



UV-curable POSS-fluorinated methacrylate diblock copolymers for icephobic coatings



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ABSTRACT

Low surface energy materials have been extensively investigated for building icephobic surfaces in recent years. Polydimethylsiloxane (PDMS) and fluoropolymers have been introduced to this field, while control of their structures is of importance to produce deicing surfaces. In this work, fluorinated methacrylate block copolymers containing polyhedral oligomeric silsesquioxane (POSS) moieties were synthesized by reversible addition-fragmentation chain transfer polymerization and transformed into thiolated-copolymers by aminolysis to adjust the self-assembly and modify surface morphology. The icephobic coatings were developed via UV-curable thiol-ene reaction with tunable amounts of thiol-modified POSS-fluorinated methacrylate diblock copolymers with vinyl-functionalized PDMS and thiol-functionalized PDMS. Characterizations of atomic force microscopy, X-ray photoelectron spectroscopy, and contact angle showed the evidence of the POSS-fluorinated diblock copolymers on the outmost surface of the coatings. Owing to the crystallization of perfluoroalkyl side groups, the coatings containing thiol-modified poly(methacrylisobutyl POSS)-*b*-poly(2-perfluorooctylethyl methacrylate) (**S17F**) exhibited excellent icephobicity, and water droplets could rebound completely on all **S17F**-containing surfaces at both normal and tilt modes before freeze even at $-15\text{ }^{\circ}\text{C}$. The ice shear strengths of the prepared UV-cured coatings were about one-eighth of that on bare aluminum surface, while the coating containing 5% **S17F** achieved the lowest ice shear strength of $105 \pm 12\text{ kPa}$. It was found that the icephobicity of these coatings were attributed primarily to the synergistic effect of the POSS-fluorinated methacrylate diblock copolymer and the PDMS component.

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1. Introduction

Ice adhesion and accumulation on surfaces can bring about severe problems on telecommunication towers, wind turbines, aircraft wings, and ships [1–3]. To avoid the detrimental environmental consequences and substantial energy consumption caused by the active deicing methods, extensive investigations have been conducted to tailor inherent material properties for building icephobic surfaces via eliminating ice formation or reducing ice adhesion [3,4].

Most notably, fluoropolymers, ascribed to the low dielectric constant and low surface energy, have been widely utilized to prepare anti-icing and icephobic coatings [5–10], including

fluoroalkylsilane [5], polytetrafluoroethylene (PTFE) [6,7] and poly(fluoroalkyl acrylate) [8–10]. Compared with PTFE, the flexible dangling fluoroalkyl groups of poly(fluoroalkyl acrylate)s can affect the molecular aggregation and the surface properties [8–14]. Particularly, with longer fluoroalkyl side groups, poly(fluoroalkyl acrylate)s exhibit crystallization properties, thus inhibit surface reorientation when contacting with water, which is important for hydrophobicity and icephobicity [8,11–14]. For example, poly(perfluorodecyl acrylate) can act as a steric barrier resisting local surface reorganization, forcing the reduction of undesirable contact angle hysteresis and low values of the ice adhesion strength [8]. Therefore, control of the molecular aggregation structure of fluoropolymers is an important issue for modifying the deicing surfaces.

Polyhedral oligomeric silsesquioxanes (POSS) are molecules with special cage-like nano-scaled organic/inorganic hybrid structures [15–20]. Importantly, owing to suitable substituent groups, POSS and its derivatives are demonstrated to be easily incorporated into various hybrid polymers [16,17]. By

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copolymerization, methacrylisobutyl POSS (MAPOSS) has been used to modify the anti-wetting properties of coating materials, due to their low surface energy and hydrophobicity [18]. Expanding on utility, combining of fluorinated groups and POSS into synthetic materials, fluorodecyl POSS has been employed to tune surface energy and surface morphology for building icephobic films [19,20].

Owing to the incompatibility of block compositions, microphase separation could occur both in bulk and on surface of the block copolymers [9,10]. In a microphase-separated block copolymer, blocks with lower surface energy migrate to the surface preferentially [9,10,21]. With the developments of reversible addition-fragmentation chain transfer (RAFT) polymerization and atom transfer radical polymerization, well-architected fluorinated block copolymers [9,13,21] and POSS-containing copolymers [17,18,22–26] have been obtained. Block copolymers containing POSS moieties are particularly attractive because they undergo self-assembly and microphase separation into block domains. Long-range structural ordering and hexagonally packed cylinders can be obtained by crosslinking of POSS-containing block copolymers [24]. On the other hand, anti-wetting coatings could be obtained by the self-assembly of fluorinated block copolymers due to their active self-orientation and self-migration to the surfaces [9,17,21]. Interestingly, in the previous work, we have found that nano-scaled morphologies obtained by the self-assembly and self-aggregation of block copolymers could be beneficial to icephobic coatings [9,10,26–28]. Fluorosilicone block copolymers polydimethylsiloxane-*b*-poly(fluorinated acrylate) [9], POSS-containing fluorosilicone block copolymers [10,18,26,27] and polymethyltrifluoropropylsiloxane-polyacrylate [28] have been synthesized in our lab, and the crosslinked coatings exhibited significant reduction in ice shear strength. Combining both POSS and fluoropolymer by RAFT polymerization, the advanced POSS-fluorinated diblock copolymers with extraordinary surface properties are expected.

