RSC Advances

ROYAL SOCIETY OF CHEMISTRY

www.rsc.org/advances

Synthesis and characterization of photoresponsive POSS-based polymers and their switchable water and oil wettability on cotton fabric

Jianbao Huang[1], Yangen Huang[1]*, Chuanglong He[1], Yu Gao[2]*

1 College of Chemistry, Chemical Engineering and Biotechnology, Donghua University, 2999 North Renmin Road, 201620 Shanghai, China

2 Research Institute of Donghua University, Donghua University, 2999 North Renmin Road, 201620 Shanghai, China

*Corresponding author.

Tel.: 86-21-67792176; Fax: 86-21-67792176. E-mail: gaoyu@dhu.edu.cn

Abstract

Fast photoresponsive polymers containing polyhedral oligomeric silsesquioxane (POSS) and fluorinated azobenzene groups were successfully prepared via radical polymerization and characterized by NMR, FTIR, XRD, GPC, TGA, etc. The photoresponsive properties of the polymers were investigated through ultraviolet-visible absorption spectra. The *trans-cis* photoisomerization of the polymers in solution conformed to the first-order reaction kinetics equation. Superhydrophobicity and high oleophobicity of the cotton fabric coated with the polymer was observed when POSS mole ratio was 3.0 %. More importantly, the surface wettability of both water and oil on the coated fabrics could be intelligently controlled by applying UV irradiation in short time.

Keywords: photoisomerization, switchable wettability, azobenzene, POSS, fluoropolymer

Introduction

Photo-switchable wettability of surface has been drawing increasing attention for their potential applications in self-cleaning materials [1, 2], microfluidic devices [3, 4], and photochemical micropatterning [5, 6]. The low energy *trans*-isomeric state of azobenzene-containing compounds can be switched reversibly to *cis*-isomeric state upon

exposure to UV light resulting in a change of surface wettability. The reversible photoisomerization of low-molecular-weight molecules or polymers containing azobenzene group have been investigated [7]. A variety of monomer layers and polymer surfaces with azobenzene group in either backbone or side chain were reported [8-12].

In order to achieve higher hydrophobicity, even superhydrophobicity, the fluorine-containing azobenzene compounds were applied [13-16]. A trifluoromethyl modified azobenzene containing polymer was applied to prepare Langmuir-Blodgett (LB) film and the water contact angle (CA) on it was 85± 1° and 74 ±1° before and after UV light irradiation [10]. The light-driven surface changes of a series of polymers with 4-perfluoroalkyl (C_nF_{2n+1}, n=4, 6, 8) modified azobenzene side groups on silicon wafers were also investigated [17]. The water CA of them were higher than 110° before UV light irradiation, but the changes of water CA after UV light irradiation were no more than ~10° [17].

The typical values for the water CA changes on flat caused by the photoisomerization of azobenzene are on the order of 10 ~ 15° at maximum [15]. Such modest changes encouraged efforts to design and study new responsive surfaces via constructing special surface morphology to amplify the changes, such as plasma etching [18], photolithographic technique [5], dual-size surface construction with nano particles [1, 13], hybrid film prepared by anion-exchange reaction [19], electro spinning [20] and so on. However, the procedures were usually complicated or with rigorous requirements. In addition, these studies were mostly focused on the photoresponsive wettability of water, with little emphasis on oil.

In the past decades, polyhedral oligomeric silsesquioxane (POSS) with its special performances has been used in preparation materials with oxidation resistance, fire retardation, good mechanical property, etc. [21-26], but few has been reported on POSS-based polymers with photoresponsive wettability.

In this report, a series of POSS-based polymers with 4-perfluoroalkyl-modified azobenzene pendants were investigated for their photoisomerization. Herein, we have focused our attention on the study of synthesis, characterization and isomerization behavior of the polymers, as well as influence of POSS addition on photoresponsive wettability of the polymer coated cotton fabric. With the surface structure resulted from POSS nano cages and

fabric texture, the larger CA changes than the typical ones on flat are expected.

Experimental sections

Materials

1,1,1,2,2,3,3,4,4,5,5,6,6,7,7,8,8-heptadecafluoro-8-iodooctane were purchased from Qinba Chemical Scientific Ltd. (Shanghai, China). Octavinyl polyhedral oligomeric silsesquioxane (Ov-POSS) (99%) was purchased from Shenyang Meixi Fine Chemicals Co. Ltd. (Shenyang, China) and dried under vacuum before use. All other chemicals were purchased from Sinopharm Chemical Reagent Co. Ltd. (Shanghai, China). Methyl methacrylate (MMA) was distilled from calcium hydride under vacuum before use. 2,2′-Azobisisobutyronitrile (AIBN) was recrystallized from methanol. Tetrahydrofuran (THF) was distilled from sodium/benzophenone immediately prior to use.

Measurements

Nuclear magnetic resonance (NMR) spectra were recorded at ambient temperature on Bruker AV400 spectrometer at 400.0, 377.0 and 79.6 MHz for corresponding ^{1}H, ^{19}F and ^{29}Si nuclei, respectively. Tetramethylsilane (TMS) was applied as the internal chemical shift reference for ^{1}H NMR spectra and CFCl$_3$ as an external standard for ^{19}F NMR spectra. Fourier transform infrared (FT-IR) spectra were recorded on a FT-IR spectrometer (Avatar 380) using KBr crystal in the infrared region $4000 \sim 400$ cm^{-1}.

Molecular weight and distribution were determined by gel permeation chromatography (GPC) using a series of three linear Styragel columns. Waters 1515 pump and Waters 2414 differential refractive index (RI) detector (set at 35 °C) were used. A commercial calibration kit of polystyrene standards was utilized to calibrate the GPC elution traces. As a result, the molecular weights (Mw, Mn) and their distributions were thus evaluated.

X-ray powder diffraction (XRD) patterns of the polymers were recorded using an X-ray diffractometer (PW 1830, Philips, Netherlands) with Cu Kα Ni-filtered radiation at 2θ ranging from 5 to 60° in steps of 0.02°.

Thermogravimetric analyses (TGA) were carried out under N$_2$ atmosphere with a heating

rate of 10°C /min up to 900 °C by using a Netzsch TG 209 F1 analyzer.

The structural and surface morphology of the polymers on cotton fabrics were characterized by field emission scanning electron microscopy (FE-SEM) (S-4800 FE-SEM, Hitachi, Japan).

