Supporting Information for

Simple Approach towards Fabrication of Highly Durable and Robust

Superhydrophobic Cotton Fabric from Functional Diblock Copolymer

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Pressure Tests of Water Droplets on SCF Samples. Two pieces of similarly sized cotton fabrics, which were modified in PGMA-*b*-PTFEMA solutions according to the optimized process described in the experimental section, were attached to a glass slide to obtain two identical superhydrophobic surfaces. A 5 μL water droplet was placed onto the SCF. Subsequently, the droplet was pressed from above by another identical cotton surface with a certain pressure. A series of images of the droplet were recorded with a camera on an optical contact angle measuring device

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over a varying compression range when the pressure was applied and released. The WCAs of the droplet were determined from the mages recorded over the pressure range.

The internal pressure (p) was evaluated using the Laplace equation: $p = 2 \times \gamma \times |\cos\theta| \times \chi^{-1}$, where γ is the surface tension of water, θ is the contact angle under compression, and χ is the distance between the samples. Therefore, $p = (2 \times 72.75 \times 10^{-3} |\cos(110°)|)/(0.6 \times 10^{-3}) = 227$ Pa

WCAs of Homogeneous Films Cast from the Copolymers. The homogeneous films were prepared by dispensing a few droplets of PGMA-*b*-PTFEMA solution (50 mg mL^{-1} in cyclohexanone) onto a clean glass slide and then placing the samples in a sealed desiccator at 25 °C until the solvent had evaporated.

Evaluation of the Amount of Copolymer Attached onto the SCF. Because of the small weight differences involves, it was difficult to obtain an accurate value of the weight difference between the coated and uncoated cotton fabrics directly. However, we could estimate the weight difference between the copolymers before and after the coating process was performed using a microbalance and then calculating the amount of the copolymer that had become attached to the cotton fabric.

In a typical trial, 0.5 g of P4-5 was dissolved in 10 mL of THF, 10 μL of triethylamine was added, and then five pieces of cotton fabrics were added to this solution, which was subsequently stirred for ~10 min. The five pieces of cotton fabrics were collected from the solution and dried in an oven at 110 °C for 2 h. Subsequently, the fabrics were refluxed in 50 mL of clean THF for 12 h to remove unbound unimer chains and micelles of PGMA-*b*-PTFEMA, which were physically adsorbed (but not covalently bound) to the cotton fibers. The refluxed THF solvent

was collected and combined with the reaction solution. After rotary evaporation was performed to remove most of THF, the samples were subsequently dried under vacuum before the sample was weighed to obtain the mass of the residual polymer. Subsequently, we could estimate the amount of copolymer that had become grafted onto surfaces of cotton fabrics.

Estimation of the Thickness of the Copolymer Layer Covering the SCFs. To estimate the thickness of the copolymer layer covering the SCF, it was assumed that the cotton fabric was covered by a single layer of fibers, whose density (ρ) is ~1.55 g cm^{-3}. Therefore, for 100 mg of cotton fabric (m), we calculated the volume (V) of an individual cotton fiber as: $V = m/\rho = 0.1/1.55 = 0.065$ cm^3.

Therefore, this corresponded to $L = V/[\pi \times (D/2)^2] = 0.065/[3.14 \times (12/2 \times 10^{-4})^2] = 5.7 \times 10^4$ (cm), where L is the length of a single fiber. Assuming that the surface of the fibers was smooth, the total surface area (S) of the fibers of the cotton fabric was calculated as: $S = L \times \pi \times D = (5.7 \times 10^4) \times 3.14 \times (12 \times 10^{-4}) = 0.021 \times 10^4$ cm^2, where D is the average diameter of the fibers of the SCF, the value of D is measured from the SEM.

The weight of the grafted polymer for each piece of the cotton fabric (100 mg) was ~2 mg. Assuming that the copolymer density was ~1.1 g cm^{-3}, the volume (V_2) of the copolymer that had become grafted onto each piece of cotton would correspond to 1.81×10^{-3} cm^3. The thickness (h) of the polymer layer can be calculated as: $h = V_2/S = (1.81 \times 10^{-3})/(0.21 \times 10^3) = 86.1$ nm.

