Polyacrylates containing hexafluoroisopropoxy pendant functions

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A series of new polyacrylates was synthesized by incorporating the hexafluoroisopropoxy unit pendant to the backbone. The fluorinated monomers were synthesized by reacting 4-fluoro(2-hydroxyhexafluoroisopropyl)benzene with acrylic or methacrylic acid chlorides. The polymers were obtained by bulk, free-radical polymerization techniques using α,α′-azobisisobutyronitrile as initiator. The polymers had viscosities ranging from 0.15 to 1.41 dl g^{-1} and had good film-forming properties. Thermogravimetric analysis showed that they had thermal stability up to 370°C in N_2; glass transition temperatures were in the range 64 to 119°C.

(Keywords: 1,1,1,3,3,3-hexafluoroisopropylidene; 2-aryl hexafluoroisopropanol; polyacrylates; polyfluoroacrylate; hexafluoroisopropoxy; fluorination; synthesis)

Introduction

Polymers prepared from acrylates and methacrylates have been long recognized for their optical clarity and stability upon ageing under severe conditions[1]. These characteristics, coupled with their versatility and the relative ease with which these polymers can be tailored to specific applications, have made them prime candidates for numerous and diverse uses.

This paper reports the synthesis and characterization of some new fluorinated acrylate monomers and polymers. We anticipate that these polymers will be of interest for dental, biomedical and optical applications due to the low moisture uptake and expected surface properties[2].

Experimental

Materials. The 4-fluoro(2-hydroxyhexafluoroisopropyl)benzene (HFAF) was obtained from Tokyo Research Centre, Central Glass Company, Japan, and was distilled under argon prior to use. The acryloyl and methacryloyl chlorides, supplied by Aldrich Chemical Company, were used as received. The α,α′-azobisisobutyronitrile (AIBN), obtained from Kodak Laboratory Chemicals, was recrystallized twice from a mixture of nine parts of methanol and one part of chloroform and then dried *in vacuo*. The hydroxyethylmethacrylate (HE) and hydroxypropylmethacrylate (HP) were supplied by Aldrich Chemical Company and were purified (99.9% by gas chromatography) by the procedure described in the literature[3]. The solvents and reagents used were commercial grade or reagent grade and were purified according to standard techniques[4].

Characterization. I.r. spectra were obtained on a Perkin–Elmer 1600 FT-IR Spectrometer, using KBr pellets and films. ^1H nuclear magnetic resonance (n.m.r.) spectra were obtained on an IBM 80 MHz spectrometer, using deuterated dimethylsulfoxide or chloroform as a solvent. Elemental analyses were performed by Desert Analytics, Tucson, AZ, USA. Differential scanning calorimetry (d.s.c.) was performed on a DuPont 9900 Thermal Analyzer at Texas Research Institute, Austin, TX, USA, and thermogravimetric analyses were done by Shimadzu Scientific Instruments, Columbia, MD, USA. Solution viscosities were determined at a concentration of 0.25 g dl^{-1} in chloroform or dimethylformamide (DMF) at 26°C using a 100 or 50 Cannon–Fenske viscometer. The water absorption of the polymer was studied by drying a thin film to constant weight in a desiccator (24 h) and then placing it in deionized water at room temperature. At 1 day intervals the film was removed, wiped dry and weighed until a constant weight was again realized (2–4 days).

Monomer synthensis. 2-(4-Fluorophenyl)-2-hexafluoropropyl acrylate (FA). A dry, 250 ml, three-neck, round-bottom flask was charged with 10.49 g (0.040 mol) of distilled HFAF and 50 ml of freshly distilled tetrahydrofuran (THF). The flask was equipped with a constant-pressure addition funnel, stirring bar, and argon inlet and outlet tubes. To this mixture, 8.3 ml (0.060 mol) of triethylamine was added under a flow of argon. The solution of acryloyl chloride (18.96 g, 0.060 mol) in 20 ml of THF was poured into the addition funnel while the reaction mixture was stirred and cooled to 0°C in an ice–water bath. The acryloyl chloride solution was slowly dripped into the reaction flask over a 2-h period, during which time the colourless solution gradually turned light orange. After the addition was completed, the ice–water bath was removed and the reaction mixture was stirred overnight at room temperature. The reaction mixture was then poured into approximately 200 ml of distilled water to give an orange–yellow liquid, which was extracted with diethylether. The organic layer was collected, washed several times with warm water and dried over anhydrous $MgSO_4$. This solution was decanted from the desiccant and concentrated by reduced-pressure evaporation to yield (85%) crude monomer.

