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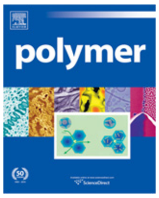

A facile strategy for the fabrication of highly stable superhydrophobic cotton fabric using amphiphilic fluorinated triblock azide copolymers

Guang Li, Haiting Zheng, Yanxue Wang, Hu Wang, Qibao Dong, Ruke Bai*

CAS Key Laboratory of Soft Matter Chemistry, Department of Polymer Science and Engineering, University of Science and Technology of China, Hefei 230026, PR China

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ABSTRACT

Amphiphilic triblock azide copolymers containing poly(ethylene glycol) (PEG) and poly(2,2,3,4,4,4-hexafluorobutyl acrylate) blocks have been synthesized through room temperature RAFT polymerization using redox initiation and were successfully used to fabricate superhydrophobic cotton fabric by a facile approach. The copolymers were covalently attached to the surface of the cotton fabric by the reaction of azide groups with the cotton fibres based on nitrene chemistry via UV irradiation. Due to introducing the fluorinated polymer chains, the cotton fabric was transformed from hydrophilicity to superhydrophobicity with a water contact angle of 155°. Since the fluorinated polymer chains were covalently attached on the surface of the cotton fabric, the superhydrophobic cotton fabric possessed high stability and chemical durability.

1. Introduction

Since the discovery of phenyl azide [1] and the first proposal of nitrenes [2] as reaction intermediates over 100 years ago, the chemistry of azides and nitrenes has attracted the attention of chemists. Organic azides are particularly useful intermediates in synthetic chemistry because azide groups can be transformed into a variety of functional groups such as amino, azo, and isocyanate groups [3]. Azide compounds and polymers are widely used as crosslinking materials [4–6], high energetic materials [7–13], and the materials for surface modification [14–18]. Comparing with the traditional methods for the preparation of azide polymers, such as chemical modification of polymers using sodium azide and chlorinated polymers with uncontrolled azide content in the polymer [4,11,19–21] and living cationic ring-opening polymerization of cyclic ether azides with very stringent polymerization conditions [7–13], room-temperature reversible addition fragmentation chain transfer (RAFT) polymerization using a traditional redox system (benzoyl peroxide (BPO)/*N*,*N*-dimethylaniline (DMA)) has been proved to be a facile strategy for the preparation of azide polymers in our lab [22].

The fabrication of superhydrophobic surface on textile substrates endowing the textile with self-cleaning properties has become an attractive subject for both academic research and industrial application in recent years [23–27]. Superhydrophobic surfaces with water contact angles larger than 150° can be achieved mainly from the combination of the rough surface and the low-surface-energy materials, such as organic fluorine and silicon compounds [28–36]. Many methods have been developed for the fabrication of the superhydrophobic surfaces on rigid substrates, but a few for soft materials, such as cotton fabric. To our knowledge, up to now, only few approaches such as dyeing technology [37], dipping-drying-curing method [38], and chemical vapor deposition approach [39–41], have been successfully used to the fabrication of superhydrophobic cotton fabric. However, these approaches are still subject to some limitations, such as complex fabrication process, severe conditions, and relative poor durability of the fabric due to weak physical interaction. Therefore, facile and effective approaches for the modification of soft substrates need to be explored.

It is well known that azide group can easily decompose to nitrene under thermal or UV conditions and the nitrene has very high reactivity with almost any C–H bonds or C=C bonds of an adjacent organic molecule, therefore, azide compounds and polymers are widely used as crosslinking materials [4–6] and the materials for surface modification [14–18]. And so azide polymers containing other functional groups will become good materials for the chemical modification of the substrates. Azide-thermolysis process needs high temperature and long reaction time [18,42–44], but azide-photolysis process can be conducted at ambient

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* Corresponding author. Tel.: +86 551 3600722; fax: +86 551 3631760.
E-mail address: bairk@ustc.edu.cn (R. Bai).

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temperature and even with high reaction speed [17,45–47]. And so comparing with azide-thermolysis, azide-photolysis process is more suitable for practical application. Herein, we present a facile strategy for the preparation of the amphiphilic fluorinated triblock azide copolymers and a one-step approach for transforming hydrophilicity to superhydrophobicity of cotton fabric through UV irradiation at ambient temperature.

2. Experimental

2.1. Materials

Methyl acrylate (MA) (Shanghai Chemical Co., China) and 2,2,3,4,4,4-hexafluorobutyl acrylate (HFA) (Harbin Xeogia Fluorine–Silicon Chemical Co., Ltd.) were passed through a neutral alumina column before use. Benzoyl peroxide (BPO) (Shanghai Chemical Co., China) was recrystallized from chloroform. *N*,*N*-dimethylaniline (DMA) (Shanghai Chemical Co., China) was distilled under reduced pressure and the pure DMA was collected below 135 °C. Polyethylene glycol monomethyl ether ($M_n = 5000$, Fluka) dried by azeotropic distillation of its toluene solution. S-1-dodecyl-S′-(α,α′-dimethyl-α″-acetic acid)trithiobonate [48], 4-azidophenyl methacrylate (APM) [22] and Benzyl 1*H*-imidazole-1-carbodithioate (BICDT) [49] were synthesized according to the references respectively. Cotton fabric was purchased from a general store. All other chemicals were analytical-grade reagents and used as-received.

