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Synthesis and polymerization of novel fluorinated acrylates and methacrylates bearing alkoxyl groups derived from radical addition reaction of perfluoroisopropenyl ester

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Abstract

Radical addition of 2-benzoxypentafluoropropene [$CF_2{=}C(CF_3)OCOC_6H_5$] (BPFP) with alcohols such as ethanol and 2-propanol was investigated to afford fluorinated alcohols. Radical addition of BPFP with cyclic ethers such as tetrahydrofuran, 1,3-dioxolane and tetrahydropyran was also achieved to afford addition products followed by hydrolysis to yield fluorinated alcohols possessing cyclic structures. Novel fluoroalkyl acrylates and methacrylates were synthesized from the fluorinated alcohols with (meth)acryloyl chlorides. Radical polymerization of the fluoroalkyl (meth)acrylates yielded polymers of 1.2×10^5 as the highest molecular weight.

Keywords: Fluoropolymers; Radical polymerization; Perfluoroisopropenyl group; Radical addition; Methacrylate

1. Introduction

As has previously been reported the radical addition of 2-benzoxypentafluoropropene [$CF_2{=}C(CF_3)OCOC_6H_5$] (BPFP) with large excess of tetrahydrofuran (THF) in feed affords 1:1 addition product in high yield [1]. 1:2 addition product was preferable to 1:1 adduct when the addition of BPFP was carried out with 1,4-dioxane and the structure of the product was determined by X-ray crystallographic analysis to show 2,6-diaddition [2]. An easy way of carbon–carbon bond formation was achieved under mild reaction condition and the reaction was found to be applicable to wide variety of organic compounds possessing carbon–hydrogen bonds [3]. The radical addition of perfluorovinyl compounds are well-known reaction to produce many fluorinated organic compounds [4–18]. The reaction of bifunctional compound, bis(α-trifluoromethyl-β,β-difluorovinyl) terephthalate [$CF_2{=}C(CF_3)OCOC_6H_4COOC(CF_3){=}CF_2$], afforded novel fluorinated polymers bearing such organic segments in polymer main chains as 1,4-dioxane, diethyl ether, dimethoxyethane, 18-crown-6, triethylamine, glutaraldehyde and alkanes which have never been supposed as direct starting compounds for preparation of polymers by developing the radical addition reaction to polyaddition [19].

This report concerns about the syntheses of fluorinated alcohols by radical addition of BPFP with ethanol and 2-propanol. Syntheses of acrylates and methacrylates were carried out by the reaction of acryloyl chloride or methacryloyl chloride with fluorinated alcohols produced and the radical polymerization reactivity of these acrylate derivatives was examined. The fluorinated compounds derived from BPFP with cyclic ethers such as THF, 1,3-dioxolane and tetrahydropyran were also synthesized followed by hydrolysis to afford fluorinated alcohols from which fluoroalkyl acrylates and methacrylates bearing cyclic structures were yielded, and polymerization of the acrylate derivatives was investigated. A polymer possessing fluoroalkyl group with cyclic structures might be applicable to photoresist lithography [20].

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2. Experimental

All experiments related to reaction and polymerization were carried out under a purified nitrogen atmosphere to preclude oxygen and moisture.

2.1. Reagents

BPFP was synthesized by the reaction of benzoyl chloride with 2 eq. of lithium enolate derived from 1,1,1,3,3,3-hexafluoropropan-2-ol (HFIP) with butyllithium in THF described in the literatures [21,22]. HFIP (Central Glass Co.) was dried by refluxing over calcium hydride and distilled under reduced pressure. Commercial butyllithium in a hexane solution was used after determination of concentration by titration. Commercial ethanol, 2-propanol, THF, 1,3-dioxolane, tetrahydropyran and toluene were purified by usual methods. Acryloyl chloride and methacryloyl chloride were used after distillation. Benzoyl peroxide (BPO) and 2,2′-azobisisobutyronitrile (AIBN) were precipitated from chloroform and then recrystallized in methanol at 0 °C. Di-*tert*-butyl peroxide (DTBP) was used as received.

2.2. Measurements

Measurement of vapor phase chromatography was carried out with a Hewlett-Packard 6890 equipped with flame ionization detection with a ZB-2, wide-bore fused silica capillary column (15 m × 0.53 mm, film thickness: 1.5 μm). The column temperature was programmed from 80 to 320 °C at 20 °C min^{-1}. The mass spectra were measured on a JEOL JMS-SX102. Isobutane was used as a reagent of chemical ionization (CI). Size exclusion chromatography (SEC) was measured with a TOSOH HLC-802A apparatus at 40 °C with Shodex KF 805L (2×) using THF as an eluent (flow rate 1.0 ml min^{-1}). The molecular weight measured by SEC was calculated from the calibration curve for standardized polystyrene. NMR spectra were recorded on a JEOL JNM-ECP500 Fourier transform NMR spectrometer at 500 MHz for ^{1}H, 125 MHz for ^{13}C and 470 for ^{19}F NMR using deuterated chloroform as a solvent. ^{13}C and ^{19}F NMR spectra were measured under proton decoupling conditions. Chemical shift of ^{19}F NMR was determined based on absolute magnetic field intensity.

