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Perfluoroalkylated diblock-alkyl methacrylate monomers for biomedical applications
Wettability of their copolymers with HEMA and DEGMA

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Dedicated to Prof. Richard D. Chambers on the occasion of his 70th birthday.

Abstract

The intermediate perfluoroalkylated diblock hydrophobic–hydrophilic secondary alcohols (**9**–**11**), which were prepared by the reaction of monomethyl ethers of oligomeric ethyleneglycols with 2-[(perfluoroalkyl)methyl]oxiranes (**7** and **8**), resulted in the formation of the title monomers (**12**–**14**) by the acylation with methacryloyl chloride. Copolymers of **12**–**14** with HEMA and DEGMA prepared under radical conditions display enhanced swelling properties.

Keywords: Epoxide ring opening; Perfluoroalkylated oligoethers; Double-tail methacrylates; Perfluoroalkylated methacrylates; Wettability of methacrylate copolymers

1. Introduction

Fluorinated polymeric materials exhibit unique properties that can be exploited in technical and/or biomedical areas [1,2]. Among them, polymers and copolymers of acrylates and methacrylates of fluorinated alcohols have been used in a number of applications, viz. textile finishing [3], special polymerization surfactants [4], microelectronics [5,6], optoelectronics [7], oxygen carriers [8], human prosthetics [8,9], and highly sensitive electron beam or X-ray resists [6,10,11]. Classical hydrophilic polymers (hydrogels) based on hydrophilic methacrylate polymers and copolymers have frequently been applied as biocompatible materials [12–14], e.g. for contact lenses, tissue prostheses, treatment of burns, etc. However, the ophthalmologic HEMA-based materials suffer from insufficient oxygen transport in particular cases that can cause irritation or inflammation of eye tissue. Very likely, the properties of the materials could be improved by the introduction of hydrophilic moieties in perfluoroalkylated monomers.

Hydro-swelling properties measured as water content in polymethacrylates are dependent on the hydrophilicity of ester groups as demonstrated in Scheme 1 [15,16]: polymeric HEMA (**1**) exhibits the highest wettability (equilibrium swelling) among the materials tested [17], while the presence of fluorinated blocks in the ester groups causes decrease in swelling (copolymers of **2** or **3**). The presence of fluorinated segments in the ester groups of methacrylate monomers can increase oxygen transport in the corresponding polymeric materials as shown for copolymers of HEMA (**1**) with the monomers **2** or **3** relatively to polyHEMA (Scheme 1). It has also been observed (Scheme 1) that the presence of hydrophilic groups

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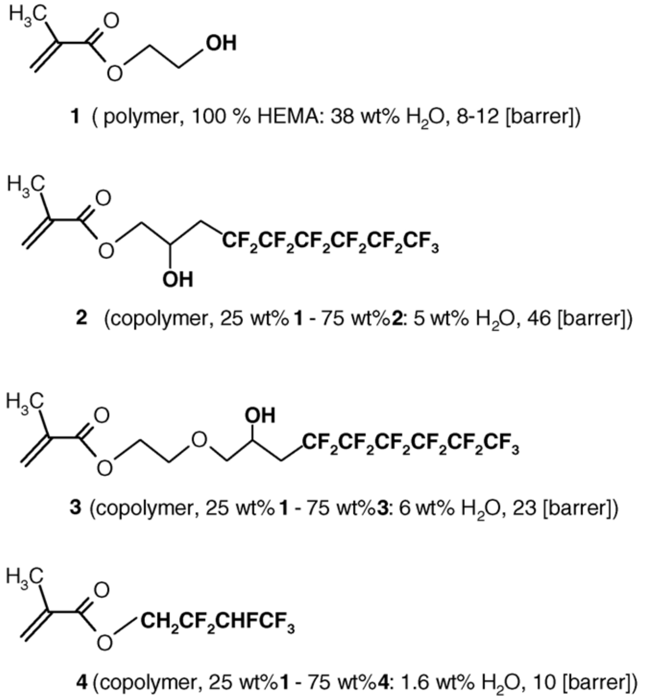


Scheme 1. Comparison of equilibrium swelling (wettability; wt.% content of water) and oxygen permeability (in barrer units [15]) for polymeric HEMA (**1**) [17] and copolymers of **2**–**4** with HEMA [16].

or blocks in the ester groups can increase oxygen transport (diffusion) as deduced from the comparison of the oxygen diffusion (permeability) values for the copolymers of **2** or **3** versus methacrylate **4** (Scheme 1) [16].

