Superhydrophobic Electrospun POSS-PMMA Copolymer Fibres with Highly Ordered Nanofibrilar and Surface Structures

Yuhua Xue[a,b], Hongxia Wang[b], Dingshan Yu[c], Lianfang Feng[a], Liming Dai[c], Xungai Wang[b], Tong Lin[b]

[a] *State Key Laboratory of Chemical Engineering, College of Materials Science and Chemical Engineering, Zhejiang University, Hangzhou 310027, China*

[b] *Centre for Material and Fibre Innovation, Deakin University, Geelong, VIC 3217, Australia. Fax: 61-3-52272539; Tel: 61-3-52271245; E-mail: tong.lin@deakin.edu.au*

[c] *Department of Chemical and Materials Engineering, The University of Dayton, Dayton, OH 45469, USA*

ELECTRONIC SUPPLEMENTARY INFORMATION

S 1. Experimental section

S1.1 Materials and characterisations

Methyl methacrylate (MMA 99%) was washed with 5% (w/v) of aqueous NaOH solution to remove all the inhibitor, and then dried with calcium chloride overnight and distilled in vacuum. The purified MMA was stored in a flask sealed under N_2. Methacrylisobutyl POSS [(propyl methacrylate)(isobutyl)$_7$Si$_8$O$_{12}$] (MA-POSS) from Hybrid Plastics Co. and 4,4'-Azobis(4-cyanovaleric acid) (ACVA), tetrahydrofuran (THF), toluene and dimethylformamide (DMF) from Aldrich were used as received.

Molecular weights and distributions of all polymer samples were characterized by gel permeation chromatography (GPC) performed in THF (1.0 ml/min) at 25°C using a Waters GPC instrument, with a Waters 2414 Refractive Index Detector. ^{1}H NMR was measured with a Bruker 400 NMR spectrometer at 25 ºC, using deuterio-chloroform ($CDCl_3$) as solvent and tetramethylsilane (TMS) as the internal standard. The morphology of the electrospun fibres was observed under a scanning microscope (SEM, Leica S440) and a transmission electron microscopy (TEM, JEOL JEM-2100) at an acceleration voltage of 200 kV. Fourier transform infrared spectra (FTIR) were measured on a FTIR spectrometry (Bruker Optics) in ATR mode. X-ray diffraction (XRD) was performed on a powder diffractometer (Philips 1140/90) using Cu radiation 1.54Å. The samples were analysed at room temperature over a 2θ range of 5~50° with sampling intervals of 0.04°. Water contact angles were measured using a contact angle meter (CAM101, KSV Instruments Ltd). Topographic images were obtained using an AFM (DME type DS 45-40, Denmark) in tapping mode at room temperature.

Time-of-flight secondary ion mass spectrometry (*ToF-SIMS*) analyses were performed using a ToF-SIMS IV (Ion-TOF GmbH, Germany) instrument with a reflectron analyzer, a Bi cluster ion gun (25 keV), and a pulsed electron flood source for charge neutralization. The

primary pulsed Bi+ ion beam current was 2.5 pA, and the primary ion dose density was below the static SIMS limit of 1013 ions ·cm^{-2}. For spectral acquisition, positive and negative ion mass spectra were acquired from a 100×100 μm^2 area using a cycle time of 100 μs with a resulting mass resolution >7000 at m/z). Peak assignments were made based on the Munster High Mass Resolution Static SIMS library.

