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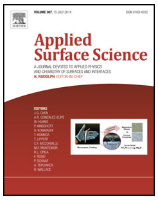

Superhydrophobic surfaces of electrospun block copolymer fibers with low content of fluorosilicones

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ABSTRACT

A series of well-defined poly[methyl(3,3,3-trifluoropropyl)siloxane]-*b*-poly(methyl methacrylate) (PMTFPS-*b*-PMMA) diblock copolymers with low content of PMTFPS were synthesized by atom transfer radical polymerization (ATRP) of MMA from PMTFPS macroinitiators (PMTFPS-Br). The polymerization result reveals that the ATRP of MMA from PMTFPS-Br is fist-order with respect to MMA under different polymerization conditions, demonstrating a typical characteristic of living polymerization. The results also show that PMTFPS-*b*-PMMA diblock copolymers can exhibit a total surface tension (γ_S) varying from 25.28 mN/m to 21.87 mN/m with the change of PMTFPS contents from 2.6 wt% to 22.2 wt%. Moreover, the water contact angles of electrospun PMTFPS-*b*-PMMA surfaces could be higher than 150° with water roll-off angles less than 10°, which denotes a superhydrophobic property. However, the electronspinning conditions, especially the concentration of spinning solution, would have important effect on the surface morphology, surface composition and wetting behavior of electrospun films. It was found that bead-free fibers with uniform diameter as well as good superhydrophobic property could be prepared on condition that the polymer concentration of spinning solution was as high as 32 wt% in the mixed solvent of DMF and THF.

1. Introduction

Superhydrophobic surfaces exhibiting contact angles greater than 150° along with a low rolling angle for water have attracted intense interest for many years [1,2], which largely due to their potential applications in self-cleaning interfaces [3–5], anticorrosion layers [6,7], electrowetting-based applications [8–10], and so on. There are many investigations on the fabrication of artificial superhydrophobic surfaces as well as the mechanisms involved in these superhydrophobic properties, and the results indicated that the chemical composition and surface geometrical structure of the solid surfaces have a great influence on the surface wettability [1,2]. So, the superhydrophobic surface could be successfully obtained by controlling the surface roughness and the chemical nature of the surface with low surface energy materials [11–14].

Many physical and chemical methods can build a suitable surface roughness with hierarchical microstructures and nanostructures to obtain hydrophobic surface, such as electrospinning [15–18] or electrospraying [19], plasma etching [20], sol–gel [21], chemical vapor deposition [22,23], chemical etching [24,25], electrochemical deposition [26], solution–immersion [27], and so on. Among these methods, electrospinning is a simple and practical way to produce a required roughness and morphology for surperhydrophobic surface [15–18]. Electrospinning is a technology which imposes a high voltage on the polymer droplets extruded from micro-injection pump, which can produce charged jets from the polymer solutions or melts [28,29]. By adjusting the electrospinning parameters (solution feeding rate, tip-to-collector distance, applied voltage), polymer solution properties (surface tension, viscosity, conductivity and molecular weight of the polymer) and the environment conditions (temperature, humidity), we can use this way to obtain either submicrometer polymer fibers or polymeric particles on a surface [30–32].

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After the surface roughness is developed, on the other hand, the chemical nature of the surface need to be considered to fabricate superhydrophobic surfaces [1,2]. A common method is to treat the rough surface with hydrophobic agent such as silanes, fluorinated chemicals or fluoropolymers. However, some fluorinated polymers or chemicals with long length of fluorinated tail associated with the problems of perfluorooctane sulfonate (PFOS) [33] or perfluorooctanoic acid (PFOA) [34] are often used to enhance the hydrophobic or oleophobic properties of film surfaces. Now, fluorinated chemicals or fluoropolymers without PFOS/PFOA and environmentally friendly methods have attracted intense attention in fabricating superhydrophobic and oleophobic surfaces [35]. Moreover, there are also some particular problems for electrospinning as fluoropolymers do not hold charge and therefore do not spin well [2]. Our challenge is to fabricate superhydrophobic surfaces of electrospun block copolymer fibers with low content of 3,3,3-trifluoropropyl substituted fluorosilicones.

Many techniques have been used to synthesize polysiloxane-containing block copolymers with controlled macromolecular structure [36]. Among these methods, the method combining anionic ring-opening polymerization (ROP) with atom transfer radical polymerization (ATRP) is a useful techniques to synthesize well-defined fluorosilicone-containing block copolymers with predictable molecular weights [37]. In this work, a series of well-defined poly[methyl(3,3,3-trifluoropropyl)siloxane]-*b*-poly(methyl methacrylate) (PMTFPS-*b*-PMMA) diblock copolymers with low content of fluorosilicones were synthesized by a combination of anionic ROP of 1,3,5-trimethyl-(1,3,5-trifluoropropyl)cyclotrisiloxane (F_3) and ATRP of MMA from PMTFPS macroinitiators. And then, the surface wettability and surface properties of electrospun PMTFPS-*b*-PMMA diblock copolymer fibers were investigated via contact angle measurement (CAM), scanning electron microscopy (SEM), and X-ray photoelectron spectroscopy (XPS) analysis.

