

Superhydrophobic electrospun POSS-PMMA copolymer fibres with highly ordered nanofibrillar and surface structures†

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A POSS-PMMA copolymer has been synthesised by conventional free-radical polymerisation reaction. Uniform electrospun fibres from this copolymer showed a water contact angle as high as 165° with a sliding angle as low as 6°. For the first time, we found that the electrospun fibres had a bundled nanofibrillar secondary structure with an ordered POSS morphology on the fibre surface.

Polyhedral oligomeric silsesquioxanes (POSS) are hybrid molecules composed of a well-defined cubic octameric silica cage surrounded by eight organic corner functional groups.¹ The excellent mechanical and thermal properties of the silica cage and tuneable chemical reactivity of the corner functional groups make POSS an ideal building block for high performance polymer composites in aerospace, material, biological and electronic applications.^{2–5} POSS-containing polymers,^{6–13} prepared by either grafting or co-polymerisation, have also been reported to show not only better dispersing ability than the corresponding pure polymers but also some special properties such as low-dielectric,^{14,15} excellent thermal stability,¹⁰ and high mechanical strength.¹⁶

Electrospinning is a simple and effective technique to produce continuous polymeric nanofibres.^{17–20} This technique has recently been used to prepare fibrous POSS/polymer membranes with interesting surface properties. As reported by McKinley *et al.*,²¹ a fibre membrane electrospun from a fluorodecyl POSS and polymethylmethacrylate (PMMA) mixture showed both super water-repellent and super oil-repellent surface features. On the other hand, a membrane electrospun from POSS-grafted poly(vinyl alcohol) (PVA) exhibited an amphiphilic surface.²²

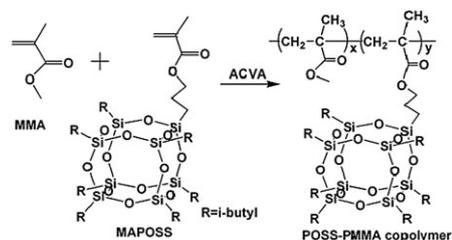
Depending on the nature of the starting material and electrospinning conditions, beaded-fibres, bead-only structures, and/or uniform fibres can be electrospun, along with controlled fibre orientations,^{23–25} surface roughness,²⁶ or bicomponent cross-sectional configurations.²⁷ Although fibres with superhydrophobic surfaces have been directly produced

by electrospinning,^{21,28–30} most of the superhydrophobic electrospun membranes are based on either beaded-fibres or beads-only structures with poor mechanical properties. Electrospun membranes of uniform fibres usually have a weak hydrophobicity with either water contact angles less than 150° or a very large contact angle hysteresis.³¹ It is still a challenge to produce a superhydrophobic membrane from uniform electrospun fibres that has a high water contact angle and a low contact angle hysteresis.

In this paper, we report the first electrospinning of a POSS-PMMA copolymer (Scheme 1) into uniform fibres that can form a highly superhydrophobic membrane with a water contact angle > 160° and a very low hysteresis. More interestingly, the bead-free electrospun fibres showed a nano-fibrillated structure under electron microscopic observations and ordered surface molecular arrangement on atomic force microscope (AFM). These features have not been reported for any electrospun fibres.

Scheme 1 depicts the route for synthesising the POSS-PMMA copolymer. As can be seen, two monomers, methyl methacrylate (MMA) and (propyl methacrylate) (isobutyl)₇Si₈O₁₂ (MA-POSS), were copolymerised at 68 °C in a mixture of toluene–tetrahydrofuran (THF), 4 : 1 (v/v), via a conventional free-radical reaction induced by an azo initiator, 4,4'-azobis(4-cyanovaleric acid) (ACVA). The POSS : MMA ratio was set at 50 : 50 (wt/wt). For comparison, pure PMMA was also synthesised under the same conditions. Gel permeation chromatography (GPC) measurements indicated a unimodal molecular weight distribution for both the resultant copolymer and pure PMMA. The number-averaged molecular weight (M_n) for the POSS-PMMA copolymer was found to be 113 400 g mol⁻¹ with a polydispersity index (PDI) of 1.91, typical for copolymers synthesised by free-radical polymerisation. For the pure PMMA, the M_n and PDI were found to be 135 000 g mol⁻¹ and 2.06, respectively.

The FTIR spectrum of the POSS-PMMA copolymer showed combined features for PMMA and MA-POSS



Scheme 1 Synthetic route for POSS-PMMA copolymer.