S1.2 Synthesis of POSS-PMMA copolymers

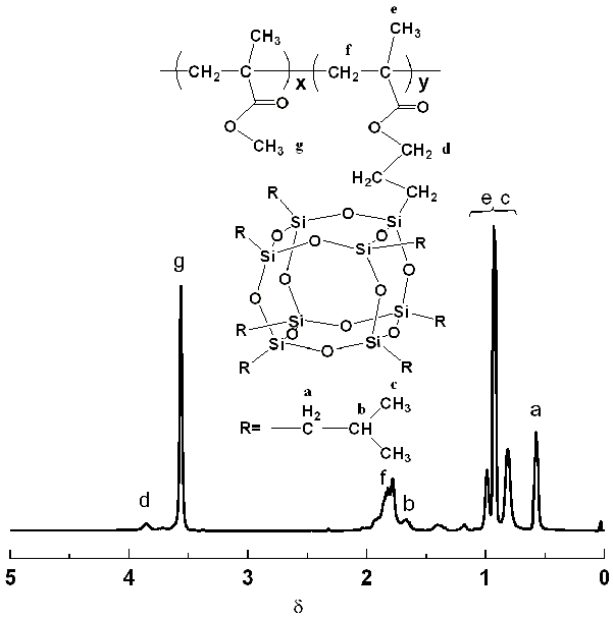
A POSS-PMMA copolymer containing equal weight of the monomers, MA-POSS and MMA, has been synthesised by free-radical polymerisation. The typical synthesis process is described as follows: In a 50 ml round bottom flask, MA-POSS (2.0 g, 2.12 mmol), MMA (2.0 g, 20.0 mmol) and ACVA (0.025g, 0.155 mmol) were dissolved in toluene (16 ml) and THF (4 ml) under a nitrogen atmosphere. The mixture was heated to 65 ºC under constant magnetic stirring to initiate the polymerisation reaction, and the polymerisation was then carried out at the elevated temperature for 24 hrs. After the reaction, the reaction solution was poured into excess methanol to precipitate the polymer. The polymer was then purified via several dissolving/precipitating cycles, and finally dried at 80 ºC in vacuum for 24 hrs.

S1.3 Electrospinning

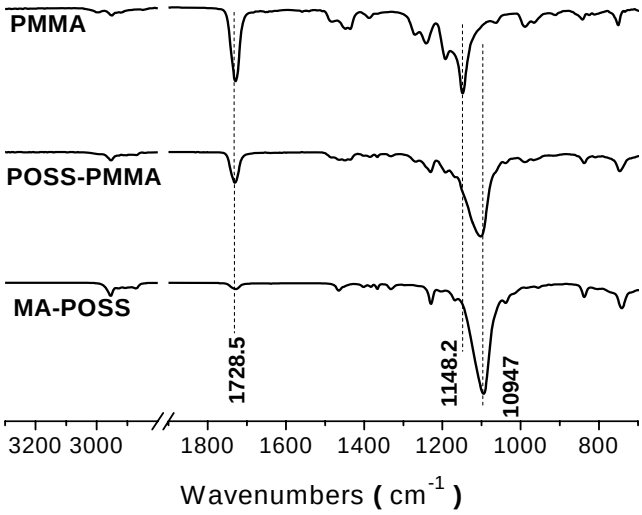
A purpose made electrospinning apparatus which included a high voltage power supply (ES30P, from Gamma High Voltage Research), a syringe with a flat-end metal needle, a syringe pump (Aldrich), a stainless steel collecting screen covered with an aluminium foil, was used to produce POSS-copolymer fibre membranes. In a typical electrospinning experiment, a POSS-copolymer solution (solvent DMF/THF 1:1 vol/vol), was added into a syringe and delivered to the tip of the needle by the syringe pump at a feeding rate of 3 ml/hr.

Electrospinning was carried out under an applied voltage of 20 kV with fibre collecting distance of 25 cm.

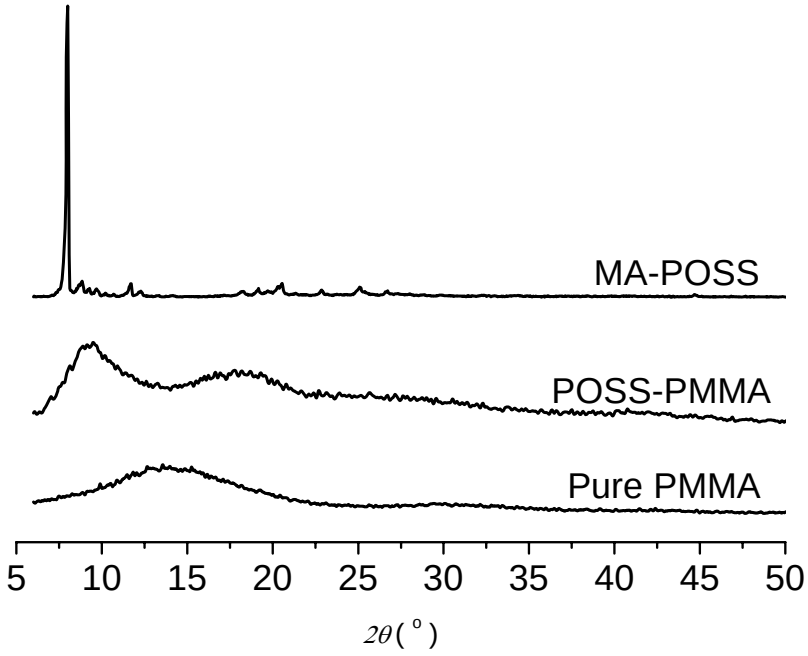
S 2. ^{1}H-NMR spectrum of POSS-PMMA copolymer ($CDCl_3$)