2. Experimental

2.1. Materials

Tetrahydrofuran (THF, 99%; YongDa Chemical Reagent Co. Ltd.) was refluxed over sodium in the presence of benzophenone until a deep purple color was attained. 1,3,5-Trimethyl-(1,3,5-trifluoropropyl)cyclotrisiloxane (F_3, 99%; Shanghai 3F Co. Ltd.) was first dried over 3 Å molecular sieves, then refluxed with CaH_2 in vacuo for several hours, and finally distilled before use and diluted with a small amount of pure THF. Methyl methacrylate (MMA, 99%; HuaDong Medicine Co. Ltd.) were extracted three times with 5% aqueous NaOH, washed with distilled water, and then dried over CaH_2 and distilled into the ampule in vacuum. *n*-Butyllithium (*n*-BuLi, 2.5 M in hexane, 99%; Acros), dimethylchlorosilane ($(CH_3)_2SiHCl$, 98%; Sigma–Aldrich), Karstedt's catalyst (2% Pt in xylene; Sigma–Aldrich), 4-dimethylaminopyridine (DMAP, 99%; Acros) and *N*,*N*,*N*′,*N*″,*N*‴,*N*‴-hexamethyltriethylene-tetramine (HMTETA, 99%; Sigma–Aldrich) were used without further pretreatment. Triethyl amine (TEA) was stirred over CaH_2 and distilled before use. CuBr (98%; Acros) was washed with glacial acetic acid, followed by pure ethanol and ethyl ether, and then dried under vacuum. The liquids for contact angle measurements, formamide (99%; HuaDong Medicine Co. Ltd.), diiodomethane (CH_2I_2, 99%; Sigma–Aldrich Co.), were also used without further purification.

2.2. Synthesis of PMTFPS-*b*-PMMA

The anionic ROP of F_3 and the synthesis of α-bromoisobutyryl-terminated PMTFPS (PMTFPS-Br) (as shown in Supplementary data) was performed via the procedure described previously [37]. Then, PMTFPS-Br was used as a macroinitiator for the ATRP of MMA. The ATRP polymerizations of MMA were carried out in a 50 mL Schlenck flask equipped with a magnetic stir bar under nitrogen atmosphere. As an example, the purified MMA (4.6 mL, 0.040 mol), CuBr (0.0056 g, 0.040 mmol), HMTETA (0.022 mL, 0.080 mmol), cyclohexanone (16.60 mL), and PMTFPS-Br (0.144 g, 0.040 mmol) were added to the flask which was filled with pure nitrogen and evacuated previously by using high-vacuum techniques (about 10^{-3} Pa). The solution was purged with nitrogen for 30 min until the Cu complex had formed, with a change of the solution from cloudy and colorless to clear and light green. And then, the flask was placed in a water bath with a constant temperature at 65 °C or 75 °C for different reaction time. After polymerization, the solvent was removed under vacuum, and the resultant polymers were dissolved in THF and passed through a column of active aluminum oxide to remove the metal complex. Finally, the obtained PMTFPS-*b*-PMMA diblock copolymers were precipitated into methanol and then dried more than 48 h under vacuum.

2.3. Electrospinning process

PMTFPS-*b*-PMMA diblock copolymers were dissolved in DMF or a mixed solvent of DMF and THF (DMF/THF = 1:1, v/v) at room temperature and stirred to form transparent solution. Then, the polymer solution was placed in the injection syringe of the eletrospinning instrument equipped with a syringe pump (WZS-50F6, Smiths Medical Instrument (Zhejiang) Co. Ltd.), a high voltage power (ES50P-10W/DDPM, GAMMA, USA), a dehumidifier (AR-160, Hangzhou DOROSIN electrical equipment CO., LTD) and a collector connected to the ground and covered by aluminum foil. Finally, the polymer solution was electrospun, and the operating parameters as solution flow rate (0.6 ml/h), electrospun time (4 h), electrical potential (15 kV, DC), the humidity in the electrospun device (50%), jet diameter of the syringe tip (1.0 mm or 0.3 mm) and the collecting distance between syringe tip and collector screen (15 cm or 25 cm) were fixed or adjusted in order to investigate their effects on the wettability and morphology of electrospun films.

2.4. Measurements

2.4.1. Gel permeation chromatography (GPC)

GPC analysis was performed on a Waters 1525/2414 GPC system consisting of a Waters 1525 binary HPLC pump, a Waters 2707 autosampler, three Waters Styragel columns (Styragel HR1, HR3, and HR4), and a Waters 2414 Refractive Index Detector. THF was used as the eluent at a flow rate of 1.0 mL/min at 30 °C. Calibration curve was made by polystyrene standard (Waters).

2.4.2. Proton-nuclear magnetic resonance (^1H NMR)

^1H NMR analysis was conducted by using a Bruker Avance AV 400-MHz Digital FT-NMR Spectrometer and carried out with 5 wt% solution in $CDCl_3$ at room temperature. The number average molecular weight of PMTFPS block ($M_{n,PMTFPS}$) was calculated from the characteristic proton integrals.

2.4.3. Contact angle measurement (CAM)

The contact angles or hysteresis of electrospun PMTFPS-*b*-PMMA diblock copolymer films were measured by contact angle goniometry using a DSA20 contact angle measurement device (Krüss, Germany) at room temperature and ambient humidity. All liquids were added drop wise to the film surface and the