

Rapid Communication

SYNTHESIS OF PERFLUORO-1-OCTANESULFONATED FULLERENE AND THE FRICTION PROPERTIES OF ITS THIN FILM*

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Abstract A star-shaped compound of perfluoro-1-octanesulfonated fullerene was synthesized. The measurement of the friction for its spin-coating film by friction force microscopy (FFM) reveals that the films possess lower friction force compared to that of the star-shaped C₆₀-polystyrene films.

Keywords Perfluoro-1-octanesulfonated fullerene, Thin film, Friction force microscopy (FFM)

The study of microtribological properties in ultrathin organic or polymeric films has focused recently on development of a new type of low friction lubricants^[1, 2], especially for application in high-density magnetic recording systems^[3, 4]. The C₆₀-containing polymers have been synthesized for the lubricating investigation, in which the soft polymer chains attached to C₆₀ are responsible for reducing friction force, and C₆₀ cores attached to polymer chains in thin film are expected to be beneficial for load-bearing capacity^[5, 6]. Fluorocarbon compounds are of great interest due to their potential use as lubricants. Surface modified C₆₀ with fluorocarbon chain as arms incorporated in the thin films should be favorable for friction and wear properties. Here we report the synthesis of a star-shaped compound of perfluoro-1-octanesulfonated fullerene and the comparison of microtribological properties between star-shaped C₆₀-polystyrene and star-shaped C₆₀-perfluoro-1-octanesulfonate.

A perfluoro-1-octanesulfonated fullerene was prepared from fullerol [C₆₀(OH)_n] and perfluoro-1-octanesulfonyl fluoride [CF₃(CF₂)₇SO₂F]. Fullerol was synthesized according to references^[7, 8]; the procedure described briefly as follows: 0.8 g of NaOH and 50 mL of benzene containing 50 mg of C₆₀ were placed in a 100 mL three necked flask and the mixture was vigorously stirred. Then 1 mL of tetrabutylammonium hydroxide solution (10% in water) was added. The mixture was stirred 24 h at room temperature under N₂, the solution turned colorless and some black precipitate formed after a few hours. The precipitate was separated by filtration and washed with a large quantity of water, then dried under reduce pressure to give 69 mg brown powder. It was dissolved in *N,N*-dimethyl formamide (DMF). From the elemental analysis, the “*n*” of C₆₀(OH)_n can be calculated to be 14–17. The perfluoro-1-octanesulfonyl fluoride was used as received from Shanghai Institute of Organic Chemistry (Chinese Academy of Sciences). A mixture of fullerol (100 mg), DMF (100 mL, purified before use) and triethylamine (3 mL) was placed in a three necked flask; after bubbling dry nitrogen for 5 min to remove the oxygen, the solution was stirred at 0°C for 10 min. 2.5 g Perfluoro-1-octanesulfonyl fluoride was dissolve in 25 mL diethyl ether and then added dropwise.

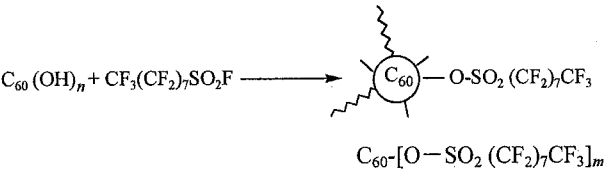
The reaction was kept at 0°C for 3 h then 50°C for 10 h. Volatiles were removed at reduced pressure to yield a brown residue, which was dissolved in 10 mL DMF then precipitated by 150 mL of diethyl ether, filtered and

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dried, to give 260 mg brown powder of product. 3400, 1282, 1240, 1209, 525 cm^{-1} in the FTIR spectrum reveal the chemical bond of $\text{—O—SO}_2\text{—}$ to be formed. The reaction between fullerol and perfluoro-1-octanesulfonyl fluoride can be illustrated as follows:



From elemental analysis, the oxygen content of the product is 13.81%–14.54%, and the arm number “ m ” can be calculated to be 3.

The thin films of star-shaped C_{60} -perfluoro-1-octanesulfonate on silicon wafers (immersed in 30% H_2O_2 and concentrated H_2SO_4 in 3:7 volume ratio before use) were prepared by spin-coating with 0.5 or 1.0 mg/mL DMF solutions. The films were kept at N_2 for 3 days, then in reduced pressure for 3 days at 60°C before measurement. The thin films of star-shaped C_{60} -polystyrene^[6] were prepared in our laboratory for comparison investigation.

The contact angles of films were further determined in water using JJC-1 Contact Angle Goniometer at 25°C as shown in Table 1.

