Res Chem Intermed
https://doi.org/10.1007/s11164-018-3411-3

Synthesis of novel perfluoroalkyl ether derivatives

Xiang Shi[1] · Hongxin Shi[1] · Hongke Wu[1] · HaiMin Shen[1]

Received: 12 October 2017 / Accepted: 26 March 2018

Abstract A series of novel fluoroether-containing monomers has been designed and prepared based on the commercially available perfluoroalkyl ether acid fluoride. Treating acid fluoride with allyl alcohol, 2-hydroxyethyl methacrylate or *N*-allylmethylamine allowed for the direct formation of corresponding vinyl-containing fluorinated monomers. High yields of the fluorinated epoxy monomers could be obtained from acid chloride with glycidol; meanwhile, fluorinated diol was prepared from diethanolamine or 3-amino-1,2-propanediol. Moreover, fluorinated monoamine, fluorinated monoalcohol and fluorinated dichloride were also obtained. Most of these fluorinated monomers were liquid at room temperature and exhibited good solubility in common organic solvents.

Keywords Fluorinated monomers · Oligomers of hexafluoropropylene epoxide · Acylation reactions

Introduction

Water-repellent and oil-repellent films for coating many materials have been extensively investigated. As is well known, lowering the surface tension of a film contributes to formulating nonwettable coatings. Notably, one of the most popular and successful strategies for lowering the surface tension of a film is incorporating a fluorine-containing group into the polymers [1, 2]. Such low-surface-tension groups can naturally segregate to the surface, which has been observed by various analytical methods including contact angle, XPS, static SIMS and neutron

✉ Xiang Shi
xiangshi_zmh@163.com

[1] School of Chemical Engineering, Zhejiang University of Technology, No. 18 Chaowang Road, Hangzhou 310032, China

Published online: 02 April 2018

reflectivity measurements [3, 4]. Many fluorinated monomers, such as fluorinated acrylates, fluorinated diols, fluorinated monomalcohols and fluorinated epoxides, have been synthesized. The copolymerization of fluorinated with nonfluorinated monomers has produced various fluorinated polymers, which have aroused growing attention [5–13].

Generally speaking, the surface properties of a fluorinated polymer depend on the fluorine content of the surface. Fluorinated polymers can be classified into three types based on the position of the fluorine-containing functional group in the polymer chain. The quantity of fluorine migrating to the surface of fluorinated polymer with a fluorinated unit in the main chain does not work well, which can be attributed to the restricted movement of the entire molecular chains [14–16]. Fluorine in fluorinated polymers with fluorinated side groups or fluorinated terminating groups can easily segregate to the air–polymer interface, thus promoting the surface properties of the fluorinated polymer [17–20]. In addition to their surface properties, fluorinated monomers can also be used for the modification of energy conversion and storage devices, which are expect to play a major role in the development of sustainable technologies to alleviate the energy and environmental challenges we are currently facing [21–23].

Thus far, few studies have been reported on the preparation of fluorinated monomers with a branched perfluoroalkyl ether pendent group. Compared with the perfluoroalky group-containing polymer, the flexible ether group can significantly modify the surface properties of corresponding polymers.

In the light of the above findings, we envisaged that a molecule containing both a perfluoroalkyl ether group and a reactive functional group should be suitable for preparing a fluorinated polymer with water repellency, oil repellency and soil repellency. The design and synthetic process of a number of fluorinated monomers containing a perfluoroalkyl ether group using acylating reaction has been elaborated in this study.

Experimental

Chemicals

Perfluoro-2-methyl-3-oxa-hexanoic acid fluoride and perfluoro-2,5-dimethyl-3,6-dioxa-nonanoic acid fluoride (perfluoroalkyl etheracid fluoride; PFEF) were purchased from WengJiang Reagent and used as received. Glycidol, dithanolamine, ethanolamine, 3-amino-1,2-propanediol and 2-hydroxyethyl methacrylate were bought from Aladdin Reagent and were subjected to vacuum distillation prior to use. N,N-dimethylformamide, allyl alcohol and ethylenediamine from Shanghai Lingfeng Chemical Reagent were dried with calcium hydride and purified by distillation before use. Thionyl chloride was refined by distillation at atmospheric pressure before use. Dichloromethane, chloroform, triethylamine and tetrahydrofuran were dried through refluxing over sodium benzophenone, which was freshly distilled prior to use. *N*-allylmethylamine and trifluoroacetic acid were obtained from Energy Regent and used as received.

General methods and instrumentation

^{1}H NMR (500 MHz), ^{13}C NMR (125 MHz) and ^{19}F NMR(125 MHz) spectra were recorded on a Bruker AV500 spectrometer. Chemical shift values in ppm for ^{1}H NMR spectra and ^{13}C NMR spectra were determined referenced to TMS as internal standard, and those for ^{19}F NMR spectra were referenced to CCl_3F as external standard. FTIR spectra were recorded on a Thermo Electron Nicolet 6700 FTIR spectrophotometer in the range from 4000 to 600 cm^{-1}. Most of the volatile fluorinated monomers were analyzed on a GCT Premier gas chromatography time-of-flight mass spectometer (Waters) with an OV-17 column (3 m × 3 mm, 50% phenylmethylpolysiloxane). The detector and injector temperatures were both 250 °C. The analysis was performed at a temperature starting from 50 °C and reaching 250 °C at a heating rate of 20 °C/min.

Preparation of perfluoroalkyl ether acid chloride

An amount of 117.5 g perfluoro-2,5-dimethyl-3,6-dioxa-nonanoic acid fluoride (0.35 mol) was added dropwise into 63.1 g water (3.50 mol) under agitation at room temperature, followed by 6 h of agitation at 50 °C. The two phases could be carried out separately, and the lower fluorocarbon layer was then transferred to a separating funnel and extracted 5 times with a saturated sodium chloride solution to obtain the crude acid, which was then subjected to vacuum distillation, yielding 133.5 g of pure perfluoro-2,5-dimethyl-3, 6-dioxa-nonanoic acid (85%) boiling at 80 °C at 3 mmHg. IR: 1775, 3161, 1439, 1434, 1231, 1150, 993 cm^{-1}.

The perfluoro-2-methyl-3-oxa-hexanoic acid was prepared from 167.5 g perfluoro-2-methyl-3-oxa-hexanoic acid fluoride (0.50 mol) and 90.3 g water (5.00 mol) using the same method, with a yield of 81%. IR: 1774, 3159, 1438, 1435, 1235, 1150, 993 cm^{-1}.