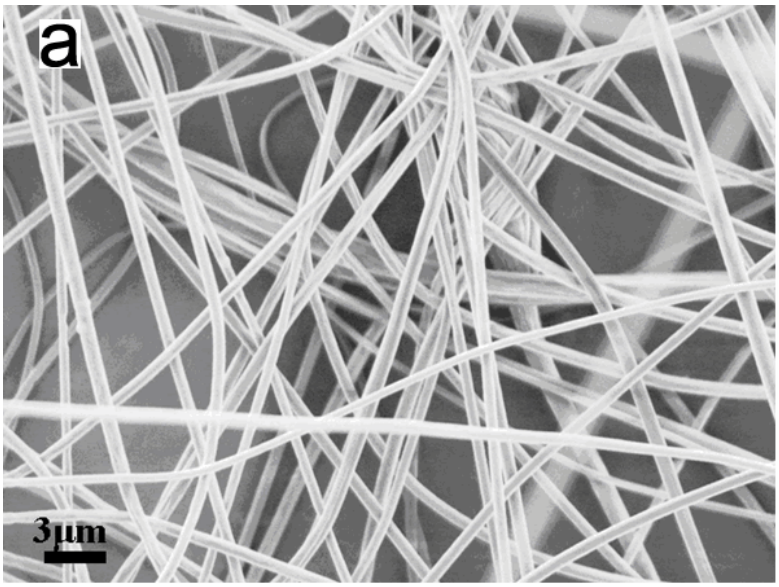
S 3. FTIR spectra of POSS-PMMS copolymer, MA-POSS and pure PMMA