2.2. Synthesis of PEG5000-CTA

PEG5000 (6.6 g, 1.32 mmol) was dissolved in 150 ml of methylene dichloride with S-1-dodecyl-S′-(α,α′-dimethyl-α″-acetic acid) trithiobonate (0.91 g, 2.5 mmol) and catalytic amount of 4-(dimethylamino)pyridine (50 mg). When the solution was homogenized by stirring, dicyclohexylcarbodiimide (0.52 g, 2.5 mmol) was added in one portion to the solution. After stirring at room temperature for 48 h, the precipitate in dicyclohexylurea was removed by filtration. The filtrate was concentrated, precipitated in excess of diethyl ether, and dried under vacuum. The crude product was dissolved in 100 ml of methylene dichloride and extracted with water at pH 9–10 for 3 times (100 ml each). After dried over anhydrous sodium sulfate for 24 h, the solution was concentrated and precipitated in excess of diethyl ether. PEG5000-CTA with yellow color was obtained by filtering and drying under vacuum at room temperature for 48 h (6.25 g, 88.5% yield).

2.3. Synthesis of PEG5000-b-P(MA-co-APM)

PEG5000-CTA (1.2 g, 0.22 mmol), APM (0.49 g, 2.41 mmol), BPO (21.6 mg, 89.2 μmol), DMA (11.2 μl, 89.2 μmol), MA (1.66 g, 19.29 mmol) and 1, 4-dioxane (1.5 ml) were placed in a glass tube. The glass tube was sealed under a vacuum after degassing with three freeze–evacuate–thaw cycles and then placed in an oil bath at 25 °C. After the polymerization was conducted for 6 h, the reaction mixture was precipitated in petroleum ether. The polymer was collected by filtration and dried in a vacuum oven at room temperature for 24 h (conversion = 75.2%, $M_{n,GPC} = 14\,800$, $M_w/M_n = 1.15$).

2.4. Synthesis of PEG5000-b-P(MA-co-APM)-b-PHFA

PEG5000-*b*-P(MA-*co*-APM) (0.3 g, 27.4 μmol), BPO (2.7 mg, 11.0 μmol), DMA (1.4 μl, 11.0 μmol), HFA (0.83 g, 3.52 mmol) and 1,4-dioxane (1.0 ml) were placed in a glass tube. The glass tube was sealed under a vacuum after degassing with three freeze–evacuate–thaw cycles and then placed in an oil bath at 25 °C. After the polymerization was conducted for 24 h, the reaction mixture was precipitated in petroleum ether. The polymer was collected by filtration and dried in a vacuum oven at room temperature for 24 h (conversion = 46.8%, $M_{n,GPC} = 30\,600$, $M_w/M_n = 1.13$).

2.5. Synthesis of P(APM-co-HFA)

BICDT (12.1 mg, 51.6 μmol), BPO (12.5 mg, 51.6 μmol), DMA (6.5 μl, 51.6 μmol), APM (59.2 mg, 0.25 mmol), HFA (1.03 g, 4.36 mmol) and 1,4-dioxane (1.5 ml) were placed in a glass tube. The glass tube was sealed under a vacuum after degassing with three freeze–evacuate–thaw cycles and then placed in an oil bath at 25 °C. After the polymerization was conducted for 12 h, the reaction mixture was precipitated in petroleum ether. The polymer was collected by filtration and dried in a vacuum oven at room temperature for 24 h (conversion = 70.1%, $M_{n,GPC} = 15\,600$, $M_w/M_n = 1.10$).

2.6. Synthesis of PEG5000-b-PHFA

PEG5000-CTA (0.2 g, 37.4 μmol), BPO (3.6 mg, 14.8 μmol), DMA (1.9 μl, 14.8 μmol), HFA (1.12 g, 4.74 mmol) and 1, 4-dioxane (1.5 ml) were placed in a glass tube. The glass tube was sealed under a vacuum after degassing with three freeze–evacuate–thaw cycles and then placed in an oil bath at 25 °C. After the polymerization was conducted for 6 h, the reaction mixture was precipitated in petroleum ether. The polymer was collected by filtration and dried in a vacuum oven at room temperature for 24 h (conversion = 32.6%, $M_{n,\ GPC} = 10\,400$, $M_w/M_n = 1.03$).