In this paper, we report the preparation of novel methacrylate monomers (**12**–**14**) bearing a branched structure in the alkoxy part of the ester group. The corresponding parent secondary alcohols (**9**–**11**) possess hydrophilic oligomeric ethylene glycol structure in one branch, while the second branch is perfluoroalkylated methyl. In the copolymeric structure, both hydrophilic and strongly hydrophobic (fluorophilic) chains could come in interactions. Such architecture of the ester group could significantly modify the material properties [18] of the corresponding (co)polymers when compared with simple fluoroalkyl methacrylates. The monomers of this type possessing a higher number of oxyethylene units have been reported [19,20] for copolymers giving good water- and oil-repellent properties to textiles.

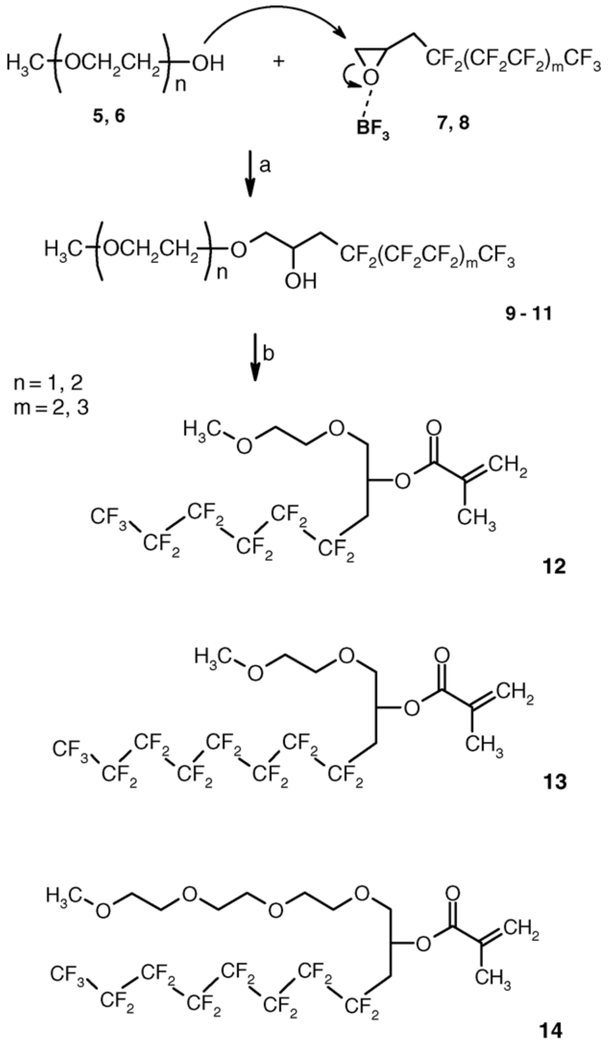
2. Results and discussion

2.1. Synthesis of new monomers

In the synthesis of the perfluoroalkylated diblock-alkyl methacrylates, we were looking for a relatively simple strategy. The precursors of the title methacrylates **12**–**14** are diblock secondary alcohols possessing one branch hydrophilic moiety and the second hydrophobic bearing a perfluoroalkyl. Such type of secondary alcohols can generally be prepared by the reaction of organometals with aldehydes [21]. In this paper, we have applied the reactions of perfluoroalkylated oxiranes as building blocks.

2.1.1. Preparation of diblock amphiphilic secondary alcohols ***9–11***

It has been found that the ring opening of [(perfluoroalkyl)methyl]oxiranes (e.g. **7** and **8**) by O-nucleophiles is completely regioselective and can also be chemoselective under appropriate reaction conditions [22] according to Scheme 2. The secondary hydroxy group is formed in the ring opening of the epoxides. An acidic catalysis is more convenient from the chemoselectivity point of view than the basic one because a base could attack acidic C–H bonds in the neighbourhood of the perfluoroalkyl causing the formation of byproducts [23]. Boron trifluoride diethyl etherate appeared to be an efficient catalyst even when the



Scheme 2. Preparation of the new monomers **12**–**14**: (a) $BF_3 \cdot Et_2O$, 100 °C, 10 h, 92.5–99%; (b) MACl, Et_3N, Et_2O, r.t., 4 h, 81–96%.

derivatives of triols or saccharides were employed in the ring opening [22,24,25], but in particular cases side reactions caused by this catalyst were observed [26].

