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Synthesis of novel polymethacrylates with siloxyl bridging perfluoroalkyl side-chains for hydrophobic application on cotton fabrics

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ABSTRACT

Three novel fluorinated methacrylate monomers with siloxyl bridging perfluoroalkyl groups were synthesized and characterized. Afterwards, the corresponding polymethacrylate latexes, namely monofluoroalkylsiloxyl polymethacrylate (PMFSMA), bisfluoroalkylsiloxyl polymethacrylate (PBFSMA) and trisfluoroalkylsiloxyl polymethacrylate (PTFSMA), were prepared and coated onto cotton fabrics to make them water-repellent. Particle size, particle size distribution, zeta potential and high-resolution transmission electron microscope (TEM) were tested to assess the emulsion stability and particle morphology. Thermal properties of PTFSMA were evaluated by thermal-gravimetric analysis (TGA). Surface properties of the coated cotton fabrics were characterized by Fourier transform infrared spectroscopy (FT-IR), scanning electron microscope (SEM), water contact angle (WCA), adhesive force and X-ray photoelectron spectroscopy (XPS). It was found that the incorporation of more perfluoroalkyl chains and the annealing process could decrease the surface free energy of polymer film to 13.7 mN/m. Furthermore, the EDS spectra of PTFSMA film after annealing showed an enrichment of fluorine in the film-air interface.

1. Introduction

In the past few decades, the market for technical textiles has been growing and the demand for textiles with special functions has strongly increased [1]. Among various natural and synthetic textiles, cotton fabric is one of the most widely used fabrics in consumer products due to its attractive characteristics, such as softness, comfort, and widespread applicability. However, the high concentration of hydroxyl groups on cotton surface makes the fabric easily stained by liquids [2]. Therefore, hydrophobicity in cotton fabrics, in particular, is one of the most desirable textile properties for consumers [3].

Conventionally, hydrophobic surfaces can be fabricated in two different ways: physical surface modification and chemical deposition [4–7]. Recently, many methods derived from above two ways have been proposed to generate hydrophobic surfaces, such as chemical coating [8–11], plasma and chemical etching [12–16], sol-gel technique [17,18], vapor deposition [19–21], electrostatic spinning [22,23], phase separation [24–26], and template method [27,28]. Of all these methods, the surface chemical coating has become a simple and effective technique for the manufacture of hydrophobic surfaces. Owing to the popularity of chemical coating, there are a large amount of waterproof finishing agents have been prepared and applied, such as polyurethanes [29,30], polysiloxanes [31,32], long chain fatty acids, fluorinated polymers, etc. [33–37].

In particular, fluorinated polymers have been thoroughly investigated as functional materials for surface coating applications due to their unique properties including excellent chemical and thermal stability, predominant hydrophobicity and oleophobicity [38–40]. Among various fluorinated materials, fluorinated polyacrylates have emerged as the most widely used hydrophobic coatings of substrates such as textiles, paper, membranes and leather [41–43]. Many researchers have prepared fluorinated polyacrylates by conventional emulsion polymerization, suspension emulsion polymerization, seeded emulsion polymerization, controlled radical polymerization, and other synthetic polymerization techniques. For instance, An et al. synthesized and characterized a series fluorinated polyacrylates [26,44]. Cengiz et al. synthesized perfluoroalkyl methacrylate copolymers in supercritical carbon dioxide [45,46]. And Zhang et al. reported the short perfluoralkyl

