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Optical Properties of Cyanoperfluoro- and Cyanochloroperfluoroalkylacrylates in "Data Communication" Field of Wave Length Around 0.85 μm

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Abstract: A number of cyanoperfluoro- and cyanochlorineperfluoro-alkylacrylates with halogenation grade equal to 66.6% has been synthesized out of ketones. Monomers are transparent colorless liquids of low viscosity able to conduct radical photopolymerization. Monomers' absorption and refraction spectra have been measured in "data communication" field of wave length around 0.85 μm . It has been proved, that monomers' coefficient of absorption ranges from 0.04 to 0.09 dB/cm, refractive index lies within the range of 1.336 - 1.457. The synthesized monomers can be used to form polymer waveguides and other elements integrally – the optical devices using UV photolithography and direct laser drawing.

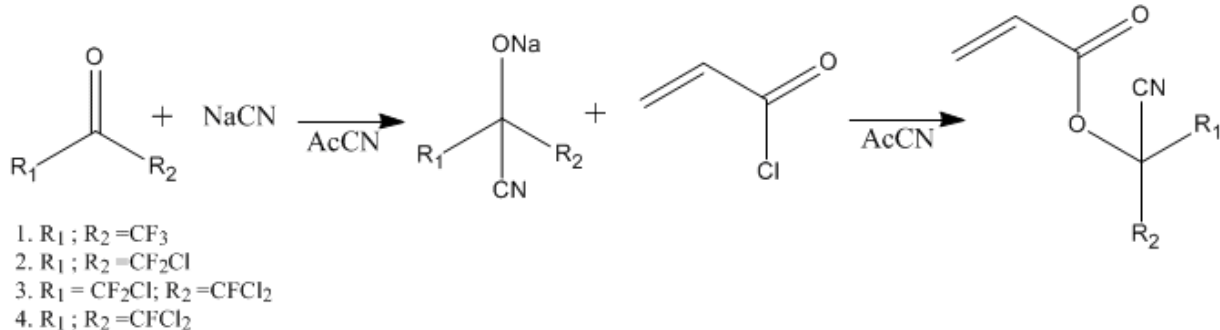
Keywords: Cyanoperfluoroalkylacrylates, cyanochlorinefluoroalkylacrylates, coefficient of absorption, refractive index, integrated optics.

Introduction

The synthesis of halogenated (fluorine and chlorine containing) monomers is one of the most intensive studied fields of organic and macromolecular chemistry. Among such monomers most attention is paid to the chemistry of fluorinated acrylates. Initially they were used as oleophobic and hydrophobic coatings in textile and leather industries. Further studies of fluoroacrylates based on primary alcohols like $\text{CH}_2=\text{CH}-\text{COO}-\text{CH}_2-\text{R}_f$, where R_f – perfluorinated radical have revealed another promising field of application – as transparent optical materials for priority direction of modern connection and information transferring technics - fibre and intergrated optics [1 - 11]. Good optic properties of these monomers and corresponding polymers in combination with high heat and moisture resistance, mechanical durability and at the same time flexibility cause their significant advantage compare to methacrylates (for example, poly(methyl methacrylate), PMMA). Nowadays many fluoroalkyl polymers of wide spectrum of refractive index have been synthesized and patented [2 - 11], that allows their using in creation of optical fibers and waveguides [12 - 16]. In terms of all said above it is advisable to synthesize and study acrylates containing tertiary alcoholic groups, and groups with one or few fluorines substituted for chlorine or cyano-groups.

Synthesis of Cyanoperfluoro- and Cyanochlorineperfluoroalkylacrylates

We have developed synthesis methods of halogenated (fluorine- and chlorine containing) monomers, we have produced cyanoperfluoro- and cyanochlorineperfluoroalkylacrylates, refer to Pic. 1. Monomers have been obtained by corresponding acetons reacting with sodium cyanide with further interaction with acroleinchloride, which led to formation of acrylates in demand. The present reaction is a single-stage process with two steps conducted in acetonitrile 0°C.



Pic. 1. Scheme of Cyanoperfluoro- And Cyanochlorineperfluoroalkylacrylates Synthesis.

