Regulation of Surface Dimpled Morphology by Using Fluorinated Polymers

Daisuke Sakae, Junji Watanabe, and Yoshiyuki Ikeda

Department of Chemistry of Functional Molecules, Faculty of Science and Engineering, Konan University

Fax: +81-78-435-2539, E-mail: junjiknd@konan-u.ac.jp, yiked@konan-u.ac.jp

2,2,2-Trifluoroethyl methacrylate (TFEMA) and 1,1,1,3,3,3-hexafluoroisopropyl methacrylate (HFIMA) are fluorinated monomers, and water repellency is expected. The monomers are copolymerized with conventional methacrylic acid derivatives for versatile synthesis. In this study, a fluorinated polymer was used to achieve water repellent properties. As fluorinated monomers, TFEMA or HFIMA were copolymerized with *n*-butyl methacrylate (BMA) by conventional radical polymerization to make poly(TFEMA-*co*-BMA) (PFB) and poly(HFIMA-*co*-BMA) (PHFB), respectively. Monomer composition and the molecular weights of PFB and PHFB were characterized by ^1H NMR and GPC. We evaluated the surface functionality by making a self-organized dimple pattern. Spin coating of the polymer solution was carried out on the substrate, and then, the solvent was evaporated under a humid environment. After that, a self-organized dimple pattern was formed. The resulting surface structure was regulated by the concentration of the polymer solution, its composition, and the solvent. The surface morphology was observed by optical microscopy, scanning electron microscopy, and atomic force microscopy. The diameters of the dimples of PFB and PHFB were roughly 0.8 μm and 0.5 μm , respectively. Homogeneous dimpled morphology was observed on the polymer-coated surfaces. The surface hydrophobicity is reported in terms of the surface morphology.

Key words: Fluorinated polymers, dimpled structure, random copolymerization, self-organization

1. INTRODUCTION

Surface properties of materials and water repellent properties are important for many products. In particular, water repellency is a fundamental aspect in a large number of living organisms (e.g., plants and insects), and it is applicable in numerous industrial processes. Fluorinated chemical agents show higher water repellencies. Fluorinated polymers are widely studied due to several unique characteristics, such as water and oil repellency, low surface tension, and low refractive index [1].

Micro-patterned surfaces are prepared by following two approaches: using physical and chemical methods. For example, plasma etching is a physical approach capable of patterning the substrate, and the final micro-pattern is precisely controlled [2]. Varieties of micro-patterned surfaces are known as spikes, pillars, or stripes. However, this method has a few disadvantages: it is time-consuming to make micro-patterned structures, and it is a labor-intensive process. In 2000, water-assisted honeycomb pattern formation was reported by Shimomura *et al* [3]. Water droplets were nicely assembled in the polymer solution and formed the template. The polymer solution was coated on the substrate under a high humidity environment, and the solvent was evaporated to make the honeycomb pattern. In this process, amphiphilic polymers are indispensable because micron-sized water droplets can be stabilized by the amphiphilic polymers. In this approach, the stable water droplet is dominant, and the droplets migrate into

the thin layer of the polymer solution.

In the present study, we focused on a hydrophobic polymer to make a micro-patterned surface. In particular, the fluorinated polymers are not major examples of micro-pattern formation and have not been extensively investigated. According to the mechanism of micro-pattern formation, no micro-pattern would be formed using fluorinated polymers without the presence of amphiphilic polymers. Recently, we have found dimpled surface morphologies on fluorinated polymer-coated substrates. The surface morphology would be associated with the floating of the water droplets exhibiting precise and homogeneous morphology. The anomalous approach would be applicable to form a micro-patterned surface. Therefore, the dimpled morphology formation is discussed in terms

Poly(TFEMA-*co*-BMA) (PFB) Poly(HFIMA-*co*-BMA) (PHFB)

Scheme 1. Structures of PFB and PHFB.

Table 1. Synthetic results of fluorinated polymers ^{a, b)}

Sample	Mole fraction of fluorinated monomers ^{c)}		Poor solvent (wt%)		Molecular weight			Yield (%)
	In feed	In copolymer	2-Propanol	Water	$M_n (\times 10^{-4})$	$M_w (\times 10^{-4})$	M_w/M_n	
PFB100	1	1	100	0	1.1	2.2	2.0	72
PFB80	0.8	0.81	80	20	1.5	2.9	2.0	85
PFB50	0.5	0.41	50	50	1.5	2.7	1.8	84
PFB20	0.2	0.18	20	80	1.5	3.3	2.2	72
PFB0	0	0	0	100	2.3	3.7	1.6	94
PHFB50	0.5	0.49	50	50	1.3	2.1	2.1	69

a) Polymerization time : 24 h.

b) Solvent : THF.

c) Determined by ¹H NMR.

of polymer composition and coating conditions.