2.7. Preparation of superhydrophobic cotton fabric

A sheet of cotton fabric was cleaned by ultrasonic washing in ethanol and water, respectively, followed by drying at 120 °C in a vacuum oven for 1 h. The cleaned fabric was allowed to soak in amphiphilic triblock copolymer solution in tetrahydrofuran (THF) for 1 min and dried at 80 °C for 10 min to remove the solvent. UV exposure was carried out by placing the hand-held UV lamp (254 nm, 6 W) directly at a distance of 5 cm from the substrate for 10 min. And then the modified cotton fabric was rinsed with abundant THF and dried at 80 °C for 20 min.

2.8. Measurements

Fourier transform infrared (FT-IR) spectra were recorded on a Bruker Vector-22 IR spectrometer using KBr pellets. The values of the number-average molecular weight (M_n) and polydispersity (M_w/M_n) were determined by means of a Waters 150C gel permeation chromatograph (GPC) equipped with 10^3, 10^4, and 10^5 Å Waters Ultrastyragel columns, using THF (1.0 ml min^{-1}) as the eluent, and the calibration was carried out with a polystyrene standard. Contact angles were measured with an optical contact angle meter (Solon (Shanghai) technology science Co. Ltd.) at ambient temperature. Water droplets were dropped carefully onto the samples surfaces, and the average value of five measurements at different positions of the sample was adopted as the contact angle. The time dependence of the apparent water contact angle measurement was conducted at a relative atmosphere humidity of 85% at 20 °C. X-ray photoelectron spectroscopy (XPS) analysis was performed on an ESCA Lab MKII instrument with Al Kα radiation as the exciting source. Scanning electron microscopy (SEM) images were recorded using a JSM-6700F field-emission microscope. Atomic force microscopy (AFM) images were recorded under ambient conditions using a Digital Instrument Multimode Nanoscope IIIa operating in the tapping mode regime.

3. Results and discussions

3.1. Synthesis of the amphiphilic fluorinated triblock azide copolymer

Due to azide group sensitivity to heat and UV light, conventional radical polymerization and photopolymerization are not suitable for the preparation of azide polymers. Until now, there are only a few papers published on the free radical polymerization of vinyl azide monomers [50–53]. We have been trying to develop facile and effective strategies for the preparation of azide polymers. Although living free radical polymerization has been first successfully used to prepare azide polymers by γ-ray initiation in our lab [54–56], γ-ray source is not available for every laboratory. A facile strategy, room-temperature reversible addition fragmentation chain transfer (RAFT) polymerization has been also successfully applied to the preparation of azide polymers by using a traditional redox system (BPO/DMA) in our lab [22]. It is obvious that the ability to conduct living free radical polymerizations at room temperature using the traditional redox system is a desirable feature from both academic and industrial application standpoint, due to less energy consumed and ease of control of the polymerization [57].

The amphiphilic fluorinated triblock azide copolymer, poly(ethylene glycol)(5000)-*b*-P(methyl acrylate-*co*-4-azidophenyl methacrylate)-*b*-P(2,2,3,4,4,4-hexafluorobutyl acrylate) (PEG5000-*b*-P(MA-*co*-APM)-*b*-PHFA), was successfully synthesized via room temperature RAFT polymerization using the traditional redox initiator (BPO/DMA) (Scheme 1). Firstly, using PEG5000-CTA as a macromolecular chain transfer agent (macro-CTA), APM was copolymerized with MA at room temperature using BPO/DMA as the redox initiator, forming the block copolymer PEG5000-*b*-P(MA-*co*-APM). And then the chain extension polymerization was carried out with 2,2,3,4,4,4-hexafluorobutyl acrylate (HFA) under the same condition as described above using PEG5000-*b*-P(MA-*co*-APM) as the macro-CTA.

