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Synthesis and Research of Optical properties of tert-perfluorinated esters of alpha-fluoroacrylic acid

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Abstract: Group of tertiary perfluorinated ether alpha-fluoroacrylic acid type $\text{CH}_2=\text{CF}-\text{CO}_2-\text{C}(\text{CF}_3)_2-(\text{CF}_2)_m-\text{CF}_3$ where $m=0, 1, 3, 5$ containing degree of fluorination from 83.3 to 90.9% were prepared. Synthesized α -fluoroacrylates (1) have high transparency in all three telecommunication ranges 0.85, 1.3 and 1.5 μm . Refractive index of monomers decreases with elongation m of aliphatic perfluorinated radical and comes to 1.313 – 1.316.

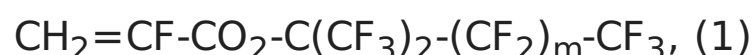
Keywords: α -fluoroacrylates, coefficient of absorption, refractive index, integrated optics.

Polymers on basis of fluorinated acrylates find wide application in industry, science and technology. [1-17]. One of the most promising field of application is fiber and integrated optics,

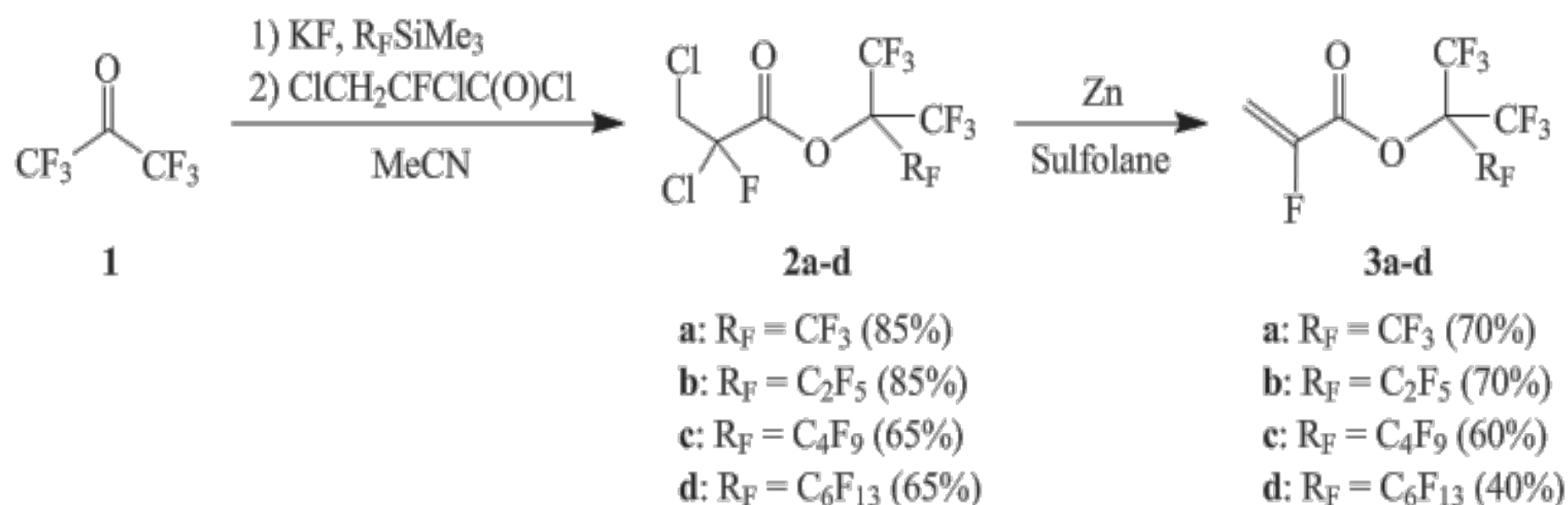
where acrylates are used as materials for creation of optical fibers and waveguides, providing high speed interconnection in "telecommunication" wavelength ranges near $\lambda = 0.85, 1.3$ and 1.55 mcm [4-9, 18-21]. Thereby the highest optical transparency in above spectral ranges have acrylates with minimum content of C-H bonds, that means with maximum degree of fluorination [22-26].