Photoisomerization of the azo-monomer (5.0×10^{-5} mol/L in THF) and terpolymers (3.8×10^{-2} g/L in THF) were measured on a Lambda 35 UV-vis spectrophotometer (PerkinElmer, USA) against a background of THF in a quartz cuvette. UV and visible light irradiation were carried out with an ultraviolet lamp (365nm, 15 W) and a visible light lamp (>400nm, 40 W), respectively. The measurement was conducted at room temperature, and UV−vis data were collected every 15 s or 30 s.

The sessile drop method was used for CA measurement at ambient temperature with an automatic video contact-angle testing apparatus (DataPhysics OCA 40, DataPhysics Instruments GmbH; Germany). The probe liquids were deionized water and salad oil. The average CA value was determined by measuring three to five different positions of the same sample with 5 μL each time. The measurement of switchable CA of the coated cotton fabrics was carried out by alternate UV/vis light irradiation procedure. The CAs of the coated cotton fabrics unexposed to UV light were determined first, then the fabrics were irradiated with 365 nm UV light (ultraviolet lamp, 500 W) for 10min and the CAs measured again. Then the same samples were kept in visible light for 1 h and the CAs measured subsequently.

Synthesis of fluorinated azo-monomer (FAM**)**

4-((4-(perfluorooctyl)phenyl)diazenyl)phenyl methacrylate was synthesized according to the literatures [27, 28] as shown in Scheme 1.
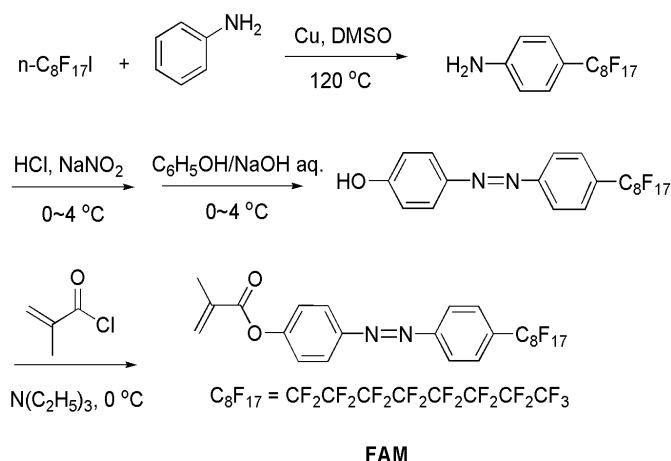
Scheme 1 Synthesis of fluorinated azo-monomer (FAM).

^{1}H NMR (400.0 MHz, CDCl$_3$), δ (ppm): 2.12 (s, 3H), 5.84(s, 1H), 6.43(s, 1H), 7.35(d, J = 8.7 Hz, 2H), 7.78(d, J = 8.3 Hz, 2H), 8.04(d, J = 8.6 Hz, 4H). ^{19}F NMR (377 MHz, CDCl$_3$), δ (ppm): −126.14 ~ −126.03(m, 2F), −122.70 ~ −121.14 (m, 10F), −110.53(t, J = 16.2 Hz, 2F), −80.75(t, J = 10.2 Hz, 3F). IR (v_{max}, cm^{-1}, KBr): 1739, 1598, 1499, 1206, 1144, 1012, 947, 852, 704, 653.

Synthesis of polymers

To a three-necked flask equipped with condenser and N$_2$ inlet, THF (5 mL), MMA (0.6 g, 6 mmol), FAM (1.4 g, 2 mmol), and Ov-POSS at desired amount were added, followed by 1 wt % of AIBN relative to monomers. After refluxed for 24 hours at 65 ^{o}C ~ 70 ^{o}C under dark, the reaction mixture was added dropwise into a 10-fold excess of chloroform/methanol (v/v, 1:30) with vigorously agitation. The precipitate was then collected by filtration and redissolved in chloroform, and reprecipitated in chloroform/methanol (v/v, 1:30). This purification process was repeated at least for three times. The polymers were finally dried at 60 °C under vacuum to give an orange powder with constant weight. The synthesis of the polymers was outlined in Scheme 2. The polymers with different POSS feeding amount of 0, 1.5 mol %, 3.0 mol % and 4.5 mol % were labeled as **P1**, **P2**, **P3**, **P4**, respectively.
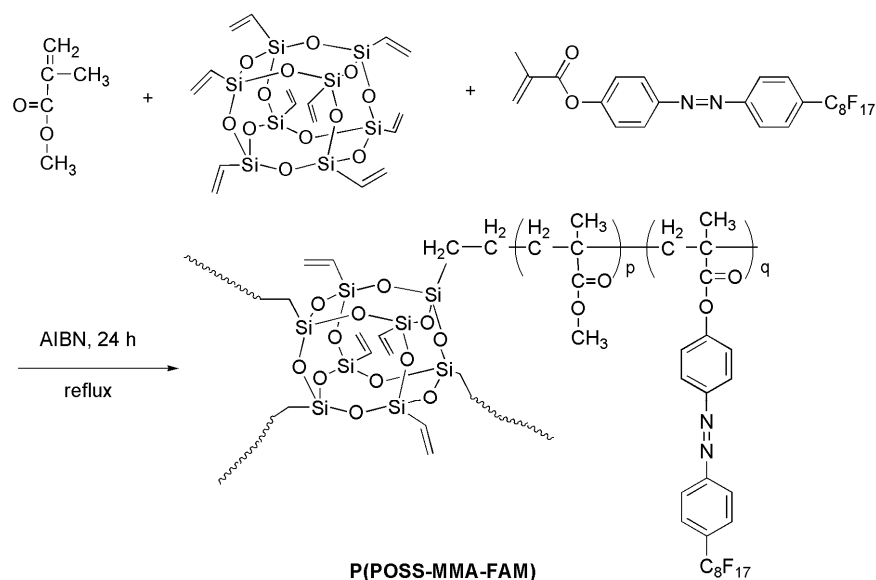
Scheme 2 Synthesis of the polymer.

