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ScienceDirect
European Journal of Medicinal Chemistry 41 (2006) 1320–1326
EUROPEAN JOURNAL OF MEDICINAL CHEMISTRY
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Original article

New perfluoroalkylated amphiphilic methacrylates bearing sulfinyl group as monomers for biomedical applications: water content and oxygen permeability of their copolymers with DEGMA

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Received 9 November 2005; revised and accepted 29 June 2006
Available online 04 August 2006

Abstract

Perfluoroalkylated methacrylates **7a–c** bearing sulfinyl group within a straight-chain ester group, i.e. $CH_2=C(CH_3)CO_2CH_2CH_2S(O)–CH_2CH_2CF_2(CF_2CF_2)_nCF_3$ ($n = 1–3$) were prepared by two alternative synthetic sequences from 2-[(polyfluoroalkyl)sulfanyl]ethanols $HOCH_2CH_2SCH_2CH_2CF_2(CF_2CF_2)_nCF_3$ ($n = 1–3$) in overall yields of 88–91%. Copolymers of **7a–c** with diethylene glycol methacrylate (DEGMA) prepared in bulk under radical conditions display high transparency, increased water content and good oxygen permeability properties, which are advantageous for their application in ophthalmology and as prosthetic materials.

Keywords: Poly(fluoroalkylsulfinyl methacrylates); DEGMA copolymers; Wettability of fluoroalkyl methacrylate copolymers; Oxygen permeability of fluorinated polymers

1. Introduction

Classical hydrophilic polymer networks (hydrogels) based on hydrophilic methacrylate polymers and copolymers have frequently been applied as biomaterials [1–3]. The task to prepare new materials for biomedical uses that combine sufficient water content with enhanced oxygen permeability, significantly higher than those for standard hydrogels, is dated since the beginning of seventies of the last century. The development of hydrogel contact lenses that form a barrier for oxygen transport to the cornea initiated a lot of studies in this area at that time. However, the preparation of suitable copolymers of highly hydrophilic monomers with extremely hydrophobic siloxane methacrylates or perfluoroalkyl methacrylates exhibiting high oxygen permeability appeared to be difficult. This great problem was solved at the beginning of this century by silicone hydrogels (Lotrafilcon A, Balafilcon A) which show high oxygen permeability (99–125 barrer) and equilibrium water content in the range of 26–36% of water [4]. However, these materials are expensive and represent relatively complicated systems with requiring exact treatment conditions. Due to these facts, new materials with enhanced oxygen permeability and sufficient and controllable equilibrium water content are demanded.

The introduction of fluorine atoms into a molecule of methacrylate monomer, especially into its ester part, causes an increase in mechanical strength and oxygen permeability. On the other hand, the materials swell badly in water and therefore their application in ophthalmology for contact lenses can be limited or excluded [5]. Hydro-swelling properties measured as water content in fluoroalkyl methacrylate copolymers can be increased, among others, by the introduction of hydrophilic

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doi:10.1016/j.ejmech.2006.06.003

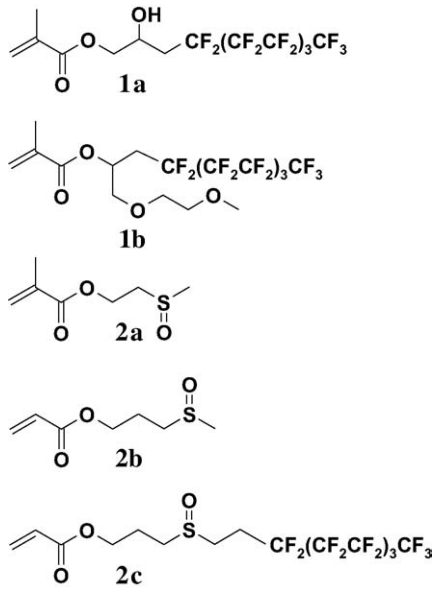


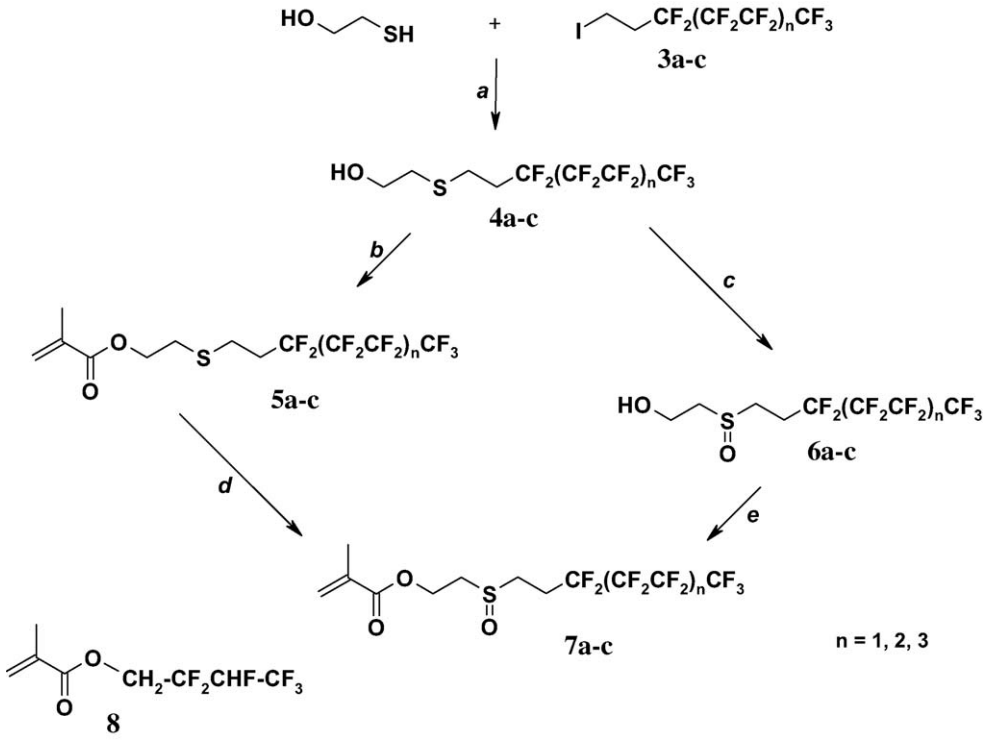
Fig. 1. Amphiphilic (meth)acrylates **1**–**2**.