Amounts of 80.0 g thionyl chloride (0.67 mol) and 5.0 g DMF were added into a dry three-neck flask and the mixture was stirred for 0.5 h. Then, 165.4 g pure perfluoro-2,5-dimethyl-3, 6-dioxa-nonanoic acid (0.33 mol) were added dropwise into the reaction mixture. The temperature of the reaction mass was then elevated to 80 °C, followed by vigorous stirring. After 5 h, the cloudy mixture was cooled to room temperature and the liquid separating into two layers was obtained. From this, the liquid in the lower layer was recovered and distilled to yield 146 g pure perfluoro-2,5-dimethyl-3,6-dioxa-nonanoyl chloride (yield 75%) boiling at 68 °C at 10 mmHg. IR: 1809, 1241, 994 cm^{-1}.

The perfluoro-2-methyl-3-oxa-hexanoic acid chloride was prepared in 65% yield from 109.6 g perfluoro-2-methyl-3-oxa-hexanoic acid (0.33 mol), 80.0 g thionyl chloride (0.67 mol), and 5.0 g DMF by means of the same procedure, with a yield of 65%. IR: 1810, 1248, 1156, 992 cm^{-1}.

Preparation of methyl perfluoroalkyl ether carboxylate

The methyl perfluoroalkyl ether carboxylate was prepared by esterfication of perfluorinated ether acid fluoride with methanol. A mixed solution of 41.11 g

anhydrous triethylamine (0.40 mol) in 47.5 g anhydrous methanol (1.48 mol) was added dropwise into 185 g perfluoro-2,5-dimethyl-3, 6-dioxa-nonanoic acid fluoride (0.37 mol) in a dry three-neck flask under agitation over a period of 2 h at 0 °C. The mixture was agitated for another 4 h and the temperature of reaction mass was maintained at room temperature. Subsequently, the reaction mixture was poured into a separating funnel. The fluorocarbon layer was washed with sodium bicarbonate solution and dried over anhydrous sodium sulfate to obtain the crude product. The crude product was distilled to give 178.43 g methyl perfluoro-2,5-dimethyl-3,6-dioxa-nonanoate (yield 94%) boiling at 145 °C at 760 mmHg. IR: 2969,1792,1290, 1237, 1145, 1040, 994 cm^{-1}. ^{1}H-NMR (500 MHz, $CDCl_3$): δ 3.99 (3H, s, C**H**$_3$).^{13}C-NMR(125 MHz, $CDCl_3$): δ 54.60 (–**C**H$_3$–).

Methyl perfluoro-2-methyl-3-oxa-hexanoate was prepared in 91% yield from 134.3 g perfluoro-2-methyl-3-oxa-hexanacid fluoride (0.40 mol), 51.2 g anhydrous methanol (1.60 mol) and 43.7 g anhydrous triethylamine (0.43 mol) using the same procedure. IR: 2970, 1792, 1292, 1233, 1152, 1040, 993 cm^{-1}. ^{1}H-NMR (500 MHz, $CDCl_3$): δ 3.96 (3H, s, C**H**$_3$). ^{13}C-NMR (125 MHz, $CDCl_3$): δ 54.57 (**C**H$_3$).

Preparation of bis(2-chloroethyl)amine

To a mechanically stirred solution of 63.7 g diethanolamine (0.60 mol) in anyhydrous chloroform (250 mL), 221.0 g thionyl chloride (1.85 mol) were added dropwise at room temperature. The reaction mixture was later heated to reflux, followed by vigorous stirring. Then, 3 h later, the reaction mixture was cooled to 0 °C. The precipitate was then filtered, washed with diethyl ether, and dried under an infrared lamp to obtain 78.1 g white solid bis(2-chloroethyl)amine hydrochloride with a yield of 72%. ^{1}H NMR (500 MHz, CD_3OD): δ 4.91 (2H, s,-N**H**$_2$), 3.96 (4H, t, –N–C**H**$_2$), 3.54 (4H, t, –C**H**$_2$–Cl).

An amount of 17.8 g bis(2-chloroethyl)amine hydrochloride (0.10 mol) was added to 200 mL dichloromethane to form a suspension. Later, 120 mL aqueous solution of sodium hydroxide (1 moL/L) were added and stirred at room temperature for 6 h. The dichlormethane layer was separated, dried over anhydrous sodium sulfate, and concentrated to obtain the crude product, which was distilled under reduced pressure to acquire the pure bis (2-chloroethyl)amine, with a yield of 70%. ^{1}H NMR (500 MHz, $CDCl_3$): δ 3.60 (4H, t, J = 4.40 Hz, –C**H**$_2$–Cl), 2.94 (4H, t, –N–C**H**$_2$), 1.88 (1H, s, -N**H**).

General procedures for the synthesis of fluorinated monomers

Procedure A To a magnetic stirred solution of 15.6 g triethylamine (0.15 mol) and 10.10 g allyl alcohol (0.17 mol) in anhydrous chloroform (150 mL) in a dry three-neck flask, 74.90 g perfluoro-2,5-dimethyl-3,6-dioxa-nonanoyl fluoride (0.15 mol) were added dropwise over a period of 3 h under agitation at 0 °C. The reaction mixture was stirred for a further 12 h, with the temperature of reaction mass being maintained at room temperature. Distilled water was added to extract the triethylammonium fluoride and the unreacted allyl alcohol at the end of the

reaction. The chloroform layer was dried over anhydrous sodium sulfate, and the major portion of the chloroform was distilled off in the vacuum of a water-jet pump over water. Additionally, the crude product was obtained and distilled under reduced pressure to give the pure product.

Procedure B To a mechanically stirred solution of 12.5 g triethylamine (0.12 mol) and 51.6 g perfluoro-2,5-dimethyl-3,6-dioxa-nonanoyl chloride (0.10 mol) in anhydrous dichloromethane (100 mL) in a dry three-neck flask, 8.25 g glycidol (0.12 mol) were added dropwise under agitation at − 10 °C and the mixture was stirred for 2 h. Then, the cryopump was removed, andthe mixture allowed to stand at room temperature for 5 h. The subsequent procedures exactly followed those in procedure A.

Procedure C An amount of 61.5 g methyl perfluoro-2,5-dimethyl-3,6-dioxa-nonanoate (0.12 mol) was added dropwise into 15.4 g ethylenediamine (0.25 mol) at room temperature under a nitrogen atmosphere. The reaction mixture was stirred at room temperature for 24 h. Later, 400 mL chloroform and 100 mL water were added into the mixture, the chloroform layer was collected and dried over anhydrous sodium sulfate, then evaporated, and the residue was distilled under reduced pressure to obtain the pure product.

