

# Synthesis and characterization of new silicon-containing fluoroacrylate monomers and polymers: 3\*

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A series of new silicon-containing fluoroacrylate polymers and copolymers (with methyl acrylate) has been prepared, starting from 1,3-bis(hexafluoro-2-hydroxy-2-propyl)benzene (1,3-HFAB). The fluorinated, silicon-containing alcohol precursor was synthesized in two steps by reacting 1,3-HFAB first with *n*-butyl lithium and subsequently with dichlorodimethylsilane. The silicon-containing alcohol was finally reacted with acryloyl or methacryloyl chloride to give the corresponding monomers. Polymers were obtained by bulk free radical polymerization using  $\alpha, \alpha'$ -azobisisobutyronitrile as initiator. The polymers, which have inherent viscosities ranging from 0.20 to 0.33 dl g<sup>-1</sup>, form brittle hydrophobic films by solution casting. The polyacrylates are stable to about 375°C (10% weight loss) in nitrogen and exhibit glass transition from 67 to 110°C. © 1997 Elsevier Science Ltd. All rights reserved.

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## INTRODUCTION

Polymers containing hexafluoroisopropylidene linking groups have received extensive study because of their desirable combination of enhanced properties when compared to non-fluorinated analogues<sup>2</sup>. Less work has been reported on polymers derived from hexafluoro-2-hydroxy-2-propyl-substituted arenes, presumably because the low reactivity of the tertiary alcohol group in these potential monomers precludes the direct formation of high polymers involving this function as a reactive site<sup>3</sup>. There are, however, several reports of polymers derived from hexafluoro-2-hydroxy-2-propyl-substituted arenes in which a reactive polymerizable function is attached to the arylhexafluoro-2-propoxy group; examples include, primarily, polyacrylates, polyurethanes and epoxy resins, all of which can be used to form highly hydrophobic coatings and films<sup>4</sup>. Specifically, polyacrylates obtained from hexafluoro-2-[3,5-bis-(2-alkoxyhexafluoro-2-propyl)phenyl]-2-propylacrylates form brittle films with water contact angles as great as 91°<sup>5,6</sup>.

Recently, as part of a continuing effort to explore further the chemistry of these interesting systems derived from 1,3-bis(hexafluoro-2-hydroxy-2-propyl)benzene (1,3-HFAB) we prepared the homopolymer and methyl acrylate copolymers of hexafluoro-2-[3-(hexafluoro-2-methoxy-2-propyl)phenyl]-2-propyl acrylate (equation (1)) and observed water contact angles as high as 106°C for the homopolymer<sup>7</sup>.

At this time, we wish to report the preparation of related acrylate (2) and methacrylate (3) monomers derived from 5-(hexafluoro-2-hydroxy-2-propyl)-1,1-dimethyl-3,3-bis(trifluoromethyl)-2-oxa-1-silaindan, **1**, a silicon-containing derivative of 1,3-HFAB (equation (2)).

These unique monomers combine trifluoromethyl groups with a dimethylsilyl group which is in an electron-deficient environment. As expected, they form highly hydrophobic homopolymers and copolymers with methacrylate.

