by measuring contact angles of five types of alkane solvents: hexane, decane, dodecane, octane and tetradecane (Figure 6). The critical surface free energy of pC7F15MAA nanoparticle film was determined as 18.6 mN m$^{-1}$ (4:1) and 18.7 mN m$^{-1}$ (1:5), respectively. This means that the surface of pC7F15MAA nanoparticle film was occupied by fluorocarbon groups.
3.2. Dissolved oxygen sensor performance

As described in Ref. [4], we have succeeded in preparing a high sensitive dissolved oxygen sensor system. Briefly, we prepared a porous and superhydrophobic pC7F15MAA nanoparticle film with platinum(II) porphyrin containing copolymer, poly(N-dodecylacrylamide-co-5-[4-(2-methacryloxyethoxycarbonyl)phenyl]-10,15,20-triphenylporphinatoplatinum(II)) (p(DDA/PtTTP)). A

Figure 6. Zisman plot of pC7F15MAA nanoparticle film in the volume of 1:4 and 5:1.

Figure 7. (left) Luminescence spectra and (right) Stern-Volmer plots of pC7F15MAA/p(DDA/PtTP) nanoparticle film in water. Reprinted in part with permission from Ref. [4]. Copyright 2015 American Chemical Society.
mixed solution of pC7F15MAA and p(DDA/PtTPP) (95:5 w/w) in AK-225 and acetic acid (4:1 v/v) was cast on a glass substrate. The cast film was kept for at least one day at room temperature to remove solvents. The pC7F15MAA/p(DDA/PtTPP) film exhibited a water contact angle of 162°, indicating a superhydrophobic surface. More interestingly, the film showed great sensitivity to dissolved oxygen. (Figure 7) The luminescence intensity ratio at two oxygen concentrations reaches 126 (=$I_0/I_{40}$, corresponding to 0 and 40 mg L$^{-1}$ dissolved oxygen concentrations). Conducting time-resolved luminescence lifetime measurements in water as well as in gas phase, we found that the equilibrium state is maintained between the entrapped gas and dissolved oxygen through the superhydrophobic surface of the pC7F15MAA/p(DDA/PtTPP) nanoparticle film. Table 2 summarizes the film-based sensor performance. For some of references, we refer to a recent review reported by Lo et al.[7] Our system has the highest oxygen sensitivity because of the porosity as well as superhydrophobic characteristics of amphiphilic fluorinated polymer nanoparticle films.

| Chromophore Support matrix | $K_S\nu$ | Sensitivity ($I_0/I$) | Ref. |
|---------------------------|---------|-----------------------|-----|
| Ru(Ph$_2$phen)$_3^{2+}$ | TEOS/MTEOS | 0.059 (not linear) | 3.5 (0-40 ppm) | [8] |
| Ru(dpp)$_3^{2+}$ | TMOS/DiMe-DMOS | 0.14 | 16 (0-100 %) | [9] |
| PtOEP | Fluorinated co-polymer matrix | not linear | 1.8 (0-40 mg L$^{-1}$) | [10] |
| Ru(Ph$_2$phen)$_3$Cl$_2$ | Fluoropolymer matrix | 0.22 | 6.5 (0-30 mg L$^{-1}$) | [11] |
| Ru(dpp)$_3^{2+}$ | TMOS/C8TMOS | 0.11 | 10 (0-100 %) | [12] |
| Ru(dpp)$_3$Cl$_2$ | TMOS/DiMe-DMOS | 0.15 | 7.3 (0-40 mg L$^{-1}$) | [13] |
| Ru(dpp)$_3$Cl$_2$ | Porous plastic fiber | 0.5523 | 8.7 (0-14 mg L$^{-1}$) | [14] |
| Ru(dpp)$_3$ | TMOS/MTEOS | not linear | 1.3 (0-45 mg L$^{-1}$) | [15] |
| PtTFPP | TMOS/C8TMOS (silica nanoparticle) | 4.18, 0.000005 (not linear) | 117 (0-40 mg L$^{-1}$) | [16] |
| p(DDA/PtTPP) | Amphiphilic fluorinated polymer | 3.1 | 126 (0-40 mg L$^{-1}$) | [4] |

4. Conclusion
In conclusion, we described a unique bottom-up approach for creating amphiphilic fluorinated polymer nanoparticle films. Casting mixed solutions of amphiphilic fluorinated polymer, pC7F15MAA allows to prepare porous superhydrophobic surfaces. We addressed preparation conditions in terms of the mixing ratio of two solvents (acetic acid and AK-225) and solution concentration. We compared our sensing system for dissolved oxygen detection based on surface wettability and oxygen sensitive luminescence with other previous reports. Because of the good oxygen permeability as well as low surface tension of fluorinated side chains, the oxygen detection was successfully demonstrated with the excellent oxygen sensitivity in water ($I_0/I_0 = 126$), which is the highest value reported so far. Other possibilities such as selective solvent extraction and wettability patterns, which are based on unique surface wettability of pC7F15MAA nanoparticle films will be clarified in the future.
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