Synthesis and application of ω-bromoperfluoroalkylvinyl ethers

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Report2: Alternative routes to synthesize anion-active fluoropolymers.

The analysis of scientific and technical literature and patents has witnessed that many processes and technologies require membrane and other materials with a certain functional activity (cationogens, anionogens, nonionic materials, ampholytes) [1,2].

In the group of anionogenic membranes the most interest, in particular as ion-exchange membranes (IEM) for a novel method to produce caustic without use of mercury and chlorine wastes, is in copolymers of tetrafluoroethylene with perfluoroalkylvinyl ethers (VEA) containing the end functional (dialkylamino)methylene group which undergoes further quaternization.

Fluoropolymers with anionic conductivity are known to be produced by several routes [1,2], the fundamentally different are the following:

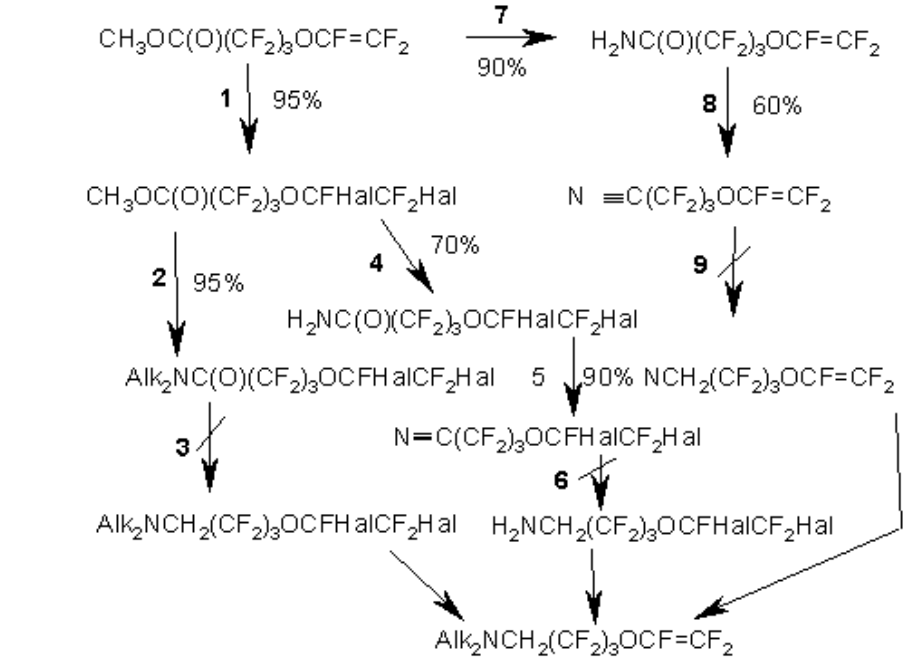
- synthesis of a monomer containing appropriate nitrogen- or phosphorus-containing functional groups and fluoromonomer copolymerization with proper components:
- using a monomer containing a functional group able to polymer-analogous conversions in the forming co-polymer followed by replacement of this group with anion-active one directly in the polymer.