## EXPERIMENTAL

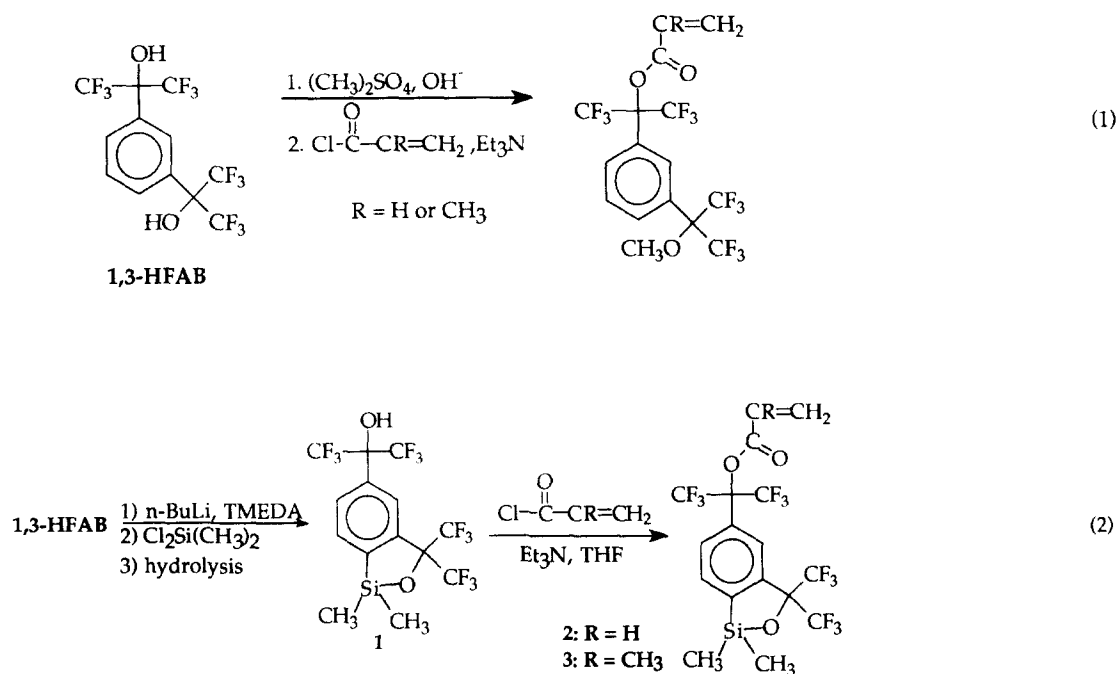
### Materials

The diol, 1,3-bis(hexafluoro-2-hydroxy-2-propyl)benzene, obtained from Central Glass Co., Tokyo, Japan, was dried (azeotropic water removal with toluene) and distilled prior to use (b.p. = 63° at 1 torr).  $\alpha, \alpha'$ -Azobisisobutyronitrile (AIBN), obtained from Kodak Laboratory Chemicals, was recrystallized twice from methanol–chloroform (9/1) and dried *in vacuo*. All other reagents were purchased from Aldrich Chemical Co. Anhydrous tetrahydrofuran and *n*-butyllithium were used as received. Tetramethylethylenediamine (TMEDA) was stored over 4 Å molecular sieves (Mallinckrodt Grade 514 GT). Dichlorodimethylsilane, methyl acrylate and methyl methacrylate were distilled (argon atmosphere) immediately prior to use. Hexane was dried by distillation from sodium.

Lithiation and silylation reactions were conducted under argon. Deuteration was performed by adding 1 ml aliquots of lithiated intermediates to excess D<sub>2</sub>O. The mixtures were then neutralized, and the deuterated

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samples were isolated by ether extraction for  $^1\text{H}$  n.m.r. analysis.

#### Measurements

Melting points were determined by using a Meltemp<sup>TM</sup> apparatus. Carbon and hydrogen analyses were obtained from Desert Analytics, Tucson, Arizona. Nuclear magnetic resonance spectra were obtained on an IBM NR-80 or a GE 500 MHz FT-n.m.r. spectrometer. Infra-red spectra were obtained on a Perkin-Elmer Series 1200 FT-i.r. spectrometer. Molecular weights were measured in THF on a Tracor 951 LC pump using a Shodex packed column by comparison to polystyrene standards. Thermogravimetric analyses and differential scanning calorimetry were performed on a Dupont 9900 thermal analyzer at Texas Research Institute (TRI), Austin, TX, USA. Contact angles were measured at 25°C on a Tante model CAM-MICRO. Solution viscosities were determined at a concentration of 0.25 g dl<sup>-1</sup> in THF at 25°C using a 50 Cannon-Fenske viscometer.

#### Monomer synthesis

*Preparation of 5-(hexafluoro-2-hydroxy-2-propyl)-1,1-dimethyl-3,3-bis(trifluoromethyl)-2-oxa-1-silaindan (1).* Following the procedure of Martin and Perozzi,<sup>8</sup> 1,3-HFAB (5.0 g, 12 mmol dissolved in 5 ml THF) was added dropwise to a stirred solution (0°C) of *n*-butyllithium (19 ml of 2.5 M hexane solution, 73 mmol) containing TMEDA (1.1 ml, 7.3 mmol). The mixture was allowed to warm and was stirred for 18 h at room temperature. Deuteration of a 1 ml aliquot indicated 80% conversion to 4-deutero-1,3-bis(hexafluoro-2-hydroxy-2-propyl)benzene.  $^1\text{H}$  n.m.r.,  $\text{CDCl}_3$ ,  $\delta$ , ppm: 8.14 (s, 1H); 7.83–7.81 (d, 1H); 7.54–7.53 (d, 1H).