The monomer was purified by column chromatography using a mixture of hexane and dichloromethane (50/50

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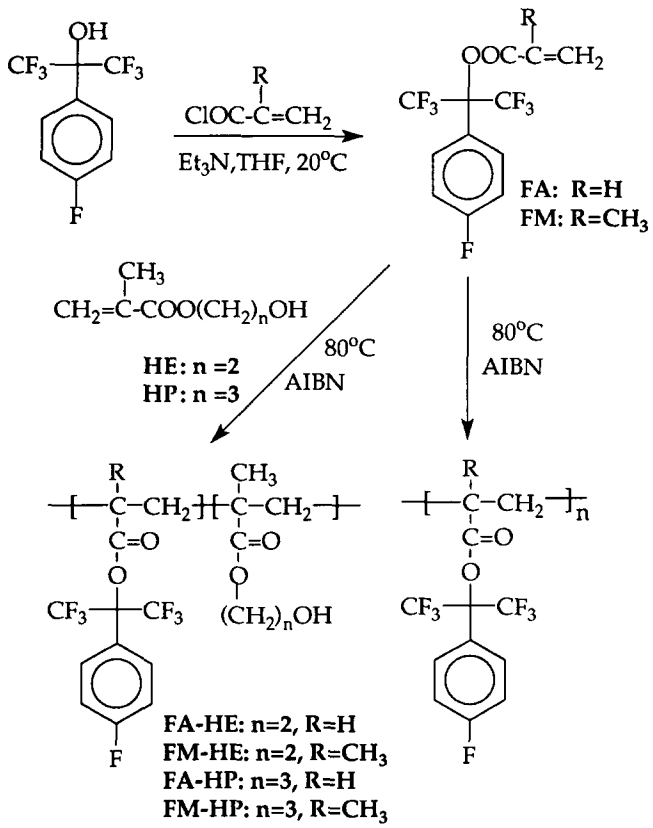

Scheme 1

by volume) as the elution solvent. After purification, the monomer was obtained as a colourless, clear liquid in 75% yield (9.48 g); b.p. 72–74°C (10^{-3} mmHg). Analysis calculated for $C_{12}H_7F_7O_2$: C, 45.56; H, 2.21; found: C, 45.42; H, 2.44. I.r. (KBr, cm^{-1}): 1762, 1633, 1246. ^1H n.m.r. ($CDCl_3$, δ): 6.30 (m, 3H, vinyl); 7.11 (m, 4H, aromatic).

2-(4-Fluorophenyl)-2-hexafluoropropyl methacrylate (FM). A similar procedure to that described above was performed, except that 5.85 g (0.060 mol) of methacryloyl chloride was used in place of acryloyl chloride to yield 10.56 g (80%) of FM as a clear, colourless liquid after column chromatography; b.p. 48–52°C (10^{-3} mmHg). Analysis calculated for $C_{13}H_9F_7O_2$: C, 47.27; H, 2.72; found: C, 47.02; H, 2.84. I.r. (KBr, cm^{-1}): 1755, 1641, 1216. ^1H n.m.r. ($CDCl_3$, δ): 2.0 (s, 3H, $-CH_3$); 5.5–6.5 (2s, 2H, $-CH_2$); 7.00–7.50 (m, 4H, aromatic).

General polymer synthesis. Scheme 1 illustrates the preparation of these polymers. The homo- and copolymerizations of these monomers with hydroxymethacrylates were effected by bulk, free-radical polymerization using AIBN as initiator at 80°C to yield fluoroacrylic polymers. The apparatus consisted of a 25 ml, three-neck, round-bottom flask equipped with a water condenser, stirring bar, and argon inlet and outlet tubes. The monomer was placed in the round-bottom flask and an inert atmosphere was maintained in the flask by a continuous flow of argon, which was bubbled through the monomer. The AIBN was added to the monomer in the reaction flask, and the apparatus was then heated in an oil bath maintained at 80°C. The monomer was converted to highly viscous polymer within about 20 min for FA homopolymer and about 5 h for FM homopolymer. Both reactions were then heated for an additional 60 min. The polymers were then dissolved in THF and precipitated into methanol. The white flakes of polymers were isolated by filtration and dried overnight in a vacuum oven at 50°C.

The same reaction procedure was used for the synthesis of different copolymers of FA and FM with HE and HP by varying the mole ratios of the monomers to 10, 30, 70 and 90%. A constant initiator-to-monomer ratio was taken for all of these polymerizations, which was about 1:520 for acrylates and 1:260 for methacrylates. These polymerizations were also conducted at 80°C, whereupon a highly viscous polymer was obtained in about 15 min for reactive monomers and about 4 h for less reactive systems (*Table 1*). The reaction was then continued for an additional 30 min. The polymers were dissolved in either DMF or THF, depending upon the solubility of the polymer, and precipitated into water or methanol. The white flakes were isolated by filtration and dried overnight *in vacuo* at 50°C.

