

## Synthesis of novel polymethacrylates bearing cyclic perfluoroalkyl groups

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Novel fluorinated methacrylic polymers and copolymers were prepared. Perfluoro(2-pyrrolidinopropionyl fluoride) and perfluoro(3-pyrrolidinopropionyl fluoride) were reduced to the corresponding 1,1-dihydroperfluoroalcohols, which were then reacted with methacryloyl chloride to give the methacrylates. The homopolymers and the copolymers with methyl methacrylate were obtained by a radical polymerization. The tough polymer films prepared by solution casting showed excellent water repellency with contact angles above 100°. © 1998 Elsevier Science Ltd. All rights reserved.

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### Introduction

Polymers with fluorocarbon chains have lower surface energy than those with hydrocarbon or silicone chains<sup>1</sup>, and therefore are used as bulk or an additive to give water and oil repellency to material surfaces. Polyacrylates and polymethacrylates having fluoroalkyl groups, which usually are polyfluorinated linear alkyl groups, are widely prepared because of their facile monomer synthesis and polymerization<sup>2–4</sup>, and used not only as repellents but also as optical and lithographic materials<sup>5–7</sup>. It is of interest to prepare novel fluorinated polyacrylates and polymethacrylates having cyclic perfluoroalkyl groups, because the bulky substituents in the polymers would affect physical properties of the polymers. Recently perfluoropolymers with a main chain containing cyclic structure were developed and now form a new class of fluoropolymers<sup>8,9</sup>.

We report upon the preparation and polymerization of novel methacrylates bearing the perfluoropyrrolidino group. Perfluoroacyl fluorides with a dialkylamino group are advantageously prepared by electrochemical fluorination because the nitrogen atom restricts cyclization of the molecules during the fluorination<sup>10</sup>. Thus perfluoroacyl fluorides with a cyclic amino group are a convenient source of fluorinated cyclic compounds with a reactive functional group.

### Experimental

Perfluoro(2-pyrrolidinopropionyl fluoride)<sup>11</sup> (0.150 mol) or perfluoro(3-pyrrolidinopropionyl fluoride)<sup>12</sup> was added dropwise to a mechanically stirred ethereal suspension (500 ml) of lithium aluminum hydride (0.090 mol) at 0°C under argon atmosphere. The mixture, stirred at 0°C for an additional 30 min., was acidified with conc. HCl. The ethereal solution was washed with water, aq. NaHCO<sub>3</sub>, and aq. NaCl, and dried over anhydrous MgSO<sub>4</sub>. The alcohol was obtained by evaporation of ether and purified by distillation.

2,3,3,3-Tetrafluoro-2-(octafluoropyrrolidino)propanol: 69% yield; b.p. 138–140°C; i.r. (neat): 3388 cm<sup>-1</sup> (O–H); <sup>1</sup>H n.m.r. (CDCl<sub>3</sub>): 4.00–4.53 ppm (m, 2H), 2.34 (t, 1H, OH,

$J = 7.3$  Hz); <sup>19</sup>F n.m.r. (CDCl<sub>3</sub>): –79.6 ppm (m, 3F), –85.4 (dm, 2F,  $J = 175$  Hz), –92.0 (dm, 2F,  $J = 175$ ), –131.6 (dm, 2F,  $J = 246$ ), –134.2 (dm, 2F,  $J = 246$ ), –158.8 (m, 1F); m.s.  $m/z$  (relative intensity): 326 (0.78) [M–F]<sup>+</sup>, 325 (1.7) [M–HF]<sup>+</sup>, 314 (3.8) [M–CH<sub>2</sub>OH]<sup>+</sup>, 306 (3.2) [M–HF<sub>2</sub>]<sup>+</sup>, 296 (4.4) [C<sub>6</sub>F<sub>11</sub>NH]<sup>+</sup>, 295 (43) [C<sub>6</sub>F<sub>11</sub>N]<sup>+</sup>, 228 (16) [C<sub>5</sub>F<sub>8</sub>NH<sub>2</sub>]<sup>+</sup>, 196 (53) [C<sub>4</sub>F<sub>7</sub>NH]<sup>+</sup>, 195 (42) [C<sub>4</sub>F<sub>7</sub>N]<sup>+</sup>, 176 (19) [C<sub>4</sub>F<sub>6</sub>N]<sup>+</sup>, 145 (13) [C<sub>3</sub>F<sub>5</sub>N]<sup>+</sup>, 131 (29) [C<sub>3</sub>F<sub>5</sub>]<sup>+</sup>, 119 (14) [C<sub>2</sub>F<sub>5</sub>]<sup>+</sup>, 114 (17) [C<sub>2</sub>F<sub>4</sub>N]<sup>+</sup>, 100 (42) [C<sub>2</sub>F<sub>4</sub>]<sup>+</sup>, 83 (26) [CF<sub>3</sub>N]<sup>+</sup>, 69 (100) [CF<sub>3</sub>]<sup>+</sup>.