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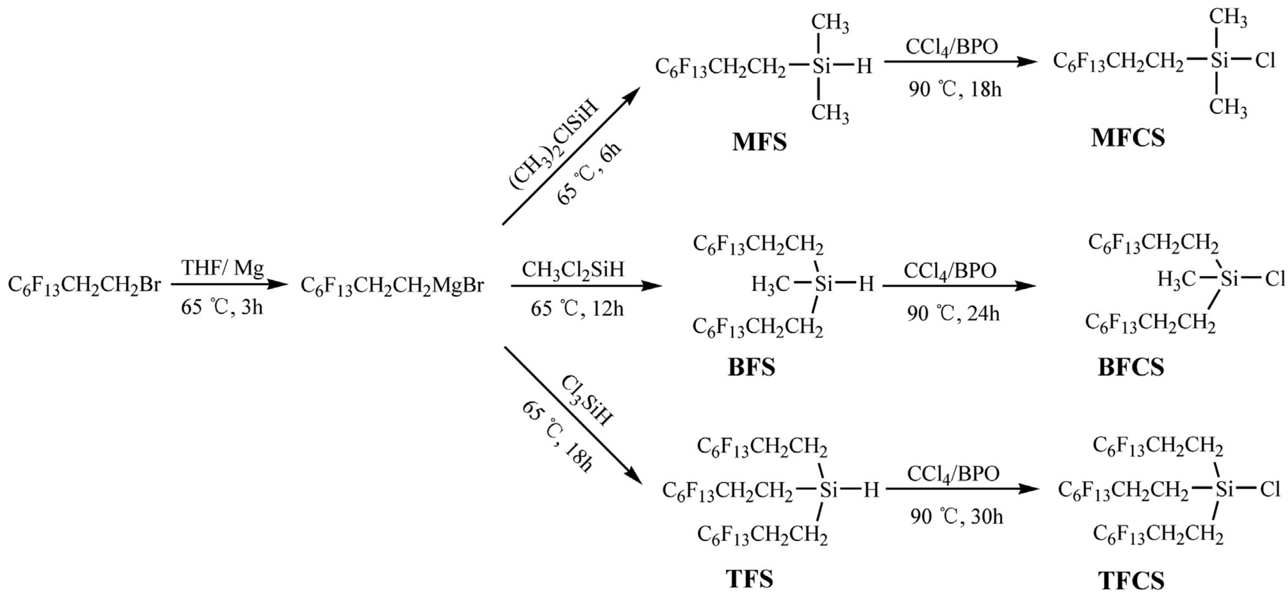
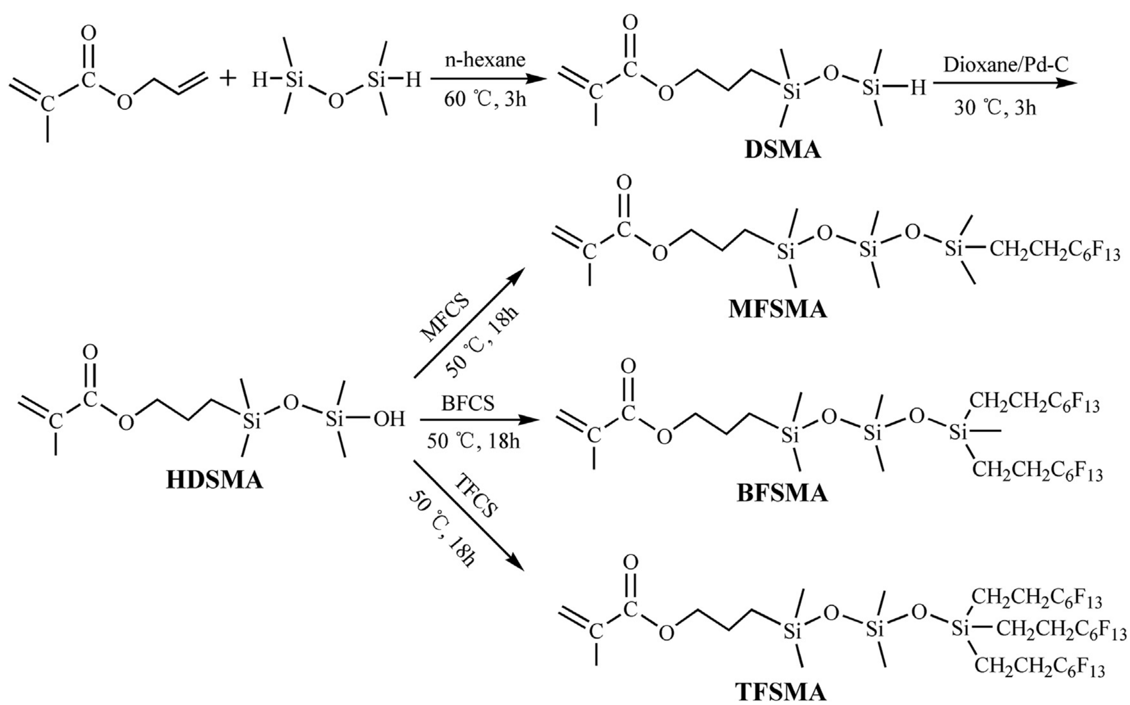


Scheme 1. Synthesis of MFCS, BFCS and TFCS.



Scheme 2. Synthetic route to MFSMA, BFSMA and TFSMA.

group containing acrylate polymers with extreme low surface energies [47,48].

It has been confirmed that surface properties of fluorinated polymers are influenced by the length of fluorocarbon groups, the fine structure and crystallinity of the perfluoroalkyl side-chains on the surface, and the type of spacer linker group located between the main chain and the fluorocarbon side-chain [47,49–51]. When the fluoroalkyl chain has more than eight fluorinated carbon atoms, the excellent dynamic water repellence is achieved because of the low surface molecular mobility [48,52]. Unfortunately, it has been reported that perfluorocarbon chain containing more than eight carbons, especially perfluorooctanoic acid (PFOA) and perfluorooctanesulfonate (PFOS), can resist degradation and bio-accumulate in human and animal tissue. These materials are cause of concern for the public, and some of them have accordingly been banned or voluntarily withdrawn from the market. Therefore, it is urgent to develop environmentally friendly materials to replace the currently used long-chain fluorinated substances.

Accordingly, the objective of our work was to synthesize three novel fluorinated methacrylates, in which short perfluoroalkyl groups were introduced onto the same silicon atom by the generation of Si—C bonds (see Scheme 1 and Scheme 2). The innovation of the current method lies in the generation of Si—C bonds, which were much easier to obtain than C—C bonds and realized the introduction of multi-perfluoroalkyl groups onto the same atom to form a close-packed perfluoroalkyl groups. Subsequently, those fluorinated monomers reacted with other acrylic monomers (BA, MMA, and HEMA) by emulsion polymerization to make corresponding