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Construction of superhydrophobic surfaces by fibrous aggregation of perfluoroalkyl chain-containing organogelators†

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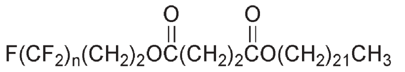
Received (in Cambridge, UK) 31st January 2006, Accepted 10th April 2006
First published as an Advance Article on the web 24th April 2006
DOI: 10.1039/b601485b

Superhydrophobic surfaces, characterized by water contact angles greater than 150°, can be produced by means of intermediate organogels, which were formed by perfluoroalkyl chain-containing organogelators with volatile organic solvents.

Superhydrophobic surfaces, characterized by water contact angles greater than 150°, have recently attracted much attention for their promising applications in various fields from daily life and industry, to agriculture. To effectively develop such functionality, it is of importance to select and/or control both the chemical compositions of compounds and the geometrical roughness of surfaces.[1–3] When measured on perfectly flat surfaces, even the surface of CF_3 terminated compounds gives contact angles less than 120°, which are known to possess the lowest free energy.[4] Therefore, designing and constructing appropriate roughness on the materials are indispensable for the formation of superhydrophobic surfaces. Various methods, such as plasma etching and polymerization,[5–7] chemical vapor deposition,[8] electrodeposition,[9] sol–gel,[10] solidification,[11,12] phase separation,[13,14] and deposition of nanoparticles,[15] have been developed. Our strategy for constructing superhydrophobic surfaces lay on the utilization of xerogels of the fibrous aggregates formed by low molecular weight organogelators.

Low molecular weight organogelators are known to form gels by heating them in appropriate organic solvents.[16,17] The removal of the solvents from the organogels gives xerogels, which have three-dimensional network structures of fibrous aggregates. The aggregates provide nanometer-scale roughness on the surface. Moreover, the evaporation of the solvent from gels is expected to result in homogenous and smooth surfaces on a macroscopic scale, because the formation of gels inhibits the deposition of crystals and/or bulky aggregates of the compounds to lead to functional materials.[18] These unique properties of the organogels have prompted us to utilize the fibrous aggregates for producing superhydrophobic surfaces. Here we demonstrate the organogel formation of new low molecular weight gelators containing perfluoroalkyl chains in various organic solvents and the surface modification of the glass plate using organogels.



$$F(CF_2)_n(CH_2)_2O\overset{O}{\overset{\|}{C}}(CH_2)_2\overset{O}{\overset{\|}{C}}O(CH_2)_{21}CH_3$$

n = 10 **1**
n = 8 **2**
n = 6 **3**
n = 4 **4**

Scheme 1 Structure of compounds **1–4**.

The compounds containing perfluoroalkyl chains **1–4** were synthesized as follows. Firstly, 1-docosanol was changed to alkylmonosuccinate by reaction with succinic anhydride, and then chlorinated by thionyl chloride. The obtained alkylmonosuccinyl chloride was converted to the compounds **1–4** by using (perfluoroalkyl)ethanol (Scheme 1).

Table 1 shows results of the gelation tests for **1–4** with the minimum gel concentrations at 20 °C. Compound **1** can gelate a wide variety of organic solvents at the minimum gel concentration of less than 10 g L^{-1}, and the value reaches 2 g L^{-1} in alcohols, DMF, acetonitrile, and silicone oil. All the gels obtained from **1** were transparent and stable for more than a month. There have been only a few examples of the gelators containing perfluoroalkyl chains for water and organic liquids.[19–23] In contrast with **1**, the compounds with shorter perfluoroalkyl chains, **2–4**, can form the organogels with restricted kinds of organic solvents, and the required minimum gel concentration is much higher. Moreover, the gels prepared from **3** and **4** were unstable and transformed to the crystals in a week. Thus, the compounds containing longer perfluoroalkyl chains have higher gelation ability, suggesting that the aggregation of perfluoroalkyl chains is crucial for forming stable organogels.

Table 1 Gelation tests for **1–4** in organic solvents[a,b] and minimum gel concentrations (g L^{-1})

Solvent	1	2	3	4
Methanol	G(2)	G(2)	G(25)	G(50)
Ethanol	G(3)	G(7)	G(25)	G(50)
1-Propanol	G(7)	G(10)	G(25)	G(100)
Benzylalcohol	G(2)	G(2)	G(25)	G(100)
Ethyl acetate	G(11)	G(100)	S	S
Acetophenone	G(3)	G(15)	C	S
DMF	G(2)	G(5)	G(30)	G(100)
Acetonitrile	G(2)	G(4)	G(30)	G(50)
Squalane	G(4)	G(6)	G(20)	G(100)
Silicone oil	G(2)	G(4)	G(17)	G(50)

[a] G = gel, S = solution, C = crystal. [b] Gelation tests were examined in the same method described in ref. 24.