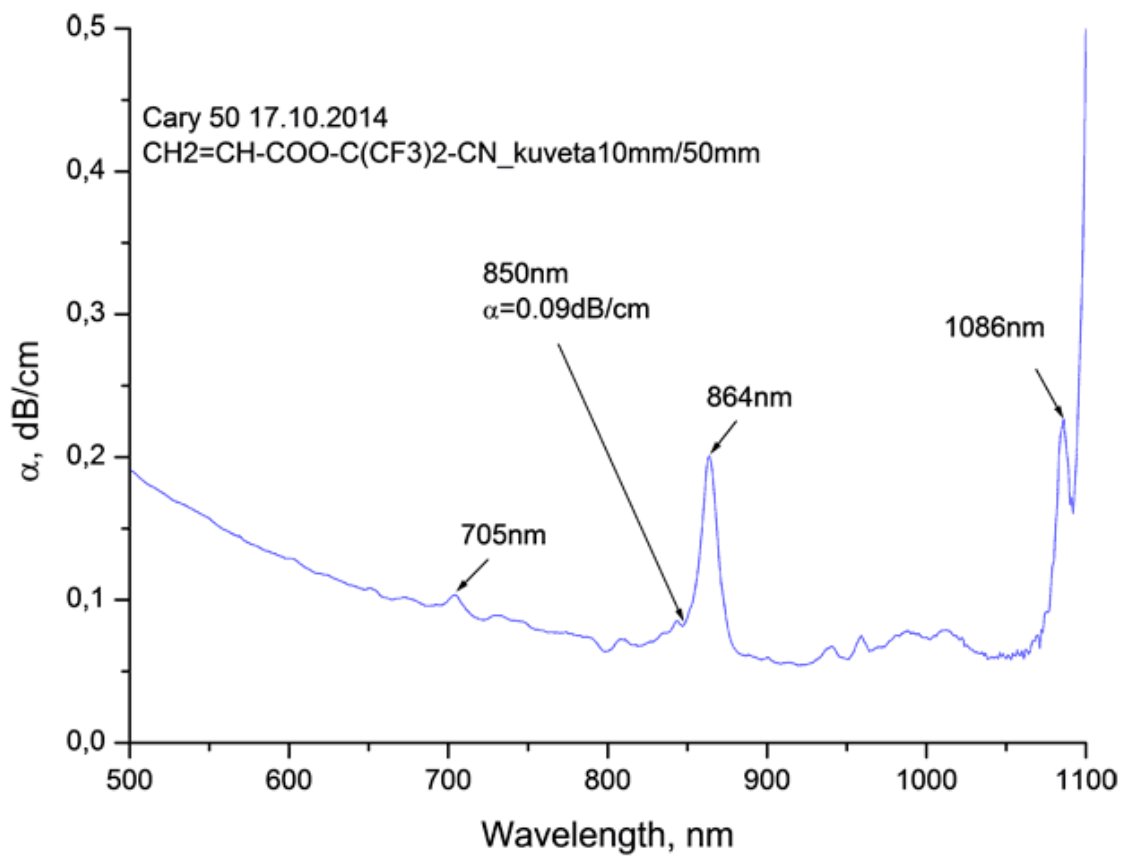
Refractive indices n_D and boiling points showings have been determined for all obtained monomers, refer to Table 1.

Table 1. Synthesized Cyanoperfluoro- And Cyanochlorineperfluoroalkylacrylates And Their Main Characteristics.