SCFs as Oil/Water Separation Membranes. To test the ability of the SCFs to separate oil/water mixtures, the coated cotton fabric was used as a separation membrane that was attached so that it covered the opening of a 50 mL beaker. A

solution mixture consisting of 20 mL of petroleum and 10 mL of water that had been stained with Chinese ink (the concentration of the ink in the water droplets is 10%) was poured slowly into the beaker through the SCF. The separated oil was collected in the beaker, while the water remained on the surface of the SCF.
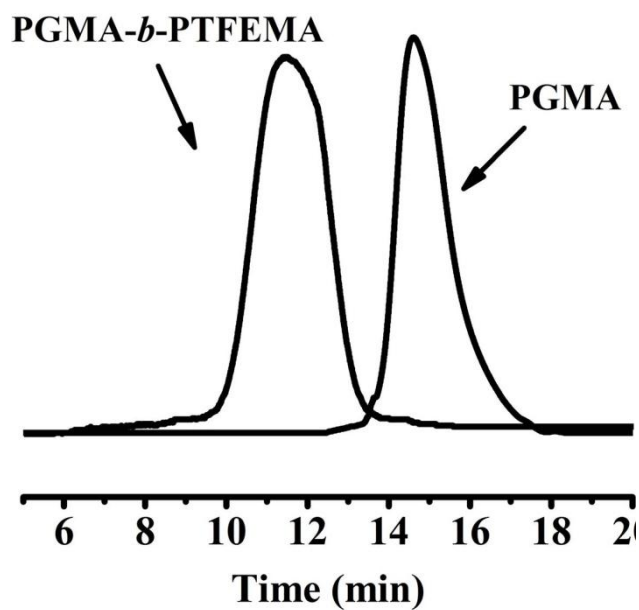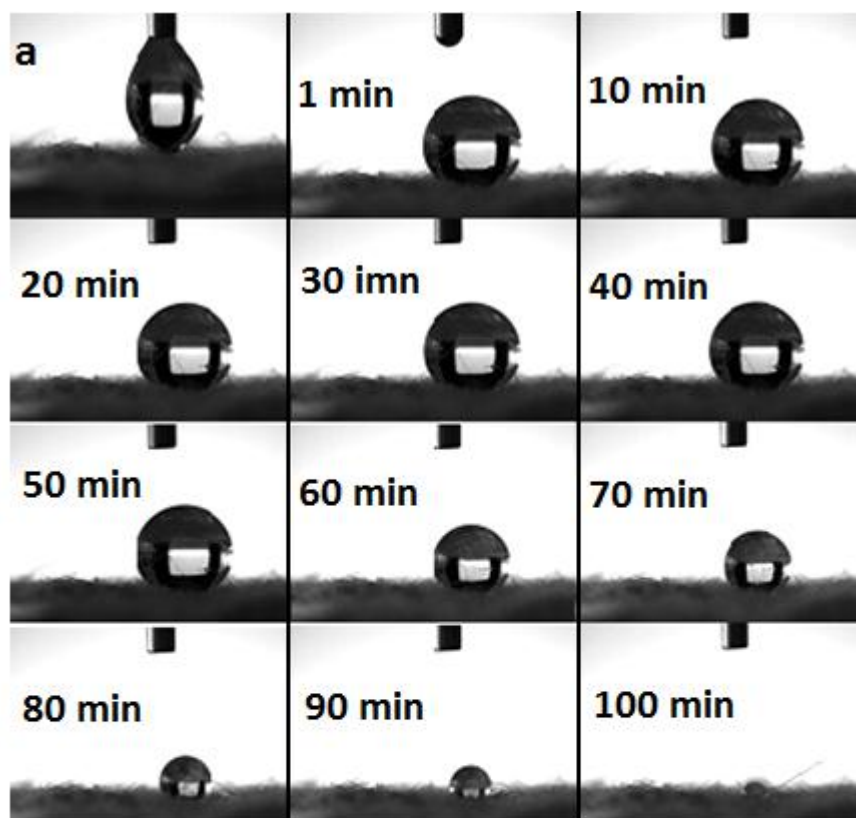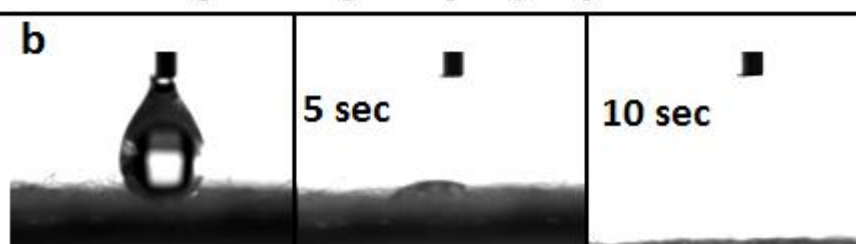
Fig. S1 SEC traces of PGMA (P4) and PGMA-*b*-PTFEMA (P4-5). A DMF solution containing 0.05 mg mL^{-1} of tetrabutylammonium bromide was used as the eluent at a flow rate of 0.6 mL min^{-1}.