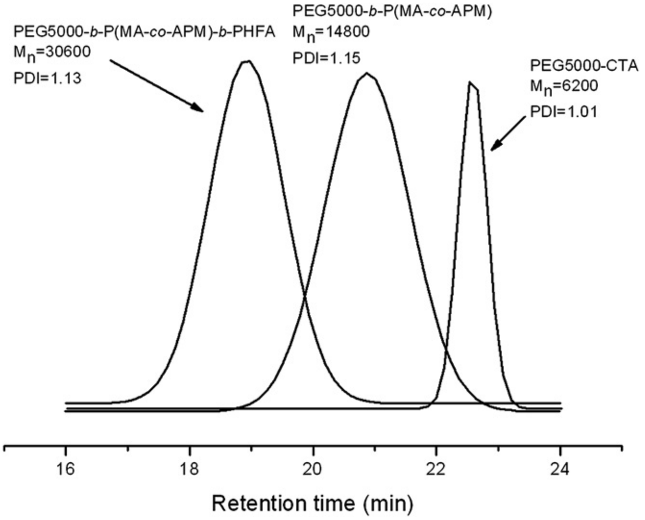
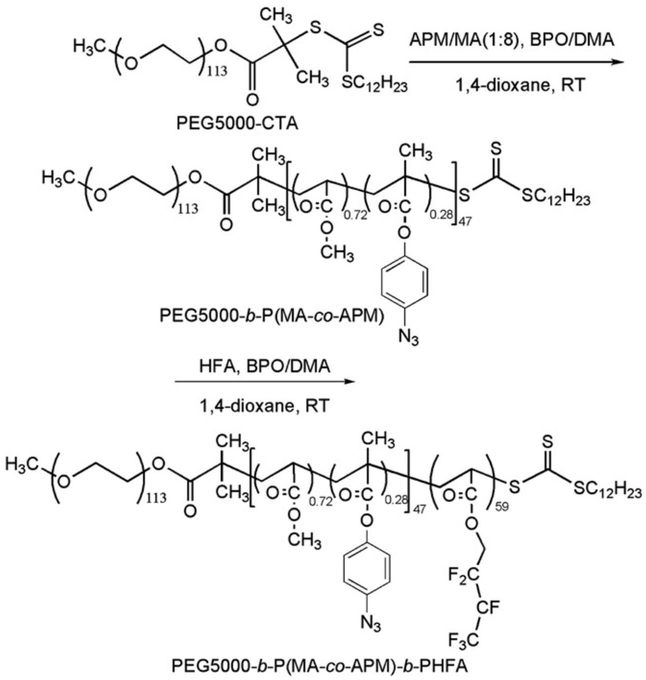


Fig. 1. GPC traces of PEG5000-CTA, PEG5000-*b*-P(MA-*co*-APM) and PEG5000-*b*-P(MA-*co*-APM)-*b*-PHFA.

Fig. 1 shows the GPC traces of PEG5000-CTA, PEG5000-*b*-P(MA-*co*-APM) and PEG5000-*b*-P(MA-*co*-APM)-*b*-PHFA. It can be seen clearly that the molecular weight of the block copolymers increases with the chain extension polymerization, and the molecular weight distribution of the block copolymers remains narrow after chain extension polymerization. The structures of PEG5000-*b*-P(MA-*co*-APM) and PEG5000-*b*-P(MA-*co*-APM)-*b*-PHFA were characterized by FT-IR spectra. Fig. 2(a) clearly shows that the azide groups remain after the polymerization, which means APM as a comonomer can be incorporated into the polymer chain to form azide copolymers via room temperature RAFT copolymerization. After the chain extension polymerization of HFA with PEG5000-*b*-P(MA-*co*-APM) as the macro-CTA at room temperature, azide group peak can still be seen clearly from the FT-IR spectrum (Fig. 2(b)), implying the formation of the amphiphilic fluorinated triblock azide copolymer.



Scheme 1. Synthesis of PEG5000-*b*-P(MA-*co*-APM)-*b*-PHFA.

3.2. Preparation of superhydrophobic cotton fabric via UV irradiation

The procedure for fabrication of the stable superhydrophobic cotton fabric is described as follows: first, a sheet of cotton fabric

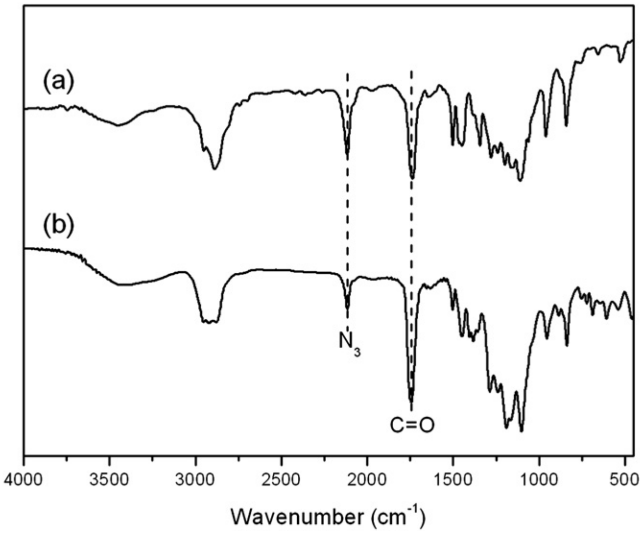


Fig. 2. FT-IR spectra of (a) PEG5000-*b*-P(MA-*co*-APM) and (b) PEG5000-*b*-P(MA-*co*-APM)-*b*-PHFA.

