

Synthesis and Application of Bifunctional Perfluoroligoethers

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To create samples of new generation appliances and equipment that meet the up-to-date consumer requirements we need new materials possessing an entire complex of positive working characteristics such as high thermal and frost-resistance, wear-resistance, resistance to aggressive medias etc.

That's why recently there has been a great interest of different fluorinated polymers, at that to synthesize different materials based on these polymers we should have corresponding functional groups in the fluoropolymer's structure. Two main ways are used for that.

The first one is the co-polymerization of fluoromonomers, which already contain functional groups needed. At that we obtain fluoropolymers with functional groups in the side chain.

The second way is a forming of functional groups right during the co-polymerization process. Thus, we obtain fluoropolymers with end groups able to transform further.

If you look from a practical point of view then heterochain polymers of different classes are of the most interest as their working characteristics are higher, than ones of their carbochain analogues. Their thermal and frost-resistance, physical and mechanical properties are much higher on conditions that chemical inertness and resistance to different aggressive media are preserved. At first these characteristics belong to polyethers, polyamides and polysulphides.

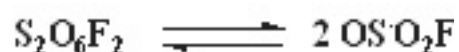
Different types of fluorinated polyethers are mostly studied in synthetical and applied terms. They are obtained either by polymerization of corresponding fluorolefines oxides, or by co-polymerization of fluorolefines together with oxygen. It is necessary to involve corresponding special reagents into co-polymerization process, especially bi-radical initiators to obtain functional end groups.

They are a narrow class of compounds many of them are not applicable to solve the problem set. Thus, bi-radical compounds of hydro carboxylic structure can't be used in reactions, where great excess of oxygen is used. Besides, during their application there is always a danger of introducing a hydrocarboxylic fragment into fluorine containing structure, what leads to sharp deterioration of physical and mechanical characteristics and change of materials obtained reactivity. Among fluororganic bi-radical compounds we can use dicarboxylic perfluorinated acids acyl peroxides: $\text{R}_\text{F}\text{C}(\text{O})\text{-O}(\text{O})\text{CR}'_\text{F}\text{C}(\text{O})\text{O-O}(\text{O})\text{CR}_\text{F}$

However, their obtaining and isolation is a rather complicated technological task and besides that they are always accompanied by formation of peroxide monoacyl, that essentially lowers the yield of target compounds.

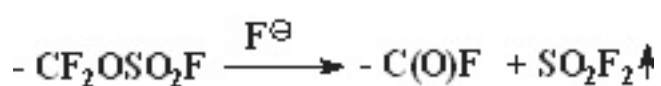
Before we had carried out a detailed analysis of a wide range of fluoro-non-organic compounds to use them as initiators of fluorolefines reactions. At that we had stated, that

peroxide compound peroxydisulphuryl difluoride meets most fully the complex of requirements, made of polymerization initiators of radical type. It is a thermal and chemical resistant compound in a wide range of temperatures, it is not sensitive to phase transfers, mechanical impacts and open fire. Peroxydisulphuryl difluoride is also low active in chemical terms. But the main thing is that peroxydisulphuryl difluoride is easily subject to homolytical decomposition according to -O-O- bond so that the molecular formula floats constantly with the radical one.



According to electron spin resonance data in radical form at minus 20°C there are 16% of compound, at 0°C - 37%, and at +20°C - 60-65%. The energy of dissociation is only 22,4 kcal/mol, that's why the peroxydisulphuryl difluoride dissociation into radical as a rule is not a limiting stage of reaction process.

Taking into account all said above we have carried out the research of tetrafluoroethylene and oxygen co-polymerization reaction in the presence of pyroxidisulfuryl difluoride for the purpose of obtaining new perfluoroligoethers - α,ω-bis-(fluorisulfonyloxy)perfluorooxalkylene alkanes of the common formula **FO₂SORFOSO₂F**, which structure contains two extremely reactive fluorosulfonate groups, which can be easily transformed into corresponding fluoroanhydrides, ethers, acids, amines etc if having fluorine atoms at neighboring carbon atom.