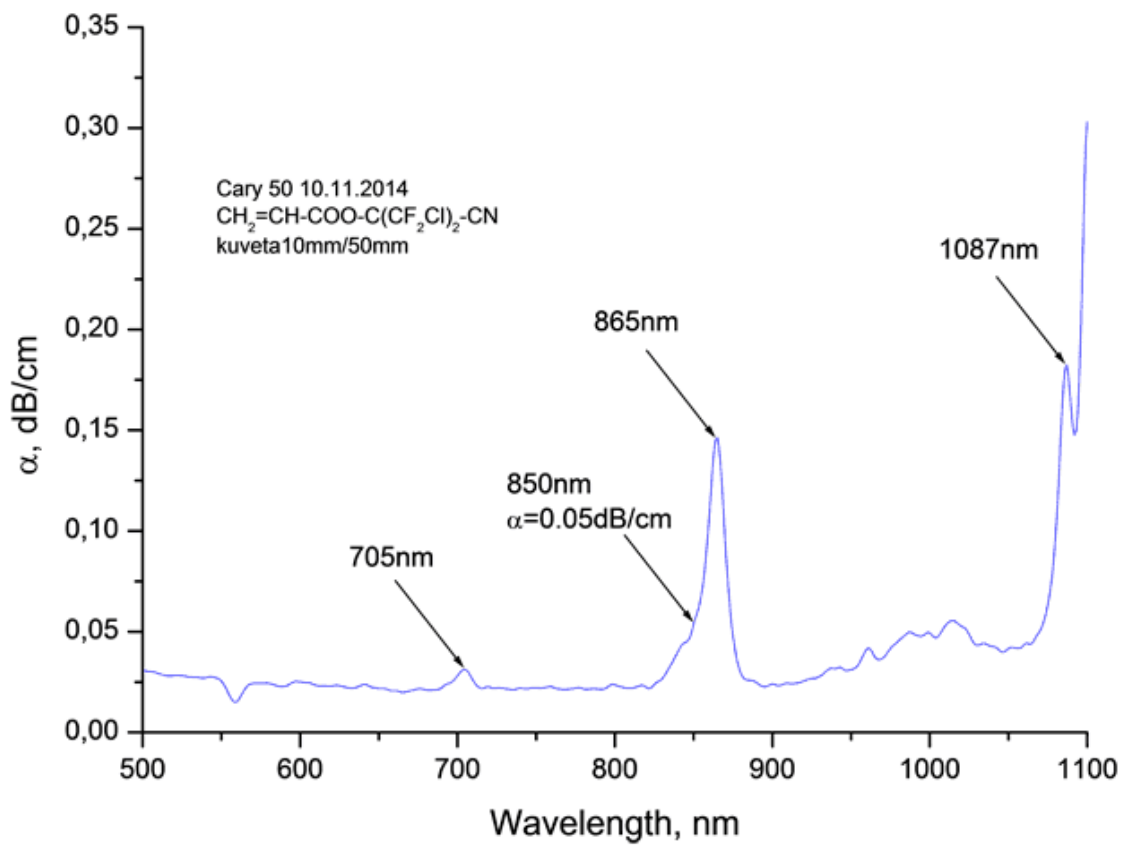
Monomer	Halogenation Grade	n_D	Boiling Point
$CH_2=CH-COO-C(CF_3)_2-CN$	66.6%	1.3417	127°C
$CH_2=CH-COO-C(CF_2Cl)_2-CN$	66.6%	1.4051	68-70°C at 20 mm Hg
$CH_2=CH-COO-C(CF_2Cl)(CFC_2)-CN$	66.6%	1.4364	90-94°C at 20 mm Hg
$CH_2=CH-COO-C(CFC_2)_2-CN$	66.6%	1.4685	116-120°C at 20 mm Hg