To increase the degree of fluorination of acrylic monomers by keeping its high activity in the process of radical UV photopolymerization, we developed methods of synthesis for

cyanoperfluoro- cyanochloroperfluoroalkylacrylates, and also tert-butyl- α -fluoroacrylates. [27,28]. The next step to increase the degree of fluorination of acrylic monomers is transfer to α -fluoroacrylates of perfluorinated tert-alcohols with extended length of aliphatic radical in alcohol part of an ester. For this purpose, we developed method of synthesis of new, previously not described monomers of homologues series

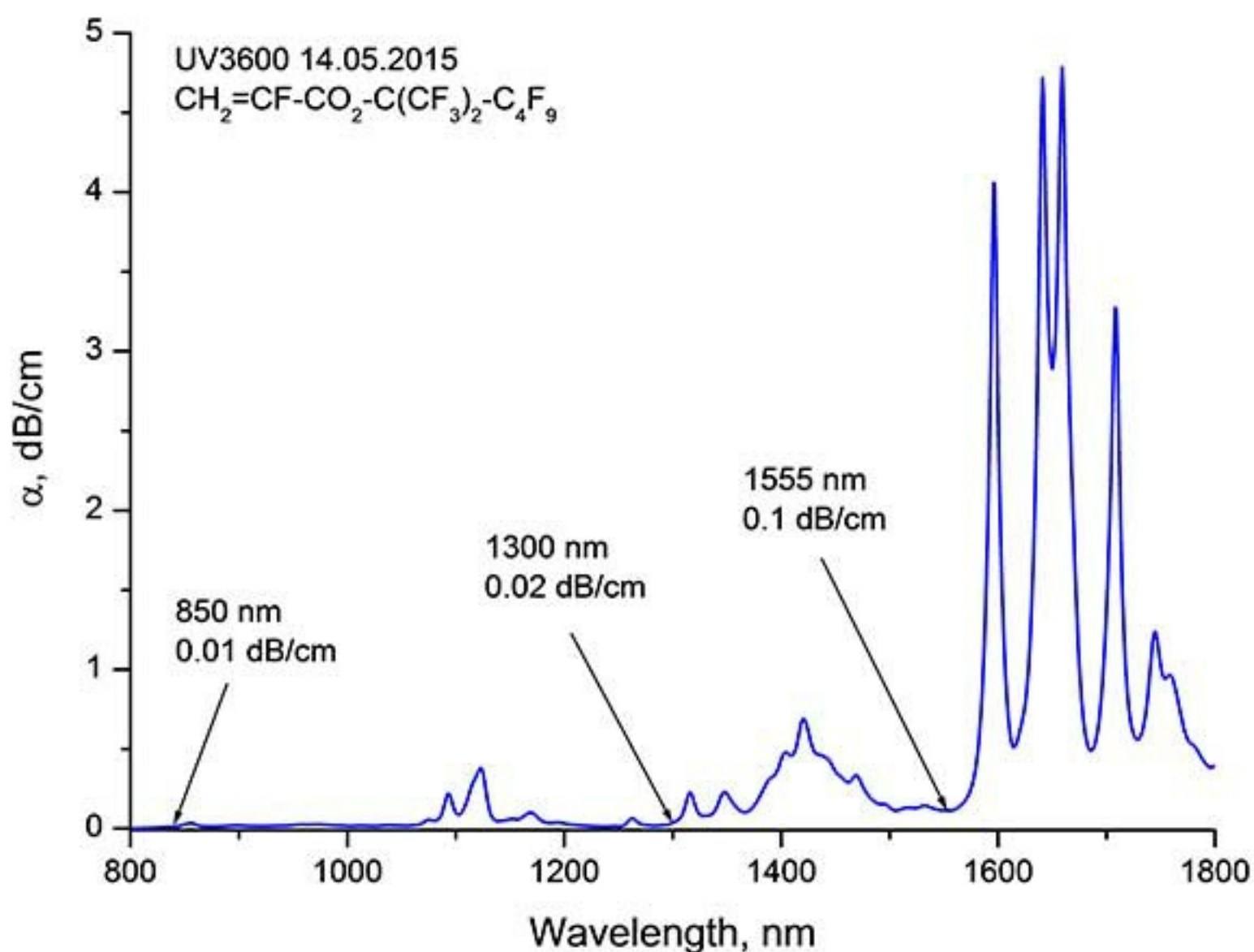


where $m = 0, 1, 3, 5$, with degree of fluorination from 83.3 to 90.9 %. The synthesis of α -fluoroacrylates (1) was conducted according to the below Scheme 1 through interaction of obtaining in situ potassium salts of perfluorotertbutyl alcohols, reaction of nucleophilic addition of perfluoroalkyl(trimethyl)silanes to hexafluoroacetone by the presence of equimolar quantity of Potassium fluoride with 2,3-dichloro-2-fluoropropionyl chloride and following dechlorination.