2,2,3,3-Tetrafluoro-3-(octafluoropyrrolidino)propanol: 68% yield; b.p. 154–155°C; i.r. (neat): 3368 cm<sup>-1</sup> (O–H); <sup>1</sup>H n.m.r. (CDCl<sub>3</sub>): 4.08 ppm (tt, 2H,  $J_1 = 13.8$  Hz,  $J_2 = 1.2$ ), 2.72 (broad s, 1H, OH); <sup>19</sup>F n.m.r. (CDCl<sub>3</sub>): –90.7 ppm (m, 4F), –94.0 (m, 2F), –123.8 (m, 2F), –133.3 (s, 4F); m.s.  $m/z$  (relative intensity): 326 (0.16) [M–F]<sup>+</sup>, 306 (1.0) [M–HF<sub>2</sub>]<sup>+</sup>, 296 (1.8) [C<sub>6</sub>F<sub>11</sub>NH]<sup>+</sup>, 295 (13) [C<sub>6</sub>F<sub>11</sub>N]<sup>+</sup>, 264 (48) [M–CF<sub>2</sub>CH<sub>2</sub>OH]<sup>+</sup>, 214 (14) [C<sub>4</sub>F<sub>8</sub>N]<sup>+</sup>, 196 (37) [C<sub>4</sub>F<sub>7</sub>NH]<sup>+</sup>, 176 (18) [C<sub>4</sub>F<sub>6</sub>N]<sup>+</sup>, 131 (31) [C<sub>3</sub>F<sub>5</sub>]<sup>+</sup>, 119 (11) [C<sub>2</sub>F<sub>5</sub>]<sup>+</sup>, 114 (26) [C<sub>2</sub>F<sub>5</sub>N]<sup>+</sup>, 100 (100) [C<sub>2</sub>F<sub>4</sub>]<sup>+</sup>, 69 (85) [CF<sub>3</sub>]<sup>+</sup>, 64 (74) [CF<sub>2</sub>N]<sup>+</sup>.

The methacrylic monomers were synthesized as follows. Methacryloyl chloride (0.0478 mol) was added dropwise to an ethereal solution (75 ml) of 2,3,3,3-tetrafluoro-2-(octafluoropyrrolidino)propanol (0.0435 mol) or 2,2,3,3-tetrafluoro-3-(octafluoropyrrolidino)propanol, and an excess amount of triethylamine (0.0652 mol) at 0°C under argon atmosphere. The mixture was stirred at room temperature, washed with water, and concentrated by evaporation of ether. Distillation of the residue under reduced pressure over ferric chloride(III) afforded the methacrylates of **1** or **2** (see Figure 1).

2,3,3,3-Tetrafluoro-2-(octafluoropyrrolidino)propyl methacrylate (**1**): 77% yield; b.p. 37.5°C/2 Torr; i.r. (neat): 2981 cm<sup>-1</sup> (C–H), 1743 (C = O), 1640 (C = C); <sup>1</sup>H n.m.r. (CDCl<sub>3</sub>): 6.21 ppm (m, 1H), 5.70 (m, 1H), 4.85 (dd, 1H,  $J_1 = 14.3$  Hz,  $J_2 = 14.0$ ), 4.66 (dd, 1H,  $J_1 = 30.0$ ,  $J_2 = 14.0$ ), 1.97 (m, 3H); <sup>19</sup>F n.m.r. (CDCl<sub>3</sub>): –80.2 ppm (m, 3F), –84.9 (dm, 2F,  $J = 175$  Hz), –93.2 (dm, 2F,  $J = 175$ ), –131.3 (dm, 2F,  $J = 246$ ), –134.8 (dm, 2F,  $J = 246$ ), –157.07 (m, 1F).