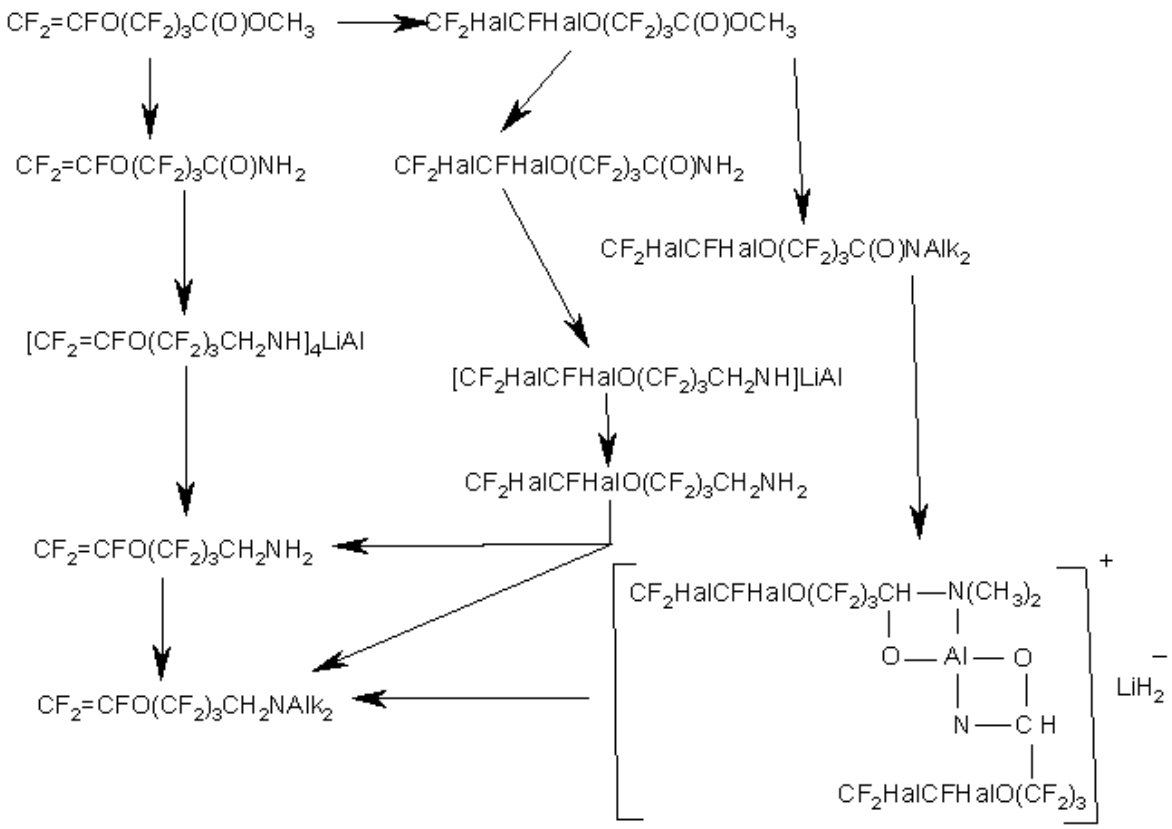
This work presents both directions.

Development of a method to synthesize VEA from FK-96 monomer.

FK-96 monomer has been produced by a number of companies of Japan and the USA for production of IEM in technology of mercury-free electrochemical production of chlorine and caustic. A similar technology has been developed in Russia also, therefore the method of VEA synthesis by substitution (or conversion) of methylcarboxyl group with (dialkylamino)methylene one seems the most simple.

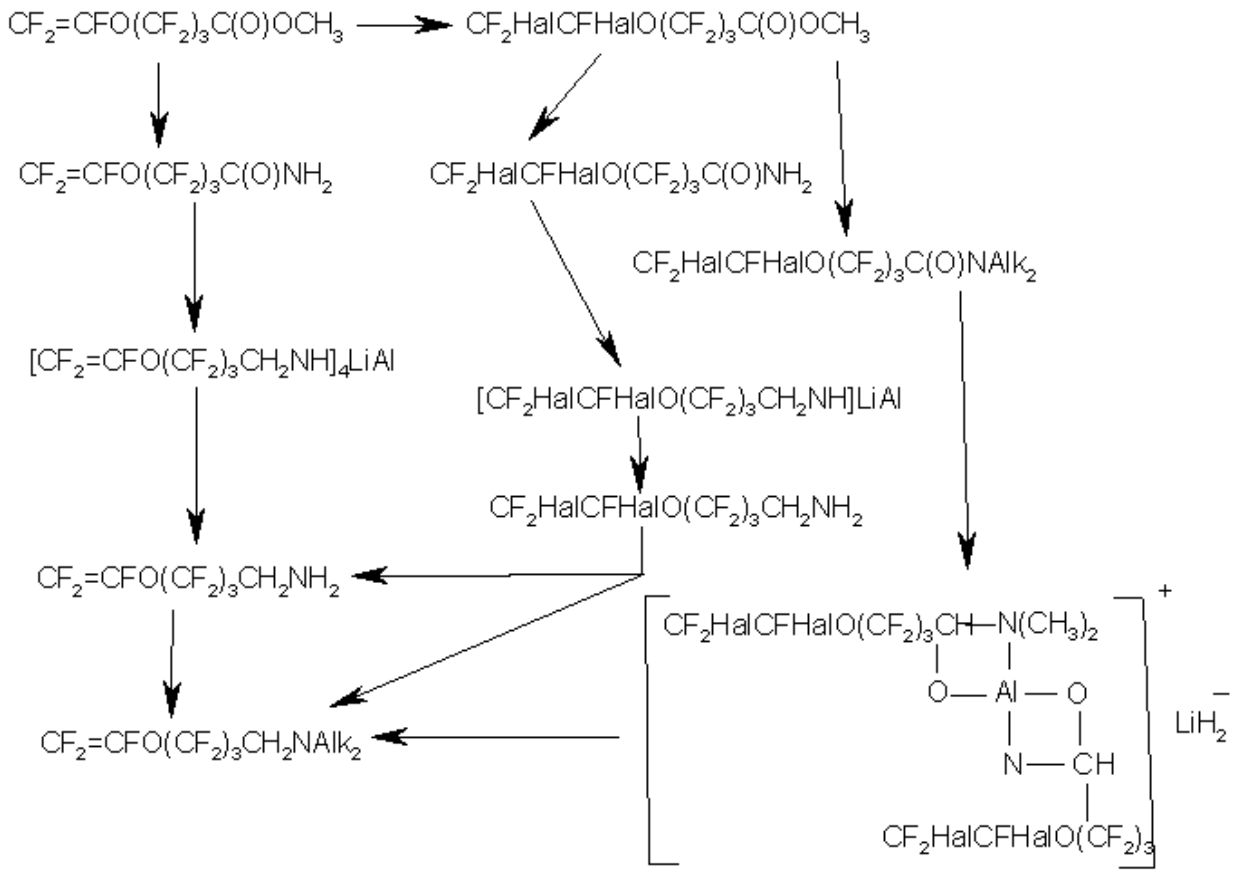
Different routes to synthesize VEA from FK-96 were worked out, many of them were found blind lead (scheme 1).





