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FLUORINE CONTAINING POLYMER MATERIALS BASED ON UNSATURAT ACIDS MODIFIED ACCORDING TO ESTER FRAGMENT AND THEIR PRACTICAL APPLICATION

V.B. No [a], *G.G. Furin* [b]

[a] PIKO Enterprise LLC , 8 Galterina str., Perm City Russia 614113.

[b] Novosibirsk Institute of Organic Chemistry named after N.N. Vorojtsov SD of RAS, 9 Acade Lavtrentiev avenue, Novosibirsk, 630090, Russia E-mail : furin@nioch.nsc.ru

Here we discuss the approach to the fluorine modification of acrylates and maleates e fragment using partly fluorinated alcohols and acrylic, methacrylic and maleic acids' derivative synthesize them. We also discuss the reactions involving multiply bond and carboxylic grou maleic acid fluorine containing mono-ester and acrylic acid esters. We analyze acryl polymerization processes their co-polymerization with other olefines, and also fluorine conta polymers' characteristics. We also take a look at practical application fields of such poly materials.

Contents

Introduction

At every stage of technical progress the role and direction of fundamental researches, especially ones of new class of organic compounds is initiated by society's need in new materials, which can't without creating fundamentally new, possessing high consumer properties and able to work u more severe conditions materials. Indeed fluorine compounds meet such requirements and can p defining part in intensification and production simplification of many goods without fundame reconstruction of existing manufactures. Perfluorinated compounds are the compounds of our pre and future. The production of such perfluorinated organic compounds has already been develo Such compounds meet up-to-date requirements by thermophysical and dielectric characteristics, can be used in a wide temperature and thermal loads ranges their practical application field is

found. The entire replacement of hydrogen atoms for fluorine in the organic molecule results in sl changing of properties, what has been used to create new generation materials possessing exce working characteristics. They began to be used for metals and alloys atmospheric and salt corro defense, and also as lubricating oils, applied at aggressive conditions, in hydraulic liquids, as h transfers, liquids for vacuum pumps, operating in corrosion active medium, as additives for oils, u at high pressure in different compressors etc. In terms of scope and level of scientific achievem and scale of their commercial implementation the fluorine chemistry is now a powerful indepen scientific and technical direction of organic chemistry.

The production of fluorine containing materials doesn't only depend on the level of our knowle regarding fluororganic compounds properties, but also on their practical application perspec which is dictated by development of technical conception.

Among fluoropolymers [1-3] an independent and intensively developing class of polymers and polymers, acrylates and methacrylates [3-7] fluorine modified fills an important place. It oc because of the fact, that acrylates based on fluorinated alcohols posses unique properties, espec high hydro- and oleophobic abilities. It makes a base to obtain polymeric suspensions for fib articles surface proccessing and creating coatings for non-organic materials. In most cases water oil-repellent agents are obtained out of polymers, which main chains are poly-acrylic polymetacrylic acid, turning acid groups into fluorocarboxylic chains ester ones (C8-C10) [8-12]. T are surfactants, sorbing at the edge of phase break sharply change surfaces' nature and proper Their specific surface activity, which can't be reached in case of hydrocarboxylic component, ma base to create materials, which achieved a strong position among commercial products. Sur energy of coatings made of such fluorine containing polymers is low, and that's why they can be ha dampened and are characterized by low friction coefficients comparatively to other solid materials said above allows creating materials for field of technics. The field of their practical application inclu different directions. For example, we can point out the water and oil-repellent properties ad chemicals for fabrics [13], materials for microelectronics [14], surfactants (SAM) for ole polymerization processes [10], systems stable to electronic strike and X-rays [15-17] etc.

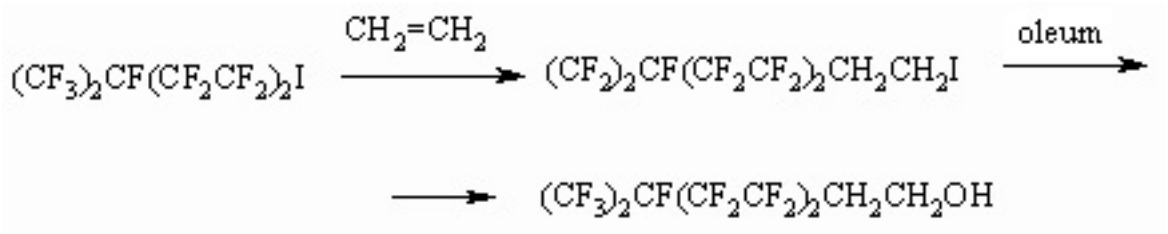
Here we see the chemical enterprises re-orientation to science intensive articles production, technologies and new products.

The synthesis of fluorine modified monomers (acrylates) is mainly carried out by interactio acrylic and metacrylic acids with linear partially fluorinated alcohols, that was boosted by patent c [18]. The interest for modified acrylates is constantly growing a great file of information on this c compounds, especially in the field of practical application. If earlier at acrylates synthesis they u linear poly-fluorinated aliphatic alcohols, then by now the interest for introduction opportunit hydophilic fragments such as ether bounds, nitrogen atoms etc into main chain of molecule is sh Such opportunity for acrylates can be implemented in hydrocarboxylic skeleton of ester part.

Acrylic and metacrylic acids are commercially produced in huge amounts. Because of this researchers paid a lot of their attention to developing of partly fluorinated alcohols obtaining meth and technology and other unsaturated organic compounds co-polymeriazation proccesses [1,3]. requirements for properties of polymer materials used for techniques, in regards to wearing quali weather resistance, incombustability, antiadhesive and anti-corrosive properties, dielectrical and o special characteristics remain high. Owing to so strict requirements for such materials and in s that their production is complicated and price is high compare to other plastics they work up market. Combination of fluorine containing polymer materials based on acrylates impr characteristics of chemical and atmosphere stable coatings.