a-a water droplet sitting on superhydrophobic cotton fabric

b-a water droplet sitting on original cotton fabric

Fig. S2 Photographs of a water droplet placed on a cotton fabric that had been modified with P4-5 (a) and on an uncoated cotton fabric (b) at 30 °C and a humidity of ~68%.
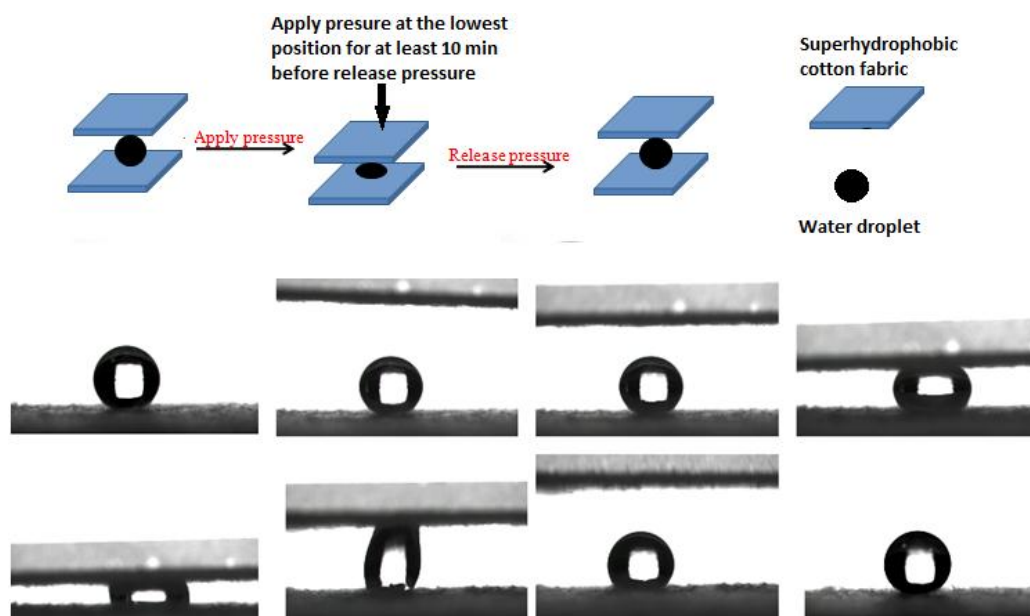
Fig. S3 Photographs of a water droplet that was placed on the surface of a SCF as it was subjected to pressure application and release experiments.