2,2,3,3-Tetrafluoro-3-(octafluoropyrrolidino)propyl methacrylate (**2**): 89% yield; b.p. 46–47°C/2 Torr; i.r. (neat):

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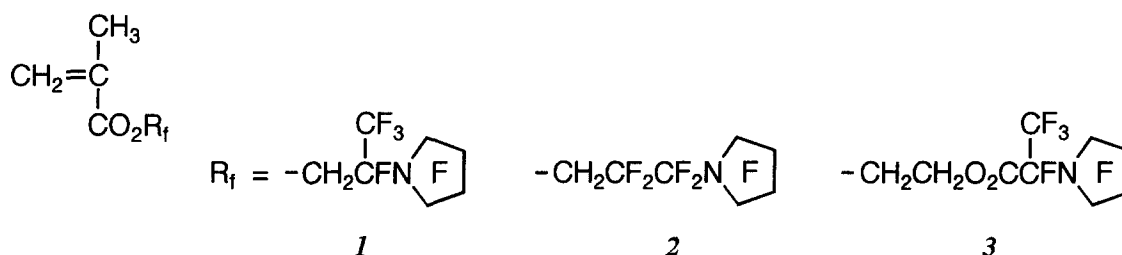


Figure 1 The monomer structures

Table 1 Homopolymerization of methacrylates bearing the perfluoropyrrolidino group<sup>a</sup>

Monomer (g)	Feed (g)	Hexanethiol (mol%)	Solvents (ml)	Polymerization time (h)	Yield (%)	Polymer			
						$\theta^b$ (°)	$\gamma_c^c$ (dyn cm <sup>-1</sup> )	$T_g$ (°C)	$T_d^d$ (°C)
1	1.00	—	THF 1.00	15	87	—	—	86	308
1	1.00	3.0	THF 0.50/F113 0.50	24	77	115	18.7	76	313
2	0.50	—	THF 0.50	24	91	118	18.6	57	268
2	0.50	3.0	THF 0.25/F113 0.25	24	86	—	—	47	337
3	0.50	—	THF 0.50	4	22	96	20.7	—	—

<sup>a</sup> *In vacuo* at 60°C with 0.5 mol% AIBN<sup>b</sup> Contact angles of water droplets to polymer films<sup>c</sup> Critical surface tensions of polymer films<sup>d</sup> 10% weight loss temperatures under nitrogen atmosphere

2970 cm<sup>-1</sup> (C–H), 1744 (C = O), 1646 (C = C); <sup>1</sup>H n.m.r. (CDCl<sub>3</sub>): 6.22 ppm (m, 1H), 5.70 (m, 1H), 4.66 (tt, 2H,  $J_1 = 12.9$  Hz,  $J_2 = 1.2$ ), 1.98 (m, 3H); <sup>19</sup>F n.m.r. (CDCl<sub>3</sub>): -90.7 ppm (m, 4F), -93.9 (m, 2F), -120.7 (m, 2F), -133.2 (s, 4F).

Similarly a slightly excess amount of perfluoro(2-pyrrolidinopropionyl fluoride) and an ethereal solution of 2-hydroxyethyl methacrylate and an excess amount of triethylamine afforded the ester of 3<sup>13,14</sup> (Figure 1).

2-[Perfluoro(2-pyrrolidinopropionyloxy)]ethyl methacrylate (3): 91% yield; b.p. 71°C/0.04 Torr; i.r. (neat): 2961 cm<sup>-1</sup> (C–H), 1787 (C = O), 1723 (C = O), 1637 (C = C); <sup>1</sup>H n.m.r. (CDCl<sub>3</sub>): 6.12 ppm (m, 1H), 5.62 (m, 1H), 4.73–4.57 (m, 2H), 4.46–4.43 (m, 2H), 1.94 (dd, 3H,  $J_1 = 1.6$  Hz,  $J_2 = 1.0$ ); <sup>19</sup>F n.m.r. (CDCl<sub>3</sub>): -75.7 ppm (m, 3F), -87.9 (dm, 2F,  $J = 172$  Hz), -93.2 (dm, 2F,  $J = 172$ ), -131.5 (dm, 2F,  $J = 247$ ), -135.9 (dm, 2F,  $J = 247$ ), -137.8 (m, 1F).

Infrared spectra were obtained with a Shimadzu FTIR-8600PC spectrophotometer. Mass spectra were taken with a Shimadzu QP-5000 instrument at 70 eV. <sup>1</sup>H n.m.r. (300.0 MHz) and <sup>19</sup>F n.m.r. (282.2 MHz) measurements were recorded on a Varian UNITY INOVA-300, the chemical shifts being defined as  $\delta$  values relative to TMS and CFCl<sub>3</sub>, respectively. Molecular weights of polymers were correlated to standard polystyrenes with a TOSOH HLC-802A gel permeation chromatograph using TOSOH GMH6 columns and tetrahydrofuran as the eluent. Glass transition and thermal decomposition temperatures of polymers were measured with Perkin-Elmer DSC7 differential scanning calorimeter and TGA7 thermogravimeter. Contact angles of water droplets to polymer film surfaces were measured with an Erma G-1 goniometer.