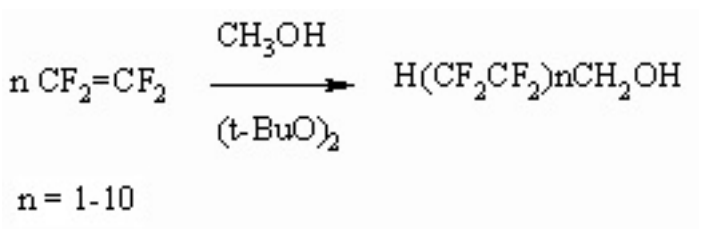
In this review we demonstrate the last decade achievements in the field of synthesis and applica of polymer materials based on acrylates and maleates, containing fluorine modified ester fragme synthesis of which is based first of all on use of partly fluorinated alcohols. These alcohols produc technology is based on the following chemical transformations. .

1) Alcohols like $R_FCH_2CH_2OH$ are produced out of R_FI perfluoroalkyliodides, which at first introduced into reaction with ethylene with further saponification of new sub-derivative [19,20].



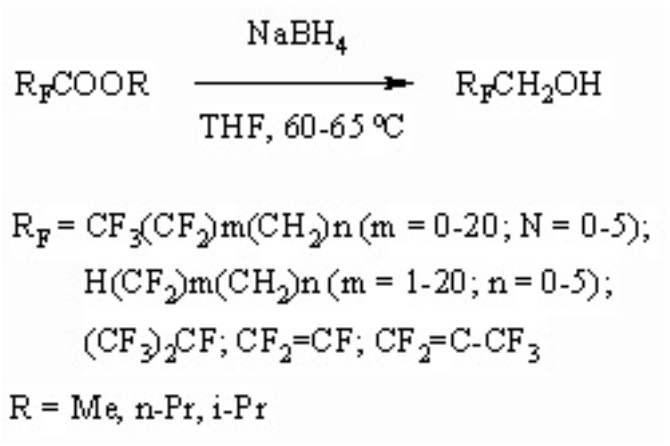
The method is implemented in commercial scale.

2) Synthesis method of $H(CF_2CF_2)_nCH_2OH$ (n = 1-15) telomeric alcohols is based on telomeriza of tetrafluoroethylene and other fluorolefines in methyl alcohol or aliphatic alcohol in presenc peroxide initiators [21-55].

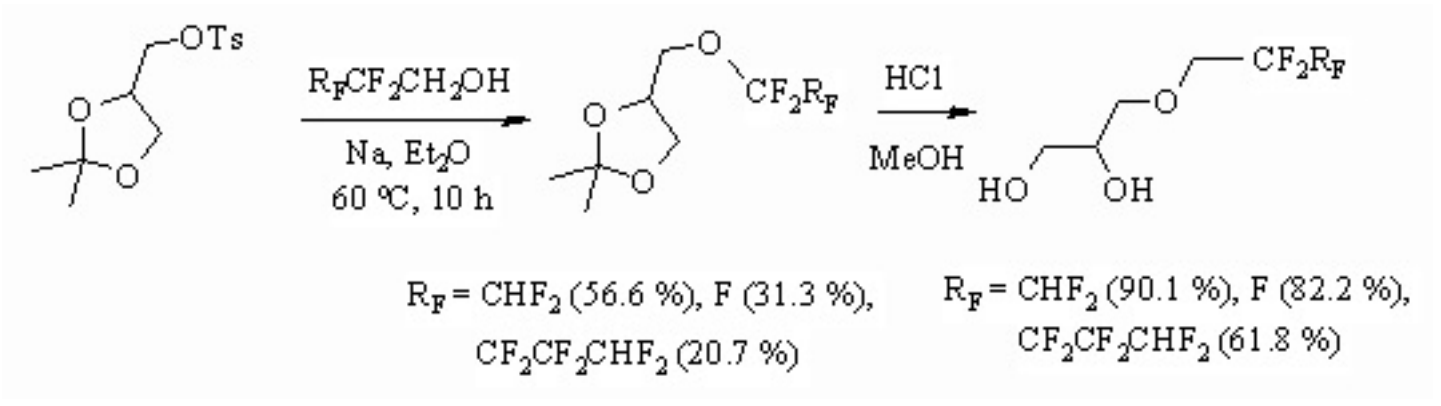


This process is implemented commercially.

3) Alcohols like R_FCH_2OH are obtained by reduction of polyfluorinated carbonyl contai compounds (perfluorocarboxylic acids ethers [51,56-69] and diketons and ketofluoroanhydrides | by $NaBY_4$ or $LiAlH_4$ action.



4) Synthesis of diols with polyfluoroalkyl groups was developed by Paleta and his co-workers. carried out by reaction of partly fluorinated alcohols and 4(hydroxymethyl)-2,2-dimethyl-1,3-dioxo tosylate with further deprotonation of reaction product [71-79].



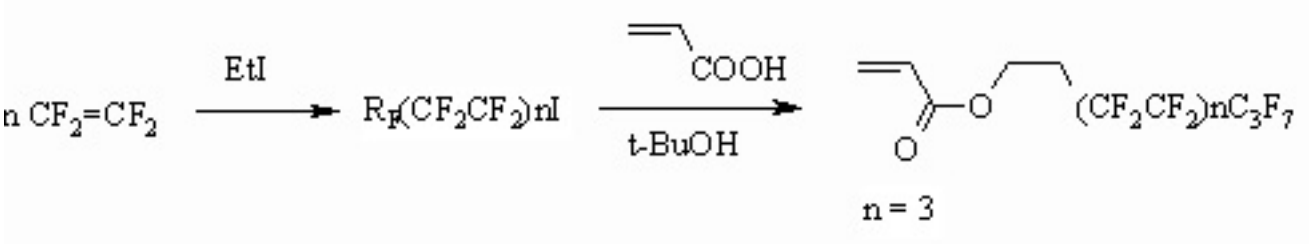
Acrylic acid itself and methacrylic acid or its chloroanhydride, anhydride, maleic acid or anhydride are used as unsaturated carboxylic acids.