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(see ESI†), including two strong vibration bands at 1729 and 1148 cm^{-1} , attributable to C=O and C–O–C stretching vibrations from PMMA, and a strong Si–O–Si stretching vibration at 1095 cm^{-1} from the POSS cage. The ^1H NMR spectrum (see ESI†) further confirmed the polymer structure. X-Ray diffraction (XRD) of the POSS-PMMA copolymer showed a pattern different from both MA-POSS monomer and pure PMMA (see ESI†). For the POSS monomer, MA-POSS, the XRD showed a sharp single peak at $2\theta = 8.0^\circ$ ($d = 11 \text{ \AA}$), arising from aggregated POSS. Several tiny peaks were also found in the range 2θ between 8.1 and 28° . However, the pure PMMA showed a broad amorphous reflection with the peak at $2\theta = 14^\circ$. In contrast, the POSS-PMMA copolymer showed no sharp peak associated with POSS, but three broad bands peaked at 8.6, 18.1 and 25.7° . This suggests that the POSS-PMMA copolymer contains no crystal-like POSS aggregates, and the PMMA blocks in the copolymer show a different morphology to that in the pure PMMA.³²

In a mixture solvent of dimethylformamide (DMF) and THF (1 : 1 v/v), the POSS-PMMA copolymer can form a viscous solution for electrospinning in air. As shown in Fig. 1, bead-free uniform fibres were produced by electrospinning the POSS-PMMA copolymer solutions with a polymer concentration in the range of 5–10 wt%. However, lower polymer concentrations led to beaded fibres. The average fibre diameters estimated from the SEM images are listed in the caption of Fig. 1. While Fig. 1(b) and (c) show uniform fibres with an average fibre diameter in the range from 2.16 to 3.67 μm , coarser fibres resulted from the polymer solution at a higher concentration (Fig. 1(a)). The beaded fibres shown in Fig. 1(d) have an average diameter of 0.6 μm .

Fig. 2 shows the water contact angle (WCA) for the electrospun POSS-PMMA copolymer membranes. All the electrospun membranes with uniform fibres (e.g. Fig. 1(b) and (c)) showed water contact angles greater than 160° , while membranes consisting of coarser fibres (e.g. Fig. 1(a)) had lower WCA values. The WCA of the beaded fibre membrane (Fig. 1(d)) was as high as 170.5° . The minimal angle for rolling

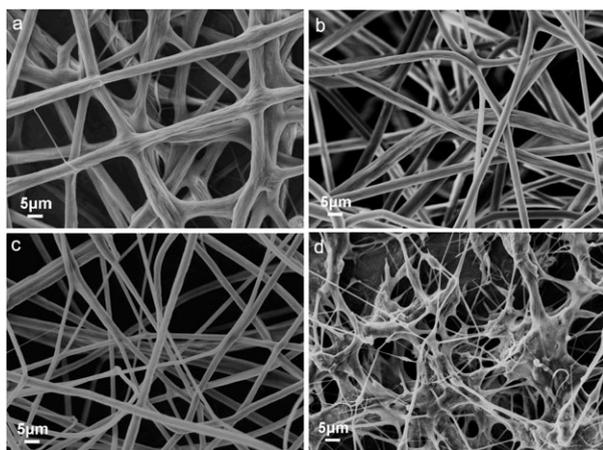


Fig. 1 POSS-PMMA fibres electrospun from the copolymer solution in DMF–THF at different polymer concentrations (a–d) 10, 7, 5, 3 wt% (grams in 100 ml solvent), the average fibre diameters are (a–d) 3.97, 3.67, 2.16, 0.60 μm , respectively.

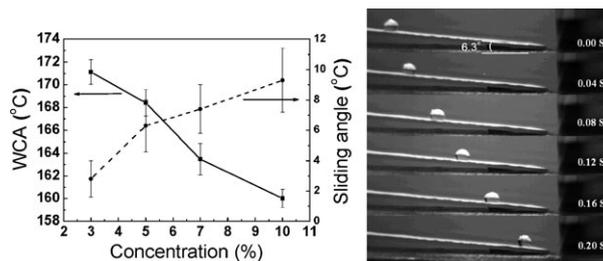


Fig. 2 (a) WCA and SA of the electrospun POSS-PMMA fibre membranes, (b) photos of a water drop sliding on the POSS-PMMA fibre mat surface (sliding angle 6.3°).

off the water drop from the surface, also called the sliding angle (SA), was used to measure the contact angle hysteresis.³³ A higher sliding angle would suggest a larger contact angle hysteresis. The sliding angle for all the samples shown in Fig. 2 is lower than 10° . The sliding angle for the uniform fibre membranes was found to be as low as 6.3° . To demonstrate the small hysteresis, the time-dependence of sliding a water drop on a fibre membrane (electrospun from 5 wt% polymer solution) was recorded and shown in Fig. 2(b).

To further understand possible effects of the surface structure on the membrane hydrophobicity, we used high-resolution SEM, TEM and AFM to study the morphology of as-spun fibres. The photo image given in Fig. 3(b) shows a secondary structure formed on the fibre surface, which is similar to the seta of a water strider's leg (Fig. 3(a)).³⁴ Such a secondary surface structure was only observed on the uniform fibres electrospun from 5–10 wt% polymer solutions (see ESI†). It was also interesting to note that such a secondary surface structure caused an apparently reduced trend in the sliding angle (Fig. 2(a)). The SEM examination (Fig. 3(b) inset) revealed that the constituent setas consisted of uniform fibril bundles. TEM images shown in Fig. 3(c) and (d) indicated that many circular nanofibrils with a diameter between 50 and 100 nm were bundled together to form the single electrospun fibre. By comparison, nanofibres electrospun from pure PMMA have a smooth surface with a uniform diameter along the fibre length (see ESI†).