Procedure D An amount of 21.0 g pre-distilled diethanolamine (0.20 mol) was added in 200 mL DMF under mechanical stirring, and then 51.5 g perfluoro-2,5-dimethyl-3,6-dioxa-nonanoyl chloride (0.10 moL) were added dropwise into the mixed solution at − 20 °C under a nitrogen atmosphere. After being stirred for 3 h, the cryopump was removed, and the reaction mixture was allowed to stand for 24 h at room temperature. The reaction mixture was acidified with hydrochloric acid; meanwhile, the solvent was removed under reduced pressure. Subsequently, the crude product was further purified by column chromatography using silica gel with methanol and chloroform as eluent.

Procedure E An amount of 9.13 g pre-distilled 3-amino-1,2-propanediol (0.10 mol) was added in a dry round-bottomed flask fitted with a stirrer, thermometer and drop funnel, and then 51.4 g methyl perfluoro-2,5-dimethyl-3,6-dioxa-nonanoate (0.10 mol) were added dropwise from the funnel. The reaction mixture was stirred for 6 h at 65 °C and then cooled to room temperature and the unreacted methyl perfluoroalkyl ether carboxylate and methanol was removed under reduced pressure The crude product was purified by column chromatography as described above under Procedure D.

Procedure F Amounts of 6.0 g trifluoroacetic acid and 30 g water were added to 61.0 g glycidyl perfluoro-2,5-dimethyl-3,6-dioxa-nonanoate (0.11 mol). The mixture was stirred vigorously for 24 h at room temperature. Next, 400 mL chloroform were added to the mixture, then the chloroform layer was washed with sodium bicarbonate solution and dried over anhydrous sodium sulfate. The chloroform was removed on a rotary evaporator, and the residue was purified by distillation under reduced pressure.

Allyl perfluoro-2-methyl-3-oxa-hexanoate (1a, FP2_Ally)

Colorless liquid, yield 75%, bp 78 °C(10 mmHg). IR: 1781, 1643, 1332, 1285, 1235, 1152, 1038, 993 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): δ 5.97–5.89 (1H, m, –C**H**=C), 5.47–5.38 (2H, m, –C=C**H**$_2$), 4.89–4.83 (2H, m, –O–C**H**$_2$–).^{13}C NMR (125 MHz, $CDCl_3$): δ 69.06 (–O–**C**H_2–), 129.29 (–**C**H–), 121.22 (=CH_2). ^{19}F NMR (500 MHz, $CDCl_3$): δ − 80.05 (m, 1F, $CF_3CF_2C\mathbf{F}_2$), − 82.09 (m, 3F, OCF(C**F$_3$**)), − 87.09 (m, 1F, $CF_3CF_2C\mathbf{F}_2$), − 82.89 (m, 3F, C**F$_3$**CF_2CF_2), − 130.30 (s, 2F, $CF_3C\mathbf{F}_2CF_2$), −132.06 (t, 1F, OC**F**CF_3). GC–MS (*m*/*z*): 69[CF_3]$^+$, 169 [C_3F_7]$^+$, 370 [M-e]$^+$.

Allyl perfluoro-2,5-dimethyl-3,6-dioxa-nonanoate (2a, FP3_Ally)

Colorless liquid, yield 83%, bp 90 °C (10 mmHg). IR: 1787, 1648, 942, 1283, 1239, 1147, 1038, 994 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): δ 5.97–5.89 (1H, m, –C**H**=C), 5.47–5.39 (2H, m, –C=C**H**$_2$), 4.90–4.82 (2H, m, –O–C**H**$_2$–).^{13}C NMR (125 MHz, $CDCl_3$): δ 69.09 (–O–**C**H_2–), 129.38 (–**C**H–), 121.35 (=CH_2). ^{19}F NMR (500 MHz, $CDCl_3$): δ − 79.0 (m, 2F, C**F$_2$**OCF(CF_3)COO), − 79.6 (m, 3F, $CF_2OCF(C\mathbf{F}_3)$-CF_2O), − 80.5 (t, 3F, C**F$_3$**CF_2CF_2), − 81.4 (m, 3F, $CF_2OCF(C\mathbf{F}_3)$COO), − 85.6 (m, 2F, $CF_3CF_2C\mathbf{F}_2$), − 128.9 (s, 2F, $CF_3C\mathbf{F}_2CF_2$), − 129.0 (s, 1F, $CF_2OC\mathbf{F}(CF_3)$-COO), − 131.0 (m, 1F, $CF_2OC\mathbf{F}(CF_3)CF_2$). GC–MS (*m*/*z*): 69 [$CF_3$]$^+$, 169 [$C_3F_7$]$^+$, 508 [M-($CH_2$=$CH_2$)]$^+$, 536 [M-e]$^+$.

Methacrylic acid-β-(perfluoro-2-methyl-3-oxa-hexanoyl) acetate (1b, FP2_HEMA)

Colorless liquid, yield 87%, bp 94 °C (3 mmHg). IR: 2968, 1789, 1727, 1640, 1235, 1152, 992 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): δ 6.11 (1H, s, –C(CH_3)=C**H**$_2$), 5.62 (1H, s, –C(CH_3)=C**H**$_2$), 4.69–4.62 (2H, m, –O–C**H**$_2$), 4.44–4.43 (2H, m, –COO–C**H**$_2$–), 1.93 (3H, s, –C(C**H**$_3$)=C). ^{13}C NMR (125 MHz, $CDCl_3$): δ 167.23 (C=C–**C**=O), 135.55 (**C**=CH_2), 126.46 (C=**C**H_2), 66.06 (–COO–**C**H_2–), 61.55 (–O–**C**H_2), 17.62 (–**C**H_3). GC–MS (*m*/*z*): 41 [CH_2CH=CH_2]$^+$, 69 [CF_3]$^+$, 169 [C_3F_7]$^+$, 442 [M-e]$^+$.