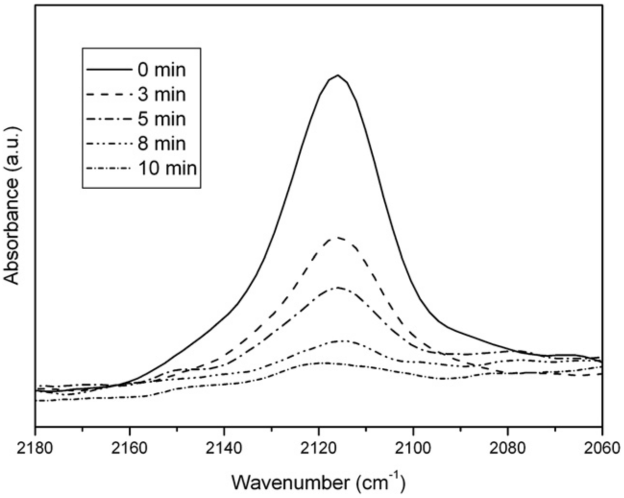


Fig. 3. FT-IR spectra of the N_3 vibration band of the copolymers with UV irradiation.

was cleaned by ultrasonic washing in ethanol and water, respectively, followed by drying at 120 °C in a vacuum oven for 1 h. Second, the cleaned fabric was allowed to soak in PEG5000-*b*-P(MA-*co*-APM)-*b*-PHFA solution in tetrahydrofuran (THF) for 1 min and dried at 80 °C for 10 min to remove the solvent. Next, UV irradiation was carried out by placing the sample under the hand-held UV lamp at a distance of 5 cm for 10 min. Finally, the modified cotton fabric was rinsed with abundant THF and dried at 80 °C for 20 min.

Fig. 3 shows the FT-IR spectra of PEG5000-*b*-P(MA-*co*-APM)-*b*-PHFA film before and after UV irradiation for different periods of time at ambient temperature, presenting the spectral changes due to the decomposition of the azide group. The characteristic band of azide group located at 2116 cm^{-1} decreases gradually upon UV irradiation and this indicate that the decomposition of the azide groups take place to give rise to the nitrenes, which are ready to react with almost any C—H bonds or C═C bonds and even with O—H or N—H bonds [4–6,14–18,42–47]. Thus, after UV irradiation of the modified cotton fabric, the formed nitrenes inserted into the C—H or O—H bonds of the cotton fibres, causing the amphiphilic copolymers to bond to the surface of the cotton fabric. As can be seen from Fig. 3, after 10 min UV irradiation of the azide copolymers, azide groups decompose completely, it means that UV irradiation is a facile and high-efficiency approach for the material modification using azide polymers.

The surface wettability of the modified cotton fabric was assessed by water contact angle (WCA) measurements. The water was absorbed rapidly by the original cotton fabric due to the perfect hydrophilicity. However, after modification of the cotton fabric using the fluorinated azide copolymers, the cotton fabric showed the superhydrophobic property. Firstly, a 2 μl water droplet was intended to be deposited on the modified surface of the cotton fabric, and it was interesting to find that the water droplet could not be placed on the surface. Consequently, the water droplet volume was increased to 6 μl and the WCA was (155 ± 1)° (Fig. 4(a)). The experimental results revealed that the WCA of the modified cotton fabric was related to the polymer concentration (Fig. 5). It was found that the WCA was measured to be (134 ± 1)° when the cotton fabric was modified by the 0.025 wt% polymer solution, and the superhydrophobic cotton fabric was obtained with WCA of (155 ± 1)° when the polymer concentration increased to 0.25 wt%. However, no apparent increase of WCA was observed even the polymer concentration was increased to 1 wt%. And so the concentration of the copolymers was set as 0.25 wt% for the modification of the cotton fabric.

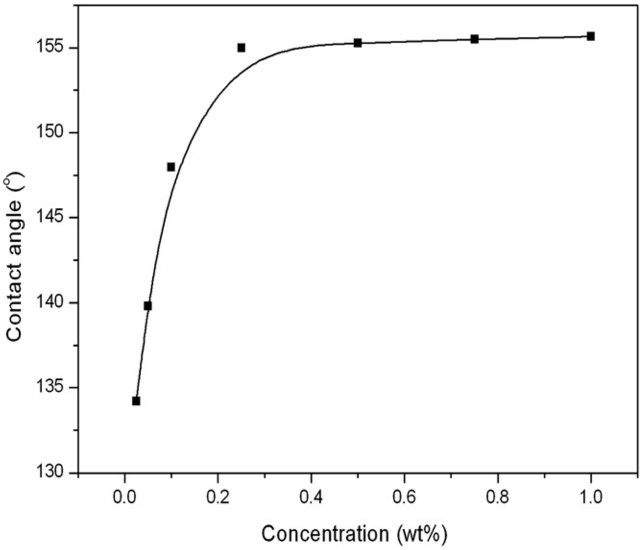


Fig. 5. The variation of contact angle with polymer concentration.