Fig. S4 Photograph of a sample of uncoated cotton fabric (below) and of an SCF sample (above) after immersion into water. A plastron layer is visible on the surface of the SCF.
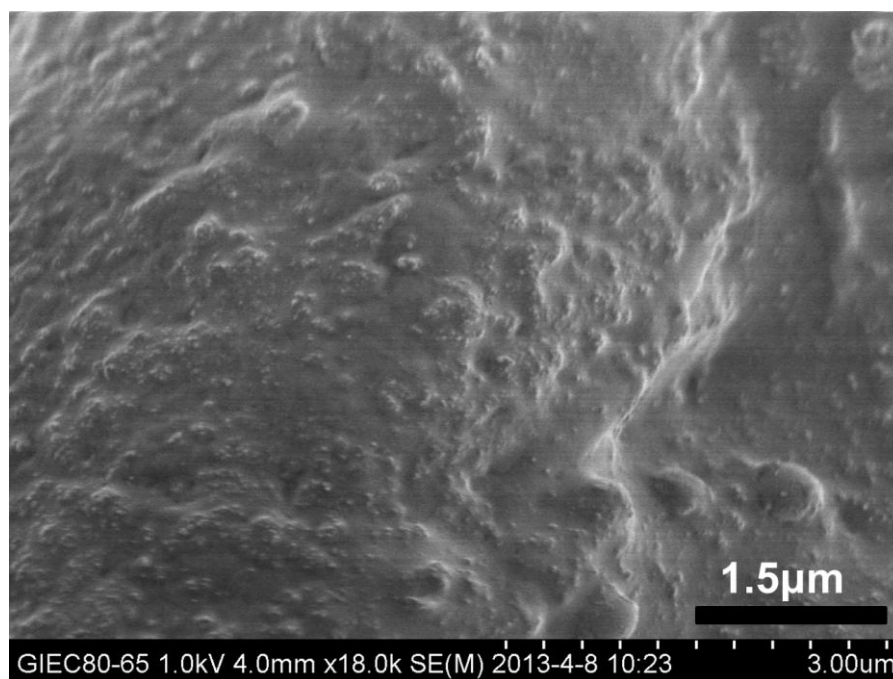
Fig. S5 High magnification SEM image of a cotton fabric that had been coated with
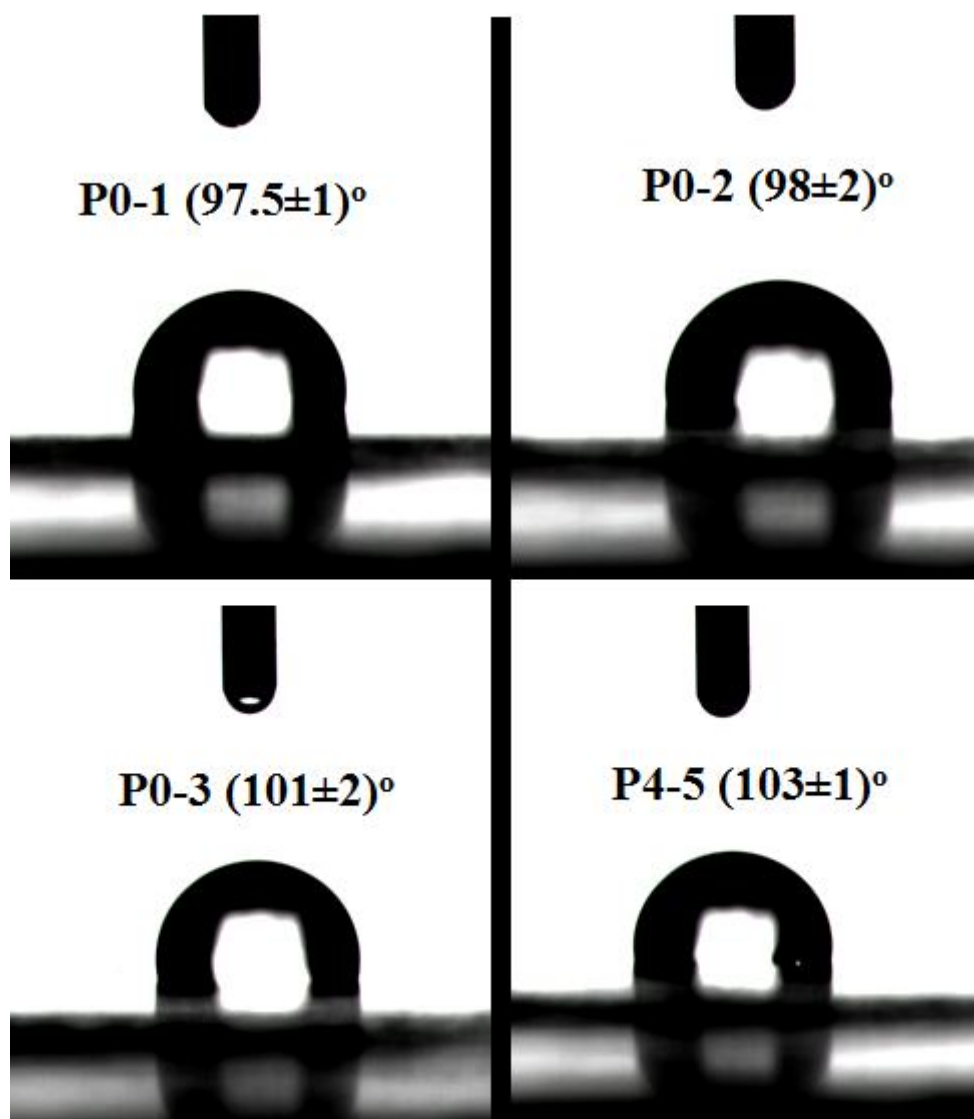
P4-5.