1. Obtaining of Fluorine Modified Acrylates Ester Fragment.

Esterification of acrylic and methacrylic acid by poly-fluorinated alcohols like $R(CF_2CF_2)_nCH_2O$ = H, F; n = 1-4) or $F(CF_2CF_2)_nCH_2CH_2OH$ (n = 1-4) is carried out in presence of acidic cata sulfocoal and concentrated sulfuric acid in toluene medium at 110 ^oC for 6-8 h [80-83]

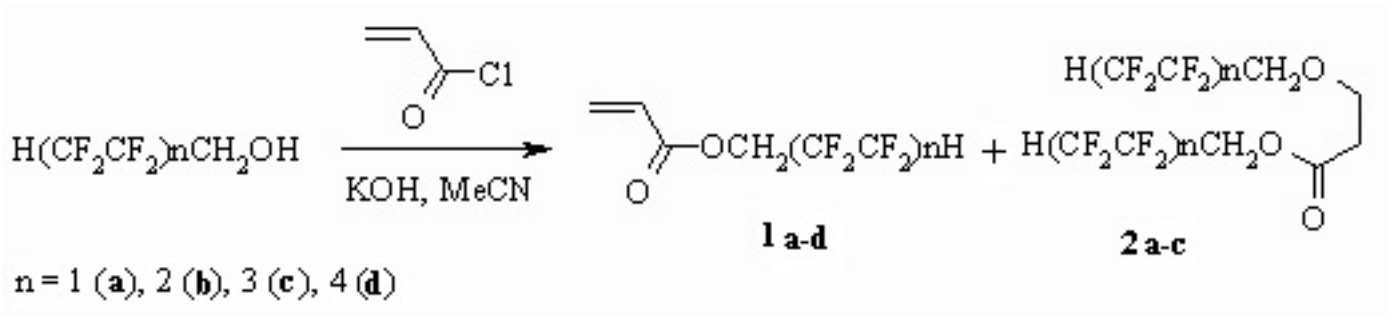
perfluoroalkylethyliodides like $(CF_3)_2CF(CF_2)_4CH_2CH_2I$ can also be used, but in this case acrylic potassium salt is used and reaction is held in presence of $C_6H_{13}N^+Et_3 \cdot I^-$ salt in isopropyl alcoh 120 ^oC for 5 h [84].

Fluorine containing acrylate synthesis can be carried out without isolating of corresponding alc Thus, the authors of the work [85] showed such an opportunity, using two apparatus. Inside the one the tetrafluoroethylene's telomerization is carried out in the presence of ethyl iodine, then reac products are put inside the second apparatus, where the acrylic acid and tert-butyl alcohol are ad that leads to formation of corresponding acrylate.

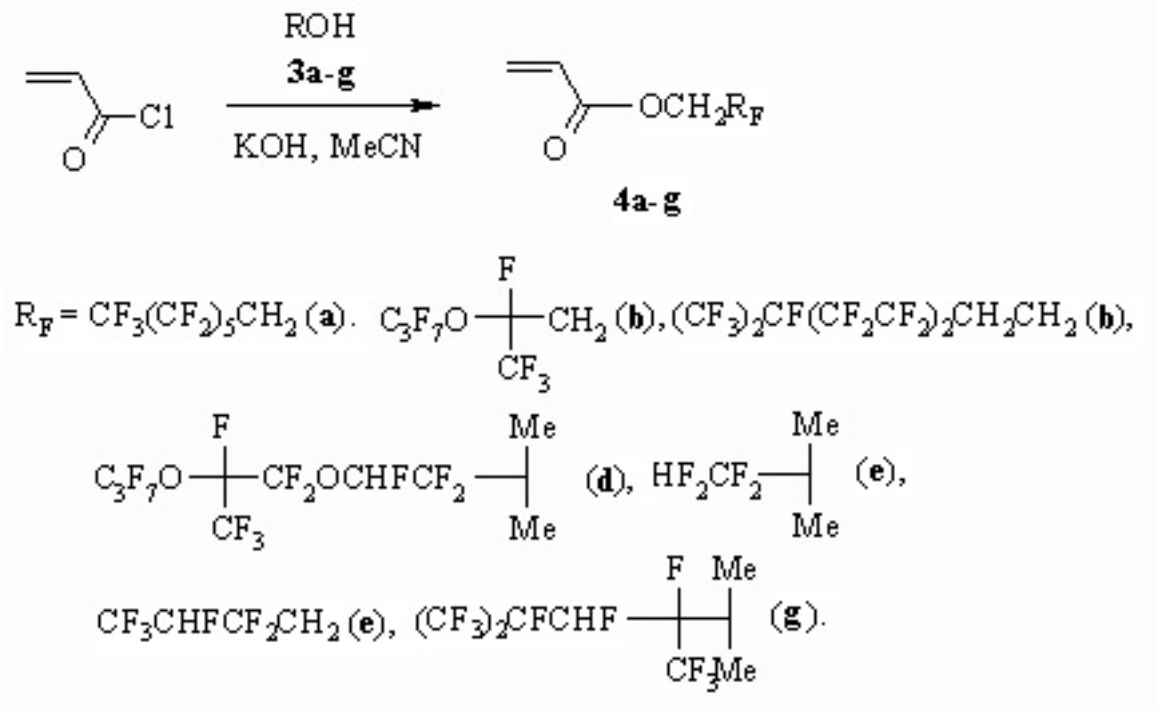


Most often acrylic and methacrylic acid chloroanhydride and anhydride are used, the reactic carried out in the presence of Et_3N.

When $H(CF_2CF_2)_nCH_2OH$ (n = 1-4) linear fluorinated alcohols are influencing acrylic chloroanhydride in the presence of bases (KOH, NEt_3) acrylates are formed in acetonitrile (**1** [30,80,81]. Here the base plays the definitive part. Thus when using potash (K_2CO_3) in acetonitril get corresponding ester of acrylic acid **1a** in the mixture of initial alcohol; NEt_3 promotes the forr of only one product **1a**, while KOH is very effective, however we get not only the **1a** product expected but also (**2a**) compound, which is a result of fluorinated alcohol addition according to C bond of reaction product **1a**. It should be noticed that before was showed [86] the formation of add product according to C=C bond of telomeric alcohols with acrylonitrile, though those authors car out their reaction in the presence of sodium metal at 40 ^oC (yield is 73 %). At present conditions acrylic acid chloroanhydride other telomeric alcohols along with **1b-d** acrylates produce also 2 compounds.

