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Synthesis and characterization of new fluorinated polyacrylates: 2*

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A series of new fluorinated acrylate polymers and copolymers (with methyl acrylate and methyl methacrylate) has been prepared starting from 1,3-bis(hexafluoro-2-hydroxy-2-propyl)benzene (1,3-HFAB). 1,3-HFAB was first reacted with dimethylsulfate in the presence of aqueous sodium hydroxide to yield 1-(hexafluoro-2-hydroxy-2-propyl)-3-(hexafluoro-2-methoxy-2-propyl)benzene which was reacted with acryloyl or methacryloyl chloride to give the corresponding fluorinated acrylate or methacrylate monomers. The polymers were obtained by bulk or solution free radical polymerization techniques with α,α'-azobisisobutyronitrile as initiator. The polymers had viscosities ranging from 0.21–0.41 dl g^{-1}, and the polyacrylates formed brittle films by solution casting. Thermogravimetric analysis showed that they had thermal stability up to 391°C in nitrogen and glass transition temperatures from 50 to 104°C. Copyright © 1996 Elsevier Science Ltd.

(Keywords: polyacrylates; fluoro polymers; polymethacrylates)

Introduction

Polymers prepared from acrylates and methacrylates have been long recognized for their optical clarity and stability upon aging under severe conditions[1]. Polyacrylates, whether linear or cross-linked, are excellent adhesives[2] and are easily fabricated into many different components and shapes.

Fluorocarbons on the other hand, have a much broader resistance to physical and chemical attack than acrylate polymers, but lack some of their advantages. This suggests that acrylates can be enhanced by the introduction of substantial amounts of fluorine, provided such an addition does not compromise their characteristic properties. Fluorocarbons also possess a range of unusual surface chemical properties which increase the versatility of polyacrylates when incorporated into the structure.

Griffith and co-workers at the Naval Research Laboratories have done extensive work in this area. Several hydrophobic polyacrylates (derived from hexafluoro-2-alkoxy-2-propyl-substituted arenes) having water contact angles of 90–91° have been prepared and characterized[3–5]. Because these fluorine-containing polymers have low critical surface energies and water absorption they have found application as coating materials in wet environments. Hexafluoro-2-phenyl-2-propoxy-containing polyacrylates have also been suggested for medical application, such as dental materials and artificial joints[6].

Increasing attention is being paid to monomers and polymers containing hexafluoroisopropylidene (6F or HFIP) groups which show promise as film formers, gas separation membranes, coatings, seals, and many other high performance applications[7]. Frequently, the inclusion of 6F groups into the polymer structure will increase the thermal stability, flame retardancy, oxidation resistance, transparency and environmental stability, while there is often a decrease in colour, crystallinity, surface energy and water absorption[8].

It is the objective of this research effort to continue the synthesis and characterization of new homo- and copolyacrylates derived from hexafluoro-2-alkoxy-2-propyl substituted arenes. To this end we report a series of homo- and co-polyacrylates and methacrylates derived from commercially available 1,3-bis(hexafluoro-2-hydroxy-2-propyl)benzene (1,3-HFAB).

Experimental

Materials. The 1,3-HFAB was obtained from Central Glass Company, Japan, and was distilled under argon prior to use. Dimethylsulfate, acryloyl and methacryloyl chlorides, supplied by Aldrich Chemical Company, USA, were used as received. The α,α'-azobisisobutyronitrile (AIBN) obtained from Kodak Laboratory Chemicals, USA, was recrystallized twice from a mixture of nine parts of methanol and one part of chloroform and then dried *in vacuo*. The methyl acrylate (MA) and methyl methacrylate (MMA) were supplied by Aldrich Chemical Company, USA, and were distilled prior to use. All other solvents and reagents used were commercial grade or reagent grade and were purified according to standard techniques[9].