Studying Optical Properties of Monomers Around to 0.85 μm

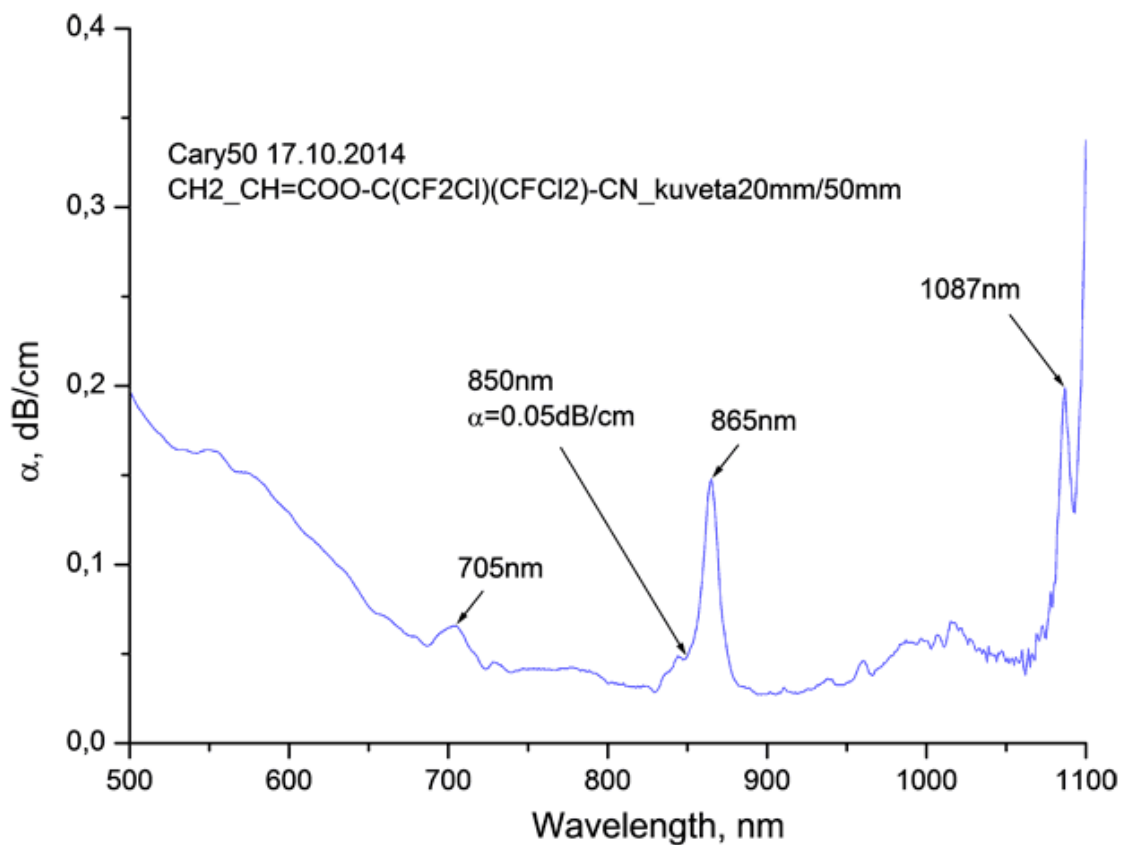
Absorption spectra of synthesized monomers in “data communication” field of wave length around 0.85 μm measured using spectrophotometer Cary-50 are listed at Pic. 2. It is obvious, that in spectra we observe the fringes of absorption caused by stretching vibrations of atoms consisting in molecule, as well as windows of transparency. Absorption lines with centres around 865 and 705 μm are caused by combination tones connected with double C=C bonds [17].



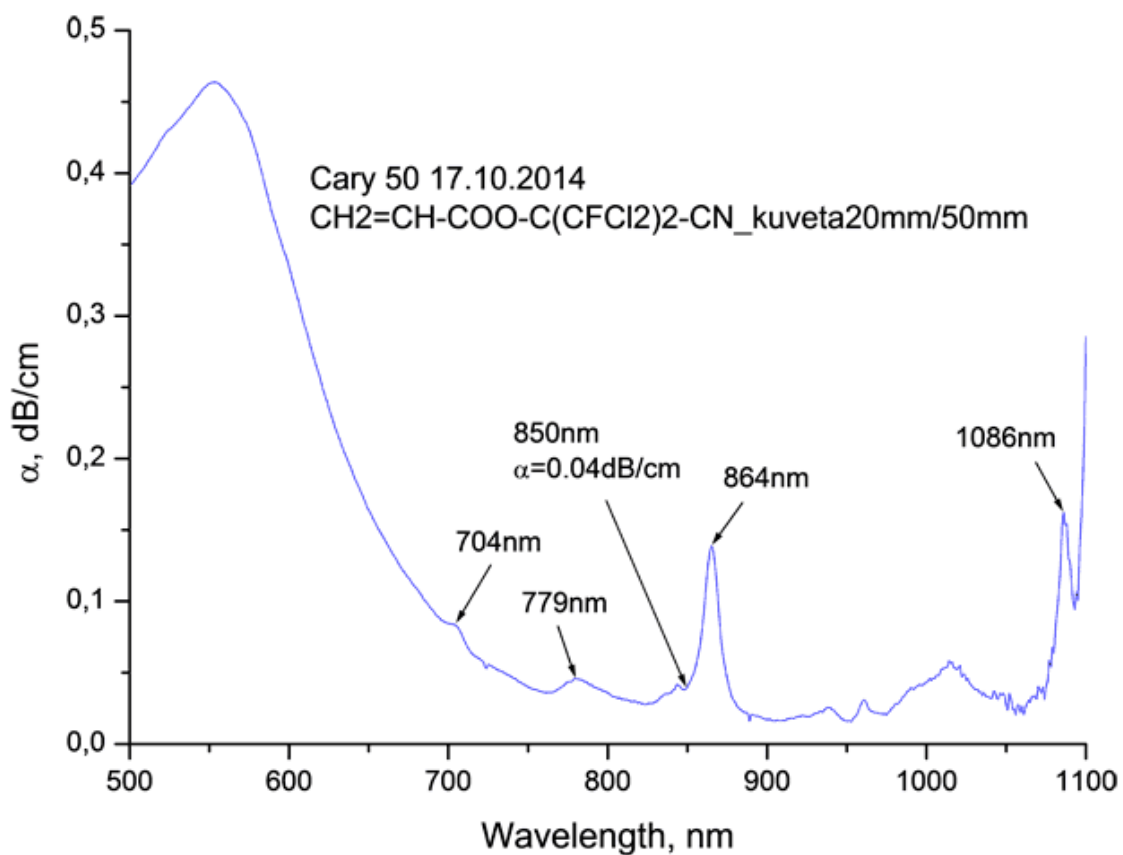
a)