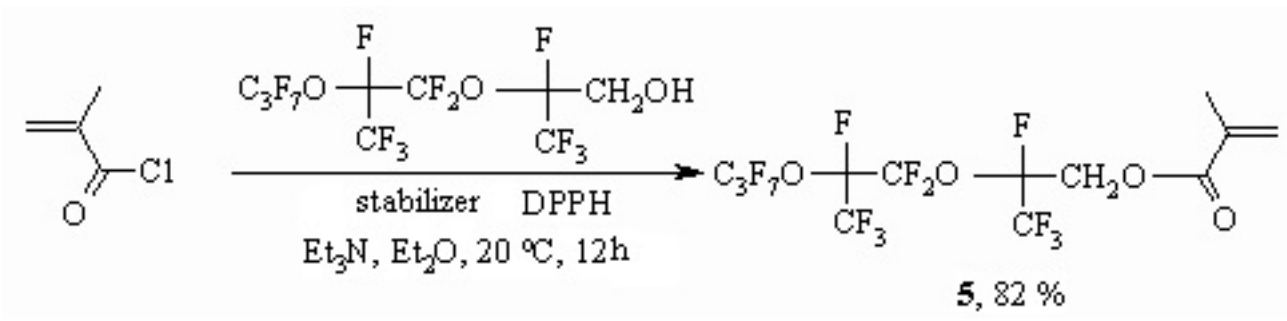


Thus, depending on fluorinated alcohol being used we should apply either triethylamine or KOH base, that dependes on their activity. Other fluorinated alcohols **3a-g** which have a branching in car chain especially in the beginning, or oxygen atoms are introduced into reaction with acrylic anhydride, at that acrylates **4a-g** were obtained [30].

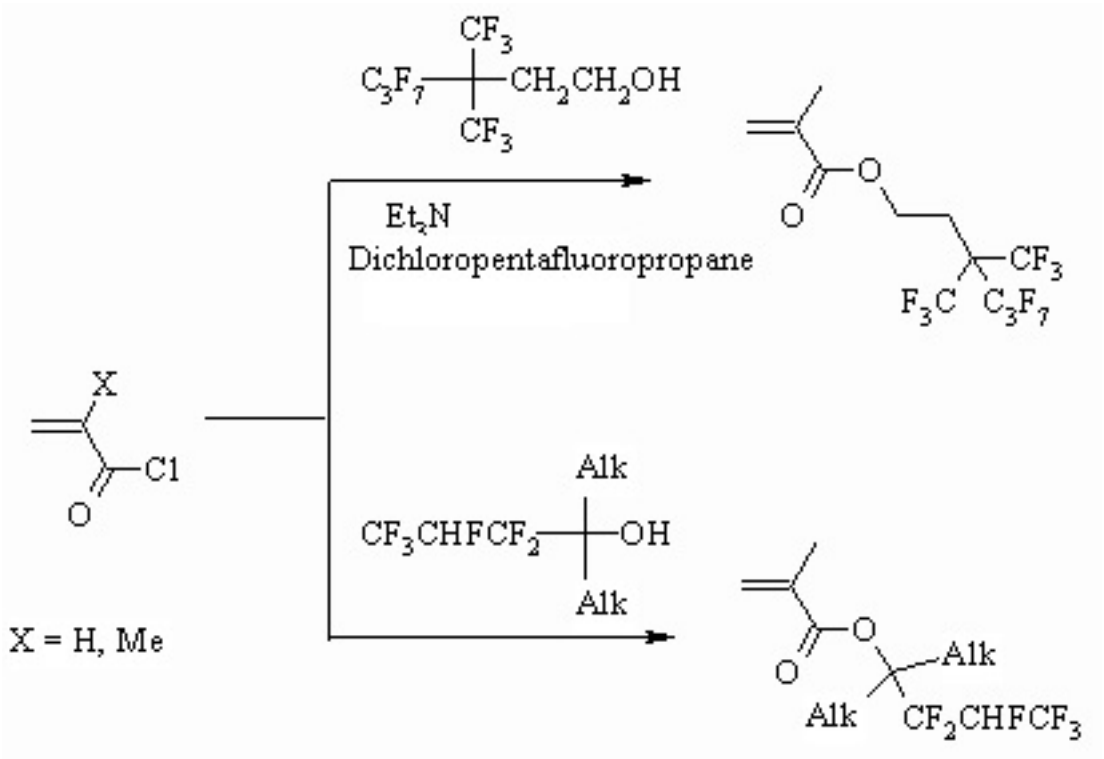


As the **3g** alcohol used had an admixture of isomeric alcohol (11 %) the **4g** acrylate formed is a mixture of two isomers with the same composition. In case of **3d** alcohol (mixture of diastereome 1:1.65 proportion) the formed **4d** acrylate is also obtained as a mixture of two diastereomers, w proportion is 1:1.1 (according to chromato-mass-spectrometry data and NMR ^{1}H and ^{19}F spectra)

By the example of **3d** alcohol reaction they show the opportunity of methacrylic acid chloanhyd introducing into reaction forming the corresponding methacrylate **5** [58].