These bifunctional perfluoroligoethers have proven to be an effective raw material to work out thermal and frost-resistant glues, jointing components etc. for working under extreme conditions, for example in aerospace systems.

The reaction is studied at a wide range of conditions. It is very sensitive to change of technological parameters of the process (temperature, initiator's concentration, contact way and reagents' concentration, stirring conditions etc.)

At conducting co-polymerization reaction in gaseous phase carbonyl fluoride and tetrafluoroethylene oxide were the main products. There were no liquid oligomerization products. At contact period of about 30 seconds the temperature of self heating was above 200 °C and in a few cases there had been self burning of reaction medium.

At conducting reaction in the medium of inert solvent (perfluorotriethylamine, trichlorotrifluoroethane) at T below 20 °C liquid perfluoroligoethers are formed.

It is stated, that obtained perfluoroligoethers are bifunctional compounds of common formula



R_F includes both **CF₂CF₂O**, and **CF₂O** fragments and also peroxide ones.

The process was carried out as follows. Initiator's solution was put into reactor equipped with jacket for thermostating and speedy stirrer, then at temperature set we separately measured out tetrafluoroethylene and mixture of oxygen and inert gas. Initiator's solution was taken in great excess to preserve its concentration constant in co-polymerization process. When we increase initiator's concentration more than 2-3% a oligomer's molecular mass sharply decreases, and at lowering concentration below 0,5% low-molecular

bifunctional fluorocarbon polymer is formed in great quantities (up to 15-20%). At temperature below -20°C the reaction rate drops noticeably because of fluorosulfonate radicals' concentration decrease. Oligomers' molecular mass ranged from 800 (at 20°C) to 20 000 (at -15°C - -25°C) depending on reaction conditions.

Difluoromethylenoxide groups content in oligomer products increases at temperature rise and their distribution is chaotic (statistic distribution). Thus at temperature -20°C - -30°C the proportion **$-\text{CF}_2\text{O}-$: $\text{C}_2\text{F}_4\text{O}$** is 2-3, and at room it reaches 10-12.

The content of undesirable peroxide fragments in oligomer composition can hardly be regulated and in a few samples the contents of active oxygen is 1%.

Best results were obtained at the following reaction conducting conditions:

temperature -15°C - -5°C
ratio C_2F_4 : O_2 = 5-7 :1
 $\text{S}_2\text{O}_6\text{F}_2$ concentration in solvent 1-2%
Dilution of oxygen with inert gas 1: 3-5

Under these conditions fluorinated bifunctional polyethers of medium molecular mass equal to 6000-8000, ratio **CF_2O : $\text{C}_2\text{F}_4\text{O}$** =4-5 and content of active oxygen about 0,5-0,7% are formed.

Fluoroligomers obtained are oily liquids of viscosity equal to 130-180 cct and density 1780-1910 kg/m^3

To obtain corresponding difluoroanhydrides of perfluoropolyoxalkylene carboxylic acids out of obtained compounds they were subject to "stabilization" by thermal processing and metal fluorides impact. At that we can observe a "linear cut" effect of polyether chain because of forming unstable fluoroformiate fragments at regeneration of fluoroanhydride groups. The process is followed by isolation of carbonyl fluoride and sulfuryl chloride. At thermal processing peroxide groups are also being destroyed isolating trifluoromethylacylfluoride and carbonyl fluoride.

Step-by-step elimination of carbonyl fluoride goes on till the main chain of perfluoropolyoxalkene and its end groups won't be separated by tetrafluoroethylene oxide fragment. At that we can observe decrease of oligoether medium molecular mass and lowering of difluoromethylenoxide and peroxide groups content.

Stabilized this way bifunctional perfluoroligoethers were tested as a raw material for synthesis of frost-resistant glues and allowed to obtain glues and jointing components samples with working range from -130°C to 300°C .

The research results fragments presented allow us to make rather determined conclusions, that at first bifunctional perfluoligoethers are perspective initial materials to obtain glues and jointing components and secondly that co-polymerization reaction of tetrafluoroethylene and oxygen in the presence of peroxidisulfuryl difluoride is a perspective direction for their synthesis.