^{1}H NMR (400.0 MHz, CDCl$_3$), δ (ppm): 0.87 ~ 2.28 (m, C$\underline{H}_2$, C$\underline{H}_3$ in backbone), 3.60 (s, OC$\underline{H}_3$), 5.96 ~ 6.08 (m, C$\underline{H}_2$=C$\underline{H}$Si), 7.25 ~ 7.94 (m, C$_6\underline{H}_4$N=NC$_6\underline{H}_4$). ^{29}Si NMR (solid, 79.6 MHz), δ (ppm): −80.15 ($\underline{Si}$–CH=CH$_2$), −66.15 ($\underline{Si}$–CH$_2$–CH$_2$). IR ($ν_{max}$, cm^{-1}, KBr): 3000 ~ 2900 (C–H st), 1734 (C=O st), 1240 ~ 1000 (C–F st, C–O st, Si–O st).

Treatment of the cotton fabric with the polymers

The desized, bleached and cleaned cotton fabrics (3 cm × 10 cm) were soaked in the polymers solution (0.01 g/mL, THF as solvent) for 2 h. The cotton fabrics were dried at 80 °C for 30 min and then cured at 160 °C for 3 min so that the polymers were deposited on the cotton fabrics and combined with the cellulose in cotton through van der Waals forces and hydrogen bonds. The cotton fabrics coated with **P1**, **P2**, **P3** and **P4** were labeled as **S1**, **S2**, **S3** and **S4**, respectively.

Results and discussion

Synthesis and Characterization

The aim of this study was to investigate photosensitive polymers with adjustable both water and oil wettability on textile surface, so the photoisomerizable monomer containing

azobenzene and fluorocarbon groups was synthesized and the series of POSS based copolymers bearing MMA, FAM units and POSS nano cages in different proportions were prepared by free radical polymerization initiated with 1 wt % of AIBN (scheme 2). The yield of the polymerization with only FAM and POSS was very low. By adding MMA, the yield was raised. Fig. 1 shows that the yield increases dramatically when the mole ratio of MMA to FAM ($n(MMA) : n(FAM)$) is raised from 1 to 3. When $n(MMA) : n(FAM)$ higher than 3, the yield increases slightly but the water CA decreases. So we choose $n(MMA) : n(FAM)$ as 3 in all polymerization. Moreover, it is notable that avoiding light during polymerization is essential to get desirable yield. The influence of the light on the polymer yield might result from the hindrance caused by photoisomerization behavior of azobenzene groups.
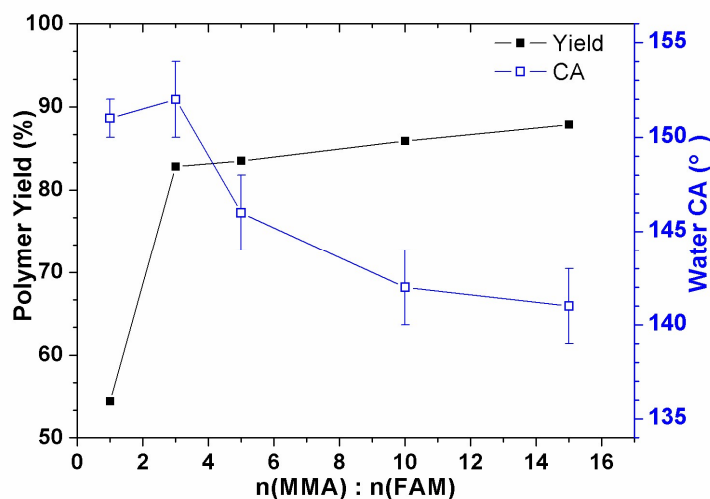

Fig. 1 Effects of MMA content on polymer yield and water CA.

^{1}H NMR spectra of FAM and **P3** (as the typical example of P(POSS-MMA-FAM) are shown in Fig. 2, in which the signals attributed to the corresponding protons are marked with numbers or letters. Compared with the spectrum of FAM, the signals of the protons of the aromatic groups from FAM unit in **P3** are detected at 7.25 ~ 7.94 ppm (in addition to the chloroform signal at 7.27 ppm), while the peaks at 5.84 ppm and 6.43 ppm attributed to the protons from $C=CH_2$ in FAM disappear in the spectrum of **P3**, which demonstrates that FAM participated in the polymerization. The protons of the methyl connected to ester group in MMA unit are located at 3.60. The peaks at 0.87 to 2.20 ppm are attributed to the methyl and

methylene protons [29-31] of MMA and FAM unit. The weak signal at ~ 6.0 ppm (**k**) in Fig. 2 indicates the existence of unreacted vinyl group in Ov-POSS segment [29]. It is potential to be endowed other functional groups from the unreacted vinyl groups in the POSS segments, and thus to be developed for various potential applications.
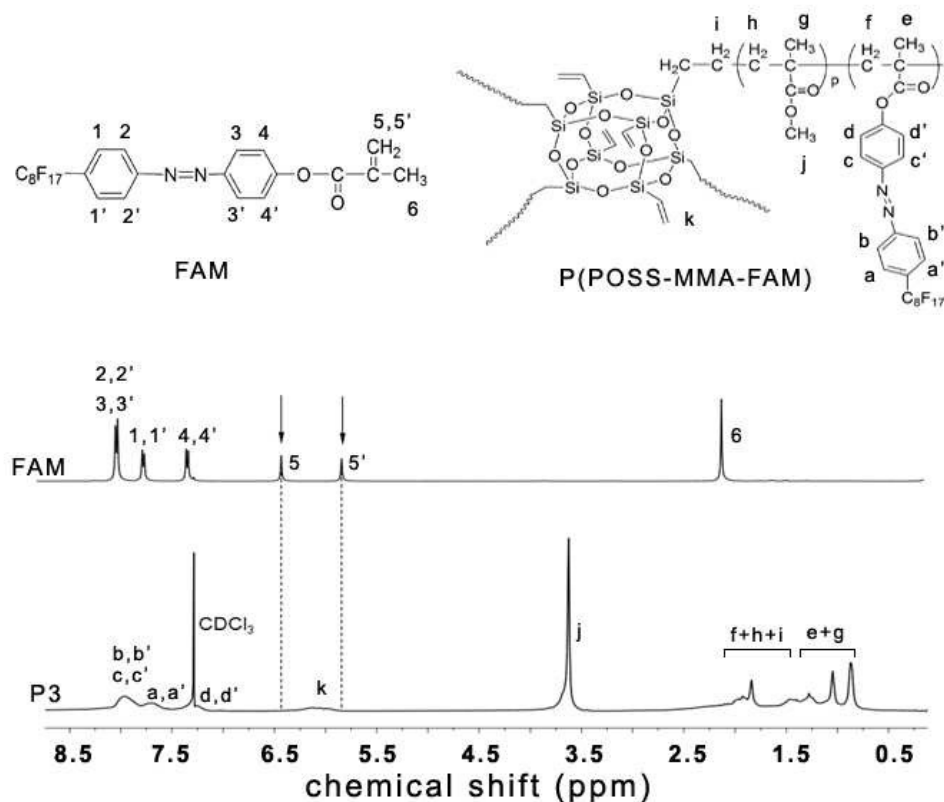

Fig. 2 ^{1}H NMR spectra of FAM and **P3**.