The solution of lithiated 1,3-HFAB was cooled (0°C), and dichlorodimethylsilane (15.0 ml, 0.12 mol) was rapidly added to it. After the mixture had been stirred at room temperature for 12 h, solvents and excess

dichlorodimethylsilane were removed *in vacuo* and the oily brown residue was hydrolysed by stirring (48 h) in 50% aqueous ethanol to which a small amount of NaOH had been added (pH = 10–12). After hydrolysis was complete, the solution was neutralized and extracted with ether to give (after drying and removal of ether) crude 1, which was washed with cold hexane and then sublimed (80°C at 0.2 torr) to give 3.1 g (59%) of 1 (m.p. = 152–153°C). Analysis calculated for  $\text{C}_{14}\text{H}_{10}\text{F}_{12}\text{O}_2\text{Si}$ : C, 36.05, H, 2.15; found: c, 36.20, H, 2.14.  $^1\text{H}$  n.m.r. ( $\text{CDCl}_3$ ,  $\delta$ , ppm): 8.03 (s, 1H); 7.90–7.88 (d, 1H); 7.76–7.74 (d, 1H); 3.36 (s broad, 1H); 0.52 (s, 6H).

*Preparation of acrylate monomers derived from compound 1.* A three-neck, round-bottom flask was charged with 5.49 g (40.9 mmol) of compound 1, 1.8 ml (12.7 mmol) of triethylamine, and 25 ml of tetrahydrofuran. The mixture was cooled to 0°C, and a solution of 12.7 mmol of either acryloyl chloride or methacryloyl chloride, dissolved in tetrahydrofuran (10 ml), was added dropwise to the reaction flask. The reaction was warmed to room temperature and stirred overnight, it was then poured into water (200 ml), and the acrylate monomer was isolated by ether extraction. The crude monomer, which was recovered by removing the ether under reduced pressure, was recrystallized from methanol. The yield was 4.0 g (65%) for the acrylate monomer, 2 (m.p. 54–55°C), and 4.4 g (70%) for the methacrylate monomer 3 (m.p. 91–92°C). Analysis calculated for  $\text{C}_{17}\text{H}_{12}\text{F}_{12}\text{O}_3\text{Si}$  (2): C, 39.23, H, 2.30; found: C, 39.63, H, 2.25. Analysis calculated for  $\text{C}_{18}\text{H}_{14}\text{F}_{12}\text{O}_3\text{Si}$  (3): C, 40.45, H, 2.62; found: C, 40.21, H, 2.57.