2.3. Procedures

The addition reaction of BPFP with ethanol was carried out by adding 171 mmol of ethanol and 21 mmol of BPFP with 4.0 mmol of DTBP in glass ampule under 120 °C for 3 days. The product was purified by distillation under reduced pressure to afford 1,1,1,3,3-pentafluoro-2-benzoxy-4-pentanol; bp 140 °C/0.03 mmHg; yield: 65%. ^{1}H NMR (in $CDCl_3$): $\delta = 1.3$ (3H, dd, CH_3), 3.9–4.4 (1H, m, CF_2CHCH_3), 6.0–6.2 (1H, m, CF_3CHCF_2), 7.4 (2H, dt, C_6H_5), 7.6 (1H, dt, C_6H_5), 8.1 (2H, dd, C_6H_5). ^{13}C{^{1}H(5 ppm)} NMR: $\delta = 14$ (s, CH_3), 66 (s, CF_2CHCF_3), 68 (s, CF_3CHCF_2), 117–121 (t, CF_2), 119–126 (q, CF_3), 127–135 (s, C_6H_5), 164 (s, COO). ^{19}F{^{1}H(5 ppm)} NMR: $\delta = -72$ (3F, s, CF_3), −119, −128 (2F, dd, CF_2). MS = 298 (electron ionization (EI), *m/z*): 233 $[M–(F)]^+$, 298 $[M]^+$, 77 $[C_6H_5]^+$, 105 $[C_6H_5CO]^+$, 121 $[C_6H_5COO]^+$; (chemical ionization (CI), *m/z*): 299 $[M+1]^+$, 105 $[C_6H_5CO]^+$.

1,1,1,3,3-Pentafluoro-2-benzoxy-4-methyl-4-pentanol was yielded by the reaction of BPFP with 2-propanol; bp 153 °C/0.1 mmHg; yield: 69%. ^{1}H NMR (in $CDCl_3$): $\delta = 1.3$ (3H, s, CH_3), 1.4 (3H, s, CH_3), 6.2 (1H, m, CH), 7.4 (2H, dt, C_6H_5), 7.6 (1H, dt, C_6H_5), 8.1 (2H, dd, C_6H_5). ^{13}C{^{1}H(5 ppm)} NMR: $\delta = 23$ (s, CH_3), 66 (m, CH), 74 (m, $C(CH_3)_2$), 117–121 (t, CF_2), 119–126 (q, CF_3), 127–135 (s, C_6H_5), 163 (s, COO). ^{19}F{^{1}H(5 ppm)} NMR: $\delta = -117$, −122 (2F, dd, CF_2), −71 (3F, s, CF_3). MS = 312 (EI, *m/z*): 77 $[C_6H_5]^+$, 105 $[C_6H_5CO]^+$, 121 $[C_6H_5COO]^+$; (CI, *m/z*): 313 $[M+1]^+$.

The addition reaction of BPFP with THF was carried out by adding 123 mmol of THF and 15.4 mmol of BPFP with 6.0 mmol of BPO in glass ampule under 80 °C for 3 days [1]. The product was purified by distillation under reduced pressure to afford 2-(1,1,3,3,3-pentafluoro-2-benzoxypropyl)tetrahydrofuran; bp 95 °C/0.1 mmHg; yield: 87%. ^{1}H NMR (in $CDCl_3$): $\delta = 1.8$, 1.9 (2H, m, C_4H_7O), 2.0, 2.1 (2H, m, C_4H_7O), 3.8, 3.9 (2H, m, C_4H_7O), 4.2, 4.3 (1H, m, C_4H_7O), 6.2 (1H, m, CF_2CHCF_3), 7.4 (2H, dt, C_6H_5), 7.6 (1H, dt, C_6H_5), 8.1 (2H, dd, C_6H_5). ^{13}C{^{1}H(5 ppm)} NMR: $\delta = 24$ (s, C_4H_7O), 25 (s, C_4H_7O), 66 (m, C_4H_7O), 69 (s, CF_2CHCF_3), 75 (d, C_4H_7O), 117–121 (t, CF_2), 119–126 (q, CF_3), 127–135 (s, C_6H_5), 164 (s, COO). ^{19}F{^{1}H(5 ppm)} NMR: $\delta = -71$ (3F, s, CF_3), −120, −125 (2F, dd, CF_2). MS = 324 (EI, *m/z*): 69 $[CF_3]^+$, 71 $[C_4H_7O]^+$. (CI, *m/z*): 323 $[M-1]^+$, 325 $[M+1]^+$.

The addition reaction of BPFP with 1,3-dioxolane was carried out by adding 143 mmol of 1,3-dioxolane and 17.9 mmol of BPFP with 3.6 mmol of BPO in glass ampule under 80 °C for 3 days [1]. The product was purified by distillation under reduced pressure to afford 2-(1,1,3,3,3-pentafluoro-2-benzoxypropyl)-1,3-dioxolane; bp 111 °C/0.1 mmHg; yield: 56%. ^{1}H NMR (in $CDCl_3$): $\delta = 4.2$ (4H, m, $C_3H_5O_2$), 5.2 (1H, m, $C_3H_5O_2$), 6.2 (1H, m, $CF_2CH(CF_3)O$), 7.4 (2H, dt, C_6H_5), 7.6 (1H, dt, C_6H_5), 8.1 (2H, dd, C_6H_5). ^{13}C{^{1}H(5 ppm)} NMR: $\delta = 66$ (s, $C_3H_5O_2$), 67 (m, $CF_2CH(CF_3)O$), 102 (t, $C_3H_5O_2$), 114 (t, CF_2), 122 (q, CF_3), 127–135 (s, C_6H_5), 164 (s, COO). ^{19}F{^{1}H(5 ppm)} NMR: $\delta = -71$, −72 (3F, s, CF_3), −117, −118, −119, −122 (2F, d, CF_2).