Fig. S6 WCA measurements for the four diblock copolymer films that were cast from

cyclohexanone at a concentration of 50 mg mL^{-1} onto glass substrates. The droplets
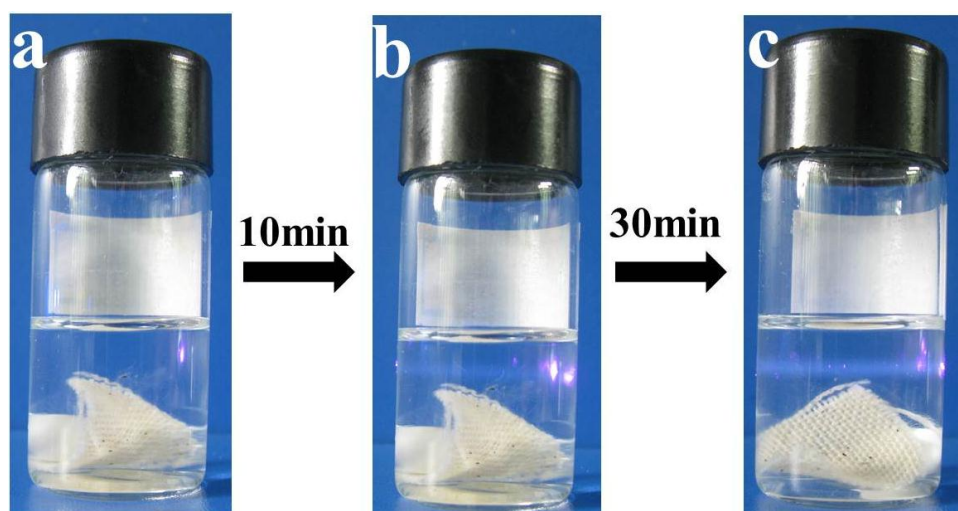
were kept in a desiccator at room temperature.