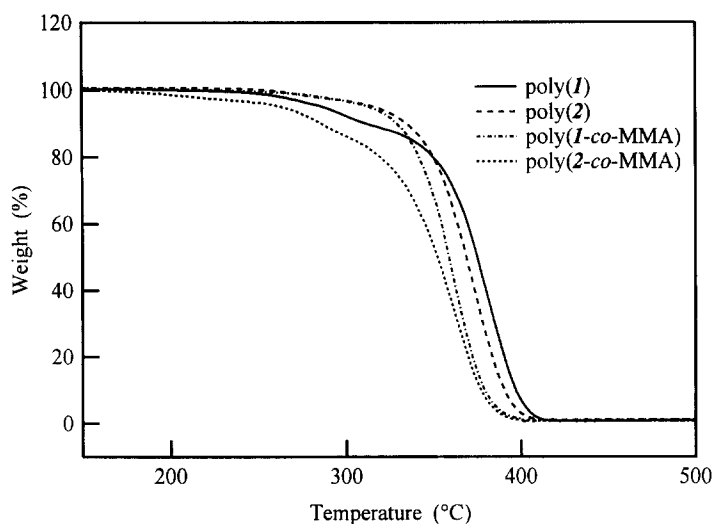
### Results and discussion

Radical polymerizations of the fluoroalkylated methacrylates (1, 2 and 3) were performed *in vacuo* in glass

ampules at 60°C with 2,2'-azobis(isobutyronitrile) (AIBN) in tetrahydrofuran (THF) and 1,1,2-trichlorotrifluoroethane (F113) in the presence or absence of hexanethiol as the chain transfer agent (Table 1). The polymerization systems became heterogeneous and gel-like owing to a solubility of formed homopolymers as polymerization proceeded. The polymers were precipitated in hexane and mostly purified by reprecipitation, while an insoluble polymer was purified by Soxhlet extraction using hexane.

Poly(2) was soluble in fluorinated solvents such as F113, hexafluorobenzene, and *p*-bis(trifluoromethyl)benzene, but insoluble in usual hydrocarbon-based solvents. Poly(1), prepared in the absence of the chain transfer agent was insoluble in all solvents tested including the fluorinated solvents in which poly(2) could dissolve, but the polymer soluble in the fluorinated solvents was obtained by using hexanethiol as the chain transfer agent, which would lower the molecular weight of the polymer. Poly(3) was soluble in F113, perfluorohexane, hexafluorobenzene, trifluoromethylbenzene and *p*-bis(trifluoromethyl)benzene, but only swellable in acetone, tetrahydrofuran, chloroform, and toluene.

Hexafluorobenzene solutions of the polymers were cast on glass surfaces, evaporation of the solvent giving films. All the films are highly water repellent with the markedly large contact angles. Poly(1) and poly(2) have similar contact angles of water and critical surface tensions despite their structural difference. In general the trifluoromethyl group gives the lowest surface tension to material surfaces among all surface chemical constitutions<sup>15</sup>. The trifluoromethyl groups in poly(1), however, would not affect significantly the surface tension of the polymer because of the large contribution of the vicinal bulky perfluoropyrrolidino groups. The water repellency of poly(1) and poly(2) is comparable to that of analogous polymers bearing linear polyfluoroalkyl groups—poly(1H,1H-pentadecafluorooctyl acrylate) and poly(1H,1H,2H,2H-heptadecafluorodecyl methacrylate) have contact angles of water equal to 110°



**Figure 2** Thermogravimetric analysis of polymethacrylates bearing the perfluoropyrrolidino groups: poly(*1*) and poly(*2*) prepared with hexanethiol as the chain transfer agent; poly(*1-co-MMA*) and poly(*2-co-MMA*) containing 5.6% of *1* and 8.8% of *2* units, respectively

**Table 2** Copolymerization of MMA and methacrylates bearing the perfluoropyrrolidino group (R<sub>f</sub>MA)<sup>a</sup>