The addition reaction of BPFP with tetrahydropyran was carried out by adding 102 mmol of tetrahydropyran and 12.8 mmol of BPFP with 5.1 mmol of DTBP in glass ampule under 120 °C for 3 days. The product was purified by distillation under reduced pressure to afford 2-(1,1,3,3,3-pentafluoro-2-benzoxypropyl)tetrahydropyran; bp 118 °C/0.1 mmHg; yield: 55%. ^{1}H NMR (in $CDCl_3$): $\delta = 1.4–2.0$ (m, 6H, C_5H_9O), 3.0–4.0 (m, 3H, C_5H_9O), 6.2, 6.3 (1H, m, $CF_2CH(CF_3)$), 7.4 (2H, dt, C_6H_5), 7.6 (1H, dt, C_6H_5), 8.1 (2H, dd, C_6H_5). ^{13}C{^{1}H(5 ppm)} NMR: $\delta = 22$, 23, 28 (s, C_5H_9O), 66, 68 (m, C_5H_9O), 72 (m, $CF_2CH(CF_3)O$), 114 (t, CF_2), 122 (q, CF_3), 127–135 (s, C_6H_5), 164 (s, COO). ^{19}F{^{1}H(5 ppm)} NMR: $\delta = -71$, −72 (3F, s, CF_3), −117, −121 (2F, s, CF_2).

Hydrolysis of 2-(1,1,3,3,3-pentafluoro-2-benzoxypropyl)tetrahydrofuran was carried out by adding 28.3 mmol of 2-(1,1,3,3,3-pentafluoro-2-benzoxypropyl)tetrahydrofuran, 33.9 mmol of methanol and 33.9 mmol of sodium hydroxide under refluxing for 24 h. After the reaction the product was extracted by diethyl ether followed by washing with saturated water solution of sodium chloride and then distilled under reduced pressure to afford 1,1,3,3,3-pentafluoro-1-tetrahydrofuranyl-2-propanol; bp 73 °C/0.1 mmHg; yield, 63%. ^{1}H NMR (in $CDCl_3$): $\delta = 1.8$, 1.9 (2H, m, C_4H_7O), 2.0, 2.1 (2H, m, C_4H_7O), 3.8, 3.9 (2H, m, C_4H_7O), 4.2, 4.3 (1H, m, C_4H_7O), 6.2 (1H, m, CF_2CHCF_3). ^{13}C{^{1}H(5 ppm)} NMR: $\delta = 24$ (s, C_4H_7O), 25 (s, C_4H_7O), 66 (m, C_4H_7O), 69 (s, CF_2CHCF_3), 75 (d, C_4H_7O), 117–121 (t, CF_2), 119–126 (q, CF_3). ^{19}F{^{1}H(5 ppm)} NMR: $\delta = -71$ (3F, s, CF_3), −120, −125 (2F, dd, CF_2).

Hydrolysis of 2-(1,1,3,3,3-pentafluoro-2-benzoxypropyl)-1,3-dioxolane was carried out by adding 26.2 mmol of 2-(1,1,3,3,3-pentafluoro-2-benzoxypropyl)-1,3-dioxolane, 31.4 mmol of methanol and 31.4 mmol of sodium hydroxide to afford 1,1,3,3,3-pentafluoro-1-(2-dioxolanyl)-2-propanol; bp 92 °C/3 mmHg; yield: 52%, ^{1}H NMR (in $CDCl_3$): $\delta = 4.2$ (4H, m, $C_3H_5O_2$), 5.2 (1H, m, $C_3H_5O_2$), 6.2 (1H, m, $CF_2CH(CF_3)O$). ^{13}C{^{1}H(5 ppm)} NMR: $\delta = 66$ (s, $C_3H_5O_2$), 67 (m, $CF_2CH(CF_3)O$), 102 (t, $C_3H_5O_2$), 114 (t, CF_2), 122 (q, CF_3). ^{19}F{^{1}H(5 ppm)} NMR: $\delta = -71$, −72 (3F, s, CF_3), −117 to −122 (2F, d, CF_2).

The hydrolysis of 2-(1,1,3,3,3-pentafluoro-2-benzoxypropyl)tetrahydropyran was carried out by adding 28.3 mmol of 2-(1,1,3,3,3-pentafluoro-2-benzoxypropyl)tetrahydropyran, 33.9 mmol of methanol and 33.9 mmol of sodium hydroxide to afford 1,1,3,3,3-pentafluoro-1-(2-pyranyl)-2-propanol; bp 110 °C/0.1 mmHg; yield: 62%. ^{1}H NMR (in $CDCl_3$): $\delta = 1.4$–2.0 (m, 6H, C_5H_9O), 3.0–4.0 (m, 3H, C_5H_9O), 6.2–6.3 (1H, m, $CF_2CH(CF_3)$). ^{13}C{^{1}H(5 ppm)} NMR: $\delta = 22$–28 (m, C_5H_9O), 66–68 (m, C_5H_9O), 72 (m, $CF_2CH(CF_3)O$), 114 (t, CF_2), 122 (q, CF_3). ^{19}F{^{1}H(5 ppm)} NMR: $\delta = -71$, −72 (3F, s, CF_3), −117, −121 (2F, s, CF_2).