In this paper, 2-[(perfluoroalkyl)methyl]oxiranes **7** and **8** were reacted with 2-methoxyethanol (**5**) or 3,6,9-trioxadecan-1-ol (**6**) according to the methodology described above. A five-fold molar excess of cheap alkanols **5** and **6** enabled complete conversion of the starting oxiranes **7** and **8** to afford the target diblock amphiphilic alkanols **9–11** (Scheme 2). The reactions were completed in 10 h at 100 °C in high isolated yields. No regioisomeric products and byproducts were detected in the reaction mixtures.

2.1.2. *Preparation of monomers **12–14***

Esters of methacrylic acid with fluorinated alkanols were prepared by several preparative methods: esterification of methacrylic acid by fluoroalkanols [27,28], transesterification of methyl methacrylate by fluoroalkanols [27,29] and acylation of fluoroalkanols by methacrylic anhydride [30] or methacryloyl chloride [11,22,27,31–33]. We applied the last method which has been mostly used by us previously: as the secondary fluoroalkanols are much less reactive than primary, methacryloyl chloride was used in 3.5–10-fold excess at room temperature. These conditions enabled the complete conversion of the fluoroalkanols **9–11** and to prepare the target amphiphilic diblock methacrylates **12–14** in yields of 81–96%.

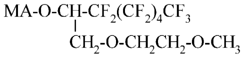
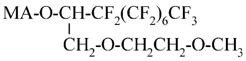
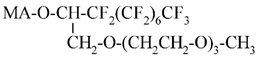
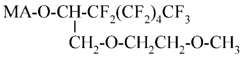
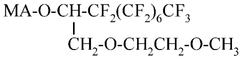
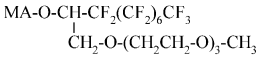
2.2. *Copolymerization with HEMA and DEGMA, swelling properties*

Fluorinated comonomers **12–14** and **15** were used for the 50:50 wt.% UV-light-induced block copolymerization with 2-hydroxyethyl methacrylate (HEMA) or diethylene glycol methacrylate (DEGMA) and with ethylene dimethacrylate (EDMA, 0.5 wt.%) as a crosslinking agent. The copolymer samples were separated from moulds mechanically and then added to distilled water to be transformed to the swollen state. The results summarized in Table 1 show the following trends: copolymer of hexafluorobutyl methacrylate (**15**) not possessing a hydrophilic block in the ester group showed very low swelling. For copolymers of **12–14** with HEMA, the swelling was almost independent on the fluorinated chain length and the length of hydrophilic polyethylene glycol blocks in the molecules **12–14**. On the other hand, for copolymers of **12–14** with DEGMA, the swelling was much higher and dependent both on the fluorinated chain length and the length of hydrophilic polyethylene glycol block in the molecules **12–14**.

3. Conclusions

The synthesis of the amphiphilic perfluoroalkylated diblock-alkyl methacrylates **12–14** was developed and optimized in the laboratory scale to obtain isolated yields of 65–78%. Copolymers prepared from amphiphilic diblock perfluoroalkyl methacrylates **12–14** generally display a higher wettability in comparison with the materials from fluoroalkyl methacrylate **15** (Table 1). Wettability of the copolymers of **12–14** with HEMA (2-hydroxyethyl methacrylate) is practically independent on the chain length of perfluoroalkyl and polyethylene glycol blocks (Table 1), while the copolymers with DEGMA (diethylene glycol methacrylate) exhibit interesting dependence (Table 1).