The ^{29}Si (solid-state) spectra of Ov-POSS and **P3** are shown in Fig. 3. The signal at –80.15 ppm is assigned to silicon atoms connected to the vinyl groups in Ov-POSS. The signal at –66.15 ppm due to silicon atoms connected to methylene groups in POSS units indicates that part of vinyl groups in Ov-POSS participated in the polymerization, which is consistent with the result from ^{1}H NMR.
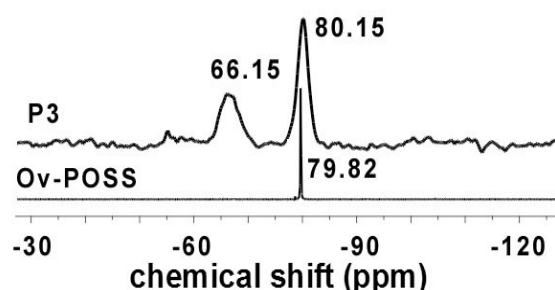
Fig. 3 ^{29}Si NMR spectra of Ov-POSS and **P3**.

It's well known that Ov-POSS is a highly crystalline material and has a characteristic dominant diffraction peak at $2\theta = 9.7°$ [32]. As seen in Fig. 4, the XRD patterns of **P2**, **P3** and **P4** are similar to that of **P1**, exhibiting amorphous structure without any peaks corresponding to Ov-POSS crystalline, which indicates that POSS units exist in the terpolymers as polymer segments without crystalline aggregates.
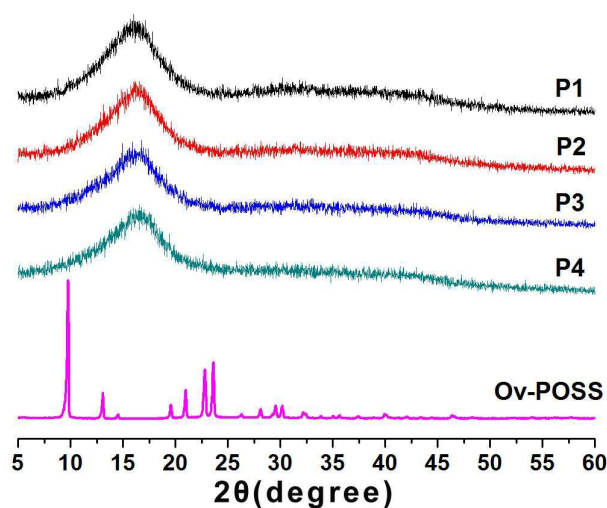

Fig. 4 XRD patterns of Ov-POSS and polymers.

The polymers **P1**, **P2, P3** and **P4** with POSS content increasing from 0 to 4.5 % (mole ratio) show good solubility in common solvents such as THF, chloroform, dichloromethane, acetone and so on. The molecular weights M_w and M_n of the polymers were measured by GPC and summarized in Table 1. For all of the polymers, M_w are higher than 2.0×10^4 g/mol and the yields of the polymers decrease slightly from 81 % to 73 % when POSS content increase from 0 to 4.5 %.

Table 1 Effects of POSS content on yield, molecular weight and thermal properties of P(POSS-MMA-FAM).

Samples	POSS feed ratio (mol %)	Yield (%)	M_w ($\times 10^4$ g/mol)	PDI (M_w / M_n)	T_{d10}[a] (°C)	Residue Char[b] (wt %)
P1	0	81	2.77	1.81	299	10.0
P2	1.5	77	3.35	1.90	307	11.7
P3	3.0	75	2.21	1.85	306	13.9
P4	4.5	73	2.61	1.85	307	16.3

[a] Temperature at weight loss of 10 %.   [b] Obtained from TGA.

Thermal Properties

All the polymers are thermally stable up to 280 °C, as shown in Fig. 5. The initial weight-loss in the region of 280 °C ~ 310 °C may be due to the exothermic decomposition of azo group (–N=N–) [33]. Subsequently, a rapid weight loss in the range of 310 °C ~ 370 °C is attributed to the degradation of backbone. The weight loss in 370 °C ~ 500 °C is due to elimination of phenyl rings. The decomposition temperatures for 10 % of weight loss (T_{d10}) of **P1** is found to be 299 °C, while that of **P2**, **P3** and **P4** is 306 °C ~ 307 °C. It shows that the polymers display high thermal stability and it is slightly improved by POSS addition. Moreover, when the polymers are heated above 800 °C to 900 °C, the weight of **P1** decreases 1.5 %, while the weights of **P2** and **P3** basically remain and the weight of **P4** is kept unchanged (Fig. 5). The residue weights increase from 10.0 wt% to 16.3 wt% when POSS mole ratio increasing from 0 to 4.5 %. In general, heating or combusting POSS-based nano composites, the POSS cage can form the thermally stable ceramic char surface layer which is able to act as a thermal shield by surface re-irradiation and as a barrier to heat or oxygen transfer from flame to the materials [29].
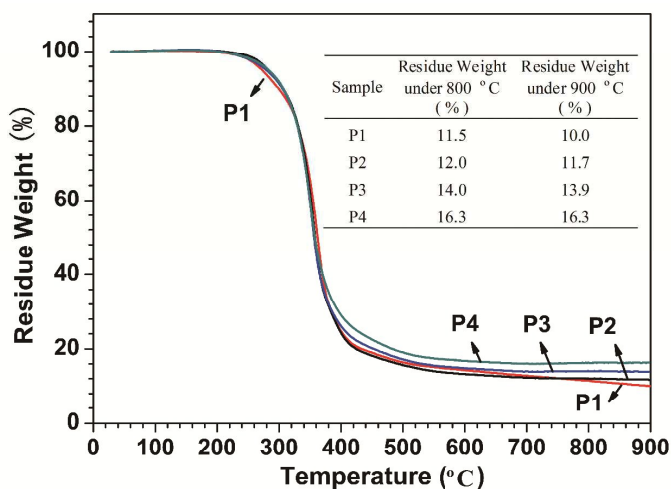
Fig. 5 TGA curves of polymers under nitrogen (inset is the residue weights of the polymers from 800 ºC to 900 ºC).