groups in the ester part (Fig. 1), e.g. hydroxyl (**1a**) [6] or ether (**1b**) [7] functional groups. Enhanced water content and oxygen permeability can also be expected for polyfluoroalkylated methacrylate materials containing highly hydrophilic sulfinyl group. As reported [8,9], the hydrogels based on non-fluorinated sulfinyl derived (meth)acrylic monomers (**2a**, **2b**) were used to enhance the penetration of pharmaceutical agents through skin. They were also applied as protein-resistant materials with high water content and minimum bioadsorption [10] for the preparation of soft contact lenses. The sulfinyl group derived materials display low electrostatic interactions which in prosthetic application lead to the reduction in protein cell adhesion. The polymers have shown a good local compatibility and no acute common toxicity at systemic levels of application [9].

Herein, we describe the synthesis of new perfluoroalkylated amphiphilic methacrylates monomers **7a**–**c** bearing sulfinyl group and some properties of their copolymers with DEGMA as optical properties, water content and oxygen permeability.

2. Chemistry

In the synthesis of the new polyfluoroalkylated methacrylates possessing sulfinyl group we were looking for a relatively simple strategy. The readily available 2-(perfluoroalkyl)ethyl iodides **3a**–**c** have been found as the most convenient starting compounds (Scheme 1). The reaction of **3a**–**c** with 2-sulfanylethanol [11] in the presence of NaOH (Scheme 1, reaction *a*) afforded 2-(polyfluoroalkyl-sulfanyl)ethanols **4a**–**c** in 86–90% yields. This substitution of iodine in **3a**–**c** by a stronger S-nucleophile was completely chemoselective. We have not observed olefins in the reaction mixtures, which are also formed by the elimination when the reagent is strongly nucleophilic but only weakly basic [12] and attacks the C–H bond in the neighborhood of the perfluoroalkyl. Thus, in bifunctional



Scheme 1. Preparation of new monomers **7a**–**c**: (a) NaOH, *t*-BuOH, reflux, 3 h, 86–90%; (b) methacryloyl chloride, Et_3N, Et_2O, r.t., 5 h, 94–96%; (c) $NaIO_4$, MeOH, water, 0 °C, 1 h, r.t., 5 h, 97–98%; (d) $NaIO_4$, MeOH, water, 0 °C, 1 h, r.t., 5 h, 94–96%; (e) methacryloyl chloride, Et_3N, Et_2O, r.t., 5 h, 91–94%.

nucleophile 2-sulfanyl-ethanol, the sulfur atom appeared to be much more reactive nucleophilic center than the oxygen atom.

The synthesis of the target monomers, 2-(polyfluoroalkylsulfinyl)ethyl methacrylates **7a**–**c** (Scheme 1), was performed by two alternative pathways, **A** (reactions *b* and *d*) and **B** (reactions *c* and *e*), both as two-step reaction sequences (Scheme 1). The pathway **A** concerns the preparation of methacrylate esters **5a**–**c**, in which the sulfide atom is subsequently oxidized to sulfinyl group. The pathway **B** includes the introduction of the sulfinyl group in hydroxy compounds **4a**–**c**, which are then combined with methacryloyl part. For the preparation of methacrylates of the hydroxy compounds **4a**–**c** or **6a**–**c** (Scheme 1) we applied the acylation by methacryloyl chloride in the presence of triethylamine [13], which afforded the products **5a**–**c** or **7a**–**c** in yields 94–96% and 91–94%, respectively. For the oxidation of the sulfide atom in the compounds **4a**–**c** or **5a**–**c**, sodium periodate in methanol–water mixture at 0 °C [9] appeared to be a highly efficient reagent. This procedure afforded the corresponding sulfinyl compounds **6a**–**c** or **7a**–**c** in yields of 97–98% and 94–96%, respectively. The total yields were 88–91% for the synthetic pathway **A** and 89–91% for the synthetic pathway **B**. The yields are high and practically the same for both the pathways.

Fluorinated co-monomers **7a**–**c** were used for the UV-light induced copolymerization with diethylene glycol methacrylate (DEGMA) and with ethylene dimethacrylate (EDMA, 0.5 wt. %) as a crosslinking agent [7]. The manipulation with a polymerization mixture was very easy. Conditions of the polymerization were similar to those recently applied [7], only polymerization time was prolonged from minutes to several hours. Disc-shape pieces (diameter 13 mm, thickness 0.5 mm) were made in open polypropylene moulds. The copolymer samples were separated from moulds mechanically and then added to distilled water to be transformed to the equilibrium swollen state within several days (check by balancing). The samples were then dried under vacuum at 50 °C to a constant weight. The water content was calculated as the ratio of the difference of weights of swollen and dry gel to the swollen gel weight in per cent quantity. The copolymers ratio and optical properties of the materials are summarized in Table 1.