Measurements. I.r. spectra were obtained on a Perkin–Elmer 1600 FT-IR spectrometer, using KBr

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pellets and films. ^1H n.m.r. spectra were obtained on an IBM NR-80 spectrometer, using deuterated chloroform as solvent. Elemental analyses were performed by Desert Analytics (Tucson, AZ, USA). Thermogravimetric analyses were performed on a DuPont 9900 Thermal Analyzer at Texas Research Institute (TRI) (Austin, TX, USA), and differential scanning calorimetry (d.s.c.) was done by either a Dupont 9900 thermal analyser, at TRI, or a Seiko Instruments, Inc. instrument. Contact angles were measured at 25°C on a Tantec model CAM-MICRO. Solution viscosities were determined at a concentration of $0.25\,g\,dl^{-1}$ in THF at 25°C using a 50 Cannon–Fenske viscometer.

Monomer syntheses. 1-(Hexafluoro-2-hydroxy-2-propyl)-3-(hexafluoro-2-methoxy-2-propyl)benzene (**1**). In a typical preparation, dimethylsulfate (8.12 g, 64.4 mmol) was added dropwise to a boiling solution of 1,3-HFAB (20.0 g, 48.8 mmol) in 15 ml of 3.5 M KOH. The mixture was heated at reflux for 14 h. The mixture was cooled; $NaHCO_3$ (5.4 g) was added, and the reaction mixture was again boiled for 0.5 h. After being cooled, the mixture was extracted with ethyl ether. The ether extract was dried over $MgSO_4$ and evaporated to yield **1** which was washed with cold hexane (−78°C) and dried *in vacuo* for 4 h to give (17 g, 82%) monomethyl ether **1** (m.p. 55°C). Analyses: calculated for $C_{13}H_8F_{12}O_2$: C, 36.80; H, 1.90; found: C, 36.49; H, 1.70. I.r. (KBr, cm^{-1}): 3309, 1271, 1159. ^1H n.m.r. ($CDCl_3$, δ): 7.5–8.0 (m, 4H, aromatic); 3.3 (s, 1H, OH); 3.5 (s, 3H, OCH_3).

Hexafluoro-2-[3-(hexafluoro-2-methoxy-2-propyl)-phenyl]-2-propyl acrylate (**2**). In a typical preparation acryloyl chloride (1.03 g, 12.7 mmol) in 10 ml of dry THF was added dropwise to a solution of **1** (5.0 g, 11.8 mmol) and triethylamine (1.8 ml, 13 mmol) in 25 ml of dry THF at 0°C. After the slow addition (1 h) was completed, the reaction mixture was warmed to room temperature and allowed to stir overnight. It was then added to 200 ml of water, extracted into ethyl ether, washed several times with water and dried over $MgSO_4$. Compound **2** was obtained by evaporating the ether *in vacuo* followed by recrystallization from methanol to yield 4.0 g (70%) of pure **2** (m.p. 42°C). Analyses: calculated for $C_{16}H_{10}F_{12}O_3$: C, 40.17; H 2.09; found: C, 40.10; H, 2.04. I.r. (KBr, cm^{-1}): 2994, 1769, 1633, 1250, 1157. ^1H n.m.r. ($CDCl_3$, δ): 7.5–8.0 (m, 4H, aromatic); 6.0–6.5 (m, 2H, $C{=}CH_2$); 6.5–7.0 (s, 1H, HC=C); 3.4 (s, 3H, OCH_3).

Hexafluoro-2-[3-(hexafluoro-2-methoxy-2-propyl)-phenyl]-2-propyl methacrylate (**3**). A procedure similar to that described above was used, except 1.23 ml (12.7 mmol) of methacryloyl chloride was used in place of acryloyl chloride to yield 3.77 g (65%) of **3** as a white solid (m.p. 51°C). Analyses: calculated for $C_{17}H_{12}F_{12}O_3$: C, 41.46; H, 2.43; found: C, 41.66; H, 2.41. I.r. (KBr, cm^{-1}): 2992, 1759, 1643, 1245, 1150. ^1H n.m.r. ($CDCl_3$, δ): 7.5–8.0 (m, 4H, aromatic); 5.7–6.5 (2s, 2H, $C{=}CH_2$); 3.4 (s, 3H, OCH_3); 2.0 (s, 3H, $C{=}CCH_3$).