Photoisomerization

The UV-visible absorption spectra measured for the polymers (**P1** and **P3**) in THF solution upon UV photoirradiation at 365 nm are shown in Fig. 6(a) and (c), which exhibit two characteristic bands of azobenzene modified molecules: a high intensity $\pi \rightarrow \pi^*$ band in the UV region (λ_{max} = 325 nm) and a low intensity n$\rightarrow \pi^*$ band in the visible region (λ_{max} = 435 nm). A gradual decrease in the absorbance at ~325 nm and an increase in the intensity of the band at ~435 nm are caused by UV irradiation due to the *trans-cis* isomerization of azobenzene groups. Furthermore, a photostationary state almost reached within 180 s because of the spectra measured after 150 s and 180 s of exposure being undistinguishable. Then, the samples were subsequently exposed to different times of visible light irradiation. As shown in Fig. 6(b) and (d), the $\pi \rightarrow \pi^*$ transition absorption increase and the n$\rightarrow \pi^*$ band intensity decrease. The spectra of the samples were almost recovered when the visible light exposure for 90 s. The similar results were observed for **P2** and **P4**.

Other polymers containing azobenzene groups in solution reported previously showed slower photo-response with *trans* to *cis* state under UV irradiation at least 20 minutes and *cis* to *trans* state under dark or visible light for hours [33, 34]. In this study, the synthesized polymers in THF solution could reversibly photoisomerize within only several minutes. At present, there are three isomerization mechanisms on the *trans-cis* photoisomerization of azobenzene: rotation, inversion and concerted-inversion mechanisms [35]. For the substituted azobenzene,

the non-nitro-substituted species are more likely to follow an inversion mechanism [36]. The previous work reported that the electron-withdrawing groups favor the inversion pathway [37] due to the strong electron-withdrawing substituent decreasing the barrier to isomerization by reducing the double-bond character of the azo group [35, 36]. In our study, the perfluoroalkyl as a very strong electro-withdrawing substituent might play the role of lowering energy barrier, resulting in the relatively fast isomerization.
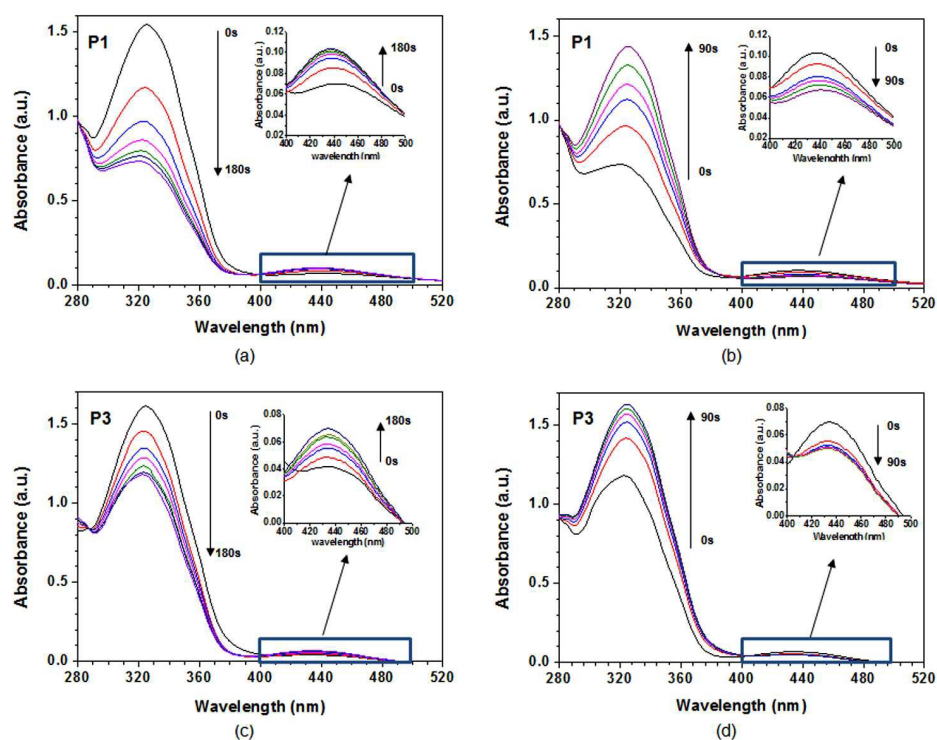

Fig. 6 UV−visible spectra of polymers. (a) and (c) UV photo-irradiation in different times of **P1** and **P3** (t = 0, 30, 60, 90, 120, 150, 180 s) at 365 nm; (b) and (d) visible photo-irradiation in different times of **P1** and **P3** (t = 0, 15, 30, 45, 60, 90 s).

To investigate the effects of POSS content on the photoisomerization rate of the polymers, the rate equations were studied. When a *trans*-azobenzene with an initial concentration of c_0 is irradiated, the rate of the change in the *trans*-azobenzene concentration, c_t, as it approaches its equilibrium value, c_∞, is given by equation (1) [38].

$$\ln \frac{c_0 - c_\infty}{c_t - c_\infty} = k_c t \qquad\qquad (1)$$

As $A \propto c$

So, $\ln \dfrac{A_0 - A_\infty}{A_t - A_\infty} = k\,t$ (2)

where A_0, A_t, and A_∞ are the absorbance at about 325 nm at time zero, time t, and infinite time, respectively.