3. Physical properties related to biomaterials

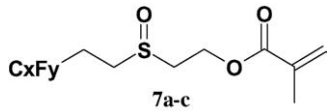
Excellent transparency of swollen copolymers is the fundamental property of a material intended for the application in ophthalmology. The data in Table 1 show that this condition is fulfilled for copolymers of monomers **7a** and **7b**, while a longer perfluoroalkyl present in the co-monomer **7c** caused opacity and/or coloration of the polymer material. The refractive index of the new materials is in the range of 1.390–1.430 (Table 1) (it is slowly increasing with decreasing water content in the swollen material (Table 2) as refractive index of water is 1.333; hydrogels based on methacrylates have set values of this quantity in dry state approximately 1.511). This is an advantage for contact lens construction contrary to high swollen hydrogels having refractive index lower than 1.380 which results in the construction of thicker lens displaying more dramatic optical curves [14].

The presence of fluorinated co-monomers **7a**–**c** in the resulting copolymers influences their mechanical properties (Table 2). Samples are stiffer relatively to standard hydrogels or silicone elastomers. This is advantageous for the manufacturing, dimensional stability, manipulation and resistance of lenses [15]. The values for modulus strains of the hydrogels (Table 2) change with the fluorinated monomer and its concentration. This effect could be caused by various lengths of perfluorinated segments in the monomers and different placements of polar sites in the pendant ester groups of the monomer units.

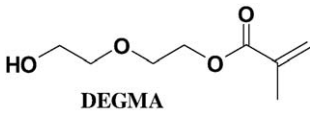
3.1. Water content in the materials

As expected, the equilibrium water content is decreasing with increasing content of the co-monomer **7** in the copolymerization mixture (Table 2). An analogous observation has been reported for the copolymers of similar amphiphilic fluorinated methacrylates [7]. The water content is higher than that or close to that for poly(HEMA) in particular cases [16] (Table 2).

Table 1
Selected optical properties of the copolymers of **7a**–**c** with DEGMA



7a-c



DEGMA

Co-monomer **7**				Properties of copolymers		
				Refractive index	Copolymer transparency	
	C_xF_y	mol%	wt.%	n_D^{20}	Dry state	Swollen state
7a	C_4F_9	9.3	20	1.396	Transparent	Transparent
7a	C_4F_9	22.7	40	1.422	Transparent	Transparent
7a	C_4F_9	40.5	60	1.444	Transparent	Transparent
7b	C_6F_{13}	7.7	20	1.415	Transparent	Transparent
7b	C_6F_{13}	18.6	40	1.426	Transparent	Transparent
7b	C_6F_{13}	32.8	60	1.431	Transparent	Transparent
7c	C_8F_{17}	6.7	20	1.389	Slightly yellow, transparent	Opaque
7c	C_8F_{17}	15.9	40	1.411	Slightly yellow, transparent	Slightly yellow, transparent
7c	C_8F_{17}	27.6	60	1.424	Slightly yellow, transparent	Slightly yellow, transparent

Table 2
Swelling, mechanical properties and oxygen permeability of copolymers of **7a**–**c** with DEGMA

Co-monomer[a] **7**				Properties of copolymers				
				Swelling properties		Mechanical properties		Transport properties
				Equilibrium swelling[b]	Coefficient of linear swelling	Modulus 5% strain	Modulus 10% strain	Oxygen permeability[b]
	C_xF_y	mol%	wt.%	$\%H_2O$	K	(kPa)	(kPa)	barrer
7a	C_4F_9	9.3	20	**47.3**	1.29	120 ± 30	180 ± 30	**31 ± 1**
7a	C_4F_9	22.7	40	**23.5**	1.12	23 ± 4	26 ± 3	**20 ± 1**
7a	C_4F_9	40.5	60	**8.6**	1.03	41 ± 9	64 ± 23	**10.0 ± 0.3**
7b	C_6F_{13}	7.7	20	**34.7**	1.18	15 ± 3	19 ± 5	**23 ± 3**
7b	C_6F_{13}	18.6	40	**21.1**	1.09	3.5 ± 0.6	4 ± 1	**19 ± 1**
7b	C_6F_{13}	32.8	60	**11.9**	1.05	15 ± 7	15 ± 9	–
7c	C_8F_{17}	6.7	20	**49.4**	1.32	42 ± 5	60 ± 7	**29 ± 2**
7c	C_8F_{17}	15.9	40	**27.3**	1.12	18 ± 8	20 ± 10	**18 ± 2**
7c	C_8F_{17}	27.6	60	**7.5**	–	120 ± 30	150 ± 40	–
	HEMA[a]	100	100	**38**[c]				**8–12**[c]

[a] Prepared by bulk radical polymerization.
[b] Average of five measurements.
[c] [16] (an appropriate value for poly(DEGMA) is not available).

This property could improve outlooks for a potential application as biomaterials.

3.2. Oxygen permeability of the materials

Against expectations, oxygen permeability decreases with increasing content of the co-monomer **7** too. It is interesting that oxygen permeability is on higher level in the comparison with standard hydrogels, e.g. polymeric HEMA (Table 2), swollen identically. The data show that the oxygen transport is not realized through water because the new materials with lower water content (**7a**, 8.6%H_2O) still exhibit higher oxygen permeability (10 barrer). This fact can be explained by mutual repulsion of perfluorinated chains: Low concentration of co-monomer **7** in the mixtures gives the possibility to fill freely the intermolecular space by pendant perfluorinated chain thus enhancing oxygen permeability. High concentration of the co-monomer **7** possessing bulky branched ester group leads to a space strain and a non-homogenity of the copolymer structure. As a result, some diffusion canals can be closed causing overall decrease in oxygen permeability. The most advantageous material appears to be the copolymer containing 9.3 mol% of the monomer **7a** (Table 2) exhibiting in addition high swelling (47.3%H_2O) and good mechanical and optical properties (31 barrer, Table 2).