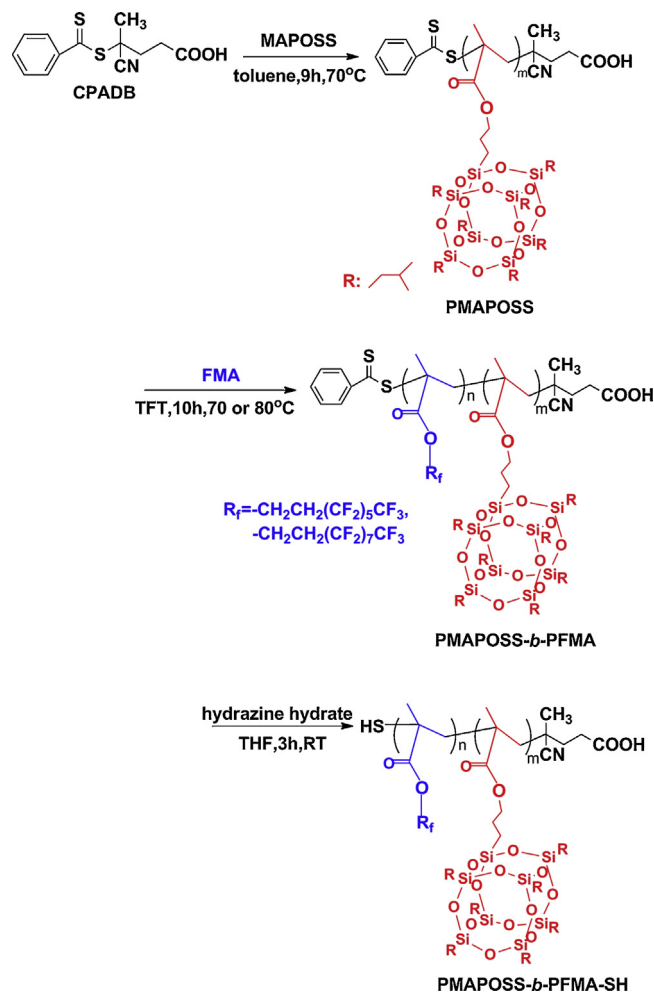
UV-curing is an efficient method to produce crosslinked materials, due to the rapid curing rate at ambient temperature, as well as low energy consumption [29–32]. It has been reported that the fluoride-containing POSS [29] and fluorinated copolymers [30] can migrate onto the surface and decrease the interface energy between UV-curable liquid acrylate resin and air. Attributed to the insensitivity to oxygen inhibition, thiol-ene reaction has also been explored in the development of crosslinked surface [31,32].

Inspired by the above successful strategies against ice adhesion and the effective UV-curing method, in this research, POSS-fluorinated diblock copolymers were initially synthesized by RAFT polymerization involving methacrylisobutyl POSS (MAPOSS) and perfluorooctyl methacrylate (13FMA) or 2-perfluorooctylethyl methacrylate (17FMA). The dithioester ends of the prepared copolymers were transformed into thiol groups and then blended with vinyl-functionalized PDMS (PDMS-V) and thiol-functionalized PDMS (PDMS-SH) for preparation of UV-cured coatings. PMAPOSS was introduced for improving hydrophobicity and the miscibility with PDMS component. The fluorinated methacrylate, 13FMA or 17FMA, was architected as the second block for facilitating block copolymers to migrate onto the surface. The morphologies and surface chemical compositions of the copolymer coatings as well as the effect of the POSS and fluorinated block on icephobic properties were investigated.

2. Experimental methods

2.1. Materials

Methacrylisobutyl POSS (MAPOSS) was purchased from Hybrid Plastics, USA, and used as received. Perfluorooctyl methacrylate



Scheme 1. Synthesis of thiol-terminated PMAPOSS-*b*-PFMA-SH via RAFT polymerization.

(13FMA) and 2-perfluorooctylethyl methacrylate (17FMA) were supplied by Xeogia Fluorin-Silicon Chemical Co., Ltd., China, and purified by passing over a column of alumina to remove inhibitor. Vinyl-functionalized PDMS (PDMS-V) (1.7 wt% of vinyl content $M_n = 24,000$) was obtained from Shandong Dayi Chemical Co., Ltd., China, and thiol-functionalized PDMS (PDMS-SH) (2.7 wt% of thiol content, $M_n = 6000$) was purchased from Shanghai Winner Silicone Materials Co., Ltd., China. 4-Cyanopentanoic acid dithiobenzoate (CPADB) was synthesized according to the reference [33]. 2,2'-Azobisisobutyrobutyl acrylate (AIBN) was obtained from Tianjin Kemiou Chemical Reagent Co., Ltd., China, and used after recrystallization by ethanol. Dimethylphenylphosphine (Me_2PPh) was obtained from Aladdin industrial Inc., China. Photoinitiator of 2,2-dimethoxy-2-phenylacetophenone (DMPA) was obtained from J&K Chemical Ltd., China. Tetrahydrofuran (THF), α,α,α -trifluorotoluene (TFT) and hydrazine hydrate (N_2H_4) were purchased from Tianjin Heowns Biochem Technologies LLC, Tianjin, China, and used without further purification.

2.2. Synthesis of POSS-fluorinated methacrylate block copolymer

POSS-fluorinated methacrylate block copolymers were synthesized by RAFT polymerization (Scheme 1). Briefly, MAPOSS (2.12 g, 1 mmol), CPADB (0.0417 g, 0.07 mmol) and AIBN (8.19 mg, 0.02 mmol) were dissolved into 4 mL of anhydrous toluene and placed in a 25-mL Schlenk tube which was thoroughly deoxygenated by five consecutive freeze-pump-thaw cycles. The tube

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