Feed		Yield (%)	Copolymer					
R <sub>f</sub> MA (mmol)	MMA (mmol)		$\bar{M}_n^b$ ( $\bar{M}_w/\bar{M}_n$ )	R <sub>f</sub> MA unit <sup>c</sup> (mol%)	$\theta^d$ (°)	$T_g$ (°C)	$T_d^e$ (°C)	
<i>1</i>	0.10	9.93	46	232 000 (2.17)	0.8	95 (68)	121	322
<i>1</i>	0.50	9.60	74	465 000 (2.41)	5.6	99 (67)	119	330
<i>1</i>	1.00	9.01	81	471 000 (2.40)	10.6	97 (66)	115	338
<i>2</i>	0.11	9.91	22	146 000 (3.82)	2.8	102 (78)	106	284
<i>2</i>	0.50	9.51	27	220 000 (2.53)	8.8	104 (83)	106	287
<i>2</i>	1.38	12.46	41	227 000 (2.33)	12.9	97 (92)	102	263

<sup>a</sup> *In vacuo* at 60°C for 3 h with 0.1 mol% AIBN

<sup>b</sup> Determined by g.p.c. correlating to standard polystyrenes

<sup>c</sup> Determined by <sup>1</sup>H n.m.r. with the resonance intensities of the protons in OCH<sub>2</sub>R<sub>f</sub> and OCH<sub>3</sub> groups in copolymers

<sup>d</sup> Contact angles of water droplets to copolymer films: the values for the air-side surfaces at film preparation, those for the glass-side surfaces in parentheses

<sup>e</sup> 10% weight loss temperatures under nitrogen atmosphere

and 123°, respectively. Poly(*3*), which has two ester linkages in a side chain and a low fluorine content in the monomer, is less repellent than poly(*1*) and poly(*2*).

Copolymerization of *1* or *2* with methyl methacrylate (MMA) were done in bulk with 0.1 mol% AIBN, and the results are shown in Table 2. All copolymers were soluble to common organic solvents and have molecular weights more than 10<sup>5</sup>. The molecular weight distributions of copolymers ( $\bar{M}_w/\bar{M}_n$ ) estimated by g.p.c. were wide but unimodal. The molecular weight increased slightly with an increase of fluoromonomer content in the feed. The copolymer films fabricated by solution casting on glass surfaces have good water repellency. The film surfaces of the copolymers that were the air-sides at film preparation have water repellency similar to that for the homopolymer films of *1* and *2*, which are attributable to surface accumulation of the fluoro-side chains in copolymers due to their low surface free energy<sup>16</sup>. Even with a few per cent incorporation of the fluoroalkylated monomers into copolymers, the film surfaces become sufficiently water repellent.

Thermogravimetric analysis of the polymers was performed under nitrogen atmosphere at the heating rate of 10°C min<sup>-1</sup>. The representative thermogravimetric curves are shown in Figure 2, and the 10% weight loss temperatures obtained are listed in Tables 1 and 2. Since the thermal stability of the polymers are as high as that for

poly(MMA) ( $T_d$ : 297°C; bulk-polymerized with 0.1 mol% AIBN;  $\bar{M}_n$ :  $1.2 \times 10^5$ ,  $\bar{M}_w/\bar{M}_n$ : 2.9 (g.p.c.)), the decomposition of fluoro-moieties in the polymers appears not to be dominant in the thermal degradation of the polymers. The homo- and co-polymers containing *1* are thermally more stable than the corresponding polymers containing *2*; the initial weight losses on heating occurred at lower temperatures in poly(*2-co-MMA*)s. Because the thermal degradation of poly(alkyl methacrylate)s, except poly(*tert*-butyl methacrylate), under inert atmosphere, involves mainly a depolymerization process in which the initiation occurs at chain ends of polymer molecules<sup>17</sup>, the reduced thermal stability of poly(*2-co-MMA*)s is attributable to their relatively low molecular weights.

The glass transition temperatures of the polymers were evaluated by d.s.c. at the heating rate of 5°C min<sup>-1</sup>. The transitions were observed at lower temperatures than that for poly(MMA). The bulkiness and low cohesive force of the fluoro-pendant groups in polymers would expand gaps between the polymer molecules, hence reducing friction of the polymer backbones<sup>3,18</sup>.

In conclusion, novel methacrylates bearing the perfluoropyrrolidino groups were synthesized from perfluoro(pyrrolidinopropionyl fluoride)s, while their homopolymers and copolymers with MMA were obtained by radical polymerization. Clear, colourless, and tough films of the polymers

were formed by the solution casting technique. Large contact angles of water to the film surfaces were observed. The copolymers having a small proportion of the fluorinated monomer units have water repellency as much as that for the homopolymers, suggesting preferential accumulation of the fluoro-pendant groups to the film surfaces. The new polymers are thermally stable, and they decompose completely with a negligible quantity of char yield under inert atmosphere.

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