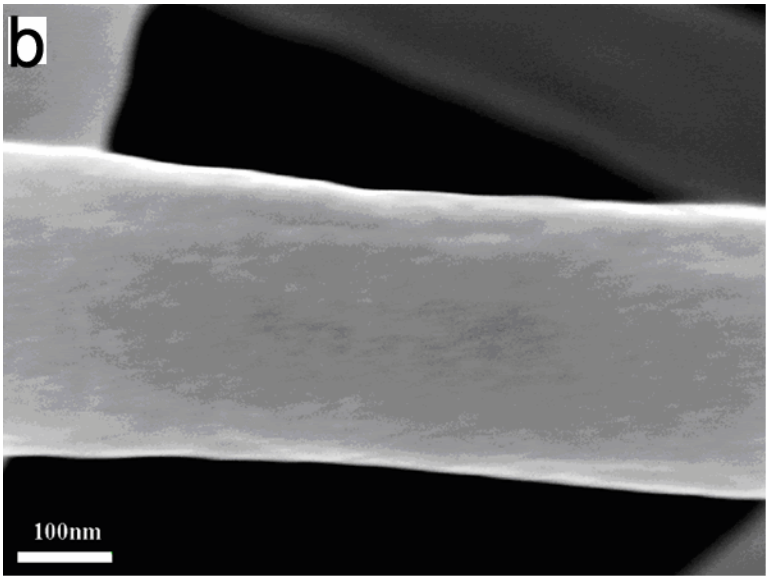


S 4. XRD patterns of POSS-PMMA copolymer, MA-POSS and pure PMMA

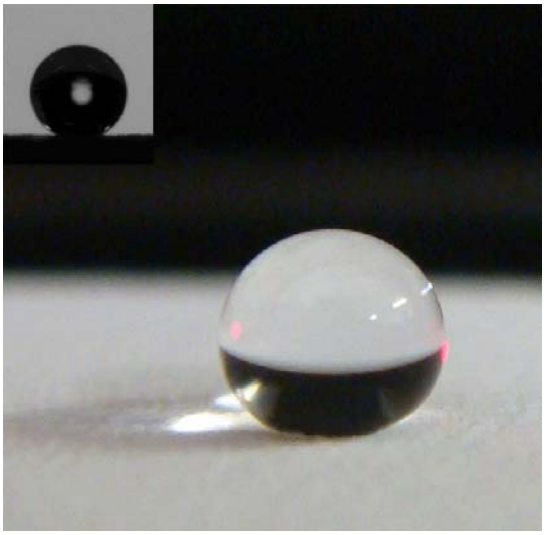


S 5. SEM images of electrospun PMMA fibres

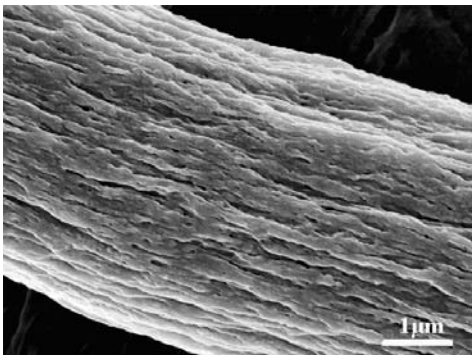


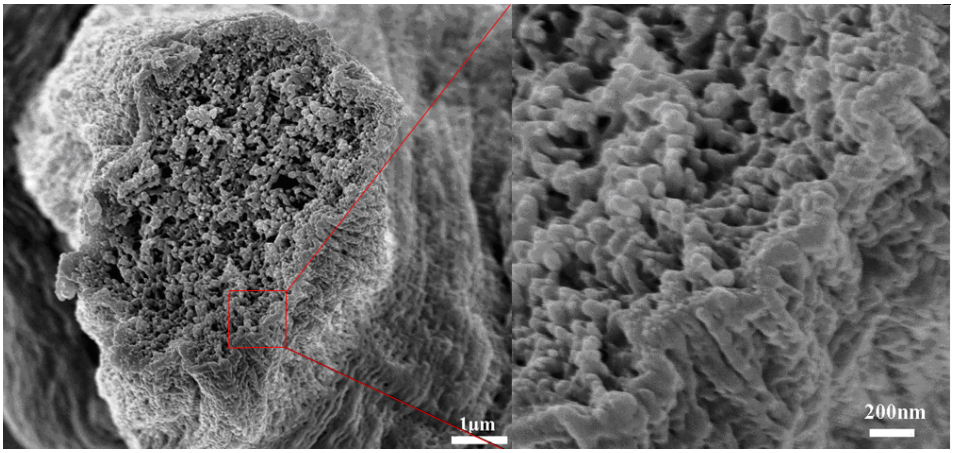


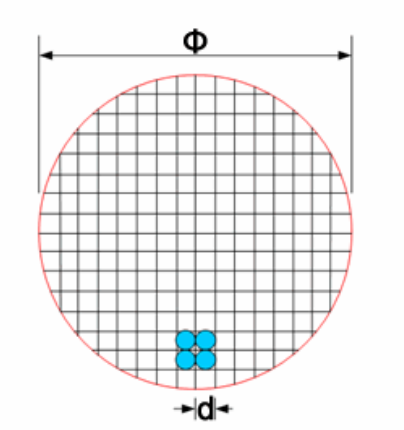
S 6. Photos of water drop on POSS-PMMA fibre membrane



S 7. SEM images of POSS-PMMA fibre and the calculation of the number of fibrils within the fibre. (Electrospun from 7wt% POSS-PMMA solution)