2. MATERIALS AND METHODS

2.1 Materials

2,2,2-Trifluoroethyl methacrylate (TFEMA) was obtained from Tosoh F-Tech Co., Tokyo, Japan. 1,1,1,3,3,3-Hexafluoroisopropyl methacrylate (HFIMA) and *n*-butyl methacrylate (BMA) were used for copolymerization to make durable coating membrane and were obtained from Tokyo Chemical Industry Co., Tokyo, Japan. Other reagents and solvents were commercially available in extra-pure grade and were used without further purification.

2.2 Synthesis of the PFB and PHFB polymers

The polymers were synthesized by free radical copolymerization. TFEMA and BMA were placed in a glass flask and 2,2'-azobisisobutyronitrile (AIBN) was added to this flask. THF was used as the solvent, and the final concentration of the total monomers was adjusted to 1 mol/L. Furthermore, 10 mmol/L of AIBN was added to the solution. The polymerization was carried out at 65°C for 24 h in a nitrogen atmosphere. The reaction mixture was poured into a large amount of a mixed solvent of 2-propanol and water to remove residual monomers and recover the polymers, and then, the resulting polymer was dried in *vacuo*. Scheme 1 shows the polymer structures of poly(TFEMA-*co*-BMA) (PFB) and poly(HFIMA-*co*-BMA) (PHFB). The chemical structures of PFB and PHFB were determined by ¹H NMR (Unity VARIAN AS-300 MHz) and IR (FT/IR-4200, JASCO Co., Tokyo, Japan) spectroscopy. The mole fractions of PFB and PHFB were determined by using ¹H NMR. The molecular weight of PFB and PHFB were determined by GPC (GPC System, JASCO Co., Tokyo, Japan) with a KF-804 column (Showa Denko K.K., Tokyo, Japan).

2.3 Polymer coating on the substrate

For polymer coating, 14 mm diameter plastic plates were first cleaned with dichloromethane. The substrates were coated in each polymer solution (PFB and PHFB: 5 wt% in dichloromethane) to make flat and dimpled morphologies. The dimpled morphology was formed by spin coating. The spin time, spin speed, humidity, and flow rate of air were 1 min, 1000 rpm, 95%, and 1 L/min, respectively.

2.4 Optical microscopy observation

An optical microscope (BX51, OLYMPUS Co., Tokyo, Japan) was used to observe the entire surface

area. To observe the dimpled morphology, 40-fold magnification was selected.

2.5 Scanning electron microscopy observation

Scanning electron microscope (SEM) (VE-9800, KEYENCE Co., Osaka, Japan) images were recorded to obtain the micro- and/or nanostructure. We measured the diameters of over 100 dimples and made a histogram.

2.6 Atomic force microscopy observation

Atomic force microscopy (AFM) (SPM-9700 SHIMADZU Co., Kyoto, Japan) was used in a dynamic mode to observe surface morphology and cross-sectional pattern.

2.7 Contact angle measurements

The polymer-coated substrate was measured by using a contact angle analyzer (Drop Master 700 KYOWA Interface Science Co. Ltd., Saitama, Japan). The contact angles were measured at 10 sec intervals with the $\theta/2$ method.

3. RESULTS AND DISCUSSION

3.1 Characterization of the polymers

Random copolymers of PFB and PHFB were obtained by radical polymerization. The chemical structure of PFB was confirmed by ¹H NMR (CDCl₃) (ppm) δ 3.9 (s, 2H, -CH₂-CH₂-CH₃), 4.3 (s, 2H, -CH₂-CF₃) and the chemical structure of PHFB was confirmed by ¹H NMR (CDCl₃) (ppm) 3.9 (s, 2H, -CH₂-CH₂-CH₃), 5.6 (s, 1H, -CH-(CF₃)₂) and IR adsorption at 660 cm⁻¹ (-CF₃). Table 1 shows the synthesis results of the polymers. A polymer yield of around 80% was achieved by changing the composition of the poor solvent. The mole fraction in the copolymer was nicely correlated with monomer composition in the feed. The number average molecular weight was 1.5×10^4 and the polydispersity was roughly 2.0. In the case of PHFB50, 0.5 mol/L of HFIMA was used for the polymerization. The resulting polymer contained 0.49 mol/L of HFIMA, which was determined by ¹H NMR. The solubilities of PFB and PHFB were similar; THF, dichloromethane, and chloroform were good solvents for polymer coating. In contrast, methanol and water were poor solvents, and they were used for surface enrichment of the polymer-coated membrane.

3.2 Evaluation of the sample surface

The flat surface was prepared by using the polymer solution (PFB50: 5wt% in 1,4-dioxane or acetone). The dimpled morphology was formed by using the polymer solution (PFB50: 5wt% in dichloromethane or

Figure 1. Optical microscope image of the dimpled morphology of PFB50.