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† Electronic supplementary information (ESI) available: Table S1 shows contact angles on glass plates coated by xerogels prepared from **1** and 12-hydroxystearic acid. See DOI: 10.1039/b601485b

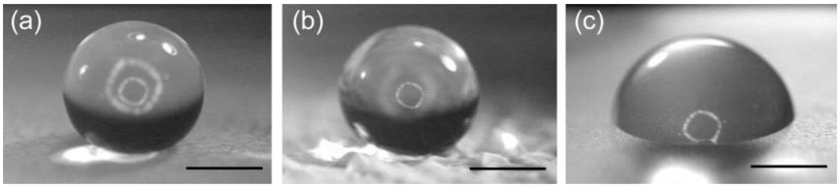

Fig. 1 Photographs of a water droplet (5.0 µL) placed on a glass plate coated by (a) xerogel of **1** from 1-propanol, (b) bulky aggregate of **1** from diethyl ether, and (c) xerogel of 12-hydroxystearic acid from cyclohexane. Scale bars, 1 mm.

The smooth surfaces coated by the xerogels of **1** on a glass plate were easily prepared by means of the intermediate organogel formation. For example, the warmed solution of **1** in 1-propanol (1 mL) at a concentration of 7 g L^{-1} (the minimum gel concentration) was dropped on a *ca.* 20 cm^2 glass plate (2.6 × 7.6 cm). When polar solvents, such as alcohols and ethyl acetate, were used, the warmed solution spread out on the glass plate without any difficulty. Then the solution on the glass turned to organogel at room temperature. The slow evaporation of the solvent in the organogel provided the xerogel coating on the glass plate. The volatile solvents that gave the organogels produced the smooth surfaces on a macroscopic scale (mm), while the solvents with which **1** cannot form the organogels efficiently (more than 100 g L^{-1}), such as diethyl ether and chloroform, led to the rough and irregular surfaces due to the partial crystallization or bulky aggregation of **1**. These rough surfaces did not give accurate measurement of contact angles, as shown in Fig. 1b. The compound **2** with some solvents also gave a smooth surface, whereas the other two compounds **3** and **4** were found to make rough or irregular surfaces irrespective of the solvents.

Fig. 1a shows a water droplet placed on the glass plate coated by the xerogel of **1** obtained from the organogel involving 1-propanol. The contact angle is 154°, *i.e.*, enough to call the surface superhydrophobic. The contact angles on the surface prepared from **1** with five solvents are greater than 150° (Table S1†). Since contact angles are less than 120° on perfectly flat surfaces,[4] the present superhydrophobicity of **1** would be ascribed not only to the chemical composition but also to the geometrical morphology of the surface prepared through the organogel formation. The compound **2** with appropriate solvents also provided the superhydrophobic surfaces.

For the sake of comparison, we measured the contact angles of the glass plate coated by the xerogels prepared from the typical organogelator of 12-hydroxystearic acid.[25] Fig. 1c shows a water droplet placed on the glass plate coated by the xerogel of 12-hydroxystearic acid in cyclohexane. The contact angle is 90°, and the image is evidently different from the case of **1**. In the same way, the contact angles on the surface prepared from other solvents also resulted in around 90° (Table S1†), indicating that this gelator is inappropriate to produce superhydrophobic surfaces irrespective of the solvents.

In order to investigate the superhydrophobic surface in detail, atomic force microscopy (AFM) images were recorded on the xerogels, which were prepared in the same way as in the case of contact angle measurements. Fig. 2a shows the image of xerogel prepared from **1** with 1-propanol, in which intertwining fibrous aggregates can be observed; the fibers are 100–200 nm in diameter. These self-assembly fibers will cause the physical gelation, as reported in the literature.[16,17,24,25] The roughness of the fibrous aggregates will contribute to the superhydrophobicity; the average surface roughness (R_a) in Fig. 2a was 60 nm. On the other hand, such fibrous aggregates cannot be observed in the xerogel prepared from 12-hydroxystearic acid, as shown in Fig. 2b. These observations support the view that the fibrous aggregates are important for producing superhydrophobic surfaces.

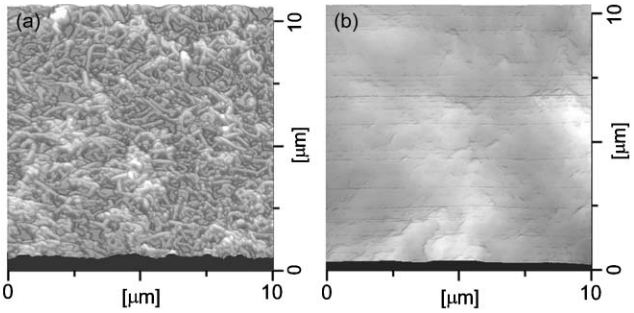

Fig. 2 AFM images of xerogels prepared from (a) **1** in 1-propanol and (b) 12-hydroxystearic acid in cyclohexane.

The present study demonstrates that the compounds with long perfluoroalkyl chains **1** and **2** are good organogelators capable of gelating a wide variety of organic solvents at a low concentration. Moreover, we exhibit a new method of preparing the superhydrophobic surfaces that are achieved by the surface roughness formed by the fibrous aggregates of the two organogelators. Compared to other methods of preparing the superhydrophobic surfaces, the present method has an advantage of its simplicity.

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