Acrylate and methacrylate derivatives were produced by the reaction of acryloyl chloride or methacryloyl chloride with alcohols obtained as mentioned above in the presence of triethylamine as a hydrochloric acid capture. Products were isolated by silica gel column chromatography by using hexane: ethyl acetate (20:1, v/v) as an eluent.

1,1,1,3,3-Pentafluoro-2-benzoxy-4-pentyl acrylate (EtA); yield: 36%. ^{1}H NMR (in $CDCl_3$): $\delta = 1.4$ (3H, d, CH_3), 5.2, 5.3 (1H, m, CH_3CHCF_2), 5.6, 6.3 (2H, dd, $CH_2{=}$), 5.8 (1H, m, $CH_2{=}CH$), 6.0 (1H, m, CF_3CHCF_2), 7.4 (2H, dt, C_6H_5), 7.6 (1H, dt, C_6H_5), 8.1 (2H, dd, C_6H_5). ^{13}C{^{1}H(5 ppm)} NMR: $\delta = 12$ (s, CH_3), 66 (s, CF_2CHCF_3), 67 (s, CF_3CHCF_2), 118–121 (t, CF_2), 119–125 (q, CF_3), 127–135 (s, C_6H_5), 134 (s, $CH_2{=}$), 135 (s, $CH_2{=}CH$), 164 (s, COO), 164 (s, $CH_2{=}CHCOO$). ^{19}F{^{1}H(5 ppm)} NMR: $\delta = -73$ (3F, s, CF_3), −122, −124 (2F, dd, $CF_2{=}$).

1,1,1,3,3-Pentafluoro-2-benzoxy-4-methyl-4-pentyl acrylate (IPA); yield: 35%. ^{1}H NMR (in $CDCl_3$): $\delta = 1.7$ (3H, s, CH_3), 1.8 (3H, s, $CH_2{=}C(CH_3)$), 5.6, 6.3 (2H, dd, $CH_2{=}$), 5.8 (1H, m, $CH_2{=}CH$), 6.2 (1H, m, CH), 7.4 (2H, dt, C_6H_5), 7.6 (1H, dt, C_6H_5), 8.1 (2H, dd, C_6H_5). ^{13}C{^{1}H(5 ppm)} NMR: $\delta = 20$ (s, CH_3), 66 (m, CH), 82 (m, $C(CH_3)_2$), 115–120 (t, CF_2), 120–125 (q, CF_3), 126–130 (s, C_6H_5), 131 (s, $CH_2{=}$), 134 (s, $CH_2{=}CH$), 163 (s, COO), 163 (s, $CH_2{=}CHCOO$). ^{19}F{^{1}H(5 ppm)} NMR: $\delta = -71$ (3F, s, CF_3), −122, −117 (2F, dd, CF_2).

1,1,3,3,3-Pentafluoro-1-tetrahydrofuranyl-2-propyl acrylate (TFA); yield: 69%. ^{1}H NMR (in $CDCl_3$): $\delta = 1.8$, 1.9 (2H, m, C_4H_7O), 2.0, 2.1 (2H, m, C_4H_7O), 3.8, 3.9 (2H, m, C_4H_7O), 4.2, 4.3 (1H, m, C_4H_7O), 5.6, 6.3 (2H, dd, $CH_2{=}$), 5.8 (1H, m, $CH_2{=}CH$), 5.9 (1H, m, CF_2CHCF_3). ^{13}C{^{1}H(5 ppm)} NMR: $\delta = 24$ (s, C_4H_7O), 25 (s, C_4H_7O), 66 (m, C_4H_7O), 69 (s, CF_2CHCF_3), 75 (d, C_4H_7O), 117–121 (t, CF_2), 119–126 (q, CF_3), 134 (s, $CH_2{=}$), 135 (s, $CH_2{=}CH$), 164 (s, COO), 164 (s, $CH_2{=}CHCOO$). ^{19}F{^{1}H(5 ppm)} NMR: $\delta = -63$ (3F, s, CF_3), −110, −118 (2F, dd, CF_2).

1,1,3,3,3-Pentafluoro-1-(2-dioxolanyl)-2-propyl acrylate (DLA); yield: 79%. ^{1}H NMR (in $CDCl_3$): $\delta = 4.2$ (4H, m, $C_3H_5O_2$), 5.2 (1H, m, $C_3H_5O_2$), 5.6, 6.3 (2H, dd, $CH_2{=}$), 5.8 (1H, m, $CH_2{=}CH$), 5.9 (1H, m, $CF_2CH(CF_3)O$). ^{13}C{^{1}H(5 ppm)} NMR: $\delta = 66$ (s, $C_3H_5O_2$), 67 (m, $CF_2CH(CF_3)O$), 102 (t, $C_3H_5O_2$), 114 (t, CF_2), 122 (q, CF_3), 134 (s, $CH_2{=}$), 135 (s, $CH_2{=}CH$), 164 (s, COO), 164 (s, $CH_2{=}CHCOO$). ^{19}F{^{1}H(5 ppm)} NMR: $\delta = -63$ (3F, s, CF_3), −110, −118 (2F, dd, CF_2).