Results and discussion

The acrylate and methacrylate monomers of HFAF (FA, FM) were readily synthesized according to *Scheme 1* in 75–80% yields as clear, colourless liquids. These monomers were satisfactorily characterized by i.r., ^1H n.m.r. and elemental analyses. The i.r. spectra of these monomers show strong C=O absorption bands at 1762–1755 cm^{-1}. The C=C stretching vibrations are found at 1633–1641 cm^{-1} and the monomers also exhibit intense absorption bands at 1246–1216 cm^{-1} arising from C–F stretches.

The acrylates, FA and FM, were homopolymerized with AIBN initiator in yields up to 65%. These polymers were soluble in common organic solvents and the inherent viscosities were 0.17–0.22 dl g^{-1}. The monomers FA and FM were also copolymerized with HE and HP using different monomer mole ratios. Designations of the copolymers, given in *Table 1*, refer to the mole per cent of each monomer in the feed. For

Table 1 Polymer characteristics

Polymers[a] (mole ratio)	Reaction time (min)	η_{inh} (dl g^{-1})	T_g (°C) by d.s.c.	T.g.a.[b] (°C) Air	T.g.a.[b] (°C) N_2	Water absorption (%)
FA	80	0.22[c]	85	360	370	0.0
FA-HE (9:1)	90	0.16[c]	64			–
FA-HE (7:3)	75	0.24[c]	85			0.6
FA-HE (1:1)	50	0.76[d]	85	260	320	–
FA-HE (3:7)	30	1.41[d]	78			–
FM	360	0.17[c]	119			–
FM-HE (9:1)	270	0.15[c]	101			–
FM-HE (7:3)	210	0.24[c]	80			5.3
FM-HE (1:1)	180	0.52[d]	74	250	295	–
FM-HE (3:7)	120	0.83[d]	–			31.0
FM-HE (1:9)	90	1.18[d]	–			–
FA-HP (1:1)	45	0.46[c]	65			1.3
FM-HP (1:1)	60	0.44[c]	83			2.7
MMA[e]	–	–	–			2.8

[a] FA, 2-(4-fluorophenyl)-2-hexafluoropropyl acrylate; FM, 2-(4-fluorophenyl)-2-hexafluoropropyl methacrylate; HE, hydroxyethylmethacrylate; HP, hydroxypropylmethacrylate
[b] Break in the major degradation curve
[c] In chloroform
[d] In dimethylformamide
[e] Commercial sample

example, FA–HE (9:1) signifies 90 mol% FA and 10 mol% HE. Similar designations apply to copolymers FM–HE, FA–HP and FM–HP.

Table 1 shows the inherent viscosities (η_{inh}) of the copolymers, which ranged from 0.15 to 1.41 dl g^{-1} when measured in DMF or chloroform at a concentration of 2.5 mg ml^{-1} at 26°C. The compositions of the copolymers were determined by ^1H n.m.r. spectroscopy, which shows that the copolymers contain the proper ratios of the monomers (equal to the monomer feed ratios), in agreement with elemental analyses.

The copolymers in which the mole per cent of HE was less than 50% were soluble in common organic solvents, such as chloroform, benzene and THF, while the polymers obtained with 50% or higher mole per cent ratio of HE were soluble only in DMF, dimethylacetamide and methanol. Clear, colourless but brittle films could be cast for each polymer from chloroform or DMF solutions.

Thermogravimetric analysis (t.g.a.) of these polymers showed that the homopolymers started decomposing at 370°C, while copolymers started decomposing at 320°C in N_2. The thermal stability in N_2/air and the glass transition temperatures (T_g) of these polymers are listed in *Table 1*. This shows that the T_g of the copolymers increased with increasing concentration of fluorinated monomer in the polymer. This is attributed to the introduction of more fluoroalkyl groups, providing a bulkier, less mobile backbone.

Moisture absorption studies were carried out using thin films of the homo- and copolymers. The films were desiccated with $CaCl_2$ before being submerged in deionized water at room temperature. The observed moisture absorptions are given in *Table 1*. The FA homopolymer does not absorb water; this is consistent with earlier work[2] reported for related polymers. Water absorption of the copolymers ranged from 0.6 to 31.0 wt%. The greater the proportion of HE units in the polymer repeat unit, the greater the moisture absorption of the copolymers.

Conclusions

New homopolymers and copolymers were obtained from 2-(4-fluorophenyl)-2-hexafluoropropyl acrylate/methacrylate monomers using a free-radical polymerization technique. Clear, colourless, brittle films were cast from solution. The glass transition temperatures and thermal stabilities of these polymers increased with fluorine content. Moisture absorption of the fluoroacrylic homopolymer is 0% whereas that of copolymers ranged from 0.6 to 31.0 wt%.

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