Table 1
Wettability (equilibrium swelling) of the 50:50 wt.% copolymers

Copolymers			
	Fluorinated monomer	Comonomer	Equilibrium swelling wt% H_2O
12	 $MA\text{-}O\text{-}CH(CH_2\text{-}O\text{-}CH_2CH_2\text{-}O\text{-}CH_3)\text{-}CF_2(CF_2)_4CF_3$	HEMA	13
13	 $MA\text{-}O\text{-}CH(CH_2\text{-}O\text{-}CH_2CH_2\text{-}O\text{-}CH_3)\text{-}CF_2(CF_2)_6CF_3$	HEMA	14.5
14	 $MA\text{-}O\text{-}CH(CH_2\text{-}O\text{-}(CH_2CH_2\text{-}O)_3\text{-}CH_3)\text{-}CF_2(CF_2)_6CF_3$	HEMA	13.5
15	$MA\text{-}O\text{-}CH_2\text{-}CF_2CHF\text{-}CF_3$	HEMA	6.3
12	 $MA\text{-}O\text{-}CH(CH_2\text{-}O\text{-}CH_2CH_2\text{-}O\text{-}CH_3)\text{-}CF_2(CF_2)_4CF_3$	DEGMA	17
13	 $MA\text{-}O\text{-}CH(CH_2\text{-}O\text{-}CH_2CH_2\text{-}O\text{-}CH_3)\text{-}CF_2(CF_2)_6CF_3$	DEGMA	27
14	 $MA\text{-}O\text{-}CH(CH_2\text{-}O\text{-}(CH_2CH_2\text{-}O)_3\text{-}CH_3)\text{-}CF_2(CF_2)_6CF_3$	DEGMA	35
	HEMA	-	38

4. Experimental

4.1. General comments

Boiling points were not corrected. Distillations of high boiling compounds were carried out using a Vacuubrand RC5 high vacuum oil pump. NMR spectra were recorded on a Varian Gemini 300 HC (FT, ^{19}F at 281 MHz) instrument using TMS and $CFCl_3$ as the internal standards. Chemical shifts are quoted in ppm (δ-scale; s singlet, t triplet, m multiplet), coupling constants J in Hz, solvent $CDCl_3$. Elemental analyses were performed on a CHN – Perkin-Elmer 2400 instrument.

The chemicals used were as follows: fluoroalkyloxiranes **3** and **4** were prepared according to our procedure [23]; 2,2,3,4,4,4-hexafluorobutyl methacrylate (**15**) was prepared according to our previous procedure [11,34]. 2-Hydroxyethyl methacrylate HEMA (Degussa-Röhm), diethylene glycol methacrylate (DEGMA) (synthesized from Fluka products by re-esterification of methyl methacrylate by diethylene glycol at IMC Prague), ethylene dimethacrylate (EDMA, 0.5 wt.%) (Sigma-Aldrich). Silica gel (60–100 μm, Merck), boron trifluoride diethyl etherate (Aldrich), triethylamine (Aldrich), di-(*tert*-octyl)pyrocatechol (Fluka), methacryloyl chloride (distilled before use, b.p. 95 °C; Fluka), 2-methoxyethanol (Aldrich), 3,6,9-trioxadecan-1-ol (Aldrich). All solvents (Penta) were dried and purified according to standard procedures.

4.2. Copolymerizations

Fluorinated comonomers **12–14** and **15** were used for the 50:50 wt.% photo-copolymerizations in block with 2-hydroxyethyl methacrylate (HEMA) or diethylene glycol methacrylate (DEGMA) and with ethylene dimethacrylate (EDMA, 0.5 wt.%) as a crosslinking agent. Disc-shaped pieces (diameter 13 mm, thickness 0.5 mm) were made in open polypropylene moulds. The copolymerizations were carried out under UV-light initiation (mercury lamp, RVK 125 W, TESLA, Prague) in nitrogen atmosphere for 2 h using benzoin ethyl ether as photoinitiator. The copolymer samples were separated from moulds mechanically and then added to water to be transformed in the swollen state within several days (check by balancing). The samples were then dried to a constant weight.

4.2.1. *9,9,10,10,11,11,12,12,13,13,14,14,14-Tridecafluoro-2,5-dioxatetradecan-7-ol (**9**)*

A flask was charged with 1,2-epoxy-4,4,5,5,6,6,7,7,8,8,9,9,9-tridecafluorononane (**7**) (13.24 g, 35 mmol), 2-methoxyethanol (**5**) (13.32 g, 175 mmol) and $BF_3 \cdot Et_2O$ (1 mL) and the mixture was heated to 100 °C for 10 h while stirring. The reaction mixture was then evaporated on rotary evaporator to remove catalyst and 2-methoxyethanol and the residue was distilled in vacuum to afford product **9** as clear liquid in a yield of 15.7 g (99 %), b.p. 120 °C/0.5 mmHg.