1,1,3,3,3-Pentafluoro-1-(2-pyranyl)-2-propyl acrylate (TPA); yield: 62%. ^{1}H NMR (in $CDCl_3$): $\delta = 1.4$–2.0 (m, 6H, C_5H_9O), 3.0–4.0 (m, 3H, C_5H_9O), 5.6, 6.3 (2H, dd, $CH_2{=}$), 5.8 (1H, m, $CH_2{=}CH$), 5.9 (1H, m, $CF_2CH(CF_3)$). ^{13}C{^{1}H(5 ppm)} NMR: $\delta = 22$, 23, 28 (s, C_5H_9O), 66, 68 (m, C_5H_9O), 72 (m, $CF_2CH(CF_3)O$), 114 (t, CF_2), 122 (q, CF_3), 134 (s, $CH_2{=}$), 135 (s, $CH_2{=}CH$), 164 (s, COO), 164 (s, $CH_2{=}CHCOO$). ^{19}F{^{1}H(5 ppm)} NMR: $\delta = -64$ (3F, s, CF_3), −112, −120 (2F, dd, CF_2).

1,1,1,3,3-Pentafluoro-2-benzoxy-4-pentyl methacrylate (EtMA); yield: 54%. ^{1}H NMR (in $CDCl_3$): $\delta = 1.4$ (3H, d, CH_3), 1.9 (3H, s, $CH_2{=}C(CH_3)$), 5.2 (1H, m, CH_3CHCF_2), 5.9 (1H, m, CF_3CHCF_2), 5.6, 6.1 (2H, s, $CH_2{=}$), 7.4 (2H, dt, C_6H_5), 7.6 (1H, dt, C_6H_5), 8.1 (2H, dd, C_6H_5). ^{13}C{^{1}H(5 ppm)} NMR: $\delta = 12$ (s, CH_3), 18 (s, $CH_2{=}C(CH_3)$), 66 (s, CF_2CHCF_3), 67 (s, CF_3CHCF_2), 118–121 (t, CF_2), 119–126 (q, CF_3), 127–135 (s, C_6H_5), 134, 135 (s, $CH_2{=}$), 164 (s, COO), 165 (s, $CH_2{=}C(CH_3)COO$). ^{19}F{^{1}H(5 ppm)} NMR: $\delta = -121$, −118 (2F, dd, CF_2), −70 (3F, s, CF_3).

1,1,1,3,3-Pentafluoro-2-benzoxy-4-methyl-4-pentyl methacrylate (IPMA); yield: 20%. ^{1}H NMR (in $CDCl_3$): $\delta = 1.6$ (3H, s, CH_3), 1.7 (3H, s, CH_3), 1.8 (3H, s, $CH_2{=}C(CH_3)$), 5.8, 6.2 (2H, s, $CH_2{=}$), 6.3 (1H, m, CH), 7.4 (2H, dt, C_6H_5), 7.6 (1H, dt, C_6H_5), 8.1 (2H, dd, C_6H_5). ^{13}C{^{1}H(5 ppm)} NMR: $\delta = 14$ (s, CH_3), 19, 20 (s, $CH_2{=}C(CH_3)$), 66 (m, CH), 82 (m, $C(CH_3)_2$), 115–120 (t, CF_2), 120–126 (q, CF_3), 127–135 (s, C_6H_5), 134, 136 (s, $CH_2{=}$), 163 (s, COO), 165 (s, $CH_2{=}C(CH_3)COO$). ^{19}F{^{1}H(5 ppm)} NMR: $\delta = -117$, −122 (2F, dd, $CF_2{=}$), −71 (3F, s, CF_3).

1,1,3,3,3-Pentafluoro-1-tetrahydrofuranyl-2-propyl methacrylate (TFMA); yield: 25%. ^{1}H NMR (in $CDCl_3$): $\delta = 1.8$, 1.9 (2H, m, C_4H_7O), 2.0, 2.1 (2H, m, C_4H_7O), 2.0 (3H, s, $CH_2{=}C(CH_3)$), 3.8, 3.9 (2H, m, C_4H_7O), 4.2, 4.3 (1H, m, C_4H_7O), 5.8, 6.3 (2H, s, $CH_2{=}$), 5.9 (1H, m, CF_2CHCF_3). $^{13}C\{^1H(5\ ppm)\}$ NMR: $\delta = 18$ (s, $CH_2{=}C(CH_3)$), 24 (s, C_4H_7O), 25 (s, C_4H_7O), 66 (m, C_4H_7O), 69 (s, CF_2CHCF_3), 75 (d, C_4H_7O), 117–121 (t, CF_2), 119–126 (q, CF_3), 134, 135 (s, $CH_2{=}$), 164 (s, COO), 165 (s, $CH_2{=}C(CH_3)COO$). $^{19}F\{^1H(5\ ppm)\}$ NMR: $\delta = -63$ (3F, s, CF_3), -110, -118 (2F, dd, CF_2).