b)



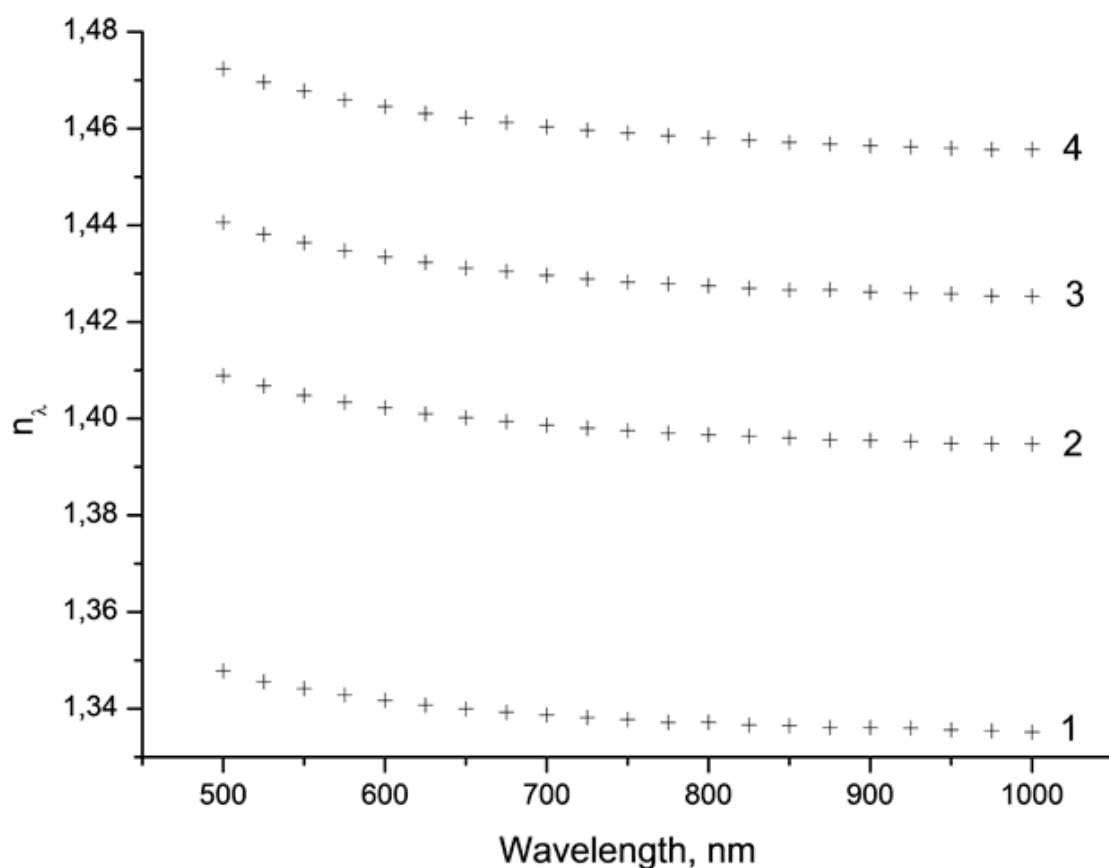
c)



d)