Scheme 1

Investigation of optical properties of monomers showed, that synthesized α -fluoroacrylates (1) have high transparency in all three telecommunication ranges 0.85, 1.3, 1.5 μm , which is provided by their high range degree of fluorination, reaching 90.9 %. Typical absorption spectrum of these monomers, provided in dB/cm is presented in picture 1. It can be seen, that attenuation coefficient comes to 0.01 dB/cm ($\lambda = 850 \text{ nm}$), 0.02 dB/cm ($\lambda = 1300 \text{ nm}$) and 0.1 dB/cm ($\lambda = 1550 \text{ nm}$) correspondingly.



Refractive index n_D on wavelength $\lambda = 589.3 \mu m$ and average dispersion $n_F - n_C$ of monomers (1) were measured with the help of Abbe refractometer IRF-454 B2M and are presented in the table 1. Table 1 shows, that refractive index of monomers decreases with elongation m of aliphatic perfluorinated radical (that means with increase of degree of fluorination) and comes to 1.313 – 1.316 , which is record-low for UV photocurable acrylates. Refractive indexes of homopolymers, produced from monomers (1), rather higher and fall within the range of 1.343 – 1.349. It is explained with weight loss and altering of chemical structure in the process of radical polymerization (opening of double $C=C$ bonds, building of polymer's macromolecules from monomer molecules and ets.)

Table. 1. Refractive index n_D on wavelength $\lambda = 589.3 \mu m$ and average dispersion $n_F - n_C$ of fluorocontaining α -fluoroacrylating monomers (1), take under 20°C.

Chemical Formula	Conversion of fluorination, %	n_D	$n_F - n_F$
$CH_2=CF-COO-C(CF_3)_3$	83.3	1.3160 ± 0.0002	6.521×10^{-3}
$CH_2=CF-COO-C(CF_3)_2-(CF_2)-CF_3$	85.7	$1.3156 \pm$	6.520×10^{-3}

		0.0002	3
$\text{CH}_2=\text{CF}-\text{COO}-\text{C}(\text{CF}_3)_2-(\text{CF}_2)_3-\text{CF}_3$	88.9	1.3148 ± 0.0002	6.516×10^3
$\text{CH}_2=\text{CF}-\text{COO}-\text{C}(\text{CF}_3)_2-(\text{CF}_2)_5-\text{CF}_3$	90.9	1.3137 ± 0.0002	6.512×10^3

The synthesized α -fluoroacrylic monomers (1) have high activity in the process of radical UV photopolymerization, which can be initiated without adding any photoinitiators under the action of UV radiation with wavelength shorter than 260 nm. These monomers are suitable for production of optical waveguides by methods of direct laser writing or UV photolithography.

Experimental

NMR ^1H , ^{19}F spectra were recorded on spectrometer "Bruker AVANCE-300" by 300 and 282 MHz correspondingly, external standard is CDCl_3 . Chemical shifts for ^1H spectra are provided in m.d with respect to tetramethylsilane. Chemical shifts of ^{19}F spectra are provided in m.d with respect to CFCl_3 . The purity of monomers were measured by method of gas-liquid chromatography (GC) on chromatograph Shimadzu 2010 + column Resteck RTX-1701 (USA) 14 % cyanopropylphenyl, 86 % polysiloxane, length 30 m, 0,32 ID, 1 mm df, flame ionization detector, carrier gas nitrogen.

General method of synthesis of fluoroacrylic monomers

To a suspension of potassium fluoride (30 g, 0.516 mol) in acetonitrile (200 ml) by stirring and temperature $-30 - -25^\circ\text{C}$ gaseous hexafluoroacetone is added (85 g, 0,512 mol) and R_fSiMe_3 (0,512 mol). After completion of exothermic reaction, as a result of which the temperature of reaction mixture rises to $0 - 5^\circ\text{C}$, the mixture is stirred by $15 - 20^\circ\text{C}$ during 2-3 hours, cooled to $0 - 5^\circ\text{C}$ and $\text{ClCH}_2\text{CFClC}(\text{O})\text{Cl}$ (92 g, 0,513 mol) drop-wise is added. The mixture is stirred by $15 - 20^\circ\text{C}$ during 2-3 hours, poured in water, the bottom layer is separated, washed 4 times with water, P_2O_5 (15g) is added and rerun in vacuum ($10 - 0,5$ torr). The product is purified by redistillation.