Attempts to carry out reaction 3 by reduction of amide with hydrazine (the Kishner reaction) failed. Similar results were obtained in hydrogenation of nitriles with hydrogen gas on nickel catalyst (reactions 6 and 9).

More effective routes are given in scheme2.

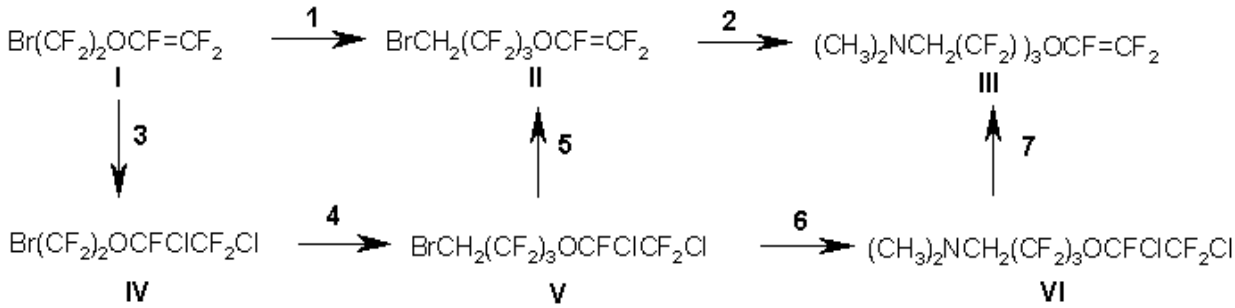


The mentioned reactions were a success only when using lithium alumohydride. Despite complex conditions of the synthesis realizations and enough exotic reagents, samples of monomers such as $CF_2=CFO(CF_2)_3CH_2NH_2$ and $CF_2=CFO(CF_2)_3CH_2N(CH_3)_2$ were produced by this route.

Development of a method to synthesize VEA fro ω- bromoperfluoroalkylvinyl ether.

Due to the complexity of the above mentioned procedure, as an alternative the authors developed a simpler route to synthesize VEA fro ω- bromoperfluoroalkylvinyl ethers (BrAVE) whose method of producing was discussed earlier by us [6].

The investigated directions of the search for a rational method to synthesize the goal monomer can be represented by common scheme 3:



The simplest and shortest route to synthesize monomer (III) according to reactions 1 and 2 (scheme3) allowed to obtain the goal product in 10-15% yield, and the final stage required a complex multi-step purification system to separate the end product of 99.8%min. purity .