Fig. 2. Absorption spectrum of monomers $\text{CH}_2\text{=CH-COO-C(CF}_3\text{)}_2\text{-CN}$ (s), $\text{CH}_2\text{=CH-COO-C(CF}_2\text{Cl)}_2\text{-CN}$ (b), $\text{CH}_2\text{=CH-COO-C(CF}_2\text{Cl)(CFCl}_2\text{)-CN}$ (c), $\text{CH}_2\text{=CH-COO-C(CFCl}_2\text{)}_2\text{-CN}$ (d) in "data communication" field of wave length around $0.85\ \mu\text{m}$.

At Pic. 3 you will find dispersion dependencies of refractive index of these monomers measured using spectroscopic refractometer created in ILIT RAS [18]. It is obvious, that dispersion of monomers is normal (around $0.85 \mu m$). Optical properties of synthesized monomers are summed in Table 2.



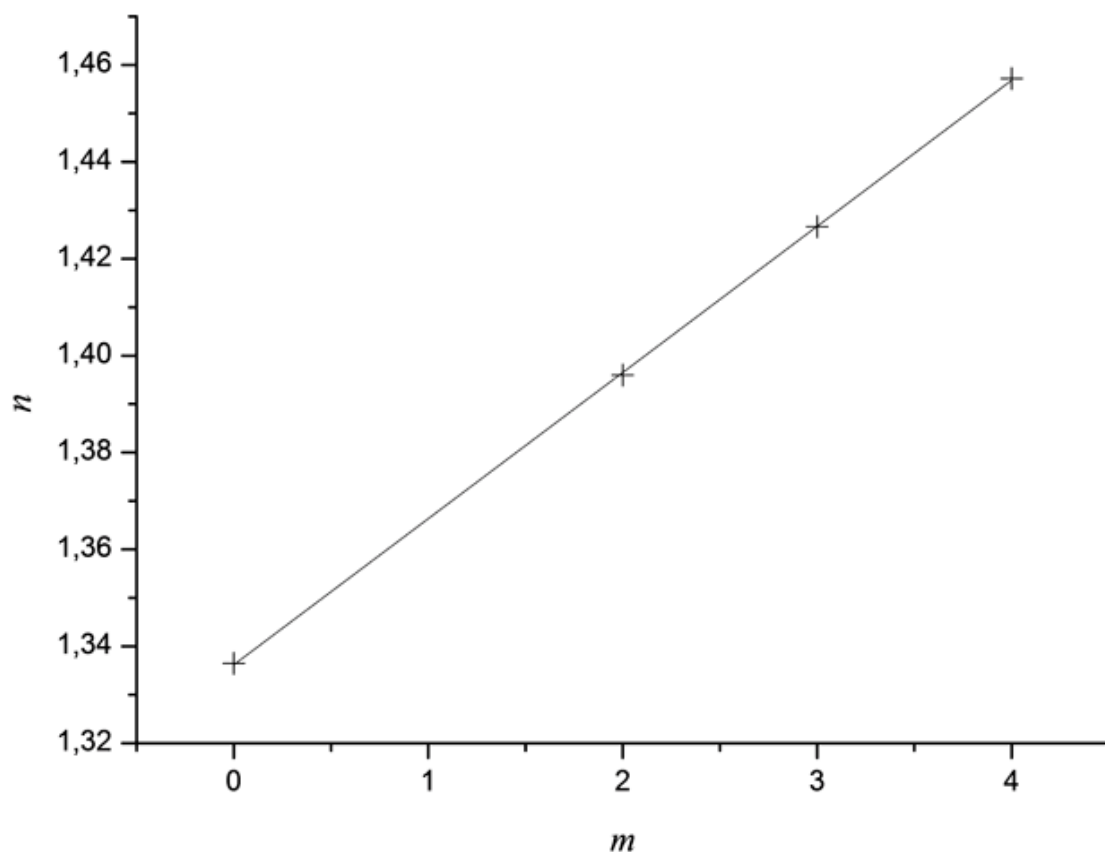
Pic. 3. Dispersion Dependencies of Monomers' Refractive Index $CH_2=CH-COO-C(CF_3)_2-CN$ (1), $CH_2=CH-COO-C(CF_2Cl)_2-CN$ (2), $CH_2=CH-COO-C(CF_2Cl)(CFCl_2)-CN$ (3), $CH_2=CH-COO-C(CFCl_2)_2-CN$ (4) around $0.85 \mu m$, measured at spectroscopic refractometer at $20^\circ C$.