Methacrylic acid-β-(perfluoro-2,5-dimethyl-3,6-dioxa-nonanoyl) acetate (2b, FP3_HEMA)

Colorless liquid, yield 94%, bp 104 °C (3 mmHg). IR: 2967, 1789, 1728, 1640, 1240, 1147, 993 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): δ 6.10 (1H, s, –C(CH_3)=C**H**$_2$), 5.61 (1H, s, -C(CH_3)=C**H**$_2$), 4.43–4.41 (2H, m, –O–C**H**$_2$), 4.43–4.41 (2H, m, –COO–C**H**$_2$–), 1.92 (3H, s, –C(C**H**$_3$)=C). ^{13}C NMR (125 MHz, $CDCl_3$): δ 168.84 (C=C–**C**=O), 135.54 (**C**=CH_2), 126.36 (C=**C**H_2), 66.08 (–COO–**C**H_2–), 61.36 (–O–**C**H_2), 17.86 (–**C**H_3). GC–MS (*m*/*z*): 41 [CH_2CH=CH_2]$^+$, 69 [CF_3]$^+$, 169 [C_3F_7]$^+$, 335 [$C_3F_7OCF(CF_3)CF_2$]$^{+\cdot}$ 523 [M-OCOCH(CH_3)=CH_2]$^+$, 608 [M-e]$^+$.

N-methyl-N-allyl-perfluoro-2-methyl-3-oxa-hexanamide (1c, FP2_NAlly)

Colorless liquid, yield 78%, bp 52 °C (3 mmHg). IR: 1687, 1648, 1235, 1146, 1105, 991, 933 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): δ 5.79–5.69 (1H, m, –C**H**=C), 5.29–5.19 (2H, m, –C=C**H**$_2$), 4.24–3.89 (2H, m, –N–C**H**$_2$–),3.03, 3.14, 3.13 (3H, t, N–C**H**$_3$). ^{13}C NMR (125 MHz, $CDCl_3$): δ 35.26 (N–**C**H_3), 52.78 (–N–**C**H_2–), 118.36 (=**C**H_2), 131.13 (–**C**=). GC–MS (*m/z*): 69 $[CF_3]^+$, 169 $[C_3F_7]^+$, 368 [M-$CH_3]^+$, 383 $[M\text{-}e]^+$.

N-methyl-N-allyl-perfluoro-2,5-dimethyl-3,6-dioxa-nonanamide (2c, FP3_NAlly)

Colorless liquid, yield 82%, bp 68 °C (3 mmHg). IR: 1687, 1648, 1238, 1146, 1105, 993, 935 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): δ 5.80–5.70 (1H, m, –C**H**=C), 5.29–5.19 (2H, m, –C=C**H**$_2$), 4.24–3.91 (2H, m, –N–C**H**$_2$–), 3.15, 3.14, 3.04(3H, t, N–C**H**$_3$).^{13}C NMR (125 MHz, $CDCl_3$): δ 35.30 (N–**C**H_3), 52.87 (–N–**C**H_2–), 118.45 (=**C**H_2), 131.05 (–**C**=). GC–MS (*m/z*): 69 $[CF_3]^+$, 169 $[C_3F_7]^+$, 534 [M-$CH_3]^+$, 549 $[M\text{-}e]^+$.

Glycidyl perfluoro-2-methyl-3-oxa-hexanoate (1d, FP2_PO)

Colorless liquid, bp 68 °C (3 mmHg). IR: 3020, 1789, 1238, 1147, 1038, 993 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): δ 4.68–4.63 (1H, m, –COO–C**H**$_2$), 4.27–4.23 (1H, m,–COO–C**H**$_2$), 3.26–3.23 (1H, m,–O–C**H**–), 2.89–2.86 (1H, m, –O–C**H**$_2$–), 2.68–2.66 (1H, m, –O–C**H**$_2$–). ^{13}C NMR (125 MHz, $CDCl_3$): δ 68.87 (–COO–**C**H_2), 47.98 (–O–**C**H–), 44.09 (–O–**C**H_2). GC–MS (*m/z*): 169 $[C_3F_7]^+$, 386 $[M\text{-}e]^+$.

Glycidyl perfluoro-2,5-dimethyl-3, 6-dioxa-nonanoate (2d, FP3_PO)

Colorless liquid, bp 76 °C (3 mmHg). IR: 3018, 1789, 1383, 1238, 1147, 1038, 993 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): δ 4.70–4.61 (1H, m, –COO–C**H**$_2$), 4.30–4.23 (1H, m, –COO–C**H**$_2$), 3.28–3.24 (1H, m, –CH_2–C**H**–O–), 2.91–2.88 (1H, m, –O–C**H**$_2$–), 2.70–2.68 (1H, m, –O–C**H**$_2$–). ^{13}C NMR (125 MHz, $CDCl_3$): 68.83 (–COO–**C**H_2), 48.00 (–O–**C**H–), 44.33 (–O–**C**H_2). GC–MS (*m/z*): 169 $[C_3F_7]^+$, 552 $[M\text{-}e]^+$.

N-(2-hydroxyethyl)-perfluoro-2-methyl-3-oxa-hexanamide (1e, FP2_MEA)

Soild, yield 82%, bp 112 °C (3 mmHg). IR: 3335, 1709, 1547, 1232, 1135, 991 cm^{-1}.^{1}H NMR (500 MHz, DMSO): δ 9.51 (1H, s, –N**H**–), 4.79 (1H, s, –O**H**), 3.48–3.44 (2H, m, –C**H**$_2$–O–), 3.34–3.23 (2H, m, –N–C**H**$_2$–).^{13}C NMR (125 MHz, DMSO): δ 40.23 (–NH–**C**H_2–), 60.75 (–C**H**$_2$–OH). GC–MS (*m/z*): 69 $[CF_3]^+$, 169 $[C_3F_7]^+$, 328 [M-(CH_2CH_2OH)], 356 $[M\text{-}OH]^+$, 373 $[M\text{-}e]^+$.

N-(2-hydroxyethyl)-perfluoro-2,5-dimethyl-3,6-dioxa-nonanamide (2e, FP3_MEA)

Soild, yield 79%, bp 127 °C (3 mmHg). IR: 3422, 1709, 1532, 1236, 1158, 994 cm^{-1}. ^1H NMR (500 MHz, DMSO): δ 9.40 (1H, s, –N**H**–), 4.75 (1H, s, –O**H**), 3.53–3.38 (2H, m, –C**H**$_2$–O–), 3.29–3.24 (2H, m, –N–**C**H$_2$–).^{13}C NMR (125 MHz, CD_3OD): δ 42.36 (–NH–**C**H$_2$–), 58.80 (–**C**H$_2$–OH). GC–MS (*m/z*): 169 $[C_3F_7]^+$, 509 $[M\text{-}CH_2O]^+$, 539 $[M\text{-}e]^+$.