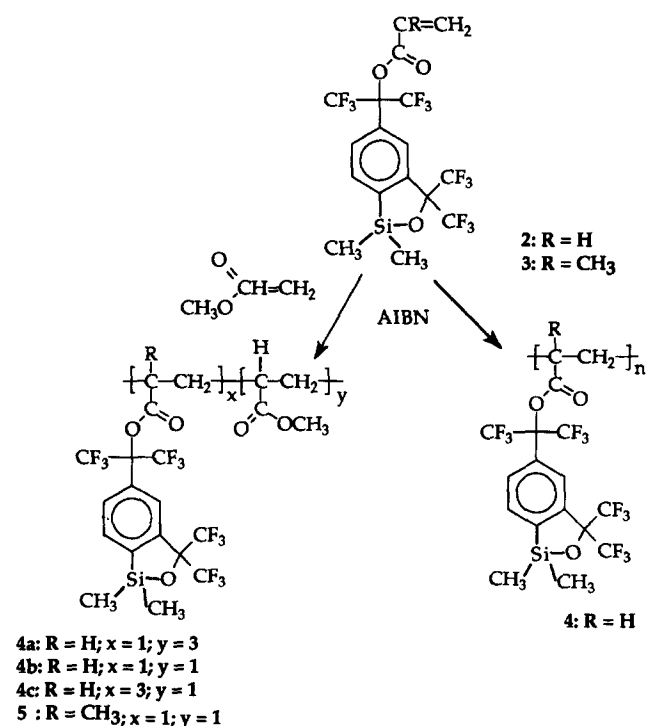
#### Polymer syntheses

Homopolymerizations of monomers 2 and 3 and copolymerizations with methyl acrylate (MA) were effected by bulk free radical polymerization using AIBN as the free radical initiator. A constant initiator-to-monomer ratio, about 1/50, was taken for all polymerizations.

In a typical experiment, a mixture of monomer **2** (0.9282 g, 1.785 mmol) and AIBN (0.006 g, 0.0365 mmol) was placed in a sealed tube under nitrogen, and the tube placed in an oil bath where the temperature was maintained at 80°C. A transparent colourless hard polymer was obtained after 12 h. The polymer was dissolved in toluene, precipitated into methanol, filtered and vacuum-dried overnight.

## RESULTS AND DISCUSSION

Perozzi and Martin observed that hexafluoro-2-hydroxy-2-propylbenzene is readily converted to lithium hexafluoro-2-(*o*-lithiophenyl)-2-propoxide which reacts with halosilanes to give a variety of derivatives<sup>8</sup>. We have



Scheme 1

found that 1,3-HFAB also reacts with *n*-butyllithium under similar conditions to form dilithium 4-lithio-1,3-bis(hexafluoro-2-oxido-2-propyl) benzene in about 80% conversion when the reaction is conducted in a mixture of THF and hexane. This trilitiated species can be easily converted to silylated derivatives by reaction with halosilanes. Compound **1** (equation (2)), which serves as a starting material for the monomer syntheses, is obtained in about 60% yield when the trilitiated 1,3-HFAB is allowed to react with dimethyldichlorosilane. Conversion of **1** to its acrylate (**2**) and methacrylate (**3**) esters is accomplished by standard procedures, in 65–70% yield. Polymerizations were conducted in bulk using AIBN as initiator (Scheme 1). The polymers, all of which were reprecipitated from toluene into methanol, are soluble in common organic solvents and form brittle water-clear transparent films from THF. Unfortunately, although the films obtained were suitable for measuring water contact angles, they were not sufficiently robust for gas diffusion measurements. Computer modelling<sup>9</sup> suggests that these silicon-containing polyacrylates should have considerably greater permeability than polymethylacrylate, which was selected as a reference material. This prediction is not unexpected; polysiloxane-based materials have long been known to be quite permeable to oxygen<sup>10</sup>.

Inherent viscosity values for the new polyacrylates range from 0.20 dl g<sup>-1</sup> for homopolymethacrylate **4** to 0.33 dl g<sup>-1</sup> for copolymer **4c** containing 32% monomer **2** and 68% MA (Table 1). Corresponding molecular weights range from 1.7 × 10<sup>4</sup> for **4** to 4.1 × 10<sup>4</sup> for **4c**. As the mole percent of monomer **2** is increased in the copolyacrylate series, both the molecular weight and inherent viscosity decrease (**4a–c** in Table 1). With the methacrylate monomer, **3**, only oligomers were obtained in an attempted synthesis of the homopolymer, but a copolymer, **5**, of molecular weight about 3.2 × 10<sup>4</sup> was obtained with methyl acrylate. Problems with polymerization of bulky acrylate monomers are commonly observed<sup>11,12</sup>.