The cross-section SEM images (Fig. 3(e) and (f)) showed that all the constituent nanofibrils aligned along the length of the electrospun fibre. The average diameter of these nanofibrils was about 55.8 nm. It can be easily estimated that a fibre of diameter about 5 μm should consist of approximately of 7000 such nanofibrils. Since the POSS silica cage is about 0.53 nm in diameter, the POSS moiety in the side chains should considerably increase the chain diameter of the POSS-PMMA copolymer. However, such a nanofibril structure should not be from a single POSS-PMMA copolymer chain. Most likely, they are bundles of entangled copolymer chains. As with electrospinning, polymer chains within the fibre can form oriented structures along the fibre length direction,³⁵ so the self-organised nanofibrils in the electrospun POSS-PMMA fibre could derive from the electrospinning process and the coarse chain size of the POSS-PMMA copolymer.

The surface morphology and chemical characteristics of the POSS-PMMA fibres were further examined by AFM and ToF-SIMS, respectively. The AFM image (Fig. 4) showed

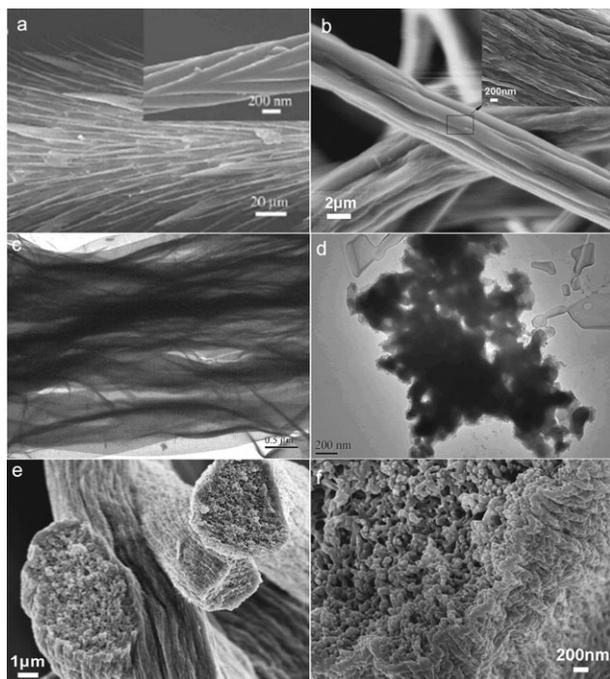


Fig. 3 (a) Photo of a water strider leg³⁴ with oriented spindly microsetae (the inset is an amplified image of a single seta [Copyright 2004 Nature Publishing Group]), (b) SEM images of POSS-PMMA fibres, (c) and (d) TEM images of side and cross-sectional views of a POSS-PMMA fibre, (e) and (f) SEM images of the cross-sectional view of POSS-PMMA fibres (the fibre was electrospun from 7 wt% POSS-PMMA solution).

an ordered surface structure at nanometre scale (also see ESI[†]), and ToF-SIMS (see ESI[†]) results clearly indicated that the surface of the electrospun fibre was mainly covered by the POSS moieties. These suggested that the fibre surface had a tertiary surface structure composed of ordered POSSs.

In the case of bead-free POSS-PMMA fibre membranes, the high superhydrophobicity and low contact angle hysteresis can be explained by the rough surface consisting of nanofibril polymers bundled with an ordered POSS surface structure. The isobutyl groups brought by the POSS moiety also facilitate to reduce the surface free-energy. However, the detailed mechanism governing the formation of hierarchical nano-/micro-structures deserves further study, which should have implications to many other systems of practical

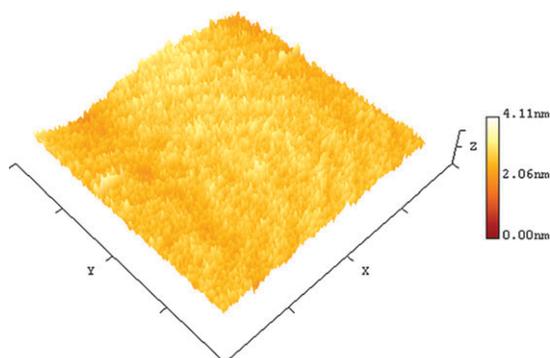


Fig. 4 AFM image of a typical POSS-PMMA fibre surface (the fibre was electrospun from 7 wt% POSS-PMMA).

significance. Also, such remarkable non-wetting functions should be very useful in the development of aquatic devices for various purposes.

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