N-(2-aminoethyl)-perfluoro-2-methyl-3-oxa-hexanamide (1f, FP2_EA)

Colorless viscous liquid, yield 66%, bp 110 °C (3 mmHg). IR: 3326, 3178, 1708, 1547, 1233, 1165, 992 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ 7.59 (1H, s, –N**H**–), 3.43–3.36 (2H, m, –N–**C**H$_2$–), 2.90–2.88 (2H, t, –C**H**$_2$–N–), 1.27 (2H, s, –NH$_2$).^{13}C NMR (125 MHz, $CDCl_3$): δ 42.49 (–NH–**C**H$_2$–), 40.23 (–**C**H$_2$–NH$_2$). GC–MS (*m/z*): 169 $[C_3F_7]^+$, 354 $[M\text{-}NH_3]^+$, 371 $[M\text{-}H]^+$.

N-(2-aminoethyl)-perfluoro-2,5-dimethyl-3,6-dioxa-nonanamide (2f, FP3_EA)

Colorless viscous liquid, yield 74%, bp 120 °C (3 mmHg). IR: 3340, 3192, 1707, 1545, 1237, 1155, 994 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ 7.38 (1H, s, –N**H**–), 3.45–3.38 (2H, m, –N–**C**H$_2$–), 2.92–2.90 (2H, t, –C**H**$_2$–N–), 1.31 (2H, s, –N**H**$_2$). ^{13}C NMR (125 MHz, $CDCl_3$): δ 42.40 (–NH–**C**H$_2$–), 40.23 (–**C**H$_2$–NH$_2$). GC–MS (*m/z*): 169 $[C_3F_7]^+$, 519 $[M\text{-}NH_3]^+$, 537 $[M\text{-}H]^+$.

Monoglyceride perfluoro-2-methyl-3-oxa-hexanoate (1g, FP2_GO)

Colorless liquid, yield 82%, bp 110 °C (3 mmHg). IR: 3445, 2963, 1787, 1454, 1228, 1154, 993 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ 4.56–4.52 (1H, m, -COO-C**H**$_2$), 4.49–4.45 (1H, m, –COO–C**H**$_2$), 4.20–4.16 (1H, m, –C**H**), 3.69–3.60 (2H, m, –C**H**$_2$**OH**).^{13}C NMR (125 MHz, $CDCl_3$): δ 69.17 (–**C**H–OH), 67.52 (COO–**C**H$_2$), 44.60 (–**C**H$_2$–OH). GC–MS (*m/z*): 169 $[C_3F_7]^+$, 373 $[M\text{-}CH_2OH]^+$.

Monoglyceride perfluoro-2,5-dimethyl-3,6-dioxa-nonanoate (2g, FP3_GO)

Colorless liquid, yield 85%, bp 122 °C (3 mmHg). IR: 3450, 2970, 1788, 1454, 1238, 1149, 994 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ 4.57–4.53 (1H, m, –COO–C**H**$_2$), 4.48–4.43 (1H, m, –COO–C**H**$_2$), 4.19–4.14 (1H, m, -C**H**), 3.68–3.58 (2H, m, –C**H**$_2$**OH**). ^{13}C NMR (125 MHz, $CDCl_3$): δ 69.16 (–**C**H–OH), 67.52 (COO–**C**H$_2$), 44.66 (–**C**H$_2$–OH). GC–MS(*m/z*): 169 $[C_3F_7]^+$, 539 $[M\text{-}CH_2OH]^+$.

N-(2,3-dihydroxypropyl)-perfluoro-2-methyl-3-oxa-hexanamide (1h, FP2_APDO)

Colorless viscous liquid, yield 71%. IR: 3344, 3081, 2949, 2888, 1708, 1545, 1234, 991 cm^{-1}. ^1H NMR (500 MHz, CD_3OD): δ 4.86 (3H, s, –N**H**–, –O**H**), 3.83–3.73 (1H, m, –C**H**OH), 3.57–3.46 (2H, m, –C**H**$_2$OH), 3.57–3.46 (1H, m, –N–**C**H$_2$–), 3.38–3.32 (1H, m, –N–**C**H$_2$–).^{13}C NMR (125 MHz, CD_3OD): δ 44.04 (–NH–**C**H$_2$–),

65.17 (–$\mathbf{C}$$H_2$–OH), 71.34 (–$\mathbf{C}$H–OH). ESI–MS (*m/z*): 426 $[M + Na]^+$, 448 $[M-H + 2Na]^+$.

N-(2,3-dihydroxypropyl)-perfluoro-2,5-dimethyl-3,6-dioxa- nonanamide (2h, FP3_APDO)

Colorless viscous liquid, yield 74%, IR: 3345, 3084, 2949, 2888, 1707, 1543, 1236, 994 cm^{-1}. ^{1}H NMR (500 MHz, CD_3OD): δ 4.88 (3H, s, –N$\mathbf{H}$–, –OH), 3.80–3.74 (1H, m, –C$\mathbf{H}$OH–), 3.56–3.45 (2H, m, –C$\mathbf{H_2}$OH), 3.56–3.45 (1H, m, –N–$\mathbf{C}$$H_2$–), 3.39–3.32 (1H, m, –N–$\mathbf{C}$$H_2$–). ^{13}C NMR (125 MHz, CD_3OD): δ 43.83 (–NH–$\mathbf{C}$$H_2$–), 64.97 (–$\mathbf{C}$$H_2$–OH), 71.18 (–$\mathbf{C}$H–OH). ESI–MS (*m/z*): 570 $[M + H]^+$, 592 $[M + Na]^+$.

N,N-bis(2-hydroxyethyl)-perfluoro-2-methyl-3-oxa-hexanamide (1i, FP2_DEA)

Colorless viscous liquid, yield 52%, IR: 3397, 2923, 1719, 1488, 1272, 1194, 975 cm^{-1}. ^{1}H NMR (500 MHz, $CHCl_3$): δ 4.23–4.20 (2H, t, –N(–C$\mathbf{H}_2$–)$_2$), 3.24–3.22 (2H, t, –N(–C$\mathbf{H}_2$–)$_2$), 3.60–3.57 (4H, m, –(C$\mathbf{H}_2$–O–)$_2$). ^{13}C NMR (125 MHz, $CDCl_3$): δ 62.15, 59.78 (–$\mathbf{C}$$H_2$–OH), 46.56, 45.34 (–N–$\mathbf{C}$$H_2$–). ESI–MS (*m/z*): 418 $[M + H]^+$.