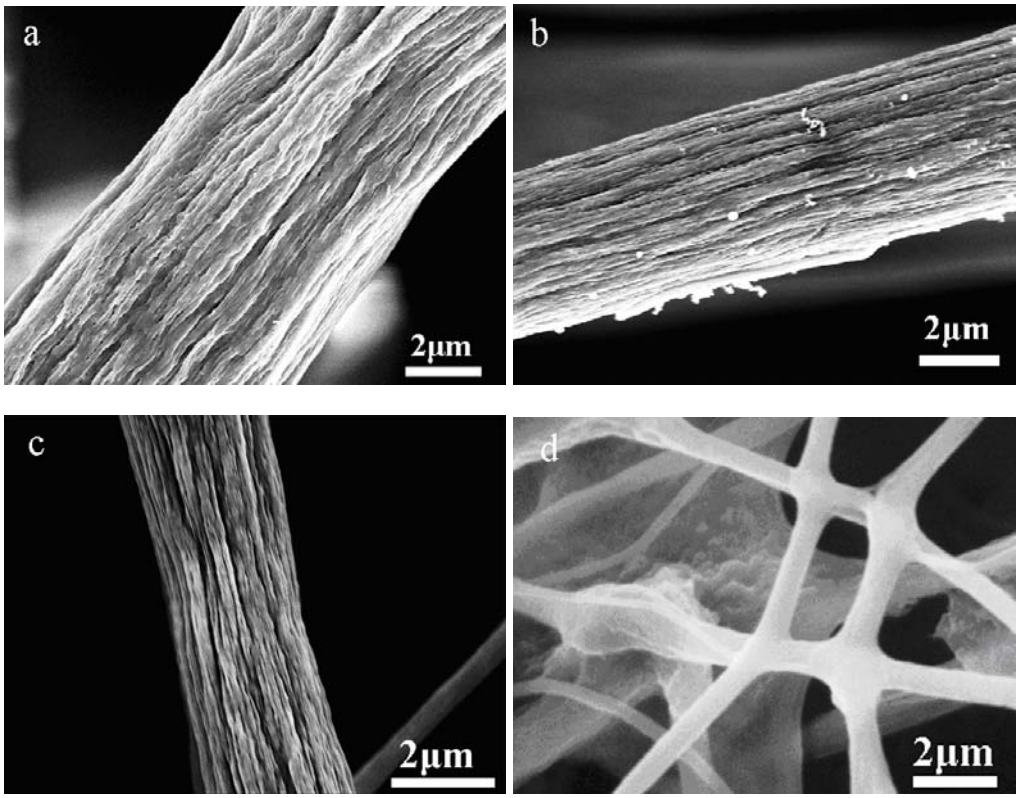




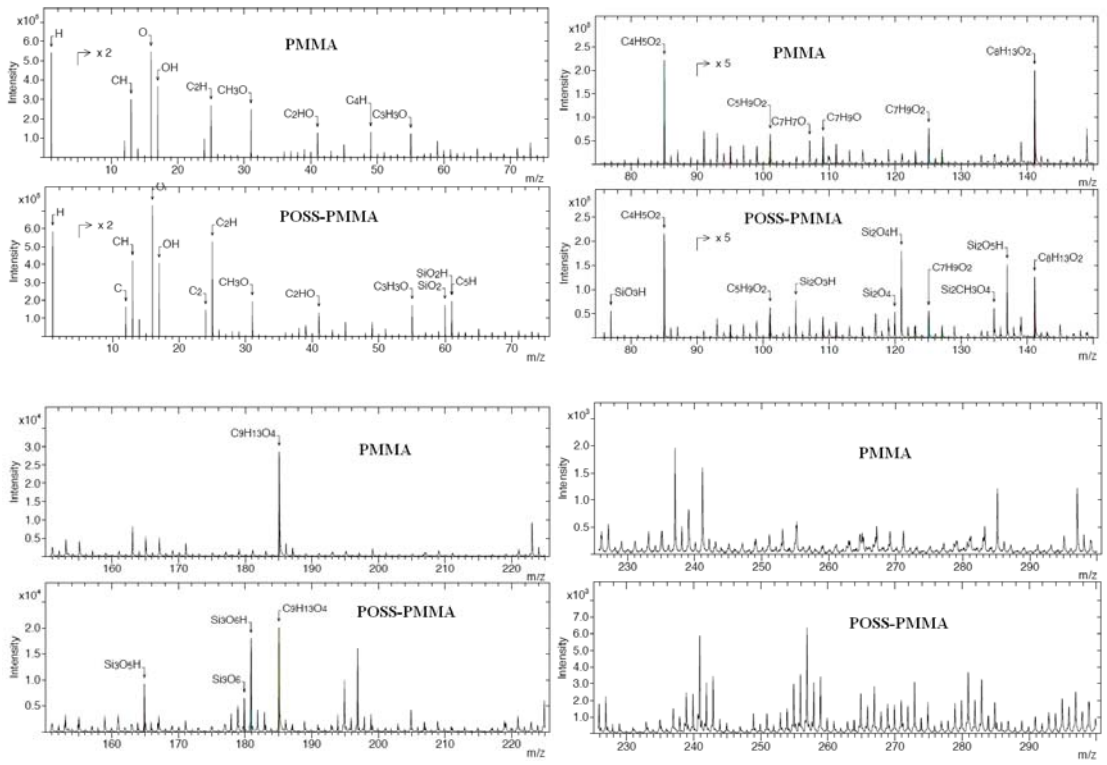


$$n = \frac{S(fibre\ or\ fibril\ bundle)}{S(unit\ square\ containing\ one\ fibril\ )} = \frac{\frac{1}{4}\pi\Phi^2}{d^2} \qquad (1)$$

S 8. Surface morphologies of POSS-PMMA copolymer fibres electrospun from different solutions (a~d), POSS-PMMA 10, 7, 5, 3 wt%



S 9. ToF-SIMS of PMMA and POSS-PMMA electrospun fibre membranes **(The fibres were electrospun from 7wt% POSS-PMMA solution)**



S 10. AFM image of POSS-PMMA fibre surface (electrospun from 7wt% solution)