Fig. S7 Photographs of the reaction mixture containing a THF dispersion of P4-5 (0.2 $\times$ 10^{-5} M) and the cotton substrates. The images were recorded after the reaction had proceeded for: 0 (a), 10 (b) and 30 min (c). When a laser beam was passed through the solution that had undergone 30 min of reaction time (c), it became clearly visible suggesting that the light was scattered due to the presence of micellar aggregates in the reaction mixture.
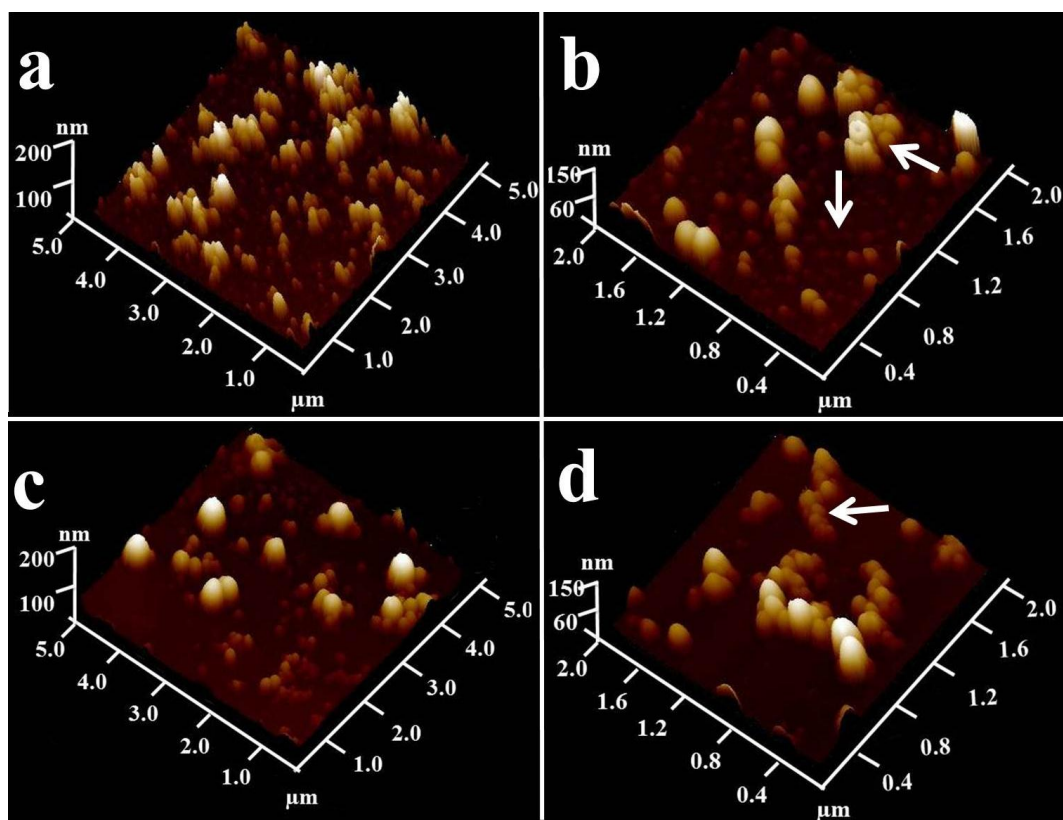
Fig. S8 AFM topography images of the aggregates that had been aero-sprayed from the reaction mixture onto silica wafers after the reaction proceeded for 10 min (a and b) and 30 min (c and d).
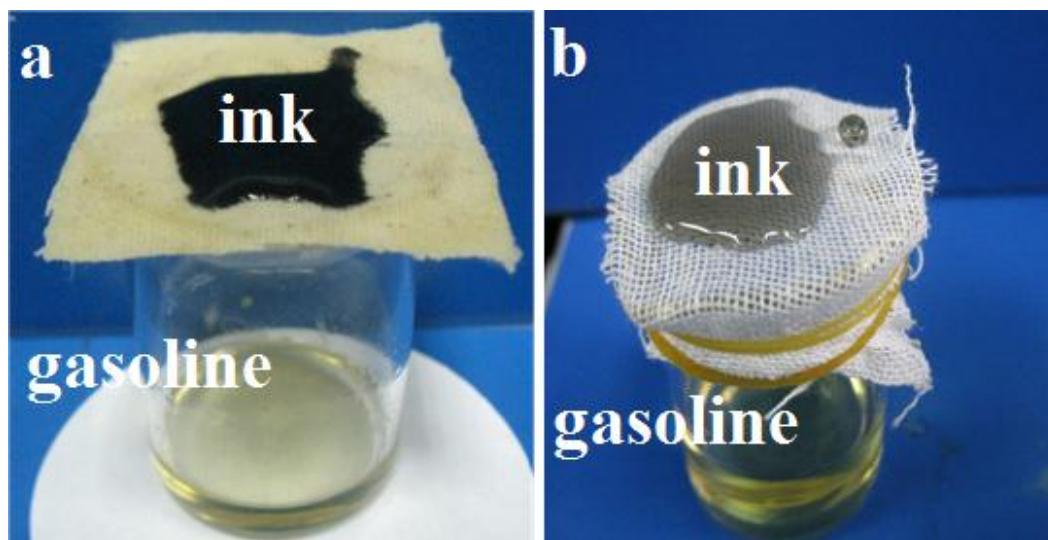
Fig. S9 Water/oil separation using two kinds of SCFs that were modified with P4-5. The SCFs in image (a) was the coated cotton fabric, and (b) was the coated cotton gauze.

Table S1. The relative amounts of various carbon bonds and all atomic ratios

obtained from high-resolution XPS spectra by peak-fitting the data into different

Gaussian components.

Sample Binding Energy (eV)	Test results (Atom%)						Theoretical results (Atom%)		
	C				O	F	C	O	F
	285	286.6	288.1	293	538	692-696	285-293	538	692-696
	C-C/ C-H	C-O-H/ C-O-C	O-C-O/ C=O	CF₃					
Original Cotton Fabric	76.5%				23.5%	0%	54%	46%	0%
	52%	17.2 %	7.3%	0%					
SCF	52.7%				23.7%	23.6%	57.5%	20%	22.5%
	39.5	5.4%	3.6%	4.2%					

Video for oil/water separation (see uploaded attachment)