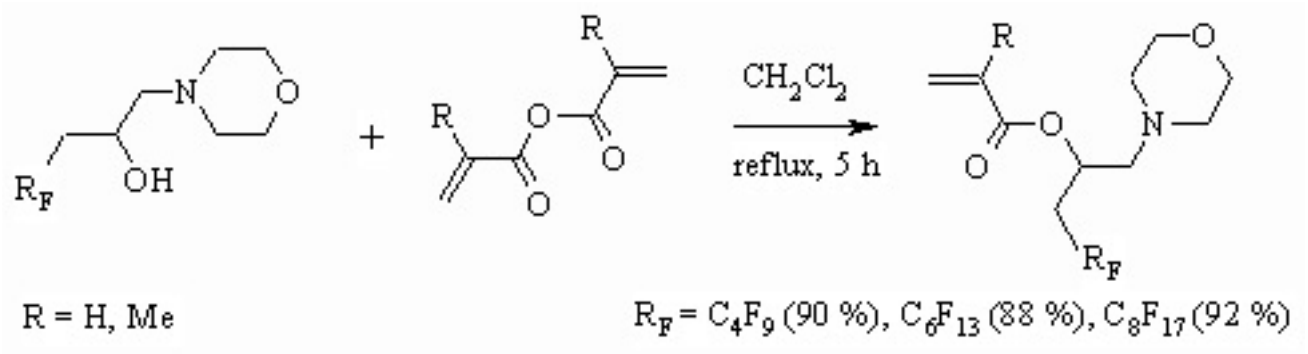


Alcohols with spatially branched carbon chains are also effective for the acrylates synthesis [87 You can look for the review on 2-phenyl-1,1,1,3,3,3-hexafluoropropan-2-ol using for polyacryl synthesis in [89].



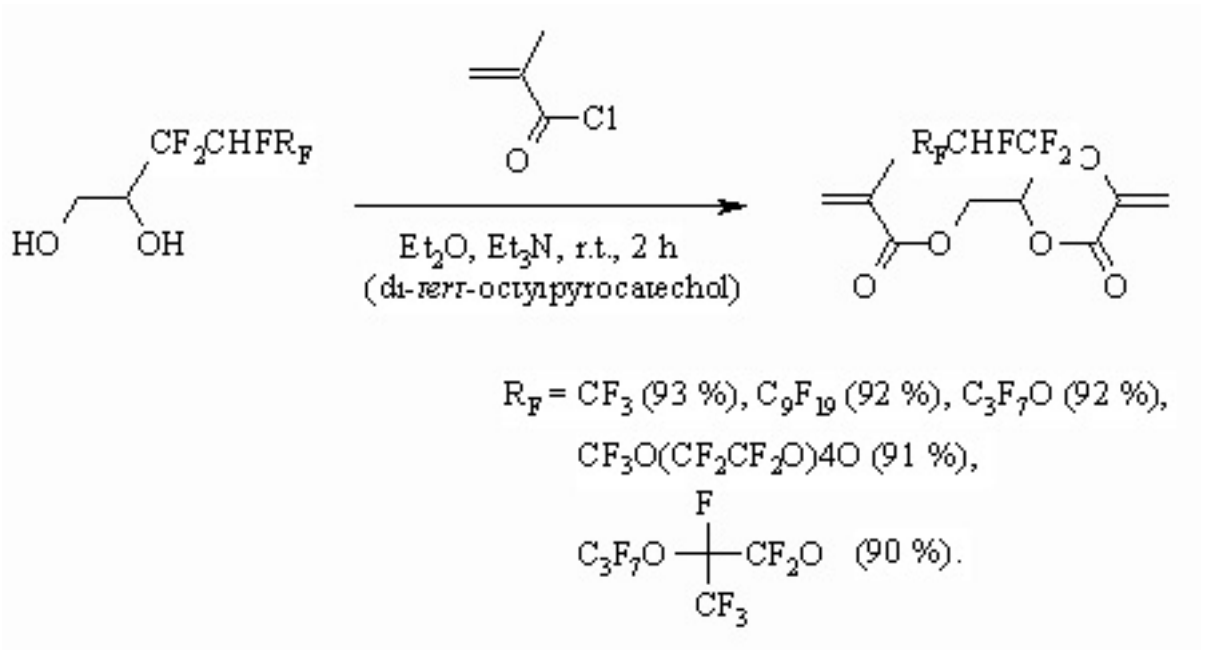
Esterification of methacrylic acid using secondary fluorocontaining alcohols in the presenc sulfuric acid isn't very much effective, that's why it is more preferable to use chloroanhydrid methacrylic acid anhydride. Thus, morpholine fluorinated metacrylate is obtained with high yield v

corresponding alcohol reacts with the methacrylic acid anhydride [60].

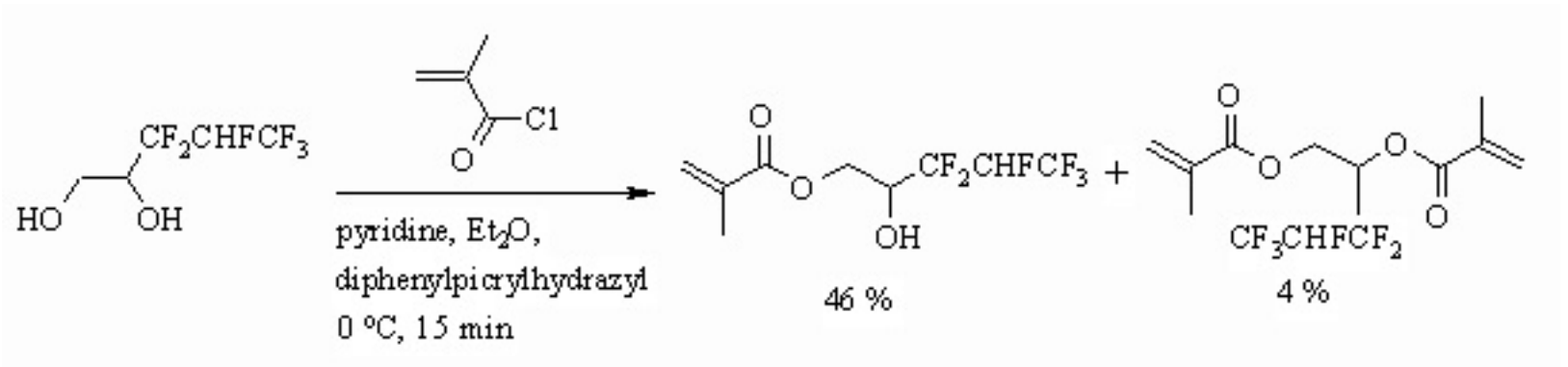


Secondary alcohols like $F(CF_2)_nCH(CH_2Cl)OH$ (n = 6,8,10) react with acrylic acid choloanhydric the presence of Et_3N in benzene at room temperature for 2 hours forming the corresponding acry with high yield [90].