Examples of first-order plots according to equation (2) for the *trans-cis* photoisomerization of **FAM**, **P1** to **P4** are shown in Fig. 7. It's observed that both the monomer and the polymers display the similar isomerization behavior. It demonstrates that the experimental data are in accordance with first order rate equation in the most reaction time but deviate from first order in the later stage of the reaction, which is consistent with similar results reported before [38]. As seen in Fig. 7, the photoisomerization rates of terpolymers are slower than **P1** (without POSS), which could be resulted from the hindering effect of POSS cage. In this study, when POSS content reaching 4.5 mol%, *trans-cis* photoisomerization of the polymer deviates from first order greatly in the later stage of the reaction (seen in Fig. 7 **P4**).
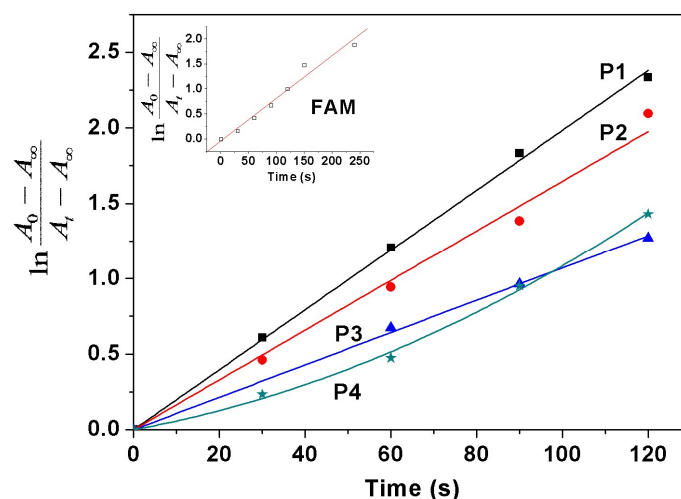

Fig. 7 First-order plots for *trans-cis* isomerization of FAM and polymers.

Morphology and Wettability of the Coated Fabrics

The water and oil CAs of **S1** to **S4** before and after UV irradiation are shown in Fig. 8. With low surface free energy from the fluorocarbon chain in the coated polymers, **S1** shows

high hydrophobicity and oleophobicity, although, as well known, cotton fabric is highly hydrophilic and oleophilic. When the coated polymer containing POSS, the average water CAs of **S2**, **S3** and **S4** increase to higher than 150° and oil CAs of **S2** and **S3** higher than 140°, which means it's beneficial to improve the water and oil repellency by incorporation of POSS.
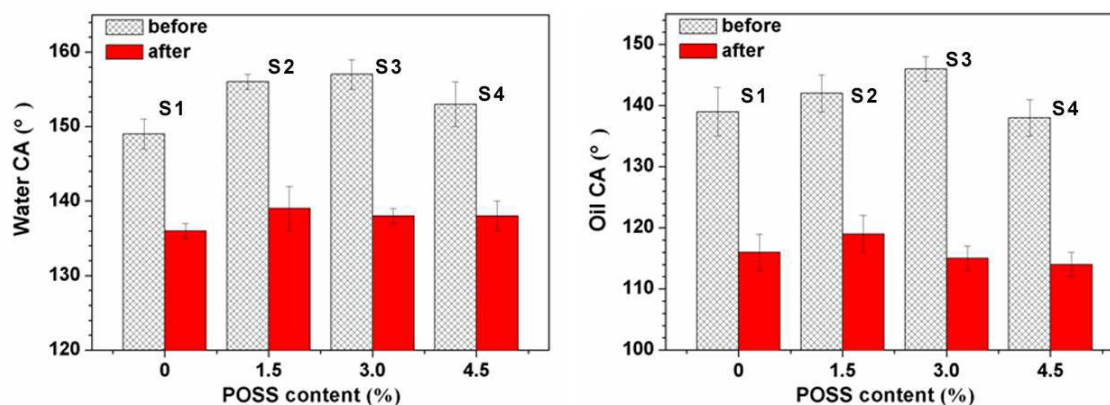

Fig. 8 Effects of POSS content on the wettability of the coated fabrics before and after UV irradiation.

As seen in Fig. 8, both the water and oil CAs show the tendency of increasing first and then decreasing when POSS mole ratio ranged from 0 to 4.5 %. It is well known that super-hydrophobic/oleophobic surfaces are usually achieved by the combination of surface geometrical structure and low surface free energy chemical compositions. On one hand, increasing POSS content in the polymer is helpful to increase surface roughness to improve water and oil CAs; and on the other hand, with POSS content increasing, the fluorine content in the polymer decreases inevitably, resulting in the hydrophobicity and oleophobicity of the cotton fabrics being lower consequently.

Apart from surface chemistry, the surface topography is also the key factor for wettability of the surface. Fig. 9 shows the surface morphology of the polymers coated cotton fabrics. The surface of **S1** has no white particles due to the absence of POSS unit in **P1**. In contrast, white particles are distributed on the surfaces of the cotton fabrics coated with **P2**, **P3** and **P4** (Fig. 9 **S2**, **S3** and **S4**). Compared with **S1**, the FE-SEM images of **S2** to **S4** show rougher surface resulted from POSS agglomeration in the polymers. The proper roughness is helpful to increase water and oil CAs of the coated fabrics.
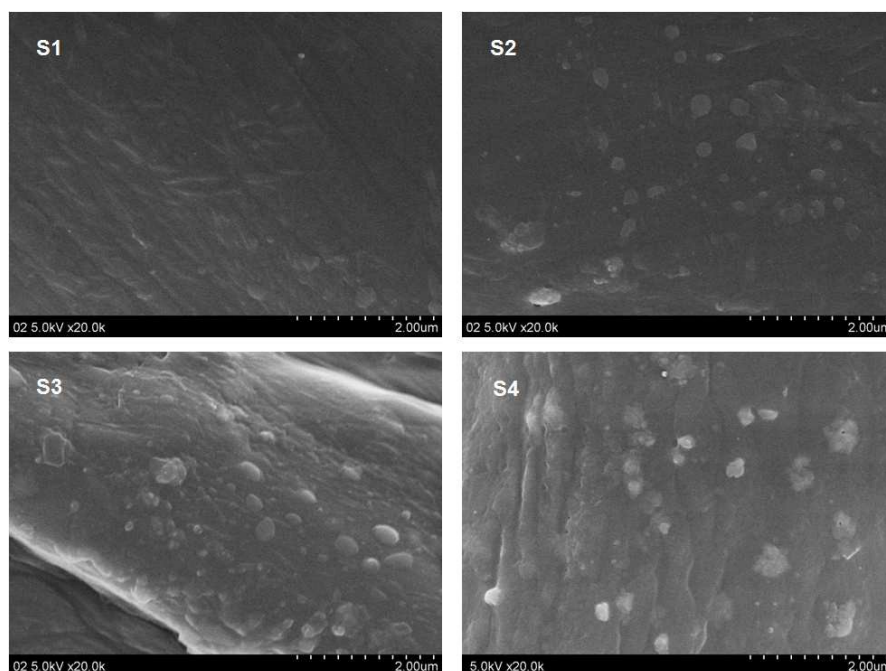
Fig. 9 FE-SEM images of coated cotton fabrics surfaces.