1,1,3,3,3-Pentafluoro-1-(2-dioxolanyl)-2-propyl methacrylate (DLMA); yield: 30%. ^1H NMR (in $CDCl_3$): $\delta = 2.0$ (3H, s, $CH_2{=}C(CH_3)$), 4.2 (4H, m, $C_3H_5O_2$), 5.2 (1H, m, $C_3H_5O_2$), 5.8, 6.3 (2H, s, $CH_2{=}$), 5.9 (1H, m, $CF_2CH(CF_3)O$). $^{13}C\{^1H(5\ ppm)\}$ NMR: $\delta = 18$ (s, $CH_2{=}C(CH_3)$), 66 (s, $C_3H_5O_2$), 67 (m, $CF_2CH(CF_3)O$), 102 (t, $C_3H_5O_2$), 114 (t, CF_2), 122 (q, CF_3), 134, 135 (s, $CH_2{=}$), 164 (s, COO), 165 (s, $CH_2{=}C(CH_3)COO$). $^{19}F\{^1H(5\ ppm)\}$ NMR: $\delta = -63$ (3F, s, CF_3), -110, -118 (2F, dd, CF_2).

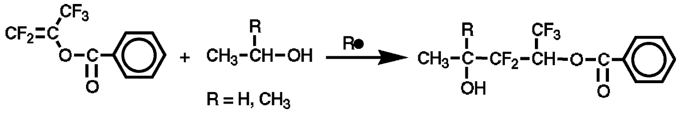
1,1,3,3,3-Pentafluoro-1-(2-pyranyl)-2-propyl methacrylate (TPMA); yield: 20%. ^1H NMR (in $CDCl_3$): $\delta = 1.4$–2.0 (m, 6H, C_5H_9O), 2.0 (3H, s, $CH_2{=}C(CH_3)$), 3.0–4.0 (m, 3H, C_5H_9O), 5.8, 6.3 (2H, s, $CH_2{=}$), 5.9 (1H, m, $CF_2CH(CF_3)$). $^{13}C\{^1H(5\ ppm)\}$ NMR: $\delta = 18$ (s, $CH_2{=}C(CH_3)$), 22, 23, 28 (s, C_5H_9O), 66, 68 (m, C_5H_9O), 72 (m, $CF_2CH(CF_3)O$), 114 (t, CF_2), 122 (q, CF_3), 134, 135 (s, $CH_2{=}$), 164 (s, COO), 165 (s, $CH_2{=}C(CH_3)COO$). $^{19}F\{^1H(5\ ppm)\}$ NMR: $\delta = -64$ (3F, s, CF_3), -112, -120 (2F, dd, CF_2).

Radical polymerization of fluoroalkyl acrylates and methacrylates was carried out by adding monomer, BPO or AIBN as an initiator in glass ampule. Polymer was isolated by reprecipitation with large excess amount of methanol and dried thoroughly. The molecular weight of the polymer was determined by SEC. The structure of the resulting polymer was confirmed by ^1H, ^{13}C and ^{19}F NMR.

3. Results and discussion

3.1. Addition reaction of BPFP with alcohols

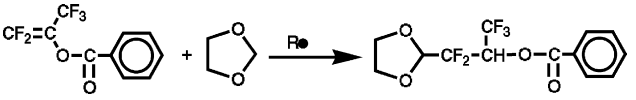
Radical addition of polyfluorinated vinyl compounds with alcohol is well-known reaction as mentioned in introduction part. BPFP also affords addition products with ethanol and 2-propanol in the yields of 65% and 69%, respectively, as described in the Section 2. The product of BPFP with ethanol might be 1,1,1,3,3-pentafluoro-2-benzoxy-4-pentanol since the absorption of 3.9–4.4 ppm in ^1H NMR is assignable to methine hydrogen of *sec*-alcohol structure; which is in accord with the results of the reaction of perfluoropropene with alcohols [17]. The reaction was then concluded to take place as shown in Eq. (1).



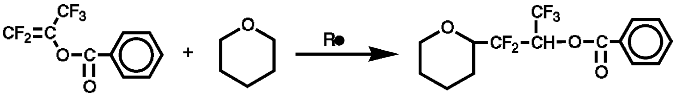
(1)

3.2. Addition reaction of BPFP with cyclic ethers

As has previously been reported the radical addition of BPFP with THF affords the 1:1 adduct in high yield [1]. The addition reaction has been reported to take place at 2-position of THF moiety. Similar reactions are found to take place in the case of 1,3-dioxolane and tetrahydropyran in high yields as mentioned in the experimental part. The reaction of BPFP with 1,3-dioxolane might take place at 2-position since the absorption at 5.2 ppm in ^1H NMR is assignable to methine hydrogen at 2-position of 1,3-dioxolane moiety (Fig. 1). The reactions are then illustrated in Eqs. (2) and (3).



(2)



(3)

3.3. Hydrolysis of addition product

Hydrolysis of addition products of BPFP with cyclic ethers was carried out in order to obtain fluorinated alcohols. The yields of fluorinated alcohols are 63%, 52% and 61% from the adducts of THF, 1,3-dioxolane and tetrahydropyran, respectively, to afford pentafluoro-2-propanol derivatives having cyclic structures. The absorption at 5.2 ppm in ^1H NMR of 1,1,1,3,3-pentafluoro-1-(2-dioxolanyl)-2-propanol was also