1,1,1,3,3,3-Hexafluoro-2-(trifluoromethyl)propan-2-yl-2,3-dichloro-2-fluoropropanoate (2a)

bp $50 - 52^\circ\text{C}/15$ torr

NMR ^1H δ : $4,0 \div 4,2$ (m, CH_2Cl); NMR ^{19}F δ : $-125,4$ (m, 1F, CFCl), $-71,7$ (m, 9F, CF_3).

1,1,1,3,3,4,4,4-Octafluoro-2-(trifluoromethyl)but-2-yl-2,3-dichloro-2-fluoropropanoate (2b)

bp $73 - 75^\circ\text{C}/15$ torr

NMR ^1H δ : $3,9 \div 4,2$ (m, CH_2Cl); NMR ^{19}F δ : $-125,4$ (m, 1F, CFCl), $-118,5$ (m, 2F, CF_2),

-81,8 (m, 3F, CF₃), -69,0, -68,6 (m, 6F, CF₃).

1,1,1,3,3,4,4,5,5,6,6,6-dodecafluoro-2-(trifluoromethyl)hex-2-yl-2,3-dichloro-2-fluoropropanoate (2c)

bp. 110-113°C/15 torr

NMR ¹H δ: 3,9÷4,1 (m, CH₂Cl); NMR ¹⁹F δ: -127,8 (m, 2F, CF₂), -125,3 (m, 1F, CFCl), -122,2 (c, 2F, CF₂), -113,8 (m, 2F, CF₂), -83,5 (m, 3F, CF₃), -68,6, -68,2 (m, 6F, CF₃).

1,1,1,3,3,4,4,5,5,6,6,7,7,8,8,8-hexadecafluoro-2-(trifluoromethyl)octan-2-yl-2,3-dichloro-2-fluoropropanoate (2d)

bp 100-103°C/0,5 torr

NMR ¹H δ: 4,0÷4,2 (m, CH₂Cl); NMR ¹⁹F δ: -127,3 (m, 2F, CF₂), -125,4 (m, 1F, CFCl), -122,2 (m, 4F, CF₂), -121,5 (m, 2F, CF₂), -113,8 (m, 2F, CF₂), -83,6 (m, 3F, CF₃), -68,6, -68,2 (m, 6F, CF₃).

To a suspension of zinc powder (9,81 g 0,15 g-atom) activated by adding of trimethylchlorosilane (1ml) in sulfolane (50ml) in vacuum 10 - 0,5 torr by stirring and temperature 30 -40 °C ester 2a-d drop-wise is added (0,1 mol), the reaction product is distilled into cooled till 0°C receiver. The obtained product is additionally purified by rectification. The purity of monomers by GC comes to 96-99 %.

1,1,1,3,3,3-Hexafluoro-2-(trifluoromethyl)propan-2-yl-2-fluoroacrylate (3a)

bp 19-20°C/15 torr

NMR ¹H δ: 5,7÷6,2 (m, CH₂=); NMR ¹⁹F δ: -119,4 (m, 1F, CF), -71,7 (m, 9F, CF₃).

1,1,1,3,3,4,4,4-Octafluoro-2-(trifluoromethyl)but-2-yl-2-fluoroacrylate (3b)

bp 28-30°C/15 torr

NMR ¹H δ: 5,7÷6,2 (m, CH₂=); NMR ¹⁹F δ: -119,4 (m, 1F, CF), -118,5 (m, 2F, CF₂), -81,8 (m, 3F, CF₃), -69,0, -68,6 (m, 6F, CF₃).

1,1,1,3,3,4,4,5,5,6,6,6-Dodecafluoro-2-(trifluoromethyl)hex-2-yl-2-fluoroacrylate (3c)

bp 70-71°C/15 torr

NMR ¹H δ: 5,7÷6,2 (m, CH₂=); NMR ¹⁹F δ: -127,8 (m, 2F, CF₂), -122,2 (c, 2F, CF₂), -119,4 (m, 1F, CF), -113,8 (m, 2F, CF₂), -83,5 (m, 3F, CF₃), -68,6, -68,2 (m, 6F, CF₃).

1,1,1,3,3,4,4,5,5,6,6,7,7,8,8,8-Hexadecafluoro-2-(trifluoromethyl)octane-2-yl-2-fluoroacrylate (3d)

Bp 60-63°C/0,5 torr

NMR ¹H δ: 5,7÷6,2 (m, CH₂=); NMR ¹⁹F δ: -127,3 (m, 2F, CF₂), -122,2 (m, 4F, CF₂), -121,5 (m, 2F, CF₂), -119,4 (m, 1F, CF), -113,5 (m, 2F, CF₂), -83,6 (m, 3F, CF₃), -68,9,

-68,4 (m, 6F, CF₃).

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