4. Conclusions

A convenient three-step synthesis of the new amphiphilic methacrylates **7a**–**c** bearing sulfinyl group was developed starting from industrial (2-perfluoroalkyl)ethyl iodides. The overall yields were 75–78%. Copolymers of **7a**–**c** with DEGMA prepared in bulk generally display some advantageous properties, e.g. transparency, sufficient water content with significantly enhanced oxygen transport, which predetermines the materials advantageous for applications in ophthalmology as contact lenses.

5. Experimental

5.1. General comments and chemicals

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, bs broad singlet, t triplet, q quartet, m multiplet), coupling constants J in Hz, solvent $CDCl_3$. GC–MS analysis was accomplished on an HP 6890 instrument coupled with AUTOSPEC-Ultima (Waters, UK). Elemental analyses were performed on a CHN–Perkin–Elmer 2400 instrument.

The chemicals used were as follows: 2-(perfluoroalkyl)ethyl iodides **3a**–**c** (Atofina S.A., France); 2-mercaptoethanol (2-sulfanylethanol), sodium periodate, ethylene glycol dimethacrylate (EDMA), benzoin ethyl ether (BEE), triethylamine (all from Sigma Aldrich); methanol, 2-methylpropan-2-ol, chloroform, dichloromethane, hexane, ethyl acetate, diethyl ether, magnesium sulfate, sodium hydroxide (Lachema, Czech Republic); DEGMA (synthesized from Fluka products by re-esterification of methyl methacrylate by diethylene glycol at IMC Prague), methacryloyl chloride (distilled before use, b.p. 95 °C; Fluka); silica gel (60–100 μm, Merck). All solvents were dried and purified according to standard procedures.

5.2. Chemistry

General procedure for preparation of 2-(polyfluoroalkylsulfanyl)ethanols **4a**–**c**. A mixture of 2-sulfanylethanol (10.94 g, 140 mmol), powdered sodium hydroxide (5.6 g, 140 mmol), and *tert*-butyl alcohol (60 ml) was heated at reflux under nitrogen for 15 min. 2-(Perfluoroalkyl)ethyl iodide (**3a**–**c**, 140 mmol) was then added during 0.5 h while stirring vigorously and the mixture

was refluxed for additional 3 h. The solvent was evaporated and the residue extracted with chloroform. Undissolved part was filtered off and the filtrate was evaporated in vacuum to afford the products **4a**–**c** as viscous liquids or waxy solids in a 99% purity (check by ^{1}H and ^{19}F NMR).

2-[(3,3,4,4,5,5,6,6,6-Nonafluorohexyl)sulfanyl]ethanol (**4a**). Yield: 39.1 g (86%); b.p. 58–59 °C/106 Pa (Ref. [11]: 70 °C/173 Pa); ^{1}H NMR ($CDCl_3$): δ 2.15 (bs, 1H, OH); 2.25–2.50 (m, 2H, CH_2R_F); 2.68–2.82 (m, 4H, CH_2SCH_2); 3.76 (q, 2H, CH_2O, $^{3}J_{HH} = 5.8$) ppm; ^{13}C NMR ($CDCl_3$): δ 22.45 (t, 1C, $R_FCH_2CH_2$, $^{3}J_{CF} = 4.35$); 32.00 (t, 1C, CH_2R_F, $^{2}J_{CF} = 21.9$); 35.22 (s, 1C, CH_2S); 60.59 (s, 1C, CH_2OH); 100–125 (m, 4C, 3 × CF_2 and CF_3) ppm; ^{19}F NMR ($CDCl_3$): δ –76.77 (t, 3F, CF_3, $^{3}J_{FF} = 10$); –108.24 (m, 2F, CH_2CF_2); –117.44 (m, 2F, CF_2); –119.03 (m, 2F, CF_2) ppm.

2-[(3,3,4,4,5,5,6,6,7,7,8,8,8-Tridecafluorooctyl)sulfanyl] ethanol (**4b**). Yield: 51.7 g (87%); b.p. 80–83 °C/160 Pa (Ref. [11]: 110–115 °C/2.66 kPa); ^{1}H NMR ($CDCl_3$): δ 2.04 (t, 1H, OH, $^{3}J_{HH} = 5.9$); 2.22–2.44 (m, 2H, CH_2R_F); 2.67–2.80 (m, 4H, CH_2SCH_2); 3.71 (q, 2H, CH_2O, $^{3}J_{HH} = 5.9$) ppm; ^{13}C NMR ($CDCl_3$): δ 22.47 (s, 1C, $R_FCH_2CH_2$); 32.10 (t, 1C, CH_2R_F, $^{2}J_{CF} = 21.9$); 35.27 (s, 1C, CH_2S); 60.57 (s, 1C, CH_2OH); 100–125 (m, 6C, 5× CF_2 and CF_3) ppm; ^{19}F NMR ($CDCl_3$): δ –81.30 (t, 3F, CF_3, $^{3}J_{FF} = 10$); –114.79 (m, 2F, CH_2CF_2); –122.39 (m, 2F, CF_2); –123.37 (m, 2F, CF_2); –123.91 (m, 2F, CF_2); –126.65 (m, 2F, CF_2) ppm. MS: *m/z* 424 (M^+). Anal. $C_{10}H_9F_{13}OS$ (C, H, S): C, 28.31; H, 2.14; S, 7.56; Found: C, 28.42; H, 2.16; S, 7.52.