N,N-bis(2-hydroxyethyl)-perfluoro-2,5-dimethyl-3,6-dioxa-nonanamide (2i, FP3_DEA)

Colorless viscous liquid, yield 49%, IR: 3395, 2923, 1724, 1532, 1272, 1194, 975 cm^{-1}. ^{1}H NMR (500 MHz, $CHCl_3$): δ 4.25–4.21 (2H, t, –N(–C$\mathbf{H}_2$–)$_2$), 3.26–3.24 (2H, t, –N(–C$\mathbf{H}_2$–)$_2$), 3.64–3.58 (4H, m, –(C$\mathbf{H}_2$–O–)$_2$). ^{13}C NMR (125 MHz, $CDCl_3$): δ 62.04, 59.38 (–$\mathbf{C}$$H_2$–OH), 46.34, 45.12 (–N–$\mathbf{C}$$H_2$–). ESI–MS(*m/z*): 584 $[M + H]^+$.

N,N-bis(2-chloroethyl)-perfluoro-2-methyl-3-oxa-hexanamide (1j, FP2_DECl)

Colorless liquid, yield 72%, bp 80 °C(3 mmHg). IR: 2970, 1686, 1234, 1146, 994 cm^{-1}. ^{1}H NMR (500 MHz, $CHCl_3$): δ 4.09–3.62 (8H, m). ^{13}C NMR (125 MHz, $CDCl_3$): δ 52.73, 51.66 (–C$\mathbf{H}_2$–Cl), 41.12, 39.88 (–N–$\mathbf{C}$$H_2$–). GC–MS (*m/z*): 169 $[C_3F_7]^+$, 404 $[M\text{-}CH_2Cl]^+$, 418 $[M\text{-}Cl]^+$, 453 $[M\text{-}e]^+$.

N,N-bis(2-chloroethyl)-perfluoro-2,5-dimethyl-3, 6-dioxa-nonanamide (2j, FP3_DECl)

Colorless liquid, yield 76%, bp 96 °C(3 mmHg). IR: 2972, 1685, 1238, 1152, 993 cm^{-1}. ^{1}H NMR (500 MHz, $CHCl_3$): δ 4.10–3.63 (8H, m). ^{13}C NMR (125 MHz, $CDCl_3$): δ 52.91, 51.79 (–C$\mathbf{H}_2$–Cl), 41.18, 39.95 (–N–$\mathbf{C}$$H_2$). GC–MS (*m/z*): 169 $[C_3F_7]^+$, 570 $[M\text{-}CH_2Cl]^+$, 584 $[M\text{-}Cl]^+$, 619 $[M\text{-}e]^+$.

Results and discussion

Synthesis of fluorinated monomers

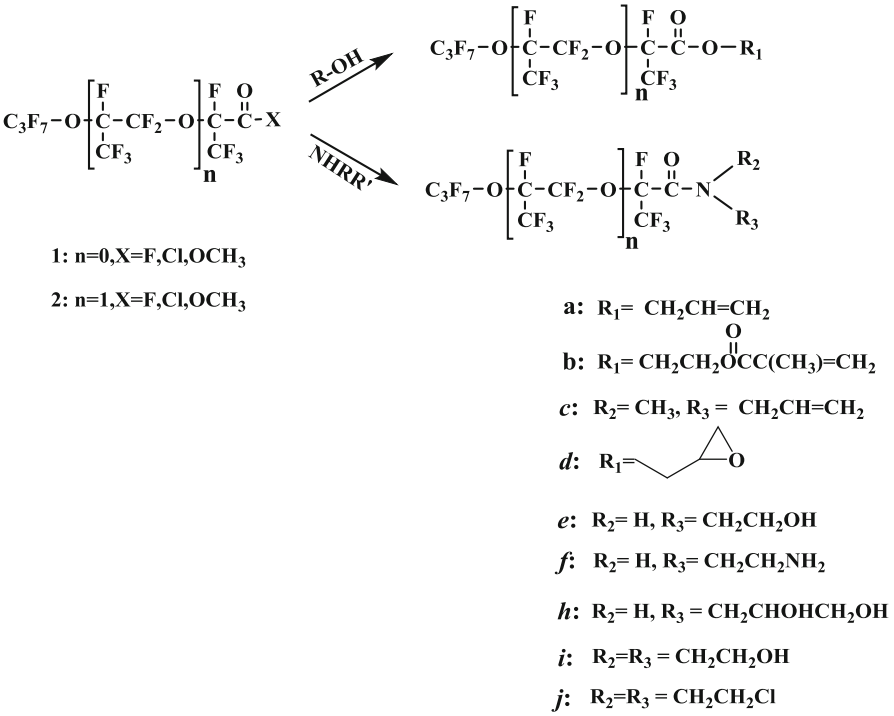
PFEF, perfluoroalkyl ether acid chloride (PFEC) and methyl perfluoroalkyl ether carboxylate (PFEM) are the desirable starting materials for synthesizing respective fluorinated monomers. Furthermore, the functionalized fluorinated monomers can be typically synthesized by the reactions of PFEF, PFEC or PFEM with the corresponding alcohols or amines. The chemical structures of the target compounds are shown in Schemes 1 and 2, while the formulas and corresponding abbreviations for the prepared fluorinated monomers are presented in Table 1.

Preparation of PFEC and PFEM

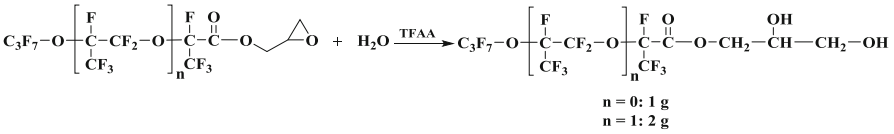
PFEC is the more reactive acylating agent for many organic reactions. Unfortunately, it is not available from commercial sources. Thus, it can be prepared from the corresponding acid by chlorination with thionyl chloride. However, such a reaction is associated with a greatly diversified yield, ranging from low to excellent. Treating acid with thionyl chloride would generally not give rise to perfluoroalkyl ether carbonyl chloride at elevated temperatures. In addition, a higher yield of carbonyl chloride could be obtained using thionyl chloride in the presence of DMF. Differences in the yields could be attributed to the chlorinating regents in the reaction. The actual chlorinating reagent was the Vilsmeier reagent formed from the reaction of DMF with thionyl chloride. It was a superior chlorinating reagent for preparing perfluoroalkyl ether carbonyl chloride from the corresponding acid. PFEM could be obtained in a single step by means of the reaction of anhydrous methanol with the corresponding PFEF in the presence of triethylamine. Importantly, the generated triethylamine hydrofluoride was immiscible with PFEM, which could be further purified through vacuum distillation; thus, the colorless liquid could be obtained: IR: 2939, 2939, 1477, 1835, 1229, 1171, 1035, 846 cm^{-1}.^{1}H NMR (500 MHz, $CDCl_3$): δ 0.76 (9H, q, –C**H**$_3$), 2.58 (6H, t, –N–C**H**$_2$), 9.22 (3H, s, HF). Triethylamine trihydrofluoride, the obtained by-product, is a good fluorinating reagent widely used in organic fluorination reactions [24–26].