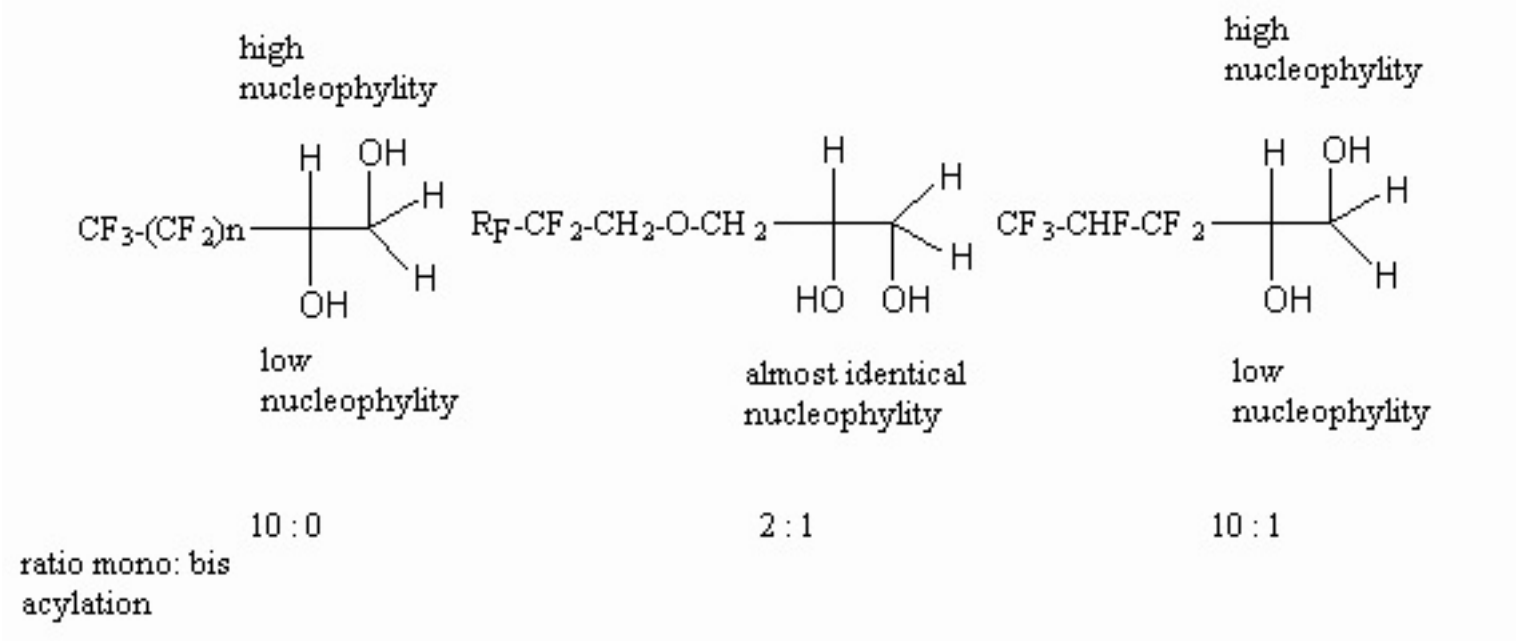
1-(Polyfluoroalkyl)ethan-1,2-diols produce corresponding bis-metacrylates [73] when methac acid chloroanhydride influence them. We should note, that process conditions essentially influence proportion of monoester and diester. Thus, using the medium of pyridine, diethyl ether and boiling 72 h- produces solely monoether [74], while in the system of triethylamine, diethyl ether, r temperature and 2 h time of reaction we get solely diether [73].

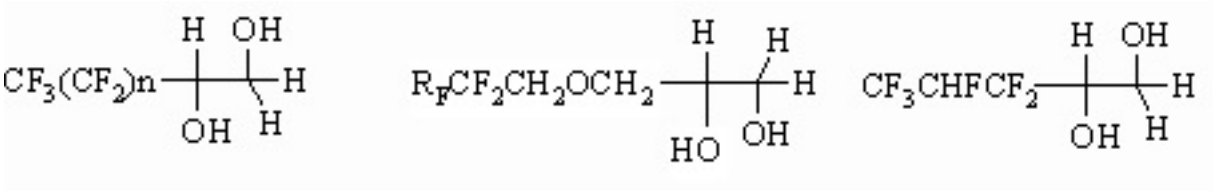


The authors of work [71] point out an important role of process conditions for the conversion lev fluorocontaining 1,2-diol with methacrylic acid chloroanhydride.