Figure 2. SEM images of the dimpled morphology prepared at 25°C and 95% relative humidity. Spreading 100 μ L of polymer solution (5wt%). (a) $\times 2500$ PFB50, (b) $\times 2500$ PHFB50, (c) $\times 5000$ PFB50, (d) $\times 5000$ PHFB50.

chloroform). By using polymer solution (PFB50: 5wt% in dichloromethane), uniformly sized dimpled morphology was observed on the surface. By using polymer solution (PFB50: 5wt% in chloroform), the surface showed non-uniform dimpled morphologies. Conversely, by using polymer solution (PFB50: 5wt% in toluene), a flat surface was made. These results indicate that the micron-sized water droplet evaporated before forming the film of the polymer due to the higher boiling point of toluene compared with chloroform.

Figure 1 shows an optical microscope image of the morphology of the membrane, which was organized fully and evenly. The total area of the optical microscope was roughly $50 \times 70 \mu\text{m}$. However, the surface morphology was indeterminate as truly dimpled. Therefore, the surface morphology was observed by SEM. By comparing Figure 2(a) and Figure 2(b), PHFB50 had a much more densely organized dimpled morphology than that of PFB50. The dimple diameters of PHFB50 were smaller than that of PFB50. The dimpled morphology was formed by water flowing in the hydrophobic polymers, as the solvent was evaporated. A histogram of the dimple diameter was obtained using SEM images. Figure 3 shows the histogram of the diameter and its cumulative percentage. The diameters of the dimples on PFB were observed to be 0.7–0.9 μm , in the case of PHFB, with 0.4–0.6 μm diameter being the most common. The surface morphology was more clearly observed by using

Figure 3. A histogram of the diameter of dimples. (a) PFB50 ($n=134$), (b) PHFB50 ($n=350$).

magnified SEM images (Figures 2(c) and 2(d)). Clear edges on the dimples were observed. Further investigation of the dimpled morphologies is warranted. Figure 4 shows AFM images of the surface with a cross-sectional view. The dimpled sizes and morphologies observed with AFM were quite similar to those obtained with SEM images. The cross-sectional information was monitored by line scanning as indicated in Figure 4(a) and 4(b). The dimpled morphology of the depth direction was 350–500 nm. The bottom shape was a little bit anomalous, showing a sharp edge on the bottom. Flat or hemispherical morphology could be easily imagined, because the fundamental mechanism of the dimpled morphology should be the template of the water droplet. The template of the water droplet was formed by centrifugal force and aqueous friction. The centrifugal force would be enhanced on the outmost surface of the polymer coating layer instead of the bottom side of the layer. Thus, asymmetric morphology in the cross-section was formed.

The surface wettability was evaluated by using the flat and dimpled surface. Figure 5(a) shows static contact angles of the flat surfaces on PFB50 with time in water or methanol immersion effects of the fluorinated monomer composition in PFB. From Figure 5(b), at 50 mol% of the TFEMA, there was an onset of change in the contact angle. Figure 5(c) shows the contact angle of the flat surface treated by methanol. PHFB was much more hydrophobic than that of PFB50. Figure 5(d) shows a change in the contact angle with surface morphology on PHFB50 after treatment by methanol. The hydrophobicity of the dimpled morphology was much higher than that of the flat surface in spite of same fluorinated polymer. The difference in the contact angle was roughly 15° . PFB50 and PHFB50 were compared with flat and dimpled morphology, and the dimpled

Figure 4. AFM images of the dimple morphology showing top view and cross-section; (a) PFB50 (b) PHFB50.

Figure 5. Static contact angle of the flat and dimple surface on different wet treatment. (a) change in solvent. (b) Change over time with a change in composition. (c) Immersed in methanol on PHFB and PFB. (d) Immersed in methanol on dimple and flat surface.

morphology did better than the flat surface in terms of the contact angle. In the immersion conditions, regardless of the angle, the dimpled morphology did better. The contact angles in water were significantly adjustable with surface morphology.

4. CONCLUSIONS

The fluorinated monomers TFEMA and HFIMA were copolymerized with BMA by radical copolymerization and a hydrophobic polymer was obtained. Regardless of the surface of the copolymer films, immersion in different solvents switched the contact angle. Samples with a flat polymer surface were compared to samples exhibiting dimpled morphology on the surface. Hydrophobic property was accretion on the dimpled structure comparing with flat surface. Two species fluorinated polymers, as large-again diameter of dimpled was observed by histogram. Hydrophobic property was accretion by dimpled structure and the number of fluoro group ($-\text{CF}_3$). Further, the regulation of surface morphology and alteration of hydrophobicity was achieved.

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