^{1}H NMR ($CDCl_3$): 2.05–2.55 (m, 2H, CH_2–R_F), 3.35 (s, 3H, CH_3), 3.40–3.90 (m, 7H, 3× CH_2–O and OH), 4.15–4.30 (m, 1H, CH–O); ^{13}C NMR ($CDCl_3$): 34.5 (t, 1C, CH_2–R_F, $^{2}J_{CF}$ = 21 Hz), 58.8 (s, 1C, CH_3), 64.2 (s, 1C, CH), 70.6 (s, 1C, CH_2–O), 71.9 (s, 1C, CH_2–O), 74.9 (s, 1C, *CH_2*–CH), 103–124 (m, 6C, 5× CF_2 and CF_3); ^{19}F NMR ($CDCl_3$): −81.4 (t, 3F, CF_3, $^{3}J_{HF}$ = 10.0 Hz), −113.2 (m, 2F, CH_2–CF_2), −122.3 (m, 2F, CF_2), −123.3 (m, 2F, CF_2), −124.1 (m, 2F, CF_2), −126.6 (m, 2F, CF_2). Anal. Calcd for $C_{12}H_{13}F_{13}O_3$: C, 31.9, H, 2.9; found: C, 32.0, H, 3.05.

4.2.2. *9,9,10,10,11,11,12,12,13,13,14,14,15,15,16,16,17,17,17-Heptadecafluoro-2,5-dioxahexadecan-7-ol (**10**)*

Analogous procedure to that for **9**: 1,2-epoxy-4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11,11-heptadecafluoroundecane (**8**) (10.47 g, 22 mmol), 2-methoxyethanol (**5**) (8.37 g, 110 mmol) and $BF_3 \cdot Et_2O$ (0.70 mL). After removing volatile components from the reaction mixture, the brown residue was purified by column chromatography (silica gel, 180 g, petroleum ether/acetone 4:1) to afford the product **10** as a slightly yellow liquid, yield 11.91 g (98%).

^{1}H NMR ($CDCl_3$): 2.16–2.50 (m, 2H, CH_2–R_F), 3.32 (s, 3H, CH_3), 3.38–4.00 (m, 7H, 3× CH_2–O and OH), 4.14–4.35 (m, 1H, CH–O); ^{13}C NMR ($CDCl_3$): 33.8 (t, 1C, CH_2–R_F, $^{2}J_{CF}$ = 22.2 Hz), 58.5 (s, 1C, CH_3), 64.5 (s, 1C, CH), 70.3 (s, 1C, CH_2–O), 71.8 (s, 1C, CH_2–O), 74.5 (s, 1C, *CH_2*–CH), 104–124 (m, 8C, 7× CF_2 and CF_3); ^{19}F NMR ($CDCl_3$): −81.5 (t, 3F, CF_3, $^{3}J_{HF}$ = 10.9 Hz), −112.8 (m, 2F, CH_2–CF_2), −122.1 (m, 2F, CF_2), −122.3 (m, 4F, 2× CF_2), −123.2 (m, 2F, CF_2), −123.7 (m, 2F, CF_2), −126.7 (m, 2F, CF_2). Anal. Calcd for $C_{14}H_{13}F_{17}O_3$: C, 30.45, H, 2.35; found: C, 30.3, H, 2.40.

4.2.3. *15,15,16,16,17,17,18,18,19,19,20,20,21,21,22,22,22-Heptadecafluoro-2,5-dioxadocosan-13-ol (**11**)*

The same procedure as that for **10**: 1,2-epoxy-4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11,11-heptadecafluoroundecane (**8**) (10.47 g, 22 mmol), 3,6,9-trioxadecan-1-ol (**6**) (18.06 g, 110 mmol) and $BF_3 \cdot Et_2O$ (0.70 mL). Product **11** was obtained in a yield of 13.05 g (92.6%) as a slightly yellow liquid.