3.3. Measurements of superhydrophobic cotton fabric

Water droplets on modified cotton fabric had advancing contact angle of (155 ± 2)° and receding contact angle of (153 ± 2)°. The small contact angle hysteresis of the modified cotton fabric makes the water droplets move freely on the surface even when the surface was only slightly tilted lower than 5°. Fig. 6 shows a water droplet rolling over a dusted modified cotton fabric and removal of the dust along the path of the rolled droplet, indicating that the surface has self-cleaning effect just like the lotus leaf. The time

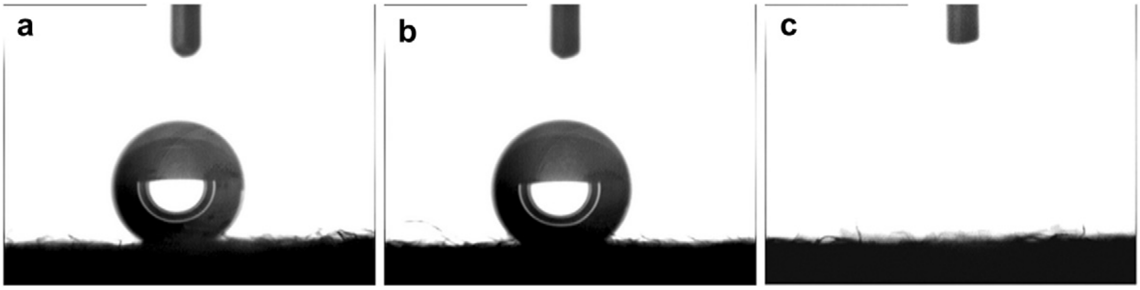


Fig. 4. A water droplet on the modified cotton fabric using (a) PEG5000-*b*-P(MA-*co*-APM)-*b*-PHFA with UV irradiation (155°), (b) P(APM-*co*-HFA) with UV irradiation (138°) and (c) PEG5000-*b*-P(MA-*co*-APM)-*b*-PHFA without UV irradiation.

Fig. 6. Image showing the self-cleaning ability of a dusted modified cotton fabric surface.

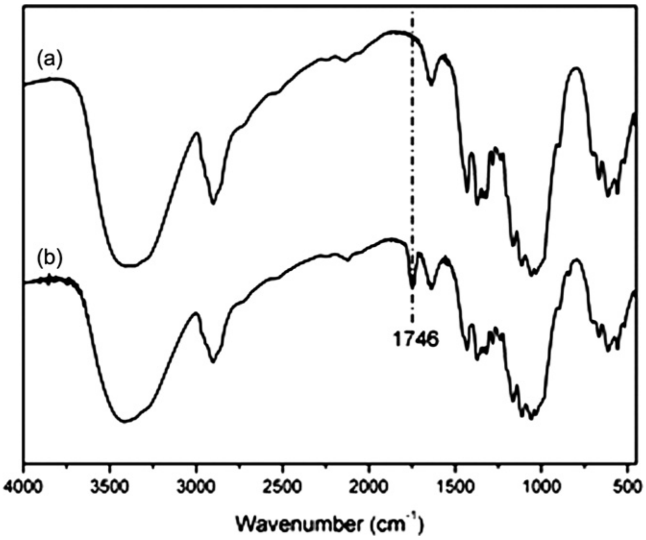


Fig. 8. FT-IR spectra of (a) the original cotton fabric and (b) the superhydrophobic cotton fabric.

dependence of the water contact angle for the modified cotton fabric is shown in Fig. 7. The contact angle of water droplet remains constant even after 1 h, and the modified cotton fabric has the essentially constant WCA value after 1 month storage in air, indicating that the superhydrophobic cotton fabric has good long-term stability.

These results demonstrate that the surface of the cotton fabric is transformed from hydrophilicity to superhydrophobicity due to the introduction of the fluorinated copolymers. It is reasonable that hydrophilic PEG blocks tend to locate in the interface between the block copolymer coating and cotton fibres due to the H-bond interaction of PEG with the hydroxyl groups of the cotton fibres, and the fluorinated blocks aggregate in the outermost of the coating contributing to the superhydrophobicity of the modified cotton fabric. In order to prove this, a control experiment was performed. P(APM-*co*-HFA) was synthesized and used to modify the cotton fabric at the concentration of 0.25 wt% with UV irradiation. The WAC was measured to be 138° (Fig. 4(b)). By comparison of the WACs, we can conclude that the amphiphilic triblock copolymers are more suitable for fabricating the superhydrophobic surface of the cotton fabric. It should be pointed out that UV irradiation is necessary for the modification of cotton fabric with the amphiphilic fluorinated triblock azide copolymers. The controlled experiment revealed that the modified cotton fabric without UV irradiation behaved the same hydrophilic property as the original one because the uncrosslinked copolymers were washed away from the surface of the modified cotton fabric by THF (Fig. 4(c)). Moreover, when a block copolymer, PEG5000-*b*-PHFA without azide groups was used to modify the cotton fabric under UV irradiation for 10 min, and then washed with THF, the hydrophilic property of the modified cotton fabric was observed no change comparing with that of the original cotton fabric. Therefore we can conclude that it is important to introduce azide groups into the polymers for the fabrication of the superhydrophobic cotton fabric.