General polymer synthesis. Homopolymerizations of monomers **2** and **3** and copolymerizations of **2** and **3** with MA and MMA were effected by solution and bulk free radical polymerization using AIBN as a radical initiator. A constant initiator-to-monomer ratio was taken for all of these polymerizations, which was about 1 : 50.

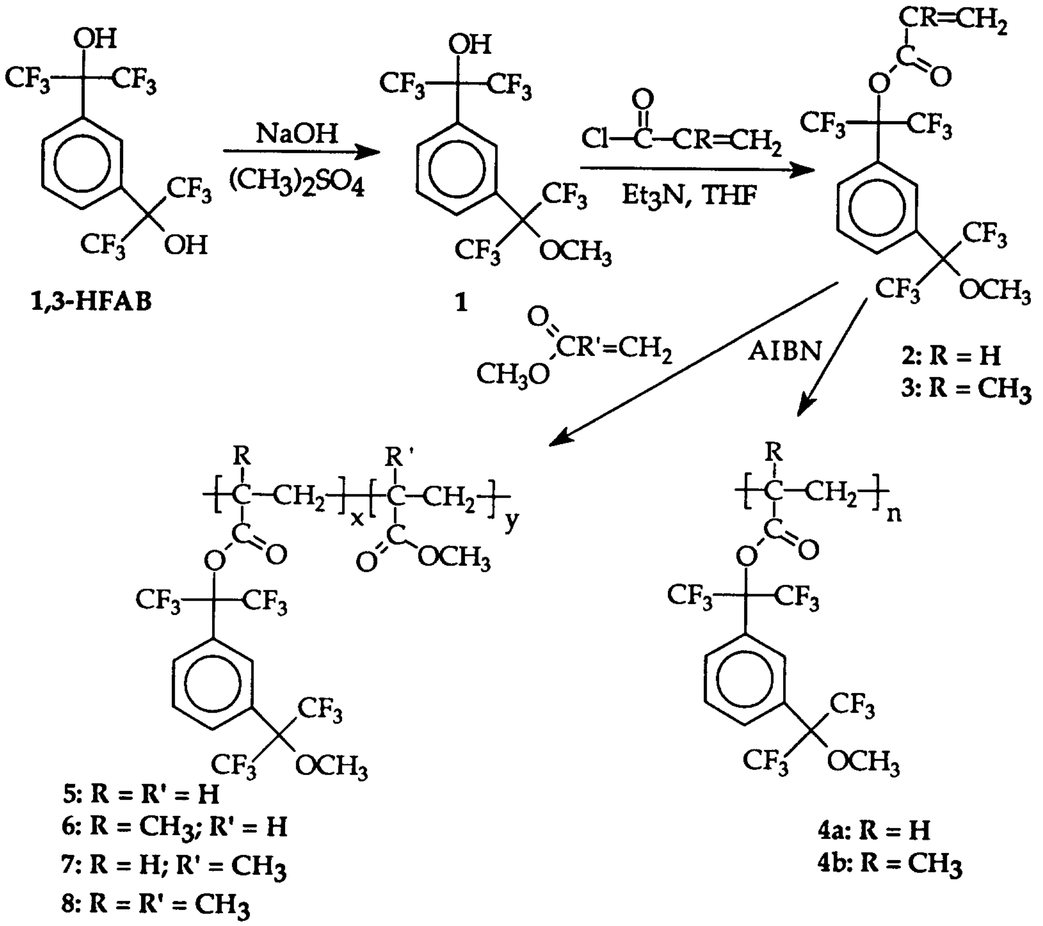
Solution polymerization. In a typical reaction, monomer **2** (1.1376 g, 2.38 mmol) and AIBN (0.008 g, 0.049 mmol) dissolved in toluene (1 ml) were placed in a capped tube under argon. The polymerization tube was kept for 36 h at 55°C, then for a further 3 h at 90°C. The solution was then cooled to room temperature, diluted with additional toluene, and poured into methanol. The white precipitate was filtered and vacuum dried overnight to yield the fluoroacrylate polymer as a white powder.