2-[(3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-Heptadecafluorodecyl) sulfanyl]ethanol (**4c**). Yield: 66.2 g (90%); yellowish wax, m.p. 71–72 °C (Ref. [17]: 73 °C); ^{1}H NMR ($CDCl_3$): δ 2.13 (bs, 1H, OH); 2.27–2.52 (m, 2H, CH_2R_F); 2.70–2.82 (m, 4H, CH_2SCH_2); 3.72–3.83 (m, 2H, CH_2O) ppm; ^{13}C NMR ($CDCl_3$): δ 22.50 (s, 1C, $R_FCH_2CH_2$); 32.14 (t, 1C, CH_2R_F, $^{2}J_{CF} = 21.9$); 35.33 (s, 1C, CH_2S); 60.56 (s, 1C, CH_2OH); 100–125 (m, 8C, 7 × CF_2 and CF_3) ppm; ^{19}F NMR ($CDCl_3$): δ –76.51 (t, 3F, CF_3, $^{3}J_{FF} = 10$); –107.99 (m, 2F, CH_2CF_2); –114.97 (m, 2F, CF_2); –115.47 (m, 4F, 2× CF_2); –115.93 (m, 2F, CF_2); –116.53 (m, 2F, CF_2); –119.13 (m, 2F, CF_2) ppm.

General procedure for preparation of 2-(polyfluoroalkylsulfanyl)ethyl methacrylates **5a**–**c**. Methacryloyl chloride (4.18 g, 40 mmol) in diethyl ether (10 ml) was added dropwise (for 0.5 h) by a syringe through septum to a mixture of 2-(polyfluoroalkylsulfanyl)ethanol (**4a**–**c**, 20 mmol), triethylamine (4.55 g, 45 mmol) and diethyl ether (140 ml) in a flask while stirring under argon and the mixture was then stirred at r.t. for 5 h. The reaction was then quenched by dropwise-addition of methanol (10 ml) and stirred for 1 h. The volatile components were removed on rotary evaporator, the salts were filtered off and washed with diethyl ether. The filtrates were combined, solvent was removed on rotary evaporator and the residue was distilled in vacuum to afford the products **5a**–**c** as clear liquids in 99% purity (check by ^{1}H and ^{19}F NMR).

2-[(3,3,4,4,5,5,6,6,6-Nonafluorohexyl)sulfanyl]ethyl methacrylate (**5a**). Yield: 7.38 g (94%); b.p. 86–87 °C/160 Pa; ^{1}H NMR ($CDCl_3$): δ 1.90 (s, 3H, CH_3); 2.24–2.50 (m, 2H, CH_2R_F); 2.76–2.86 (m, 4H, CH_2SCH_2); 4.31 (t, 2H, CH_2O, $^{3}J_{HH} = 6.6$); 5.54–5.60 (m, 1H, =CH); 6.07–6.12 (m, 1H, =CH) ppm; ^{13}C NMR ($CDCl_3$): δ 18.12 (s, 1C, CH_3); 22.96 (t, 1C, $R_FCH_2CH_2$, $^{3}J_{CF} = 4.4$); 30.73 (s, 1C, CH_2S); 31.97 (t, 1C, CH_2R_F, $^{2}J_{CF} = 22$); 63.68 (s, 1C, CH_2O); 100–125 (m, 4C, 3× CF_2 and CF_3); 125.89 (s, 1C, $=CH_2$); 135.98 (s, 1C, C=); 167.08 (s, 1C, COO) ppm; ^{19}F NMR ($CDCl_3$): δ –76.73 (m, 3F, CF_3); –108.16 (m, 2F, CH_2CF_2); –117.40 (m, 2F, CF_2); –118.98 (m, 2F, CF_2) ppm. Anal. $C_{12}H_{13}F_9O_2S$ (C, H, S): C, 36.74; H, 3.34; S, 8.17; Found: C, 36.66; H, 3.45; S, 8.03.

2-[(3,3,4,4,5,5,6,6,7,7,8,8,8-Tridecafluorooctyl)sulfanyl] ethyl methacrylate (**5b**). Yield: 9.45 g (96%); b.p. 80–83 °C/40 Pa (Ref. [12]: 90 °C/53 Pa); ^{1}H NMR ($CDCl_3$): δ 1.86 (s, 3H, CH_3); 2.22–2.43 (m, 2H, CH_2R_F); 2.67–2.80 (m, 4H, CH_2SCH_2); 4.27 (t, 2H, CH_2O, $^{3}J_{HH} = 6.6$); 5.50–5.55 (m, 1H, =CH); 6.63–6.67 (m, 1H, =CH) ppm; ^{13}C NMR ($CDCl_3$): δ 18.24 (s, 1C, CH_3); 23.03 (s, 1C, $R_FCH_2CH_2$); 30.78 (s, 1C, CH_2S); 32.08 (t, 1C, CH_2R_F, $^{2}J_{CF} = 21.8$); 63.71 (s, 1C, CH_2O); 100–125 (m, 6C, 5× CF_2 and CF_3); 126.00 (s, 1C, $=CH_2$); 135.96 (s, 1C, C=); 167.09 (s, 1C, COO) ppm; ^{19}F NMR ($CDCl_3$): δ –81.22 (t, 3F, CF_3, $^{3}J_{FF} = 10$); –114.71 (m, 2F, CH_2CF_2); –122.34 (m, 2F, CF_2); –123.29 (m, 2F, CF_2); –123.82 (m, 2F, CF_2); –126.57 (m, 2F, CF_2) ppm. MS: *m/z* 492 (M^+). Anal. $C_{14}H_{13}F_{13}O_2S$ (C, H, S): C, 34.16; H, 2.66; S, 6.51; Found: C, 34.12; H, 2.61; S, 6.48.