Synthesis of O-functionalized fluorinated monomers

The O-functionalized fluorinated monomers (1*a–b*, 2*a– b*, 1*d*, 2*d*) are typically synthesized in the manner of the reaction of PFEF or PFEC with a slightly excessive amount of the corresponding alcohols, and with triethylamine being served as an acid acceptor. However, large discrepancies can be seen in the reactions of vinyl-containing alcohols and glycidol with PFEF. Treating vinyl-containing alcohols with PFEF or PFEC could directly result in corresponding vinyl-containing fluorinated monomers, which could be incorporated into the polymer through radical copolymerization. However, the reaction of glycidol with PFEF gives rise to several by-products which are difficult to separate. The structures of these by-



Scheme 1 Synthesis route of fluorinated monomers



Scheme 2 Synthesis route of monoglyceride perfluoroalkyl ether carboxylate

products were characterized using infrared spectroscopy (Fig. 1). As shown in Fig. 1, the typical absorption peak of hydroxyl group can be observed at 3385 cm^{-1}, resulting from the ring-opening of the epoxide compound. The instability of the strained three-membered ring in the epoxy compound was responsible for such a phenomenon. The hydrogen fluoride and triethylamine trihydrofluoride formed in the reaction had increased the susceptibility of the ring-opening reaction by nucleophiles. It is concluded that the ring-opening reaction between glycidol and PFEF indeed takes place.

It was discovered in this study that ring-opening of the epoxide moiety, which was the side reaction, could be efficiently prevented using PFEC as the acylating agent with excessive triethylamine as the acid acceptor. No ring-opening by-products were observed; moreover, the triethylamine hydrochloride could be removed through filtration. Glycidyl perfluoroalkyl ether carboxylate could be obtained at a yield of over 70% under such conditions. Monoglyceride

Table 1 Synthesis of fluorinated monomers

Compound	Formula	Abbreviation	Solvent	Method
1*a*	$C_6F_{11}O_3$–C_3H_5	FP2_ALLY	$CHCl_3$	A
2*a*	$C_9F_{17}O_4$–C_3H_5	FP3_ALLY	$CHCl_3$	A
1*b*	$C_6F_{11}O_3$–$C_6H_9O_2$	FP2_HEMA	$CHCl_3$	A
2*b*	$C_9F_{17}O_4$–$C_6H_9O_2$	FP3_HEMA	$CHCl_3$	A
1*c*	$C_6F_{11}O_2$–C_4H_8N	FP2_NALLY	$CHCl_3$	A
2*c*	$C_9F_{17}O_3$–C_4H_8N	FP3_NALLY	$CHCl_3$	A
1*d*	$C_6F_{11}O_3$–C_3H_5O	FP2_PO	CH_2Cl_2	B
2*d*	$C_9F_{17}O_4$–C_3H_5O	FP3_PO	CH_2Cl_2	B
1*e*	$C_6F_{11}O_2$–C_2H_6N	FP2_MEA	THF	A
2*e*	$C_9F_{17}O_3$–C_2H_6N	FP3_MEA	THF	A
1*f*	$C_6F_{11}O_2$–$C_2H_7N_2$	FP2_EA	None	B
2*f*	$C_9F_{17}O_3$–$C_2H_7N_2$	FP3_EA	None	B
1*g*	$C_6F_{11}O_2$–$C_3H_7O_3$	FP2_GO	None	F
2*g*	$C_9F_{17}O_3$–$C_3H_7O_3$	FP3_GO	None	F
1*h*	$C_6F_{11}O_2$–$C_3H_8NO_2$	FP2_APDO	None	E
2*h*	$C_9F_{17}O_3$–$C_3H_8NO_2$	FP3_APDO	None	E
1*i*	$C_6F_{11}O_2$–$C_4H_{10}NO_2$	FP2_DEA	DMF	D
2*i*	$C_9F_{17}O_3$–$C_4H_{10}NO_2$	FP3_DEA	DMF	D
1*j*	$C_6F_{11}O_2$–$C_4H_8NCl_2$	FP2_DECl	CH_2Cl_2	A
2*j*	$C_9F_{17}O_3$–$C_4H_8NCl_2$	FP3_DECl	CH_2Cl_2	A

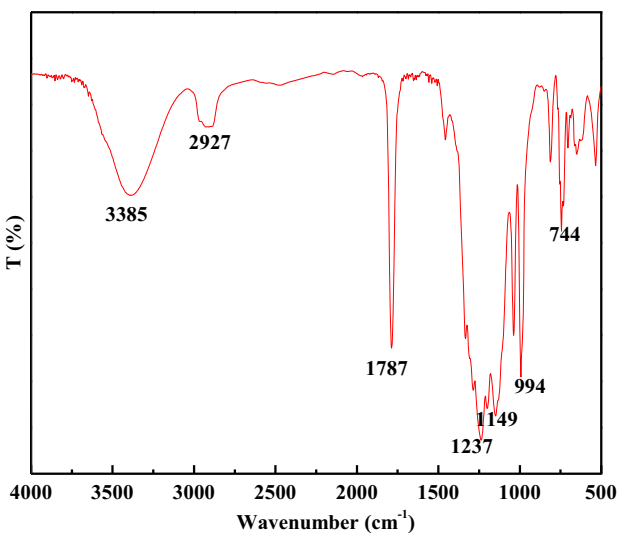


Fig. 1 FTIR spectra of byproducts from glycidol and PFEF

perfluoroalkyl ether carboxylate (1*g*, 2*g*) was prepared form the ring-opening of the synthesized epoxy monomer with water using trifluoroacetic acid (TFAA) as the catalyst (see Scheme 2).