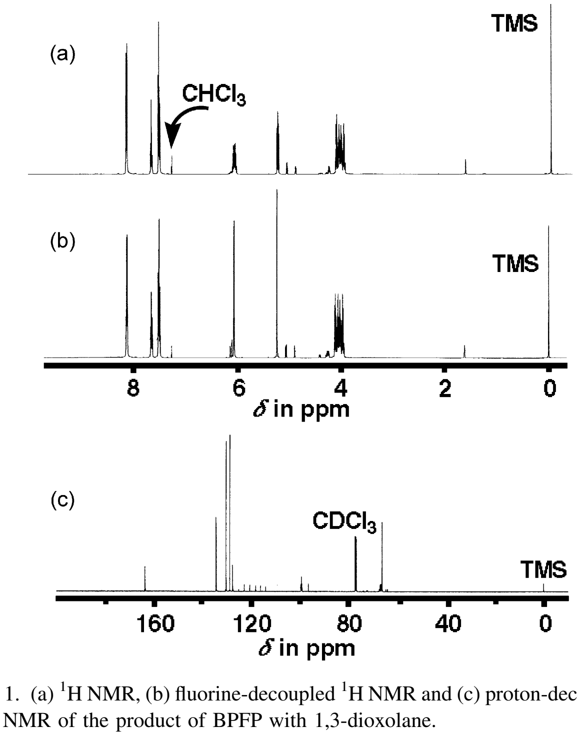
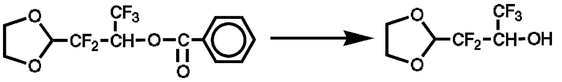


Fig. 1. (a) ^1H NMR, (b) fluorine-decoupled ^1H NMR and (c) proton-decoupled ^{13}C NMR of the product of BPFP with 1,3-dioxolane.

observed, which gives the confirmation of 2-substituted 1,3-dioxolane derivative produced, as shown in Eq. (4).


(4)

3.4. Synthesis of acrylate and methacrylate

EtA, IPA, TFA, DLA, TPA, EtMA, IPMA, TFMA, DLMA and TPMA were synthesized from fluorinated alcohols with acryloyl chloride or methacryloyl chloride, respectively, in fairly high yields as stated in Section 2. No boiling points were determined since these compounds were purified by column chromatography. The detailed analytical data are also shown in Section 2.

3.5. Radical polymerization of fluoroalkyl acrylate and methacrylate

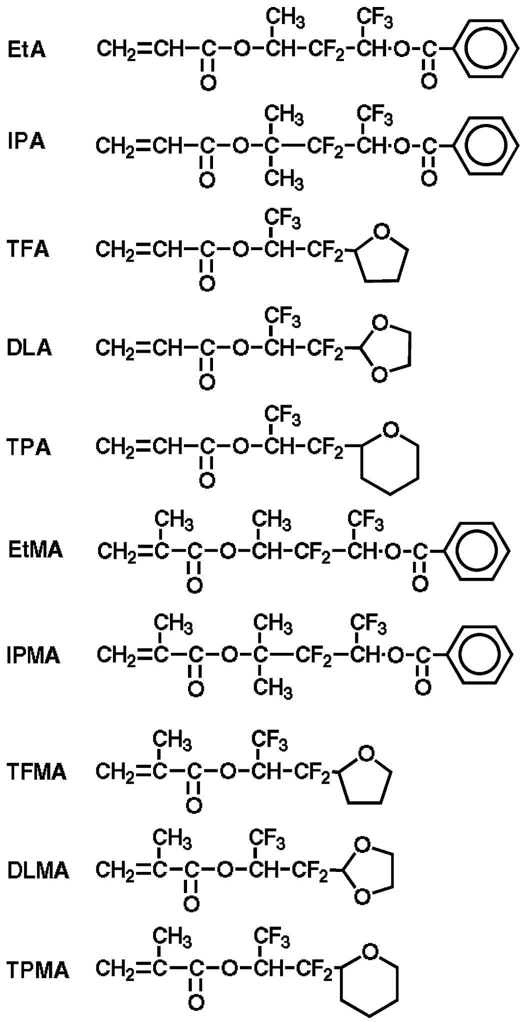
The results of radical polymerization of fluoroalkyl acrylates and methacrylates synthesized here are summarized in Table 1. The structures of monomers are illustrated in Scheme 1. The yields of polymers produced are found to be fairly low compared to those of methyl acrylate or methyl methacrylate. This is probably because low-molecular weight polymers would be soluble in methanol as a reprecipitation solvent since the solubility of fluorine-containing acrylate polymers are higher than that of non-fluorinated ones [23]. Gel formation in the case of acrylate derivatives took place, presumably because radical chain transfer reaction frequently took place at the protons of acrylate moiety and cyclic groups in ester groups.

Table 1
Radical polymerization of fluorine-containing acrylates and methacrylates