In a previous report<sup>13</sup>, we observed that both hexafluoro-2-(4-fluorophenyl)-2-propylacrylate and methacrylate also form low molecular weight homopolymers,

Table 1 Properties of new polymers

Polymer	Mol% of <b>2</b> or <b>3</b>	Mol% methylacrylate	Elemental analyses (Obs. (Calc.))	$[\eta]^d$ (dl g <sup>-1</sup> )	Molecular weight <sup>c</sup> (×10 <sup>4</sup> )	T.g.a. <sup>f</sup> N <sub>2</sub> T <sub>g</sub> (°C)	D.s.c., N <sub>2</sub> T <sub>g</sub> (°C)	Water contact angle <sup>g</sup>
<b>4</b>	100 ( <b>2</b> )	–	–	0.20	1.7	386	67	106°
<b>4a</b>	75 ( <b>2</b> )	25	40.21 (40.09) %C 2.59 (2.55) %H	0.21	2.5	374	110	102°
<b>4b</b>	65 ( <b>2</b> )	35	40.44 (41.58 <sup>a</sup> ) %C 2.57 (2.97) %H <sup>a</sup>	0.25	3.4	371	78	99°
<b>4c</b>	32 ( <b>2</b> )	68	43.50 (44.43 <sup>b</sup> ) %C 3.52 (3.68) %H <sup>b</sup>	0.33	4.1	368	75	97°
<b>5</b>	75 ( <b>3</b> )	25	41.27 (42.58 <sup>c</sup> ) %C 2.74 (3.23) %H <sup>c</sup>	0.23	3.2	158	92	98°

<sup>a</sup> Calculated value for 50 mol% **2**/50 mol% methylacrylate in monomer feed; observed value indicates reported 65/35 mol% ratio in polymer obtained

<sup>b</sup> Calculated value for 25 mol% **2** in feed; observed value indicates 32/68 mol% in polymer obtained

<sup>c</sup> Calculated value for 50 mol% **3** in feed; observed value indicates 75/25 mol% ratio in polymer obtained

<sup>d</sup> Measured at 25°C in THF at a concentration of 2.5 g/l<sup>-1</sup>

<sup>e</sup> By g.p.c.

<sup>f</sup> 10% weight loss

<sup>g</sup> Average of 10 measurements

but much higher molecular weight copolymers with less sterically demanding hydroxyethyl or hydroxypropyl methacrylate. Similar behaviour was observed for the closely related monomer, hexafluoro-2-[3-(hexafluoro-2-methoxy-2-propyl)phenyl]-2-propyl acrylate and its methyl acrylate copolymers<sup>7</sup>. The attachment of the bulky hexafluoro-2-propoxy group directly to the acrylate monomer probably makes the incorporation of the monomer into the growing polymer chain sterically difficult, thus preventing the molecular weight of the polymer from increasing. Minimized computer-simulated structures for monomer **2** and polymers **4** and **4b** indicate rather severe steric crowding in the polymers.

The acrylate polymers (*Table 1*) containing monomer **2** show typical thermal stability for compounds of this type, with the homopolymer **4** being stable to 386°C (10% weight loss). The copolymers decrease slightly in thermal stability as the mole percent of the silicon- and fluorine-containing monomer, **2**, is decreased. The methacrylate polymer, **5**, is expected for polymethacrylates, much less stable thermally, decomposing at 158°C. All polymers decompose with minimum char yield. The  $T_g$ s for the polymers range from 67°C for the homopolymer **4** to 100°C for **4a**.

The contact angle between deionized water and each polymer surface was determined for the polyacrylates and is also listed in *Table 1*. The new polyacrylates are very hydrophobic. The water contact angle for **4** is 106° while polymers **4a–c** and **5** have water contact angles ranging from 97° to 103°. Maximum fluorine content is necessary to increase the contact angle to the maximum amount; however, even polymer **4c** with only 32 mol% of **2** is quite hydrophobic, with a water contact angle of 97°. Teflon, for comparison, has a water contact angle of 108°<sup>14</sup>. It has been suggested, through an e.s.c.a. study of poly(fluoroalkyl methacrylates), that these materials orient at the interface of a coated surface so that the backbone aligns with the surface and the fluorocarbon tails project into the air so as to minimize the interfacial energy<sup>15</sup>.

## CONCLUSIONS

Several new polymers derived from novel silicon- and

fluorine-containing monomers have been prepared by bulk free radical polymerization. The polymers have inherent viscosities ranging from 0.20 to 0.33 dl g<sup>-1</sup>, indicating rather low molecular weight; however, clear, colourless but very brittle films can be cast from THF. Thermal stabilities of the polyacrylate series are greater than that of polymethacrylate. All polymers are highly hydrophobic.

## ACKNOWLEDGEMENTS

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