Synthesis of N-functionalized fluorinated monomers

N-functionalized fluorinated monomers were prepared by means of the reaction of PFEF, PFEC or PFEM with the corresponding amines. Treatment of ethanolamine with PFEF allowed for the controlling of the chemoselective *N*-acylation over *O*-acylation at 0 °C. However, the reactions proceeded in a quite distinct way with the amino alcohol of diethanolamine. PFEC could react with diethanolamine, which allowed for producing the expected products (1*i*, 2*i*); however, no desired products were obtained from the reaction of PFEF with diethanolamine. The potential intramolecular hydrogen bonding (N–H···O) causing poor nucleophilicity of diethanolamine might be responsible for such a result, which thus hindered the reaction of PFEF with diethanolamine. PFEC had a relatively higher electrophilicity compared with its corresponding homologues, which made it sufficiently reactive to react with diethanolamine. Additionally, it was found in this study that the hydroxyl groups of diethanolamine had been replaced by chlorine to form bis(2-chloroethy1)amine. The *N*,*N*-bis(2-chloroethyl)-substituted perfluoroalkyl ether carboxamide (1*j*, 2*j*) had been successfully prepared at low temperature (to reduce self-condensation of the amine) using PFEF as acylating reagent. Such a replacement had enhanced the nucleophilicity of the amino-nitrogen, making it sufficiently reactive to react with PFEF to form the amide. The synthesized *N*,*N*-bis(2-chloroethyl)-perfluoroalkyl ether carboxamide (1*j*, 2*j*) had two electrophilic sites, which could polmerize with monomers that had two nucleophilic sites. The ethylenediamine contains two almost identically reactive sites which were available for combination with the acylating reagent. To synthesize *N*-(2-aminoethyl)-perfluoroalkyl ether carboxylamide (1*f*, 2*f*), controling the chemoselective mono-amide formation had played a key role in the course of the synthesis and the reaction could not be sufficiently controlled using PFEC or PFEF as the acylating agent. Therefore, an efficiently chemoselective mono-amidation reaction was developed in this study with PFEM as the acylating agent. The high nucleophilicity of amino-nitrogen in 3-amino-1,2-propanediol made it sufficiently reactive to react with PEFM to synthesize *N*-(2, 3-dihydroxypropyl)-perfluoroalkyl ether carboxamide (1*h*, 2*h*). Furthermore, it was found in the current study that *N*-methyl-*N*-allyl-perfluoroalkyl ether carboxamide (1*c*, 2*c*) and *N*-(2-hydroxyethyl)-perfluoroalkyl ether carboxamide (1*e*, 2*e*) could also be obtained in high yields by the reactions of PFEM with *N*-allylmethylamine or 2-aminoethanol.

Properties of fluorinated monomers

Twenty derivatives of perfluoroalkyl ether carbonyl compounds were prepared in the current study, 12 of which are reported for the first time. Most of these compounds were liquid at room temperature. As has been reported, the melting point of an organic compound is mainly determined by three factors, the

intermolecular force, the molecular symmetry and the degree of conformational freedom of the molecule [27]. The low melting point could be attributed to the higher flexibility of the branched perfluoroalkyl ether chain structures, which could be achieved by the increased degree of conformational freedom and the decreased molecular symmetry.

Of the synthesized fluorinated monomers, the ester linkage-containing monomers showed superb solubility in common organic solvents such as dichloromethane, chloroform, alcohols, esters and ethers. In contrast, the amide linkage-containing monomers had good solubility in alcohols, ethers and amides. Surprisingly, compounds 1*i* and 2*i* were soluble in water, which could be used as surfactants that exhibited strong foamability.

Conclusions

In summary, 20 derivatives of perfluoroalkyl ether carbonyl compounds have been synthesized and characterized in this study based on perfluoroalkyl ether acid fluoride. Most of these prepared fluoroether-containing monomers are liquid at room temperature, and display excellent solubility in common organic solvents. Moreover, these fluorinated monomers, which have been designed containing at least one functional group, can be strategically used for preparing fluorinated polymers.

References

1. T. Liang, C.N. Neumann, T. Ritter, Angew. Chem. Int. Ed. **52**, 8214 (2013)
2. Schmidt, C.E. Coburn, B.M. DeKoven, Nature **368**, 39 (1994)
3. M. Penoff, W. Schreiner, P. Oyanguren, Macromol. Symp. **321**, 186 (2012)
4. K. Sugiyama, T. Nemoto, G. Koide, Macromol. Symp. **181**, 135 (2002)
5. X. Wang, J. Hu, Y. Li, J. Fluor. Chem. **176**, 14 (2015)
6. J. Li, X. Zhang, Z. Liu, J. Fluor. Chem. **175**, 12 (2015)
7. W. Xu, B. Lu, Y. Hu, Polym. Adv. Technol. **23**, 877 (2012)
8. T. Liu, L. Ye, J. Fluor. Chem. **131**, 36 (2010)
9. Z. Ge, X. Zhang, J. Dai, Eur. Polym. J. **45**, 530 (2009)
10. Q. Luo, Y. Shen, P. Li, J. Appl. Polym. Sci. **131**, 40970 (2014)
11. L. Chen, H. Shi, H. Wu, J. Fluorine Chem. **131**, 731 (2010)
12. Q. Zhang, Q. Wang, X. Zhan, Ind. Eng. Chem. Res. **53**, 8026 (2014)
13. H. Lim, Y. Lee, I.J. Park, J. Colloid Interface Sci. **241**, 269 (2001)
14. S.C. Yoon, B.D. Ratner, Macromolecules **19**, 1068 (1986)
15. S.C. Yoon, B.D. Ratner, Macromolecules **21**, 2392 (1988)
16. S.C. Yoon, B.D. Ratner, Macromolecules **21**, 2401 (1988)
17. T. Imae, Curr. Opin. Colloid Interface Sci. **8**, 307 (2003)
18. B. Ameduri, B. Boutevin, J. Fluor. Chem. **104**, 53 (2000)
19. D. Lahiouhel, B. Ameduri, B. Boutevin, J. Fluor. Chem. **107**, 81 (2001)
20. A. Synytska, D. Appelhans, Z.G. Wang, Macromolecules **40**, 297 (2007)
21. D. Pintossi, G. Iannaccone, A. Colombo, Adv. Electron. Mater. **2**, 1600288 (2016)
22. F. Bella, A. Lamberti, S. Bianco, Adv. Mater. Technol. **1**, 1600002 (2016)
23. F. Bella, G. Leftheriotis, G. Griffini, Adv. Funct. Mater. **26**, 1127 (2016)
24. Y. Akiyama, C. Hiramatsu, T. Fukuhara, J. Fluor. Chem. **127**, 920 (2006)

25. K. Suzuki, T. Fuchigami, J. Org. Chem. **69**, 1276 (2004)
26. H.W. Yu, Y. Nakano, T. Fukuhara, J. Fluor. Chem. **126**, 962 (2005)
27. R.J.C. Brown, R.F.C. Brown, J. Chem. Educ. **77**, 724 (2000)