Table 2. Optical Properties of Cyanoperfluoro- And Cyanochlorineperfluoroalkylacrylates At "Data Communication" Wave Length of $\lambda = 0.85 \mu m$.

Monomers	Coefficient of Absorption, dB/cm	Refractive Index	Dispersion $d_\lambda = dn/d\lambda$
$CH_2=CH-COO-C(CF_3)_2-CN$	0.09	1.3365	$-1.0 \cdot 10^{-5}/nm$
$CH_2=CH-COO-C(CF_2Cl)_2-CN$	0.05	1.3960	$-1.3 \cdot 10^{-5}/nm$
$CH_2=CH-COO-C(CF_2Cl)(CFCl_2)-CN$	0.05	1.4266	$-1.3 \cdot 10^{-5}/nm$
$CH_2=CH-COO-C(CFCl_2)_2-CN$	0.04	1.4572	$-1.5 \cdot 10^{-5}/nm$

As you can see from Table 2 the coefficient of absorption of monomers at wave length of $\lambda = 0.85 \mu m$

lies within the range of 0.04 - 0.09 dB/cm, the refractive index goes up from 1.336 to 1.457. The increasing of chlorination grade results in increasing of monomers' refraction, refer to Pic. 4.



Pic.4. The Dependency of Refractive Index $n(\lambda = 0.85 \mu\text{m})$ of Halogenated Acrylates Listed in Table 4 on the amount of chlorine atoms m in the monomer molecule (crosses). Firm line – linear approximation by the method of the smallest squares.

Film Forming Properties of Monomers

The synthesized monomers are capable of radical photopolymerization and film forming. That is why they can be used to form polymeric wave guides and other elements of integrated optical devices using methods of UV photolithography and direct laser drawing [19].

Experimental Part

2-Cyano-1,1,1,3,3,3-hexafluoropropan-2-yl acrylate $\text{CH}_2=\text{CH}-\text{COO}-\text{C}(\text{CF}_3)_2-\text{CN}$. To a three-neck flask of 500 ml volume 16g of sodium cyanide are added to 200 ml of dry acetonitrile while stirring, then the reaction mixture is cooled to 0°C and 50g of 1,1,1,3,3,3-hexafluoropropan-2-one are bubbled. The mixture is stirred 30 minutes more at 0°C and for 1,5 h at 20°C . Then the reaction mixture is cooled to 0°C and then 32,5g of propenoyl chloride are added drop by drop. All is mixed for 30 minutes more at 0°C and for 1,5h at 20°C . Then the reaction mixture is poured into water. The lower layer is separated, dried with magnesium sulphate, filtered and distilled in vacuum. 43g of 2-cyano-1,1,1,3,3,3-hexafluoropropan-2-yl acrylate are obtained in the form of colorless liquid. The yield is 58%. The purity is 98%. Boiling point = 127°C . Elemental analysis (calculated, %): C, 34.03; H, 1.22; F, 46.13; N, 5.67; elemental analysis (found, %): C, 34.0; H, 1.32; F, 46.06; N, 5.67.