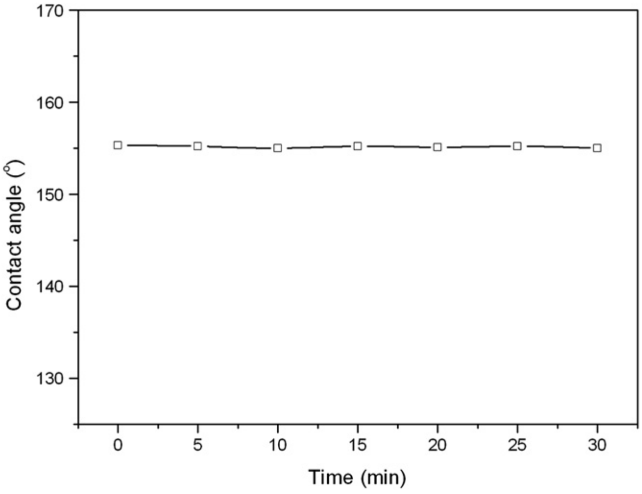


Fig. 7. Contact angle as a function of time for the modified cotton fabric.

3.4. Surface characterization of superhydrophobic cotton fabric

The superhydrophobic cotton fabric was characterized by FT-IR spectra (Fig. 8(a)) and X-ray photoelectron spectroscopy (XPS) analysis (Fig. 9). In comparison with the FT-IR spectrum of the original cotton fabric, a new peak at 1746 cm^{-1} appears, which is the characteristic stretching vibrations band of the ester C=O bonds of the copolymers (Fig. 8(b)), and the characteristic band of azide group disappeares in the spectrum of the superhydrophobic cotton fabric. It can be concluded that the copolymers are

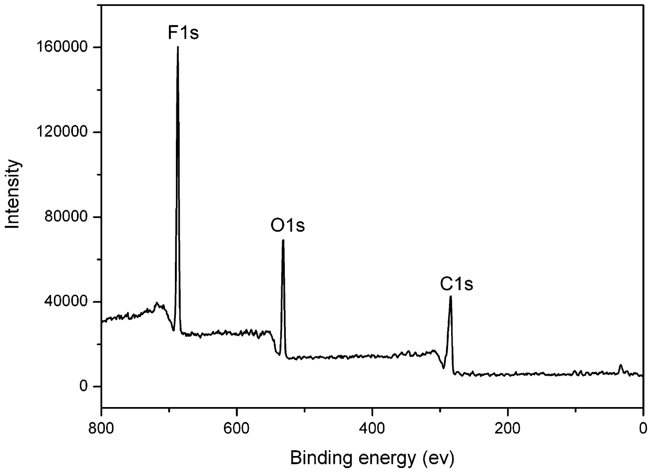


Fig. 9. XPS spectrum of the superhydrophobic cotton fabric.