^{1}H NMR ($CDCl_3$): 2.10–2.44 (m, 2H, CH_2–R_F), 3.33 (s, 3H, CH_3), 3.40–3.78 (m, 15H, 6× CH_2–O and OH), 4.23 (m, 1H, CH–O); ^{13}C NMR ($CDCl_3$): 34.4 (t, 1C, CH_2–R_F, $^{2}J_{CF}$ = 21 Hz), 58.8 (s, 1C, CH_3), 64.1 (s, 1C, CH), 70.4 (s, 1C, CH_2–O), 70.5 (s, 3C, 3× CH_2–O), 70.7 (s, 1C, CH_2–O), 71.8 (s, 1C, CH_2–O), 74.8 (s, 1C, CH_2–CH), 106–123 (m, 8C, 7× CF_2 and CF_3); ^{19}F NMR ($CDCl_3$): −81.4 (t, 3F, CF_3, $^{3}J_{HF}$ = 9.3 Hz), −112.8 (m, 2F, CH_2–CF_2), −122.1 (m, 2F, CF_2), −122.4 (m, 4F, 2× CF_2), −123.2 (m, 2F, CF_2), −123.8 (m, 2F, CF_2), −126.6 (m, 2F, CF_2). Anal. Calcd for $C_{18}H_{21}F_{17}O_5$: C, 33.8, H, 3.30; found: C, 33.6, H, 3.40.

4.2.4. *9,9,10,10,11,11,12,12,13,13,14,14,14-Tridecafluoro-2,5-dioxatetradecan-7-yl methacrylate (**12**)*

Methacryloyl chloride (10.48 g, 100 mmol) was added dropwise by a syringe through septum to a mixture of 9,9,10,10,11,11,12,12,13,13,14,14,14-tridecafluoro-2,5-dioxatetradecan-7-ol (**9**) (4.52 g, 10 mmol), triethylamine (14.16 g, 140 mmol), di-(*tert*-octyl)pyrocatechol (33.5 mg, 0.1 mmol) and diethyl ether (110 mL) in a flask while stirring and the mixture was then stirred at r.t. for 4 h. The reaction was quenched by dropwise addition of methanol (5 mL) and stirred for 1 h. The reaction mixture was washed in a dropping funnel with water (50 mL), the ethereal layer was washed with water (50 mL) and the combined water layers were extracted with diethyl ether (3 × 50 mL). Combined ethereal solutions were dried over $MgSO_4$, volatile components were then removed on rotary evaporator and the crude product was purified by column chromatography (silica gel, 200 g, diethyl ether). Product **12** was obtained in a yield of 4.92 g (96%) as slightly yellow liquid.

^{1}H NMR ($CDCl_3$): 1.90 and 1.92 (2× s, 3H, CH_3C), 2.38–2.72 (m, 2H, CH_2–R_F), 3.34 (s, 3H, CH_3–O), 3.46–3.78 (m, 6H, 3× CH_2–O), 4.27–4.66 (m, 1H, CH–O), 5.59 (m, 1H, =CH), 6.12 (m, 1H, =CH); ^{13}C NMR ($CDCl_3$): 17.7, 18.0 (2× s, 1C, CH_3–C), 32.1 (t, 1C, CH_2–R_F, $^2J_{CF}$ = 19.8 Hz), 58.8 (s, 1C, CH_3–O), 66.2 (s, 1C, CH–O), 70.9 (s, 1C, CH_2–O), 71.5 (s, 1C, CH_2–O), 71.8 (s, 1C, CH_2–O), 105–125 (m, 8C, 7× CF_2 and CF_3), 126.2 (s, 1C, CH_2=), 135.8 (s, 1C, C=), 166.1 (s, 1C, COO); ^{19}F NMR ($CDCl_3$): −81.3 (t, 3F, CF_3, $^3J_{FF}$ = 10.0 Hz), −113.2 (m, 2F, CH_2–CF_2), −122.3 (m, 2F, CF_2), −123.3 (m, 2F, CF_2), −124.1 (m, 2F, CF_2), −126.6 (m, 2F, CF_2). Anal. Calcd for $C_{16}H_{17}F_{13}O_4$: C, 36.9, H, 3.30; found: C, 36.9, H, 3.45.

