

Synthesis and application of ω -bromo-perfluoroalkylvinyl ethers.

V.M. Andrushin, N.B.Pavlova

Solution of more and more complex tasks in different fields requires development of new structural materials possessing a fundamentally different complex of field performances. Analysis of scientific and technical literature has shown that studies based on application of perfluoroalkylvinyl ethers (PFAVE) are the most priority directions in the field of development of new polymeric materials.

This is confirmed, in particular, by intensity of researches in synthesis of PFAVE monomers, in development of optimal conditions of copolymerization of PFAVE with different fluoroolefins, in studies of structure, properties and conditions of processing co-polymers produced and by more and more expanding field of their application.

Fluoropolymers containing functional groups are of a particular interest. They retain all positive features of fluoroplasts and at the same time exceed them with regard to a number of field performances such as hydrophilicity, electroconductivity, solubility, processibility, anti adhesion properties etc.

We think it reasonable in this final report ω -bromo-perfluoroalkylvinyl ethers (BrAVE) to review main conditions and fields of PFAVE application as a whole and also a possible role of BrAVE in development of new fluoropolymers on the basis of PFAVE monomers.

Japanese firms ("Daikin", "Asahi Glass", "Nitto Danki Codio Co.Ltd", "Mitsui" etc) "Du Pont" of USA and "Hoechst", Germany take their leading place in scientific, production and commercial activities in problems of synthesis, chemistry and application of PFAVE.

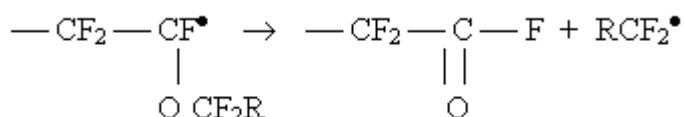
The work on development and study of new polymers derived from PFAVE are carrying out according to the following directions:

- carboxyl-containing vinyl ethers containing functional groups COOR_f , where $R_f = \text{H}$; alkyl and perfluoroalkyl $\text{C}_1\text{-C}_{10}$; alkaline metal or ammonium ion;
- sulfofluoride vinyl ethers containing functional groups SO_2R_f where $R_f = \text{F}$; OH ; OMe where $\text{Me} =$ alkaline metal or ammonium ion; alkyl and perfluoroalkyl $\text{C}_1\text{-C}_{10}$; aryl $\text{C}_1\text{-C}_{10}$; NHR_1 where R_1 is an alkyl;
- perfluorovinyl ethers containing the end CF_2R group where R is a haloid or hydrogen;
- perfluorovinyl ethers containing several functional groups, for example, two carboxyls;

- Perfluorovinyl ethers containing a ketone group or ionogenic groups of phosphonic acids; rather exotic methods of their synthesis do not allow to forecast their practical application and they will not be under review further.

The study of conditions of co-polymerization of PFAVE with tetrafluoroethylene (TFE) has shown that to obtain co-polymers with a significant number of PFAVE chains, their considerable excess regarding TFE is required. Thus, the co-polymerization constant for carboxyl PFAVE is 0.14 and 7.0 for TFE. In a reaction with sulfofluoride PFAVE the co-polymerization constants are even lower: 0.8 and 8.0 for TFE.

A careful choice of medium conditions, a co-polymerization method, initiator, pH, temperature, process regulators etc. is necessary in the synthesis of co-polymers derived from TFE and PFAVE. It is necessary to take into account that a phenomenon of fragmentation of the radical of the end chain of an ether monomer takes place in the co-polymerization process according to the scheme:



This fragmentation reduces considerably the molecular mass of the co-polymer. The fragmentation is increased with the temperature and with the increase in the length of a perfluoroalkoxyl substituent, therefore the process is recommended to carry out at the possibly lowest temperature when the activation energy of the fragmentation reaction is great.

The main methods of the co-polymerization of PFAVE with fluoroolefins is an emulsion method and co-polymerization in organic solvents. The emulsion method is preferable, it provides a more high conversion of PFAVE. Besides, the use of solvents is fraught with transfer the chain to the solvent. As a whole, the emulsion co-polymerization provides better reproducibility of the results and production of co-polymers with a greater molecular mass.

But the emulsion polymerization requires a more high level of technology and strong adherence to parameters, particularly to pH of the medium with the purpose to avoid hydrolysis of ether groups, particularly in carboxyl PFAVE.

Mechanical properties of functional perfluorinated polymers depends greatly on the type and PFAVE content. So, for example, tensile strength of carboxyl-containing polymers as sodium salts is much higher than those in the form of methyl ethers and the difference becomes more considerable with the temperature growth (it is 320 and 250 kg/cm² at 25°C and 230 and 7 kg/cm² at 90°C respectively). Relative elongation of tapes and samples containing ether groups is essentially higher than that of salts.

The glass transition temperature increases considerably at transition from ether groups to acid groups and reduces with an increase of the content of PFAVE chains.

As regards flowability of co-polymers of PFAVE with TFE, it depends on probability to form intermolecular bonds for example hydrogen bonds in co-polymers containing carboxide

groups, and on cross-linkage .

In literature BRAVE monomers are presented rather stingy and the main task of this series of reports on the synthesis, properties and application of this class of fluoromonomers is to attract attention of researchers, experts and managers to implementation of high potential capabilities of BRAVE both for creation of new materials and for modification of the existing types of fluoromonomers.

It was shown in reports 1-6 published earlier, that BrAVE monomers could be synthesized from available raw materials without using exotic experimental methods in specialized research centres possessing sufficient practice in handling fluorine and its compounds, also some data on the conditions of co-polymerization of fluoroolefins with BrAVE, main properties of the fluoropolymers produced and some conditions of their processing were given.