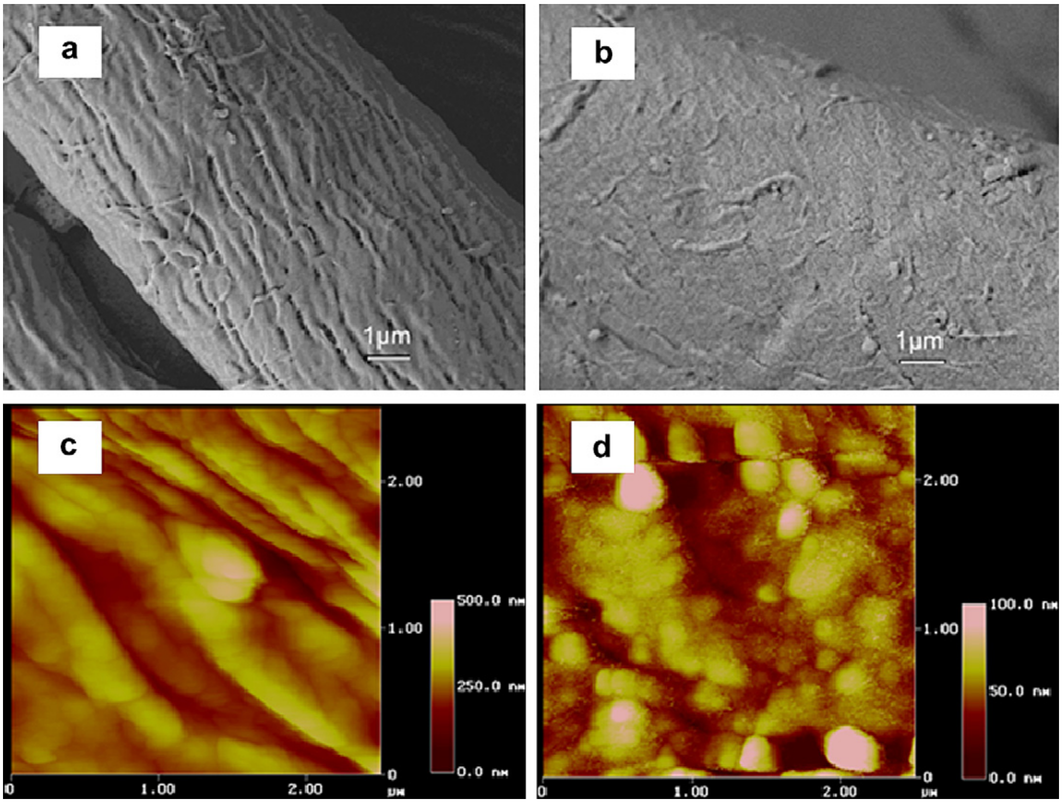


Fig. 10. SEM images of (a) original cotton fabric and (b) modified cotton fabric. AFM images of (c) original cotton fabric and (d) modified cotton fabric.

covalently attached to the surface of the cotton fabric. In the XPS spectrum of the superhydrophobic cotton fabric (Fig. 9), a strong peak with binding energy of 687 eV corresponding to F 1s, can be seen, and it proves that the cotton fabric surface is covered by the copolymers. The fluorine content of the superhydrophobic cotton fabric surface is estimated to be 32.5 wt%, which is higher than 27.5 wt% of the fluorine content in the copolymers according to ^{1}H NMR spectral analysis, this indicate that the fluorinated blocks prefer to aggregate and locate on the surface of the modified cotton fabric.

The surface morphologies of the original and the modified cotton fabric were investigated by SEM and AFM. Fig. 10(a) and (b) shows that the original cotton fabric presents a highly textured microscale fibre with a typically smooth surface, but the AFM image of the modified cotton fabric (Fig. 10(d)) reveals that the fibre surface is covered by the copolymers with some embossments causing by the aggregation of the fluorinated polymer blocks. In addition, the SEM image of the modified cotton fabric (Fig. 10(b)) shows the typical top view of the modified cotton fabric, and it can be seen that a layer of polymer is armored on the as-prepared superhydrophobic fabric surface. These results indicate that the surface of the cotton fabric is well modified by copolymers and the hydrophobicity of the fluorinated polymer blocks prevents the contact of water to the fibre surface. This is in good agreement with the WAC measurements of the modified cotton fabric.

3.5. *Chemical durability of superhydrophobic cotton fabric*

For practical applications, the chemical durability of the superhydrophobic surface is a key issue, therefore the chemical resistance of the modified cotton fabric was evaluated by measuring the change in WCA values after treating with aqueous solutions of varying pH (Fig. 11) according to the methods described previously by Li et al.[39,40] It was found that the resulting superhydrophobic fabric displayed a high durability with WCA values >147° after treatment with acidic, neutral, and basic solutions for 96 h. Due to the erosion resistance of fluorinated blocks on the cotton fabric surface, the modified cotton fabric showed excellent durability even treated with the strongly basic solution ($pH = 12$) comparing to other modification methods [39,40]. It can be concluded that the covalently attachment of fluorinated polymer chains endows the cotton fabric not only with stable superhydrophobicity, but also with the erosion resistance.

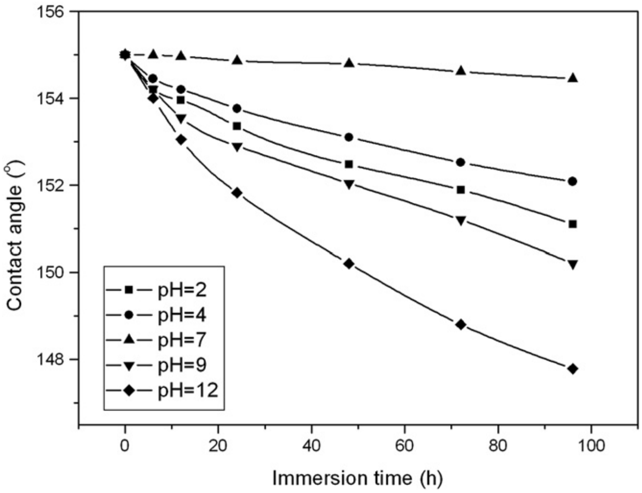


Fig. 11. The relationship between contact angles and the immersion time at varying pH for the superhydrophobic cotton fabric.

4. Conclusions

We have successfully synthesized the functionalized azide copolymers containing PEG and fluorinated polymer chains via room temperature RAFT polymerization, and developed a facile one-step approach for the fabrication of the stable superhydrophobic cotton fabric. The amphiphilic fluorinated triblock azide copolymers can be covalently attached to the surface of the hydrophilic cotton fabric through UV irradiation at ambient temperature to form a stable superhydrophobic cotton fabric. Due to covalent linkage formed between the fluorinated block copolymers and the cotton fabric, the superhydrophobic cotton fabric displays high resistance to acid, basic and organic solvents. We expect this strategy will become a promising powerful tool for the modification of various material surfaces.

Acknowledgements

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