2-Cyano-1,3-dichloro-1,1,3,3-tetrafluoropropan-2-yl acrylate $\text{CH}_2=\text{CH}-\text{COO}-\text{C}(\text{CF}_2\text{Cl})_2-\text{CN}$. To a 500ml volume three-neck flask 19g of sodium cyanide are added to 200ml of dry acetonitrile while stirring, then the reaction mixture is cooled 0°C and 70g of 1,3-dichloro-1,1,3,3-tetrapropan-2-one are added drop by drop. It is being mixed for 30 minutes more at 0°C and for 1,5 h at 20°C . Afterwards the reaction mixture is cooled down 0°C and 42g of propenoyl chloride are added drop by drop. It is being mixed for 30 minutes more at 0°C and for 1.5h at 20°C . Then the reaction mixture is poured into water. The lower layer is separated, dried with magnesium sulphate, filtered and distilled in vacuum. 85g of 1,3-dichloro-2-cyano-1,1,3,3-tetrafluoropropan-2-yl acrylate are obtained in the form of colorless liquid. The

yield is 86%. The purity is 99.3%. Boiling point = 68-70°C / 20 mm Hg. Elemental analysis (calculated %): C, 30.03; H, 1.08; F, 27.14; N, 5.00; elemental analysis (found, %): C, 30.0; H, 1.1; F, 27.1; N, 5.06.

1,1,3-trichloro-2-cyano-1,3,3-trifluoropropan-2-yl acrylate $CH_2=CH-COO-C(CF_2Cl)(CFCl_2)-CN$.

To a 500ml three-neck flask 24g of sodium cyanide are added to 250ml of dry acetonitrile while stirring, then the reaction mixture is cooled to 0°C and 98g of 1,1,3-trichloro-1,3,3-trifluoropropan-2-one are added drop by drop. It is being mixed for 30 minutes more at 0°C and for 1,5h at 20°C. Afterwards the reaction mixture is cooled to 0°C and 55g of propenoyl chloride are added drop by drop. It is being mixed for 30 minutes more at 0°C and for 1,5h at 20°C. Afterwards the reaction mixture is poured into water. The lower layer is separated, dried with magnesium sulphate, filtered and distilled in vacuum. 99g of 1,1,3-trichloro-2-cyano-1,3,3-trifluoropropan-2-yl acrylate are obtained in the form of colorless liquid. The yield is 73%. The purity is 98.6%. Boiling point = 90-94°C / 20 mm Hg. Elemental analysis (calculated %): C, 28.36; H, 1.02; F, 19.23; N, 4.72; elemental analysis (found, %): C, 28.28; H, 1.1; F, 19.27; N, 4.67.

1,1,3,3-tetrachloro-2-cyano-1,3-difluoropropan-2-yl acrylate $CH_2=CH-COO-C(CFCl_2)_2-CN$. To a

500ml three-neck flask 24g of sodium cyanide are added to 250ml of dry acetonitrile while stirring, then the reaction mixture is cooled to 0°C and then 104 g of 1,1,1,3-tetrachloro-1,3-difluoropropan-2-one are added drop by drop. It is being mixed for 30 minutes more at 0°C and for 1,5h at 20°C. Afterwards the reaction mixture is cooled to 0°C and 54,5g of acrylic acid chloroanhydride are added drop by drop. Then the reaction mixture is poured into water. The lower layer is separated, dried with magnesium sulphate, filtered and distilled in vacuum. 113 g of 1,1,3,3-tetrachloro-2-cyano-1,3-difluoropropan-2-yl acrylate are obtained in the form of colorless liquid. The yield is 80%. The purity is 97%. Boiling point 116-120°C / 20 mm Hg Elemental analysis (calculated %): C, 26.87; H, 0.97; F, 12.14; N, 4.48; elemental analysis (found, %): C, 26.75; H, 1.07; F, 12.1; N, 4.56.

Conclusion

New halogenated monomers based on cyanoperfluoro- and cyanochloroperfluoroacrylates have been synthesized. Monomers' coefficient of absorption is low (0.04 – 0.51 dB/cm) and their spectrum of refractive indices is wide (from 1.336 to 1.457) in "data communication" field of wave length around 0.85 μm. Monomers are capable of radical photopolymerization and can be used for creating different integrated optical devices using methods of UV photolithography and direct laser drawing.

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