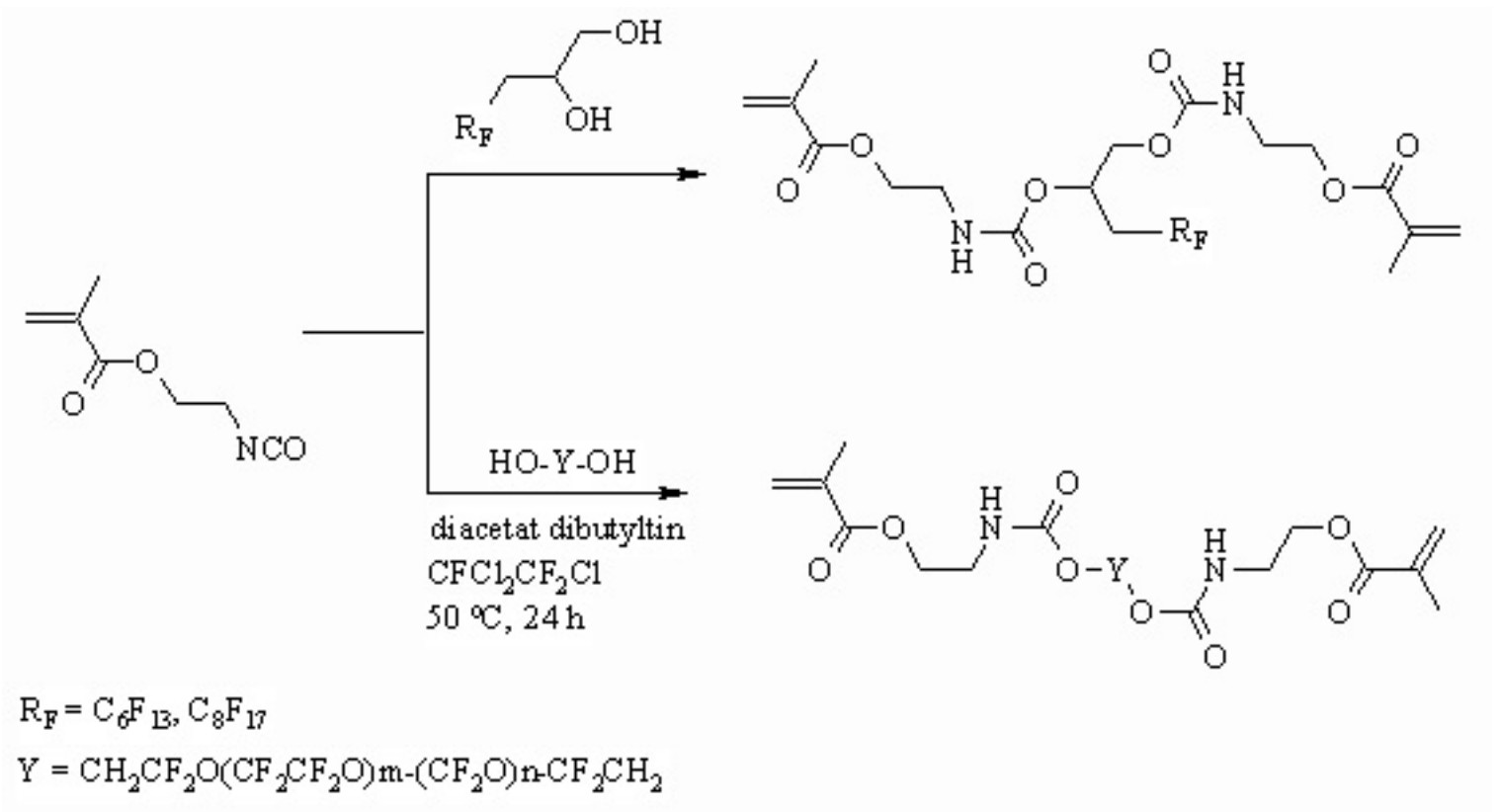


Initially only one of the two -OH groups of fluorocontaining 1,2-diol reacts. Perfluorinated gr influences its reactivity. The authors of work [71] have established the following row of activity for s of 1,2-diols.

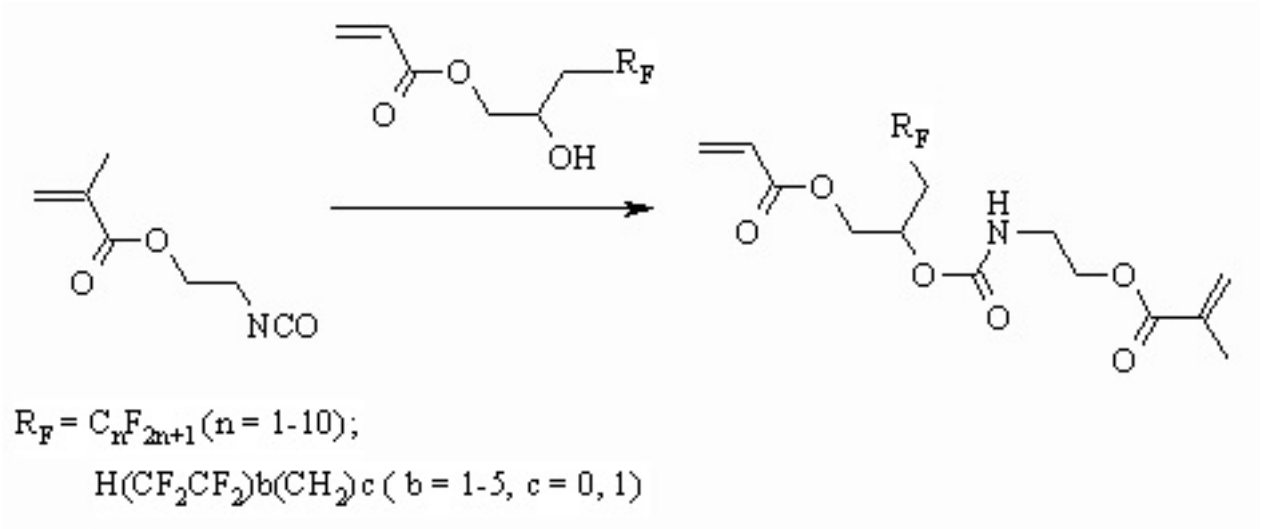




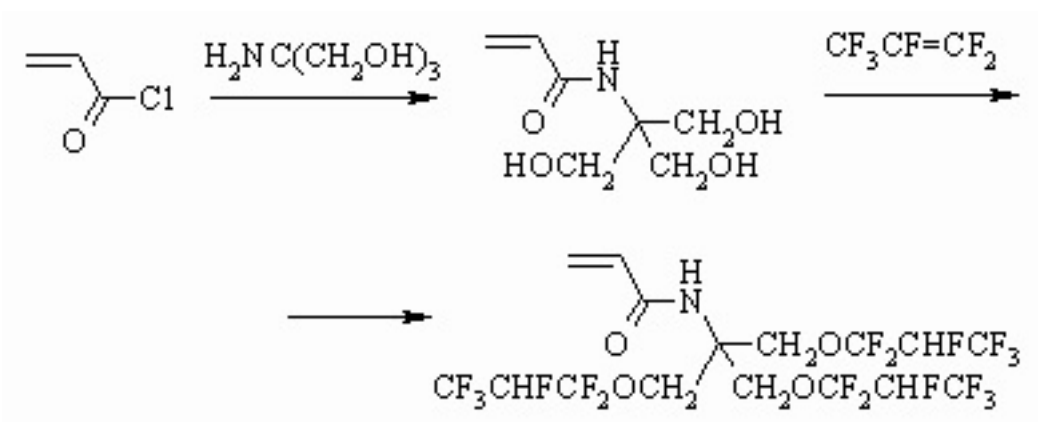
Other esters of methacrylic acid also react with 1,2-diol having perfluoralkyl group [91-93] or perfluoropolyether [94], at that the compounds, having acrylic and urethane fragments are formed