After 10 min UV irradiation at 365nm, water and oil CAs of all the samples decrease due to the *trans*-azobenzene changing to *cis*-azobenzene, which results in less fluorocarbon on the outermost of the surfaces. As seen in Fig. 8, **S1** demonstrates a static water and oil CA alteration about ~13° and ~23° after UV irradiation, respectively. A larger static water CA alteration is obtained from **S2**, where water CA changed from ~156° to ~139° upon UV irradiation. **S3** shows the most significant static CA changes. The water CA of **S3** decreases from ~157° to ~138°, changing close to 20° upon UV irradiation. With the UV irradiation, the oil CAs of **S3** decrease from ~146° to ~115° with the maximum change of ~31°. If **S3** is exposed under visible light again, the water and oil CAs almost recovered to initial levels (Fig. 10). The reversibility of CA changes of **S1** and **S3** under alternate UV and visible light irradiation are shown in Fig. 11. For each switching cycle, both water CA (WCA) and oil CA (OCA) changes of **S3** larger than those of **S1**. Cho's group investigated the effect of nanostructure on the surface dipole moment of photo-reversibly tunable superhydrophobic surfaces [13]. They found that the presence of surface nanostructures enhances the magnitude of the wettability changes. In our study, the nanostructures on the fabric surface caused by POSS addition enhance the switchable wettability, which is in agreement with the results of Cho's [13]
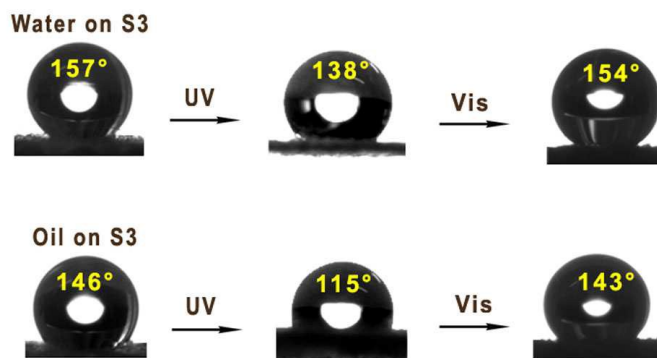
and Zhang's [16] work.

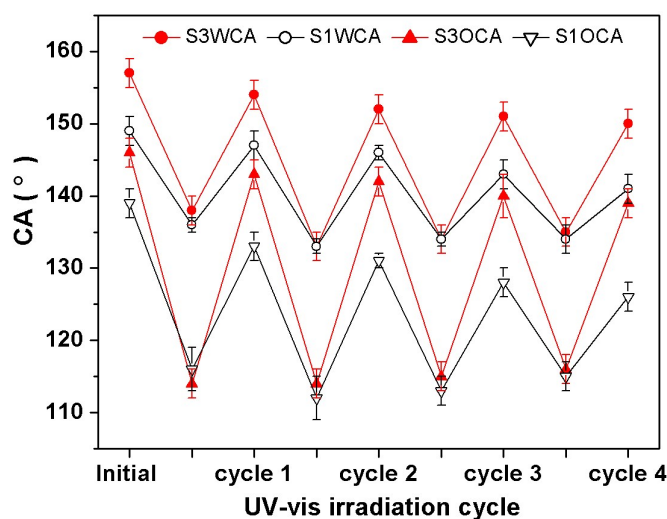Fig. 10 Wettability of **S3** before and after UV/vis irradiation.

Fig. 11 Reversible wettability transitions of **S1** and **S3** under alternate UV and visible light irradiation.

We have to point out that without any extra surface fabrication, the changes of water CAs from the POSS-based polymers coated cotton fabrics are relatively small compared to the results from the surfaces modified by anisotropic etching[15] or nanotechnology[13]. In this study, we focus on the preparation, characterization and photoisomerization behavior of the POSS-based polymer. By making use of the POSS agglomeration in the polymer and the surface structure of the cotton fabric, the higher water and oil CA changes than the typical ones on flat have been realized. The intensive study on the influences of surface structure on

the POSS-based polymer wettability will be undertaken subsequently.

Conclusions

In this work, well-defined POSS-based fluorocarbon chain modified azobenzene containing polymers were first prepared, characterized and applied to the cotton fabric for photoswitchable wetting surface. The polymers display good solubility, high thermal stability and fast photoisomerization. The *trans - cis* photoisomerization of the polymers conforms to the first-order reaction kinetics behavior. The cotton fabrics coated with these polymers possess excellent water and oil repellency and can be controlled by UV-visible light irradiation. Before and after UV light (365nm) irradiation, the changes of CAs of the coated fabrics with the series of polymers are affected by the POSS content. When POSS mole ratio increases to 3.0 %, water and oil CAs of the coated fabric are observed to be close to 20° and about 30°, respectively. The proposed polymers with good solubility, thermal stability and fast photoresponse could be applied in a wide range of fields requiring external stimuli-responsive surface.

Acknowledgements

References

1 O. Sato, S. Kubo, and Z. Z. Gu, *Acc. Chem. Res.*, 2009, **42**, 1-10.

2 S. J. Pan, R. Guo, and W. J. Xu, *Soft Matter*, 2014, **10**, 9187-9192.

3 N. M. Ahmad, M. Saqib, and C. J. Barrett, *J. Macromol. Sci., Part A*, 2010, **47**, 534-544.

4 H. Monobe, T. Ohzono, H. Akiyama, K. Sumaru, and Y. Shimizu, *Acs Appl. Mater. Inter.*, 2012, **4**, 2212-2217.

5 K. J. Lee, F. Pan, G. T. Carroll, N. J. Turro, and J. T. Koberstein, *Langmuir*, 2004, **20**, 1812-1818.

6 S. Moller, U. Pliquett, and C. Hoffmann, *Rsc Adv.*, 2012, **2**, 4792-4801.

7 N. Wagner and P. Theato, *Polymer*, 2014, **55**, 3436-3453.

8 O. Nachtigall, C. Kordel, L. H. Urner, and R. Haag, *Angew. Chem., Int. Ed.*, 2014, **53**, 9669-9673.

9 S. Abrakhi, S. Peralta, O. Fichet, D. Teyssie, and S. Cantin, *Langmuir*, 2013, **29**, 9499-9509.

10 C. L. Feng, Y. J. Zhang, J. Jin, Y. L. Song, L. Y. Xie, G. R. Qu, L. Jiang, and D. B. Zhu, *Langmuir*, 2001, **17**, 4593-4597.