A specific feature of BrAVE monomers is the presence in their structure of the perfluoroalkylene fragment, trifluorovinyl oxide group and highly reactive bromine atom in the w-position at the unsaturated bond. Their combination allows producing fluoropolymers possessing a complex of positive service properties peculiar to PFAVE co-polymers and functional activity as well. Namely the combination of the mentioned properties allows to consider BrAVE monomers in future as a base fluoromonomer together with tetrafluoroethylene, vinylidene fluoride, hexafluoropropylene etc.

Demand in functional fluoropolymers containing carboxyl, sulfate, sulfofluoride, amine, nitrile and other groups in dependence on the task under consideration is currently rather low . Therefore an idea to establish a production of BrAVE monomers and producing from them appropriate monomers with necessary functional groups can be unprofitable from economic and technical point of view. No doubt that drastic development of any route will make the original synthesis of the appropriate target PFAVE and co-polymers derived from it more expedient but these advantages can be achieved ,as a rule, in a large-scale specialized production that is unlikely in the foreseeable future.

The most interesting and perspective route of PFAVE application is their using in producing ion-exchange materials for membrane technology.

Development of the membrane technology in production of chlorine and caustic soda on an industrial scale allows to solve ecological problems (to exclude using mercury and asbestos), to obtain products of a higher quality at lower power expenses. These technologies are used most broadly in Japan, Netherlands, the USA, Germany on the basis of perfluorinated ion-exchange membranes of Japanese and American made.

Long before chlorine-alkaline electrolysis , membranes on the basis of PFAVE with sulfo groups, possessing strong oxidizing properties and providing high mobility of hydrogen, have been used as solid electrolytes in hydrogen-oxygen and hydrogen-haloid fuel elements.

Application of fluorinated membranes able to provide high current density and process effectiveness in water electrolysis is perspective in hydrogen power engineering and in

processes of separation of and drying gases. Perfluorinated sulfocationite membranes can be used as ion-selective electrodes.

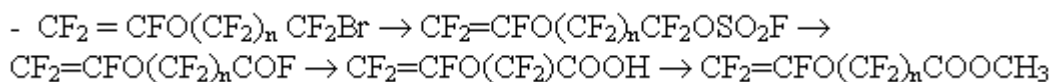
The following monomers are typical representatives of this group :



$\text{CF}_2=\text{CF}-\text{O}-[\text{CF}_2\text{CF}(\text{CF}_3)\text{O}]_n (\text{CF}_2)_m \text{AR}$ (Asahi Kasei) where $n=0.1$; $m=3-5$; $A=\text{S}$; SO_2 ; $R=\text{aryl, alkyl, perfluoroalkyl C}_1\text{-C}_{10}$



The latter monomer can be readily produced from BrAVE-2 monomer according to the scheme:



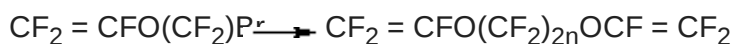
We have tested this method both in the synthesis of the monomer with 99.9% purity and in processing tapes and granules of co-polymers of TFE with BrAVE-2. The latter method of polymer-analogous transformations is of a particular interest, because the constants of BrAVE co-polymerization exceed greatly the appropriate characteristics of both sulfofluoride and carboxyl PFAVE. The co-polymerization with TFE rather readily gives fluoropolymers with BrAVE content up to 26%.

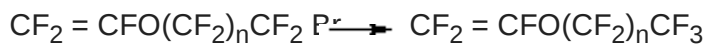
Researchers pay rapt attention to development of an available method to synthesize w-fluorosulfonylperfluoroethylvinyl ether which is urgently necessary for development of membrane technologies and which can not be obtained according to a conventional scheme of addition of hexafluoropropylene oxide to the appropriate fluoroanhydride followed by pyrolysis of salts of the acid produced.

The preliminary experiments made by us give hope for successful bromine replacement in BrAVE monomers with the sufofluoride group.

The method of producing anion-active fluoropolymers derived from TFE and BrAVE has been described in detail in report 2 of the present series. The most perspective synthetic route by the method of polymer-analogous transformations was proposed, the samples of the membranes were made and they showed high effectiveness in electrolytic processes.

To produce perfluoroalkylenedivinyl ethers from BrAVE, it is possible to use conventional reactions of debromination:





The given list of BrAVE application in processes of creation of fluoropolymers does not bear an exhaustive character, it only demonstrates a possibility to use BrAVE in the synthesis of fluoroplasts with different functional groups.

One more extremely important way of BrAVE application is their modification with participation of different fluoropolymers, because bromine atoms are convenient active centres for formation of space-linked structures. Report 4 describes the experimental results of cross-linking BrAVE fluoro-co-polymers and perfluorodiviny ethers with TFE and vinylidene fluoride using hexafluorodiphenylolpropane and triallylisocyanurate as cross-linking agents. The physical and mechanical properties of polymers of TFE and VDF with BrAVE and conditions of their processing were given in reports 5 and 6. It was determined by experiments that BrAVE monomers were highly effective modifiers of fluoropolymers. The co-polymers on their basis are stable both in acid and in alkaline media. They possess higher physical and mechanical properties and that relates equally both to TFE and to vinylidene fluoride and the polymers produced can be processed by conventional methods.

This report considers only BrAVE monomers with the linear carbochain perfluoroalkylene fragment though monomers with a different structure of the fluoroalkylene chain behave similarly in reactions of co-polymerization.

In conclusion, the authors thank all those who participated in different stages of the studies, analyses and testing the materials produced.

If we managed to attract attention of some researchers to the subject under consideration and make them to study the subject more attentively and profoundly in the original papers, we think our task has been fulfilled.