Bulk polymerization. In a typical experiment, a mixture of monomer **3** (0.8782 g, 3.57 mmol) and AIBN (0.006 g, 0.073 mmol) was placed in a sealed tube under nitrogen which was placed in an oil bath whose 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, and filtered and vacuum dried overnight.

Results and discussion

The monomethyl ether, **1**, was prepared in 82% yield as a white crystalline solid by the reaction of commercially available 1,3-HFAB as shown in *Scheme 1*. The mass spectrum of **1** is in excellent agreement with the structure as are the i.r. and ^1H n.m.r. spectra. Compound **1** was converted to the acrylate (**2**) or methacrylate (**3**) monomer in about 70% yield by reaction with acrylic or methacrylic acid chlorides, respectively, in the presence of triethylamine (*Scheme 1*). These monomers were satisfactorily characterized by i.r., ^1H n.m.r. and elemental analyses. I.r. spectra of these monomers show strong C=O absorption bands at 1769–1759 cm^{-1}, C=C stretching vibrations at 1643–1633 cm^{-1} and intense absorption bands at 1278–1275 cm^{-1} arising from C–F stretching modes.

Homo- and copolymerizations, with methyl acrylate or methyl methacrylate, of these fluoroacrylate monomers were effected by both solution and bulk radical polymerizations (*Scheme 1*). AIBN was used as the initiator because the initiation by it can be readily accomplished under mild conditions (55°C)[10]. Bulk polymerizations were conducted for 12 h at 80°C. Polyacrylates were also successfully prepared in solution (primary conversions were achieved at 55°C, final polymerizations were effected under more forcing conditions (90°C) to achieve the higher viscosities of the polymers). In both methods, yields of the polymers were between 80 and 90%. All polymers are soluble in common organic solvents, and the polyacrylates form water clear transparent films that are brittle. *Table 1* lists data for the polyacrylate series. Inherent viscosity values for this series range from $0.29\,dl\,g^{-1}$ for the homopolymer **4a** to $0.46\,dl\,g^{-1}$ for the copolymer **5c** having the composition of 40 mol% of monomer **2** and 60 mol% of methyl acrylate. As the mol% of monomer **2** is increased in the copolymer series, the inherent viscosity decreases (**5a** and **b** in *Table 1*) indicating lower molecular weights as the proportion of the hexafluoro- 2-[3-(hexafluoro-2-methoxy-2-propyl)phenyl]-2-propyl substituted acrylate



Scheme 1

moiety is incorporated into the polymer. In our previous report[11], both hexafluoro-2-(4-fluorophenyl)-2-propyl acrylate and methacrylate have also been observed to form low molecular weight homopolymers, but much higher molecular weight copolymers with hydroxyethyl or hydroxypropyl methacrylate. This may be due to the attachment of the bulky hexafluoro-2-propoxy group directly to the acrylate monomer which makes the incorporation of the monomer into the growing polymer chain sterically difficult, thus preventing the molecular weight of the polymer from increasing. Problems with polymerization of bulky acrylate monomers have been observed by others[12].

The contact angle between deionized water and each polymer surface was determined for the polyacrylates and is listed in *Table 1*. The new polyacrylates are very hydrophobic. The water contact angle for **4a** is 106° while polymers **5a–c** all have water contact angles of about 100°. Evidently maximum fluorine content is necessary to increase the contact angle to the maximum amount. Teflon, for comparison, has a water contact angle of 108°[13]. It has been suggested through an e.s.c.a.