Reaction 1 consisted of interaction of monomer (I) with vinylidene fluoride in the presence of diacylperoxide based on a dimer of hexafluoropropene oxide as an initiator of polymerization. The main product in this process was homopolymer of vinylidene fluoride.

The reaction with use of model 1,4-dibromooctafluorobutane and perfluoroacylfluoride of 7-bromo-3-oxa-2-trifluoromethylperfluoroheptanic acid ran in a similar way, the yield of the goal products of vinylidene fluoride addition attained 15%.

Substitution of bromine atom in compound (II) with dialkylamine group (scheme1,reaction 2) was carried out according to the standard procedure using dimethylamine and diethylamine at different conditions. Practically no formation of the aminolysis reaction products was found under mild conditions, but at 80^{O}C monomer destruction on the one hand and the molecule bromination across the multiple bond on the other hand took place.

As mentioned above, due to passing side reactions, the yield of the goal monomer was not high, for this reason it was necessary first to protect the perfluorovinyl fragment by treatment of compound (I) with elemental chlorine (reaction3). Chlorination passed smoothly in a high yield. A small amount of 3-oxa-1,2,5-trichloroheptafluoropentane was formed as an admixture.

Reaction 4 was carried out at conditions similar to those of reaction1. In this case the yield of the product compared with reaction 1 was essentially higher and reached 25-30%. The main admixtures were the following: homopolymer of vinylidene fluoride and also products formed as a result of dehydrohalogenation and substitution of bromine.

Aminolysis of compound (V) was carried out using dimethylamine and diethylamine at 40-130^{O}C and pressure of up to 4 atm. The reaction was found to be used for practical process working-out. The yield of compound (VI) was 40-55%. Dechlorination of compounds (V) and (VI) to produce monomers (II) and (III) in high yields was carried out in an alcohol solution using Zn powder or freshly prepared copper .

During development of the procedure to synthesize polymer on the VEA basis one could anticipate that the end dialkylamino group would display an inhibition effect in the reaction of copolymerization of monomer (III) with tetrafluoroethylene and make the process difficult. Unfortunately, the assumption was not realized completely: involving the monomers with aminomethylene and (dialkylamino)methylene groups in the copolymerization reaction failed.

As regards perfluoroalkylvinyl ethers with the end bromoethyl group, they are quite active in the reaction with TFE and appropriate copolymers were produced on their base.

Synthesis of polymers with anion-active properties.

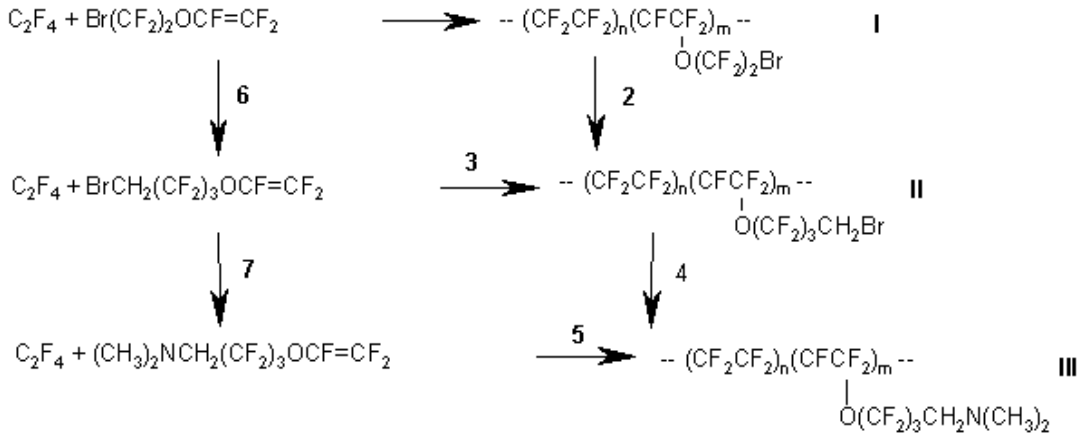
An important direction in creation of fluoropolymers of new generation has been a development of perfluoro-copolymers containing functional reactive groups able to be converted into ion exchange ones by polymer-analogous reactions with formation of high-efficient ion-conducting materials. Such materials are the most perspective due to their inherent unique properties: high heat resistance, chemical resistance in concentrated solutions of alkalis, acids, strong oxidizers, mechanical strength, possibility to make articles of any shape (films, sheets, tubes, hollow fibers, granules, film coatings etc.).