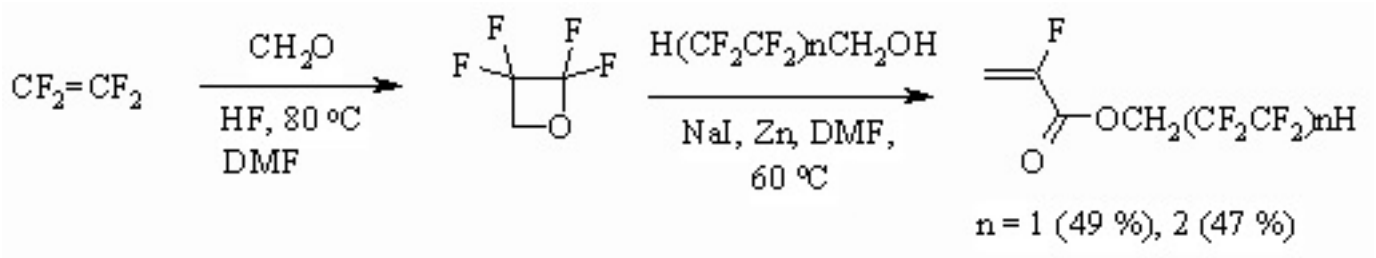
Monoester, obtained by interaction of fluorocontaining 1,2-diol and acrylic acid chloroanhyd reacts with 2- methacrylethylisocyanate and as a result we get a compound with acrylates urethane functions [95,96].



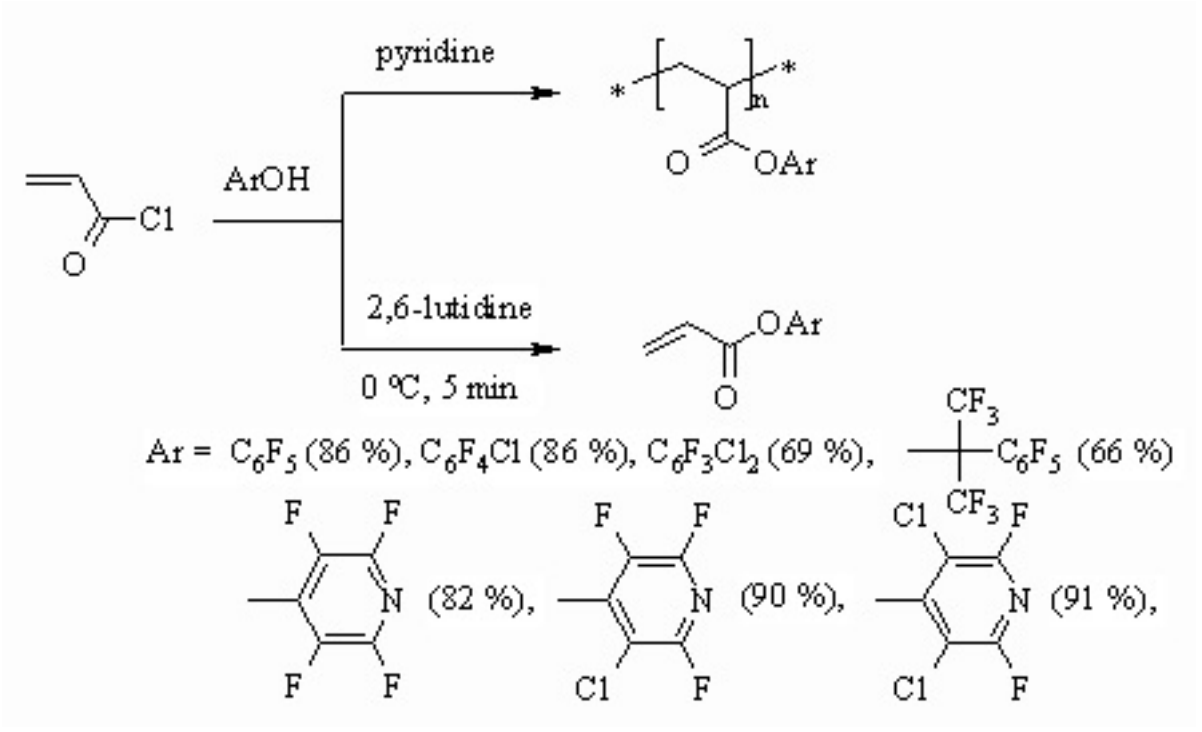
The authors of work [97] showed the opportunity of acrylates obtaining using perfluorole according to the following scheme and without using fluorinated alcohols.



α -fluoroacrylic acid fluoroanhydride, which is transformed into esters by reaction with telom alcohols[98-101], is obtained by interaction of 2,2,3,3-tetrafluoroxetane, alkali metals halogenides dehalogenizing agent in aprotic bipolar solvents in the presence of radical polymerization inhibitor.



Polymer materials based on fluorine modified acrylates and methacrylates according to e fragment are of great interest of waveguides and optical glassfiber production because they are transparent in the range of 1200-1600 nm, what is used for optical connection, along with t relatively low refracting indexes [102-104]. These properties can be enhanced by introducing fluo atoms or other heavy atoms into carbon chain. Modified derivatives of initial monomer are of inte they are obtained by introducing pentafluorophenyl group into eater part of molecule. The w [105,106], during which authors had carried out acrylates' synthesis using fluorine containing phe are devoted to this subject. It turned out, that a base used plays an important part. Thus in cas pyridine application the acrylate forming reaction goes together with polymerization process, whi the presence of 2,6-lutidine we get only acrylic acid ester.



The reactions of pentafluorophenol with α-chloroacrylate, α-fluoroacrylate and metacrylate were ea described in the [102-104].

To be continued