Run	Monomer	Initiator[a]	Solvent	Yield (%)	$\bar{M}_\mathrm{n}$[b] ($\times 10^5$)	$\bar{M}_\mathrm{w}/\bar{M}_\mathrm{n}$[b]
1	EtA	BPO		30	0.31	2.1
2		AIBN		39	0.66	2.7
3		AIBN	Toluene	45	0.10	1.3
4	IPA	BPO		76	0.34	9.0
5		AIBN		46	1.24	3.2
6		AIBN	Toluene	40	0.11	1.4
7	TFA	BPO		–	0.01	–
8		AIBN		34	0.08	6.9
9		AIBN	Toluene	0	–	–
10	DLA	BPO		Gel	–	–
11		BPO	Toluene	62	0.06	–
12		AIBN		Gel	–	–
13		AIBN	Toluene	66	0.08	–
14	TPA	BPO		Gel	–	–
15		AIBN		48	0.45	2.2
16	EtMA	BPO		11	0.69	3.9
17		BPO	Toluene	47	0.12	2.0
18		AIBN		0	–	–
19	IPMA	BPO		66	0.82	4.1
20		BPO	Toluene	61	0.74	2.2
21		AIBN		67	0.53	2.6
22	TFMA	BPO		48	0.85	4.3
23		AIBN		73	0.46	2.1
24		AIBN	Toluene	14	0.23	2.7
25	DLMA	BPO		49	0.05	–
26		AIBN		45	0.17	–
27		AIBN	Toluene	54	0.51	1.3
28	TPMA	BPO		70	0.68	6.2
29		BPO	Toluene	0	–	–
30		AIBN		15	0.11	1.6

[a] Reaction temp.: AIBN 60 °C; BPO 80 °C.

[b] Estimated by SEC (PSt standards, eluent: THF).



Scheme 1. Monomers appeared in Table 1.

4. Conclusion

Facile method to prepare polymers of fluoroalkyl acrylates and methacrylates was developed by starting from syntheses of fluorinated alcohols derived from radical addition of perfluoroisopropenyl ester with alcohols followed by the reaction with acryloyl chloride or methacryloyl chloride and then polymerization under radical conditions. Fluorinated alcohols possessing cyclic structures were also obtained by the reaction of BPFP with cyclic ethers followed by hydrolysis. Polyacrylates and polymethacrylates possessing cyclic structures in fluoroalkyl groups were easily obtained. The reaction may be applicable to syntheses of α-trifluoromethylacrylate derivatives possessing cyclic structures in ester alkyl groups which would be one of the leading candidates for resist material for lithography [24].

Acknowledgments

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References

[1] T. Narita, T. Hagiwara, H. Hamana, K. Tomooka, Y.-Z. Liu, T. Nakai, Tetrahedron Lett. 36 (1995) 6091–6094.

[2] H. Fujiwara, M. Iwasaki, T. Narita, H. Hamana, J. Fluorine Chem. 125 (2004) 1461–1464.

[3] T. Narita, H. Hamana, S. Hattori, Chem. Commun. (2004) 2340–2341.

[4] R.D. Chambers, N.M. Kelly, J.W. Emsley, J. Fluorine Chem. 13 (1979) 49–62.

[5] R.D. Chambers, N.M. Kelly, W.K.R. Musgrave, W.G.M. Jones, R.W. Rendell, J. Fluorine Chem. 16 (1980) 351–364.

[6] R.D. Chambers, B. Grievson, N.M. Kelly, J. Chem. Soc., Perkin. Trans. 1 (1985) 2209–2214.

[7] R.D. Chambers, B. Grievson, J. Chem. Soc., Perkin. Trans. 1 (1985) 2215–2218.

[8] R.D. Chambers, S.L. Jones, S.J. Mullins, A. Swales, P. Telford, M.L.H. West, in: J.C. Welch (Ed.), ACS Symposium Series 456, ACS, Washington DC, 1991, Chapter 5.

[9] O. Paleta, V. Chirkva, J. Kvicala, Macromol. Symp. 82 (1994) 111–114.

[10] H. Muramatsu, K. Inukai, T. Ueda, J. Org. Chem. 29 (1964) 2220–2223.

[11] H. Muramatsu, S. Moriguchi, K. Inukai, J. Org. Chem. 31 (1966) 1306–1309.

[12] H. Muramatsu, K. Inukai, T. Ueda, Bull. Chem. Soc. Jpn. 40 (1967) 903–907.

[13] H. Muramatsu, H. Kimoto, K. Inukai, Bull. Chem. Soc. Jpn. 42 (1969) 1155–1158.

[14] F. Liska, V. Dedek, B. Chutny, Coll. Czech. Chem. Commun. 33 (1968) 1299–1306.

[15] F. Liska, V. Kubelka, Coll. Czech. Chem. Commun. 36 (1971) 1381–1391.

[16] F. Liska, Coll. Czech. Chem. Commun. 36 (1971) 1853–1859.

[17] J.D. LaZerte, R.J. Koshar, J. Am. Chem. Soc. 77 (1955) 910–914.

[18] V. Dedek, J. Fikar, Coll. Czech. Chem. Commun. 34 (1969) 3778–3785.

[19] T. Narita, J. Polym. Sci. A: Polym. Chem. 42 (2004) 4101–4125.

[20] D.P. Sanders, E.F. Connor, R.H. Grubbs, B.P. Osborn, T. Chiba, S.A. MacDonald, C.D. Willson, Macromolecules 36 (2003) 1534–1542.

[21] C.-P. Qian, T. Nakai, Tetrahedron Lett. 29 (1988) 4119–4122.

[22] C.-P. Qian, T. Nakai, D.A. Dixon, B.E. Smart, J. Am. Chem. Soc. 112 (1990) 4602–4604.

[23] T. Narita, T. Hagiwara, H. Hamana, T. Nara, Makromol. Chem. Rapid. Commun. 6 (1985) 301–304.

[24] E. Reichmanis, O. Kalamasu, F.M. Houlihan, Acc. Chem. Res. 32 (1999) 659–667.