11 N. Delorme, J. F. Bardeau, A. Bulou, and F. Poncin-Epaillard, *Langmuir*, 2005, **21**, 12278-12282.

12 F. J. Pavinatto, J. Y. Barletta, R. C. Sanfelice, M. R. Cardoso, D. T. Balogh, C. R. Mendonca, and O. N. Oliveira, *Polymer*, 2009, **50**, 491-498.

13 H. S. Lim, W. H. Lee, S. G. Lee, D. Lee, S. Jeon, and K. Cho, *Chem. Commun.*, 2010, **46**, 4336-4338.

14 J. Y. Peng, P. R. Yu, S. J. Zeng, X. Liu, J. R. Chen, and W. J. Xu, *J. Phys. Chem. C*, 2010, **114**, 5926-5931.

15 J. Groten, C. Bunte, and J. Ruhe, *Langmuir*, 2012, **28**, 15038-15046.

16 J. Zhang, W. D. Zhang, N. C. Zhou, Y. Y. Weng, and Z. J. Hu, *Rsc Adv.*, 2014, **4**, 24973-24977.

17 M. Y. Paik, S. Krishnan, F. X. You, X. F. Li, A. Hexemer, Y. Ando, S. H. Kang, D. A. Fischer, E. J. Kramer, and C. K. Ober, *Langmuir*, 2007, **23**, 5110-5119.

18 C. H. Wanke, J. L. Feijo, L. G. Barbosa, L. F. Campo, R. V. B. de Oliveira, and F. Horowitz, *Polymer*, 2011, **52**, 1797-1802.

19 T. Chen, S. L. Xu, F. Z. Zhang, D. G. Evans, and X. Duan, *Chem. Eng. Sci.*, 2009, **64**, 4350-4357.

20 M. Chen and F. Besenbacher, *Acs Nano*, 2011, **5**, 1549-1555.

21 K. Y. Mya, C. B. He, J. C. Huang, Y. Xiao, J. Dai, and Y. P. Siow, *J. Polym. Sci., Part A: Pol. Chem*, 2004, **42**, 3490-3503.

22 Y. J. Lee, S. W. Kuo, C. F. Huang, and F. C. Chang, *Polymer*, 2006, **47**, 4378-4386.

23 L. Liu, Y. Hu, L. Song, S. Nazare, S. Q. He, and R. Hull, *J. Mater. Sci.*, 2007, **42**, 4325-4333.

24 H. Hussain, K. Y. Mya, Y. Xiao, and C. B. He, *J. Polym. Sci., Part A: Pol. Chem*, 2008, **46**, 766-776.

25 F. Zhao and Y. D. Huang, *Mater. Lett.*, 2010, **64**, 2742-2744.

26 A. Strachota, K. Rodzen, F. Ribot, M. Perchacz, M. Trchova, M. Steinhart, L. Starovoytova, M. Slouf, and B. Strachota, *Polymer*, 2014, **55**, 3498-3515.

27 Yoshino N, Kitamura M, Seto T, Shibata Y, Abe M, and K. Ogino, *Bull. Chem. Soc. Jpn.*, 1992, **65**, 2141.

28 T. Thiele, D. Prescher, R. Ruhmann, and D. Wolff, *J. Fluorine Chem.*, 1997, **85**, 155-161.

29 Y. Gao, C. L. He, Y. G. Huang, and F. L. Qing, *Polymer*, 2010, **51**, 5997-6004.

30 S. M. Gong, H. Y. Ma, and X. H. Wan, *Polym. Int.*, 2006, **55**, 1420-1425.

31 A. Bobrovsky, V. Shibaev, A. Bubnov, V. Hamplova, M. Kaspar, and M. Glogarova, *Macromolecules*, 2013, **46**, 4276-4284.

32 R. Y. Wang, S. F. Wang, and Y. Zhang, *J. Appl. Polym. Sci.*, 2009, **113**, 3095-3102.

33 P. Aruna and B. S. Rao, *React. Funct. Polym.*, 2009, **69**, 20-26.

34 X. Q. Xue, J. A. Zhu, Z. B. Zhang, Z. P. Cheng, Y. F. Tu, and X. L. Zhu, *Polymer*, 2010, **51**, 3083-3090.

35 C. R. Crecca and A. E. Roitberg, *J. Phys. Chem. A*, 2006, **110**, 8188-8203.

36 C. H. Ho, K. N. Yang, and S. N. Lee, *J. Polym. Sci., Part A: Pol. Chem*, 2001, **39**, 2296-2307.

37 G. Angelini, N. Canilho, M. Emo, M. Kingsley, and C. Gasbarri, *J. Org. Chem.*, 2015, **80**, 7430-7434.

38 I. Mita, K. Horie, and K. Hirao, *Macromolecules*, 1989, **22**, 558-563.

Graphical Abstract
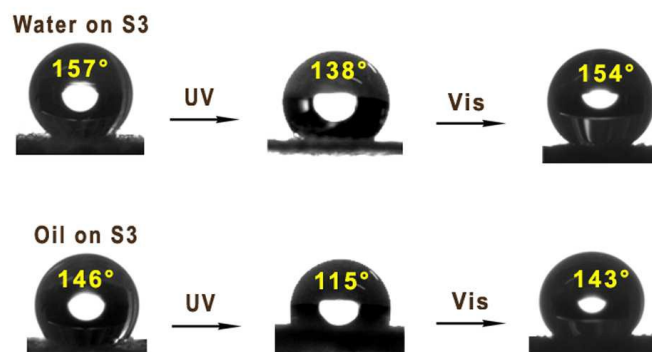
Photoresponsive polymers containing azobenzene, polyhedral oligomeric silsesquioxane (POSS) and fluorocarbon chains were successfully prepared via radical polymerization. The surface wettability of both water and oil on the POSS-based polymer coated fabrics can be intelligently controlled by applying irradiation with UV or visible light in short time.