2-[(3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-Heptadecafluorodecyl)sulfanyl]ethyl methacrylate (**5c**). Yield: 11.14 g (94%); b.p. 75–80 °C/0.53 Pa (Ref. [12]: 130 °C/40 Pa); ^{1}H NMR ($CDCl_3$): δ 1.90 (s, 3H, CH_3); 2.26–2.55 (m, 2H, CH_2R_F); 2.72–3.00 (m, 4H, CH_2SCH_2); 4.27–4.40 (m, 2H, CH_2O); 5.54–5.68 (m, 1H, =CH); 6.06–6.14 (m, 1H, =CH) ppm; ^{13}C NMR ($CDCl_3$): δ 18.13 (s, 1C, CH_3); 22.96 (s, 1C, $R_FCH_2CH_2$); 30.73 (s, 1C, CH_2S); 31.96 (t, 1C, CH_2R_F, $^{2}J_{CF} = 21.8$); 63.68 (s, 1C, CH_2O); 100–125 (m, 8C, 7 × CF_2 and CF_3); 125.91 (s, 1C, $=CH_2$); 135.97 (s, 1C, C=); 167.09 (s, 1C, COO) ppm; ^{19}F NMR ($CDCl_3$): δ –76.48 (t, 3F, CF_3, $^{3}J_{FF} = 10$); –107.96 (m, 2F, CH_2CF_2); –114.96 (m, 2F, CF_2); –115.14 (m, 4F, 2 × CF_2); –115.92 (m, 2F, CF_2); –116.51 (m, 2F, CF_2); –119.13 (m, 2F, CF_2) ppm. Anal. $C_{16}H_{13}F_{17}O_2S$ (C, H, S): C, 32.44; H, 2.21; S, 5.41; Found: C, 32.67; H, 2.31; S, 5.36.

General procedure for preparation of 2-(polyfluoroalkylsulfinyl)ethanols **6a**–**c**. A solution of sodium periodate (2.23 g, 10.4 mmol) in water (12 ml) was added dropwise to a vigorously stirred ice-cold solution of 2-(polyfluoroalkylsulfanyl)ethanol (**4a**–**c**, 10 mmol) in methanol (30 ml). The reaction mixture was stirred at 0 °C for 1 h, then at r.t. for additional 5 h. The mixture was evaporated in vacuum to dryness. The residue was extracted with chloroform on a filter and the filtrate was dried over $MgSO_4$. The solvent was then removed in vacuum and the crude product (**6a**–**c**) was purified by column chromatography (silica gel, eluent $CHCl_3/CH_3OH$ 3:1). Products **6a**–**c** were obtained as hydroscopic liquids or waxy solids in a 99% purity (check by ^{1}H and ^{19}F NMR).

2-[(3,3,4,4,5,5,6,6,6-Nonafluorohexyl)sulfinyl]ethanol (**6a**). Yield: 3.30 g (97%); ^{1}H NMR ($CDCl_3$): δ 2.46–2.78 (m, 2H, CH_2R_F); 2.86–3.15 (m, 4H, CH_2SOCH_2); 3.70 (bs, 1H, OH); 4.04–4.21 (m, 2H, CH_2O) ppm; ^{13}C NMR ($CDCl_3$): δ 24.77 (t, 1C, CH_2R_F, $^2J_{CF}$ = 22.8); 43.07 (s, 1C, CH_2S); 54.28 (s, 1C, CH_2S); 55.66 (s, 1C, CH_2OH); 100–125 (m, 4C, 3 × CF_2 and CF_3) ppm; ^{19}F NMR ($CDCl_3$): δ –77.03 (t, 3F, CF_3, $^3J_{FF}$ = 9.5); –107.47 (m, 2F, CH_2CF_2); –117.22 (m, 2F, CF_2); –119.00 (m, 2F, CF_2) ppm. Anal. $C_8H_9F_9O_2S$ (C, H, S): C, 28.24; H, 2.67; S, 9.43; Found: C, 28.31; H, 2.76; S, 9.37.

2-[(3,3,4,4,5,5,6,6,7,7,8,8,8-Tridecafluorooctyl)sulfinyl] ethanol (**6b**). Yield: 4.27 g (97%); ^{1}H NMR ($CDCl_3$): δ 2.38 (bs, 1H, OH); 2.47–2.68 (m, 2H, CH_2R_F); 2.84–3.02 (m, 4H, CH_2SOCH_2); 4.12–4.19 (m, 2H, CH_2O) ppm; ^{13}C NMR ($CDCl_3$): δ 24.90 (t, 1C, CH_2R_F, $^2J_{CF}$ = 22.4); 43.27 (s, 1C, CH_2S); 53.73 (s, 1C, CH_2S); 56.40 (s, 1C, CH_2OH); 100–125 (m, 6C, 5 × CF_2 and CF_3) ppm; ^{19}F NMR ($CDCl_3$): δ –81.19 (m, 3F, CF_3); –113.92 (m, 2F, CH_2CF_2); –122.24 (m, 2F, CF_2); –123.27 (m, 2F, CF_2); –123.57 (m, 2F, CF_2); –126.55 (m, 2F, CF_2) ppm. MS: *m/z* 440 (M^+). Anal. $C_{10}H_9F_{13}O_2S$ (C, H, S): C, 27.28; H, 2.06; S, 7.28; Found: C, 27.21; H, 2.12; S, 7.21.