Together with OSPC " Plastpolymer" a possibility to create fluoropolymers with specified properties by an alternative route has been investigated.

Introduction of reactive Br-containing groups in the chain of perfluorinated copolymers gives them ability for polymer analogous conversions including cross-linking. The formation of cross-linked structure of fluoropolymers allows improving physicomechanical properties of articles made of them, to reduce fluidity under stress, to increase heat resistance, to reduce swelling in aggressive solvents.

The method is based on introduction of active bromine-containing fragments into the polymer structure followed by their substitution directly in articles (or in granules) with required functional groups. Emulsion copolymerization of BrAVE with tetrafluoroethylene results in the formation of fluoropolymers containing -bromoperfluoroalkylvinyl fragment

We have studied a fundamental possibility to synthesize anion-active fluoropolymers taken dimethylamine as an example according to scheme 4:



Reactions 6 and 7 are mentioned above. Amination of polymer film (sch.2, reaction 4) was carried out with dimethylamine, diethylamine, triethylamine and ethylendiamine in a medium of solvents(acetone, methanol, methylene chloride) or amines themselves at a temperature of 50-140^{o}C. The reaction time was from 27 to 100h. The reaction was carried out in a steel or glass reactor depending on the temperature and used amine.

IR spectroscopy analyses have found that at temperatures up to 100^{o}C the amination reaction practically does not occur (substitution was 3%, not more), at 100^{o}C and higher there are substituted 60% of Br-groups. In this case no bands in the copolymer spectrum were found which could be assigned to -C=C- and -C=O bonds. The presence of the mentioned groups can be explained by the side reactions of dehydrofluorination according to the scheme:

$$-CH_2\,CF_2\,Br + HNEt_2 \text{ --- > } -CF=CHBr + H_2 + Et_2\,F-$$

The forming multiple bonds in the structure of macromolecules reduce in the end the content of anion-exchange groups.

The elemental analysis of the structure of the polymer containing the dimethylamine group was performed by X-ray photoelectron spectroscopy on a DHJ-5400 instrument. The analysis results are given in the table.

Table

Analytical data of X-ray photoelectron spectroscopy of anion-active polymers based cω- bromoperfluoroethylvinyl ether and tetrafluoroethylene.

Element	Starting polymer,atom%		Aminated sample, atom %				
			film				granules
	Calc.	Found	Calc.	50^{o}C, 5h	100^{o}C, 5h	130^{o}C,1h	50^{o}C,5h
C	34.2	30.00	36.6	24.42	-	-	25.51
O	2.7	10.39	2.4	7.87	-	-	3.62
Br	2.7	1.11	2.6	2.28	2.98	2.19	1.01

F	60.4	58.5	55.9	61.87	95.88	95.39	67.54
N	-	-	2.5	3.58	1.14	2.02	2.27

Note: hydrogen atom is not defined by X-ray photoelectron spectroscopy method

According to the results of X-ray photoelectron analysis one can conclude that substitution of Br atoms with $N(CH_3)_2$ group was performed most completely at 40-50^{0}C. Here the results of the analysis of film and granules `witness that at 50^0 substitution of bromine atoms with the dimethylamine groups in granules was performed more completely in comparison with film (Br content was 1.01 and 2.23% respectively). But according to the ratios of the atom content of C,O,F,N and their calculated values one can assume that partial destruction of the polymer took place in granules as well.

Similarly to the synthesis of VEA monomers, the formation of homopolymer in large amounts also took place in this scheme in stage 2 when vinylidene fluoride was used. It should be noted regarding other stages that the yields were high enough for technological development of the process. The synthesized monomers were used to make membranes, which displayed high efficiency in electrolytic processes.

Thus, a fundamental possibility to create fluoropolymers with specified properties by the alternative route using activ- bromoalkylvinyl ethers has been shown. The produced samples of materials were found to possess anion conductivity and chemical resistance in strong acid environment in the presence of active oxidizer at elevated temperatures.

References

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