Table 1. Contact angles of the polymer thin films

Film materials	Contact angle in water		
	0.5 mg/mL	1.0 mg/mL	2.0 mg/mL
C_{60} -polystyrene	34°	37°	41°
C_{60} -perfluoro-1-octanesulfonate	24°	26°	28°
Clean silicon sheet	48°		

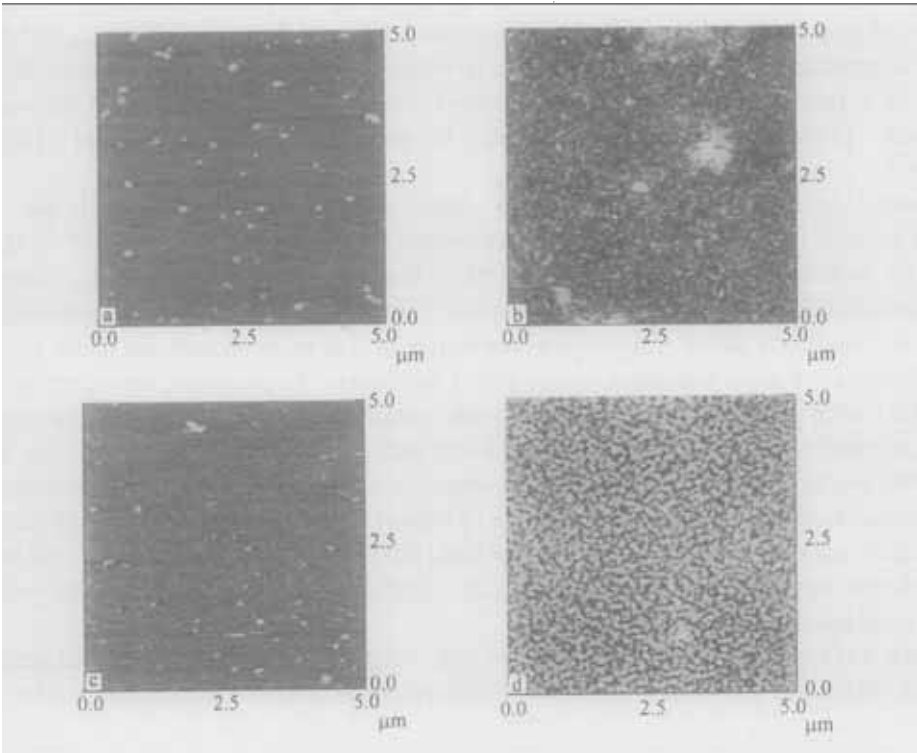


Fig. 1 AFM contact mode height images of the thin films of star-shaped C_{60} -perfluoro-1-octanesulfonate (left, conc. a 0.5%; c 1.0%) and star-shaped C_{60} -polystyrene (right, conc. b 0.5%; d 1.0%)

The contact angles of the films from star-shaped C_{60} -perfluoro-1-octanesulfonate are substantially lower than those from star-shaped C_{60} -polystyrene. It reveals that the surface of C_{60} -perfluoro-1-octanesulfonate thin film possesses the lower surface energy.

AFM and FFM images of these films were obtained on Nanoscope IIIa equipped with a bioscope G scanner ($90\text{ }\mu\text{m}$) in contact mode, a commercial Si_3N_4 cantilever with $K = 0.06\text{ N} \cdot \text{m}^{-1}$ was used at a 1.5 Hz scan rate and at 25°C and relative humidity 50% . Figure 1 provides representative height images while the scan angle is 0° .

From these images, the thin films of star-shaped C_{60} -perfluoro-1-octanesulfonate are rather flat and uniform compared to the films of star-shaped C_{60} -polystyrene. The surfaces of these films are smooth with rarely occurring macroscopic aggregation of fullerene derivates. Root mean square roughness is in the ranging of $0.6\text{--}2.4\text{ nm}$ for all films.

Friction images in trace and retrace scan directions were recorded when the scan angle is 90° , to various applied load, the friction forces (in volts) were then plotted as a function of load (nN) to yield a friction-load map (Fig. 2)

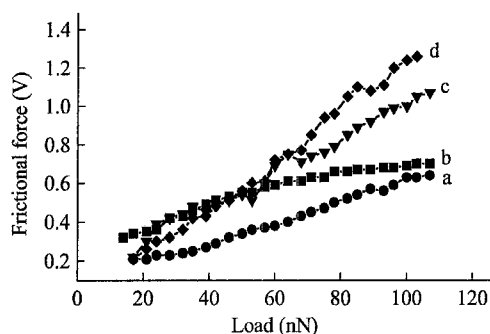


Fig. 2 Diagrams of frictional force versus load for the thin films of star-shaped C_{60} -Perfluoro-1-octanesulfonate (conc. a: 0.5% ; b: 1.0%) and star-shaped C_{60} -polystyrene (conc. c: 0.5% ; d: 1.0%)
a) Star-shaped fullerene-perfluoro-1-octanesulfonate film (0.5%)
b) Star-shaped fullerene-perfluoro-1-octanesulfonate film (1.0%)
c) Star-shaped fullerene-polystyrene film (0.5%)
d) Star-shaped fullerene-polystyrene film (1.0%)

The curves shown the non-linear relation of friction force and applied load. No evidence of film deformation and material transfer was observed during FFM measurement. The stability of these films is attributed to the additional load-bearing ability afforded by C_{60} chemically bonded in the molecular structure.

The initial investigation indicated that the star-shaped C_{60} -perfluoro-1-octanesulfonate film has a lower friction force than the star-shaped C_{60} -polystyrene film, which is expected to be a promising lubricant. It is concluded that a molecular chain with lower surface energy can give a smoother surface with lower friction force in C_{60} -containing copolymer thin films.

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