2-[(3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-Heptadecafluorodecyl) sulfinyl]ethanol (**6c**). Yield: 5.29 g (98%); ^{1}H NMR ($CDCl_3$): δ 2.51–2.76 (m, 2H, CH_2R_F); 2.81–3.20 (m, 5H, CH_2SOCH_2 and OH); 4.10–4.30 (m, 2H, CH_2O) ppm; ^{13}C NMR ($CDCl_3$): δ 24.89 (t, 1C, CH_2R_F, $^2J_{CF}$ = 21.8); 43.30 (s, 1C, CH_2S); 53.76 (s, 1C, CH_2S); 56.35 (s, 1C, CH_2OH); 100–125 (m, 8C, 7 × CF_2 and CF_3) ppm; ^{19}F NMR ($CDCl_3$): δ –76.45 (t, 3F, CF_3, $^3J_{FF}$ = 9.9); –107.24 (m, 2F, CH_2CF_2); –114.88 (m, 2F, CF_2); –115.14 (m, 4F, 2 × CF_2); –115.91 (m, 2F, CF_2); –116.28 (m, 2F, CF_2); –119.10 (m, 2F, CF_2) ppm. Anal. for $C_{12}H_9F_{17}O_2S$ (C, H, S): C, 26.68; H, 1.68; S, 5.94; Found: C, 26.45; H, 1.71; S, 5.88.

General procedure for the preparation of 2-(polyfluoroalkylsulfinyl)ethyl methacrylates **7a**–**c** from 2-(polyfluoroalkylsulfanyl)ethyl methacrylates **5a**–**c**. A solution of sodium periodate (2.23 g, 10.4 mmol) in water (12 ml) was added dropwise to a vigorously stirred ice-cold solution of 2-(polyfluoroalkyl-sulfanyl)ethyl methacrylate (**5a**–**c**, 10 mmol) in methanol (60 ml). The reaction mixture was stirred at 0 °C for 1 h and then at r.t. for additional 5 h. The mixture was evaporated to dryness in vacuum, the residue was extracted with chloroform on a filter and the filtrate was dried over $MgSO_4$. The solvent was then removed in vacuum and the crude product (**7a**–**c**) was purified by column chromatography (silica gel, eluent hexane/ethyl acetate 1:1). Products **7a**–**c** were obtained as white waxy compounds in a yield of 3.92 g (96%, **7a**), 4.83 g (95%, **7b**), 5.72 g (94%, **7c**) in a 99% purity (check by ^{1}H and ^{19}F NMR).

2-[(3,3,4,4,5,5,6,6,6-Nonafluorohexyl)sulfinyl]ethyl methacrylate (**7a**). ^{1}H NMR ($CDCl_3$): δ 1.90 (s, 3H, CH_3); 2.50–2.72 (m, 2H, CH_2R_F); 2.89–3.19 (m, 4H, CH_2SOCH_2); 4.47–4.70 (m, 2H, CH_2O); 5.58–5.63 (m, 1H, =CH); 6.08–6.14 (m, 1H, =CH) ppm; ^{13}C NMR ($CDCl_3$): δ 18.07 (s, 1C, CH_3); 24.85 (t, 1C, CH_2R_F, $^2J_{CF}$ = 23.2); 43.20 (s, 1C, CH_2S); 51.88 (s, 1C, CH_2S); 57.04 (s, 1C, CH_2O); 100–125 (m, 4C, 3 × CF_2 and CF_3); 126.61 (s, 1C, =CH_2); 135.51 (s, 1C, C=); 166.73 (s, 1C, COO) ppm; ^{19}F NMR ($CDCl_3$): δ –76.68 (t, 3F, CF_3, $^3J_{FF}$ = 9); –107.45 (m, 2F, CH_2CF_2); –117.20 (m, 2F, CF_2); –118.96 (m, 2F, CF_2) ppm. Anal. $C_{12}H_{13}F_9O_3S$ (C, H, S): C, 35.30; H, 3.21; S, 7.85; Found: C, 35.41; H, 3.19; S, 7.93.

2-[(3,3,4,4,5,5,6,6,7,7,8,8,8-Tridecafluorooctyl)sulfinyl] ethyl methacrylate (**7b**). ^{1}H NMR ($CDCl_3$): δ 1.88 (s, 3H, CH_3); 2.46–2.68 (m, 2H, CH_2R_F); 2.84–3.14 (m, 4H, CH_2SOCH_2); 4.43–4.65 (m, 2H, CH_2O); 5.54–5.58 (m, 1H, =CH); 6.05–6.08 (m, 1H, =CH) ppm; ^{13}C NMR ($CDCl_3$): δ 18.02 (s, 1C, CH_3); 24.88 (t, 1C, CH_2R_F, $^2J_{CF}$ = 23.0); 43.19 (s, 1C, CH_2S); 51.84 (s, 1C, CH_2S); 57.02 (s, 1C, CH_2O); 100–125 (m, 6C, 5 × CF_2 and CF_3); 126.35 (s, 1C, =CH_2); 135.49 (s, 1C, C=); 166.69 (s, 1C, COO) ppm; ^{19}F NMR ($CDCl_3$): δ –81.40 (m, 3F, CF_3); –114.05 (m, 2F, CH_2CF_2); –122.36 (m, 2F, CF_2); –123.39 (m, 2F, CF_2); –123.69 (m, 2F, CF_2); –126.72 (m, 2F, CF_2) ppm. Anal. $C_{14}H_{13}F_{13}O_3S$ (C, H, S): C, 33.08; H, 2.58; S, 6.31; Found: C, 33.05; H, 2.53; S, 6.28.