*4.2.5. 9,9,10,10,11,11,12,12,13,13,14,14,15,15,16,16,17,17,17-Heptadecafluoro-2,5-dioxahexadecan-7-yl methacrylate (**13**)*

The same procedure as that for **12** was applied: hydroxy compound **10** (7.18 g, 13 mmol), triethylamine (13.15 g, 130 mmol), di-(*tert*-octyl)pyrocatechol (33.5 mg, 0.1 mmol), diethyl ether (100 mL), methacryloyl chloride (10.46 g, 100 mmol). Product **13** was obtained in a yield of 7.10 g (88%) as slightly yellow liquid.

^{1}H NMR ($CDCl_3$): 1.90, 1.91 (2× s, 3H, CH_3C), 2.40–2.70 (m, 2H, CH_2–R_F), 3.33 (s, 3H, CH_3–O), 3.45–3.76 (m, 6H, 3× CH_2–O), 4.30–4.65 (m, 1H, CH–O), 5.56 (m, 1H, =CH), 6.09 (m, 1H, =CH); ^{13}C NMR ($CDCl_3$): 17.7 and 17.9 (s, 1C, CH_3–C), 32.1 (t, 1C, CH_2–R_F, $^2J_{CF}$ = 19.5 Hz), 58.8 (s, 1C, CH_3–O), 66.2 (s, 1C, CH–O), 70.9 (s, 1C, CH_2–O), 71.5 (s, 1C, CH_2–O), 71.8 (s, 1C, CH_2–O), 105–125 (m, 8C, 7× CF_2 and CF_3), 126.1 (s, 1C, CH_2=), 135.8 (s, 1C, C=), 166.1 (s, 1C, COO); ^{19}F NMR ($CDCl_3$): −81.5 (m, 3F, CF_3), −113.5 (m, 2F, CH_2–CF_2), −122.0 (m, 2F, CF_2), −122.4 (m, 2F, CF_2), −122.4 (m, 2F, CF_2), −123.2 (m, 2F, CF_2), −123.9 (m, 2F, CF_2), −126.7 (m, 2F, CF_2). Anal. Calcd for $C_{18}H_{17}F_{17}O_4$: C, 35.2, H, 2.75; found: C, 36.3, H, 2.80.

*4.2.6. 15,15,16,16,17,17,18,18,19,19,20,20,21,21,22,22,22-Heptadecafluoro-2,5-dioxadocosan-13-yl methacrylate (**14**)*

The same procedure as that for **12** was applied: hydroxy compound **11** (6.40 g; 10 mmol), triethylamine (3.54 g; 35 mmol), di-(*tert*-octyl)pyrocatechol (33.5 mg, 0.1 mmol), diethyl ether (30 mL), methacryloyl chloride (3.14 g; 35 mmol). Product **14** was obtained in a yield of 5.70 g (81%) as slightly yellow liquid.

^{1}H NMR ($CDCl_3$): 1.88 (s, 3H, CH_3C), 2.35–2.70 (m, 2H, CH_2–R_F), 3.32 (m, 3H, CH_3–O), 3.43–3.76 (m, 14H, 7× CH_2–O), 4.10–4.35 (m, 1H, CH–O), 5.54 (m, 1H, =CH), 6.07 (m, 1H, =CH); ^{13}C NMR ($CDCl_3$): 17.9 (s, 1C, CH_3–C), 32.0 (t, 1C, CH_2–R_F, $^2J_{CF}$ = 21 Hz), 58.7 (s, 1C, CH_3–O), 66.1 (s, 1C, CH–O), 70.4 (s, 1C, CH_2–O), 70.5 (s, 1C, CH_2–O), 70.5 (s, 1C, CH_2–O), 70.7 (s, 1C, CH_2–O), 70.8 (s, 1C, CH_2–O), 71.4 (s, 1C, CH_2–O), 71.8 (s, 1C, CH_2–O), 100–125 (m, 8C, 7× CF_2 and CF_3), 126.1 (s, 1C, CH_2=), 135.7 (s, 1C, C=), 166.0 (s, 1C, COO); ^{19}F NMR ($CDCl_3$): −81.4 (m, 3F, CF_3), −113.5 (m, 2F, CH_2–CF_2), −122.0 (m, 2F, CF_2), −122.4 (m, 4F, 2× CF_2), −123.2 (m, 2F, CF_2), −123.9 (m, 2F, CF_2), −126.6 (m, 2F, CF_2). Anal. Calcd for $C_{22}H_{25}F_{17}O_6$: C, 37.3, H, 3.55; found: C, 37.3, H, 3.55.

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