

# Synthesis and surface properties of novel fluoroalkylsilyl methacrylate copolymers



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## ABSTRACT

The syntheses of novel mono(1*H*,1*H*,2*H*,2*H*-tridecafluorooctyl) dimethylsilylpropyl methacrylate (MFSA), bis(1*H*,1*H*,2*H*,2*H*-tridecafluorooctyl)methylsilylpropyl methacrylate (BFSA) and tris(1*H*,1*H*,2*H*,2*H*-tridecafluorooctyl)silylpropyl methacrylate (TFSA) were achieved in two steps each in good yields. These fluoroalkylsilyl methacrylate monomers (MFSA, BFSA and TFSA) readily reacted with methyl methacrylate (MMA), butyl acrylate (BA), hydroxyethyl methacrylate (HEMA) to form their corresponding fluoroalkylsilyl methacrylate copolymers via continuous emulsion polymerization. The structures of fluoroalkylsilyl methacrylate monomers and copolymers were characterized by FT-IR, <sup>1</sup>H NMR, <sup>13</sup>C NMR and <sup>19</sup>F NMR. The stability of copolymer emulsions was determined by measuring their particle size and zeta potential, and the thermal stability of copolymers was also evaluated by using thermo-gravimetric analysis. In addition, it was observed that improving fluorine content, increasing the packing density of fluoroalkylsilyl segments, and annealing process could enhance the excellent water and oil repellency of fluoroalkylsilyl methacrylate copolymers. The surface free energies of copolymer films were calculated. Moreover, an enrichment of fluoroalkyl chains at the copolymer surface was directly verified by measuring contact angles and using atomic force microscopy.

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## 1. Introduction

Fluoropolymers present a number of peculiar and useful properties, such as high thermal stability, excellent chemical and weather resistance, low refractive indices, low coefficient of friction, high optical clarity, and the interesting water and oil repellency because of the low polarizability and the strong electronegativity of the fluorine atom [1–7]. These unique characteristics have led to a growing interest in fluorine chemistry for a wide range of applications [8]. Among various fluoropolymers, the fluorinated polyacrylates have attracted increasing interest from basic and applied polymer research communities. Because fluorinated polyacrylates exhibit unique properties including good mechanical behavior, excellent chemical and thermal stability, low refractive index, predominant hydrophobicity and oleophobicity [9–16], they have been used progressively in the fields of fabric finishing, leather, coatings and

antifouling [17–20]. Currently, the fluorinated polyacrylates with various structures, such as graft [21], random [22], hybrid nanocomposites [23] and core-shell [24–26], have been synthesized by emulsion polymerization, solvent polymerization, controlled radical polymerization, and other polymerization methods [27,28].

The hydrophobic and oleophobic properties of fluorinated polyacrylates depend on the length of fluorocarbon chains and the packing density of fluoroalkyl tails on the surface [29]. The long perfluoroalkyl side chains (*C* > 6) in fluorinated copolymers could reduce the surface energies as low as 8 mN/m and confer the optical properties [30], but they have been found to cause a series of problems, such as bioaccumulation, difficult to decomposition, and environmental unfriendliness [31,32]. On the other hand, fluoroalkyl segments show a tendency to separate from the carbon chains under appropriate temperatures. Consequently, the surface is uniformly covered with trifluoromethyl (–CF<sub>3</sub>) groups and the packing density of fluoroalkyl groups on the outermost surface of the polymer is higher than that in the internal of the polymer [33,34].

Indeed, many researchers have reported the synthesis and properties of fluorinated polyacrylates. Recently, Bertolucci and Yang independently reported the synthesis and characterization of

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the fluoroalkyl acrylate block copolymers [35,36]. Castelvetro's group examined the thermal degradation behavior of a nearly alternating copolymer of vinylidene cyanide with 2,2,2-trifluoroethyl methacrylate [37]. In addition, He's group disclosed a series of core-shell fluoroalkylsilyl methacrylate copolymers [25,26]. However, little work has been done on fluorinated polyacrylates with two or more short fluoroalkyl groups attaching to one structure unit, which could confer a low surface free energy that is similar to those of long fluoroalkyl chains, and could be considered as environmental friendly because the short fluoroalkyl chains are easy to degrade.

Herein, three novel fluorinated polymethacrylates, namely mono(1*H*,1*H*,2*H*,2*H*-tridecafluorooctyl) dimethylsilylpropyl methacrylate (MFSA), bis(1*H*,1*H*,2*H*,2*H*-tridecafluorooctyl)methylsilylpropyl methacrylate (BFSA) and tris(1*H*,1*H*,2*H*,2*H*-tridecafluorooctyl)silylpropyl methacrylate (TFSA), were synthesized *via* hydrosilylation and Grignard reaction. Subsequently, these monomers reacted with other acrylic monomers *via* continuous emulsion polymerization to obtain corresponding copolymers. The properties of the copolymer films were examined by using thermal analysis, contact angle measurement, and atomic force microscopy.