Table 1 Properties of polyacrylates

Polymer	Mol% **2**	Mol% methyl acrylate	Elemental analyses obs. (calc.)	$[\eta]^a$ dl g^{-1} bulk/sol.	T.g.a.^{b} (N_2 °C)	T_g^{c} (°C)	Water contact angles^d
4a	100	—	—	0.32/0.29	391	67	106°
5a	75	25	40.74(41.05) %C 2.13(2.37) %H	0.33/0.31	398	79	100°
5b	50	50	42.26(42.55) %C 2.33(2.84) %H	0.39/0.36	391	78	103°
5c	40	60	43.64(45.65^e) %C 3.00(3.80^e) %H	0.46/0.41	391	75	98°

[a] Measured at 25°C in THF at a concentration of 2.5 g l^{-1}
[b] 10% weight loss
[c] From d.s.c. thermograms measured in N_2
[d] ±2°
[e] Calculated values for 25 mol% **2**/75 mol% methyl acrylate in monomer feed; observed value indicates reported 40/60 mol% ratio in polymer obtained

Table 2 Properties of polymethacrylates

Polymer	Mol% 2 or 3	Mol% methyl acrylate	Mol% methyl methacrylate	Elemental analyses obs. (calc.)	$[\eta]^a$ dl g^{-1} bulk/sol.	T.g.a.^{b} (N_2 °C)	T_g^{c} (°C)
4b	100 (3)	—	—	—	0.26/0.21	371	50
6	50 (3)	50	—	43.12(34.60) %C 2.76(3.11) %H	0.41/0.38	356	76
7	50 (2)	—	50	42.63(43.60) %C 2.69(3.11) %H	0.32/0.27	402	80
8	50 (3)	—	50	44.29(44.60) %C 3.19(3.38) %H	0.33/0.29	263	104

[a] Measured at 25°C in THF at a concentration of 2.5 g l^{-1}
[b] 10% weight loss
[c] From d.s.c. thermograms measured in N_2

study of poly(fluoroalkyl methacrylates) that materials such as these 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[14]. Similar water contact angles have been observed by Griffith[3] for the closely related poly{hexafluoro-2-[3,5-bis(hexafluoro-2-methoxy-2-propyl)phenyl]-2-propyl acrylate}.

Four methacrylate polymers containing the pendent hexafluoro-2-[3-(hexafluoro-2-methoxy-2-propyl)phenyl]-2-propyl group (**4b** and **6–8**) were also prepared (*Table 2*). Although the inherent viscosity data for these polymers are similar to the results obtained for the similar polyacrylates, this series of polymers does not form films.

Thermal stabilities of these polyacrylates, although not data critical to their use, were determined by t.g.a. (temperature of 10% weight loss under nitrogen). These values, as expected, are not particularly high (up to 400°C), even in an inert atmosphere. For the acrylate copolymer series (**4a**, **5a–c**), the increased inclusion of methyl acrylate had no effect on thermal decomposition (all around 390–400°C). However, the methacrylate copolymers did respond to composition in terms of stability temperature. The inclusion of methyl acrylate with the methacrylate monomer **3** decreased the stability somewhat (ca. 15°C). Then it was observed that methyl methacrylate with the monomer **3** dropped the stability by 108°C. Thus, either comonomer lowers the stability. However, the acrylate (**2**) polymer is not affected thermally by methyl methacrylate inclusion. The authors have no resolution of this conundrum: why is the fluorinated methacrylate affected but not the acrylate? Glass transition temperatures were measured by d.s.c. for the polyacrylates and methacrylates and are in the range of 60–79°C and 50–104°C, respectively.

Conclusions

New acrylate monomers containing the hexafluoro-2-phenyl-2-propoxy group in the pendant group have been synthesized from hexafluoro-2-[3-(hexafluoro-2-methoxy-2-propyl)phenyl]-2-propanol and their homo- and copolymerizations with non-fluorinated acrylic comonomers were performed by bulk and solution free-radical methods. Clear, colourless, brittle films of the polyacrylates can be cast from solution. Inherent viscosities of these polymers ranged from 0.21 to 0.46 dl g^{-1}. A large water contact angle was observed for the polyacrylate films, suggesting a preferential orientation of trifluoromethyl groups on the surface of the polymer film. Thermal stabilities of the new polymers ranged from 263 to 402°C. The weight loss of these polymers occurred in a single step and they decomposed completely with a negligible quantity of char yield.

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