2-[(3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-Heptadecafluorodecyl) sulfinyl]ethyl methacrylate (**7c**). ^{1}H NMR ($CDCl_3$): δ 1.90 (s, 3H, CH_3); 2.50–2.76 (m, 2H, CH_2R_F); 2.88–3.24 (m, 4H, CH_2SOCH_2); 4.46–4.76 (m, 2H, CH_2O); 5.58–5.65 (m, 1H, =CH); 6.08–6.16 (m, 1H, =CH) ppm; ^{13}C NMR ($CDCl_3$): δ 18.09 (s, 1C, CH_3); 24.94 (t, 1C, CH_2R_F, $^2J_{CF}$ = 22.8); 43.23 (s, 1C, CH_2S); 51.88 (s, 1C, CH_2S); 57.05 (s, 1C, CH_2O); 100–125 (m, 8C, 7× CF_2 and CF_3); 126.65 (s, 1C, =CH_2); 135.51 (s, 1C, C=); 166.76 (s, 1C, COO) ppm; ^{19}F NMR ($CDCl_3$): δ –76.51 (t, 3F, CF_3, $^3J_{FF}$ = 9.5); –107.23 (m, 2F, CH_2CF_2); –114.89 (m, 2F, CF_2); –115.14 (m, 4F, 2× CF_2); –115.92 (m, 2F, CF_2); –116.27 (m, 2F, CF_2); –119.13 (m, 2F, CF_2) ppm. Anal. $C_{16}H_{13}F_{17}O_3S$ (C, H, S): C, 31.59; H, 2.15; S, 5.27; Found: C, 31.47; H, 2.17; S, 5.33.

General procedure for the preparation of 2-(polyfluoroalkylsulfinyl)ethyl methacrylates **7a**–**c** from 2-(polyfluoroalkylsulfinyl)ethanols **6a**–**c**. Methacryloyl chloride (5.23 g, 50 mmol) in diethyl ether (30 ml) was added dropwise (for 0.5 h) by a syringe through septum to a mixture of 2-(polyfluoroalkyl-sulfinyl)ethanol (**6a**–**c**, 10 mmol), triethylamine (5.57 g, 55 mmol) and diethyl ether (500 ml) in a flask while stirring under argon and the mixture was then stirred at r.t. for 5 h. In a flask while stirring and the mixture was then stirred at r.t. for 5 h. The reaction was then quenched by dropwise-addition of methanol (30 ml) and stirred for 1 h. The volatile components were removed on rotary evaporator, the solid residue was extracted on a filter with diethyl ether. The solvent was removed on rotary evaporator and the residual crude product (**7a**–**c**) was purified by column chromatography (silica gel, eluent hexane/ethyl acetate 1:1). Products **7a**–**c** were obtained as white waxy compound in a yield of 3.84 g (94%, **7a**), 4.73 g (93%, **7b**), 5.54 g (91%, **7c**) in a 99% purity (check by ^{1}H and ^{19}F NMR).

Copolymerization protocol. Fluorinated monomers **7a**–**c** were used for the UV-light induced (mercury lamp, RVK-125

W, TESLA, Prague; BEE as photoinitiator, 0.5 wt.%) block copolymerization with diethylene glycol dimethacrylate (DEGMA) and with EDMA (0.5 wt.%) as a crosslinking agent under nitrogen atmosphere for 2 hours. Disc-shape pieces (diameter 13 mm, thickness 0.5 mm) were made in open polypropylene moulds.

5.3. Physical properties of the new materials

Refractive index (Table 1) was measured on swollen discs mentioned above using Abbé refractometer (Carl-Zeiss, Jena, Germany). Modulus of elasticity in compression at 5% or 10% strain were measured using an Instron 5800 testing machine (Instron, High Wycombe, UK) at a speed of 10 mm/min and force 0–10 N. The tests were carried out on swollen samples (Table 2).

5.4. Physical properties of the new materials

5.4.1. Hydro-swelling

The copolymer samples (vide supra) were separated from moulds mechanically and then put in distilled water to be transformed to the equilibrium swollen state within several days (10 days as maximum, equilibrium state checked by balancing, distilled water was changed for a fresh one twice in every day; water-soluble monomers were washed out during the swelling and therefore could not influence this quantity). The samples were then dried under vacuum at 50 °C to a constant weight. The water content was calculated as the ratio of the difference of weights of swollen and dry gel to the swollen gel weight in %. Coefficient of linear swelling was calculated as a ratio of diameter of swollen and dry discs. Diameters of discs were measured with Mitutoyo toolmakers microscope TM 201 (Mitutoyo, Japan) with accuracy 0.001 mm.

5.4.2. Oxygen permeability

Oxygen permeability was determined using standard Fatt's polarographic method (determination of oxygen permeability and transmissibility with the Fatt method, ISO 9913-1/1996).

Acknowledgements

Fluorochemicals were kindly supplied by the Atofina S.A. (the former Elf Atochem S.A.). The research was supported by the Grant Agency of the Czech Republic (grant no. 106/00/1206) and partly by the Ministry of Education of the Czech Republic (project MSM 46137301).

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