## 2. Results and discussion

### 2.1. FT-IR, <sup>1</sup>H NMR and <sup>19</sup>F NMR spectroscopy

Three novel fluoroalkylsilyl methacrylate monomers were synthesized *via* hydrosilylation and Grignard reaction in two steps (see Scheme 1). The chemical structures of these newly synthesized monomers were confirmed by FT-IR. As shown in Fig. 1, all the monomers exhibit the characteristic absorption peaks of –CH<sub>3</sub> stretching vibrations at 2954 cm<sup>-1</sup> and 2880 cm<sup>-1</sup>, and the characteristic absorption peak of C=O stretching vibration at 1726 cm<sup>-1</sup>. The absorption peak at 1636 cm<sup>-1</sup> is assigned to the C=C bond. The asymmetrical and symmetrical deformation vibrations at 1457 cm<sup>-1</sup> and 1384 cm<sup>-1</sup> belong to –CH<sub>3</sub>. The absorption peaks at 1240 cm<sup>-1</sup> and 1160 cm<sup>-1</sup> are corresponding to the stretching vibrations of C–F bond. Since the chemical structures of fluoroalkylsilyl methacrylate monomers have been demonstrated, they readily reacted with methyl methacrylate, butyl acrylate and hydroxyethyl methacrylate *via* continuous emulsion polymerization to obtain corresponding copolymers (see Scheme 2). Here, the FT-IR spectra of the bisfluoroalkylsilyl methacrylate copolymers with different fluorine contents were discussed as a representative, which could be seen in Fig. 2. As shown in curves a–f, the strong stretching vibration of C=O appears at 1730 cm<sup>-1</sup>. The disappearance of characteristic absorption peak of the C=C bond at 1636 cm<sup>-1</sup>

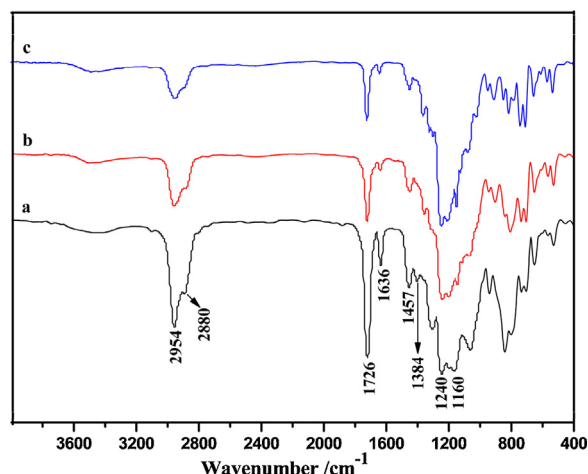


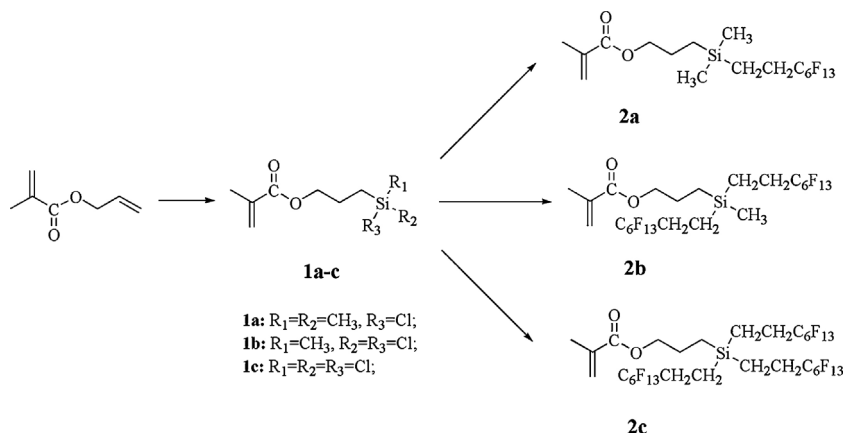
Fig. 1. FT-IR spectra of fluoroalkylsilyl methacrylate monomers: (a) MFSA; (b) BFSA; (c) TFSA.

indicates that all the monomers have reacted in the polymerization reaction. Generally, the strong peaks at 1235 cm<sup>-1</sup> and 1163 cm<sup>-1</sup> are assigned to the stretching absorption of C–F bonds, which are overlapped with the characteristic absorption peaks of –COO– at 1240 cm<sup>-1</sup> and 1160 cm<sup>-1</sup>. Moreover, it can be seen that absorptions at 1235 cm<sup>-1</sup> and 1163 cm<sup>-1</sup> become stronger as the amount of BFSA monomer increased, which indicates the effective incorporation of bisfluoroalkylsilyl methacrylate into the copolymers.

The structures of the copolymers were further confirmed by <sup>1</sup>H NMR and <sup>19</sup>F NMR. Fig. 3 presents the <sup>1</sup>H NMR spectrum of bisfluoroalkylsilyl methacrylate copolymer with 20% fluorine content. The proton NMR peaks of C<sub>6</sub>F<sub>13</sub>CH<sub>2</sub>CH<sub>2</sub> appear at 1.68 and 0.64 ppm, and the peak of SiCH<sub>3</sub> is observed at 0.07 ppm. However, the peaks of SiCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub> are observed at relatively low field, 4.03, 2.00, and 1.25 ppm, due to the adjacency to electron-withdrawing ester group. The existence of all characteristic proton peaks confirms the successful synthesis of bisfluoroalkylsilyl methacrylate copolymer. Fig. 4 shows the <sup>19</sup>F NMR spectrum of bisfluoroalkylsilyl methacrylate copolymer with 20% fluorine content. The signals of fluorine atoms appear from –81.15 ppm to –126.30 ppm, indicating the successful incorporation of bisfluoroalkylsilyl methacrylate into the copolymer.

### 2.2. Particle size and zeta potential analysis

The effect of fluorine content on the particle size was shown in Fig. 5. It clearly indicates that the particle sizes of these three



Scheme 1. Synthetic routes to fluoroalkylsilyl methacrylate monomers.

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