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TECHNOLOGY OF ORGANIC AND INORGANIC CHEMISTRY

Perfluoropolyethers. Synthesis and Application

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Perfluoropolyethers produced by oxidation of hexafluoropropylene are fully fluorinated oligomers of general formula

$$R_FO(CFCF_2O)_nR_F$$
$$\quad\quad|$$
$$\quad\quad CF_3$$

which fluorocarbon links alternate with oxygen atoms. Such oligomers have a wide range of boiling point, from 50–70°C to 240–320°C at 1 mm Hg in combination with a low freezing point, up to –60°C and below. At the same time perforpolyethers have a set of unique properties [1]: they are highly thermally stable, chemical-resistant in high aggressive media, not flammable, not toxic, have high dielectric properties, low viscosity changing properties over a wide temperature range, good lubricating properties, radiation resistance, and other. Complex of the above properties allow their use in various fields of modern technology as dielectric fluids, coolants, oils, greases.

Some properties of the individual fractions of perfluoropolyethers are listed in Table 1.

Methods for obtaining the most widely used perfluoropolyethers are based on the use of available industrial feedstock hexafluoropropylene (CF_3–$CF{=}CF_2$), one of the main fluoromonomers for different fluoroplastic brands.

The current state of development of technology for obtaining perfluoropolyethers preceded with extensive research in this field in several major countries: Russia, United States, Italy [2–5] in the years of 1970–80. A possibility of obtaining perfluoropolyethers from fluoromonomers by different ways has been investigated including gas- and liquid-phase methods at various temperatures, pressures, etc.

The work on technology perfluoropolyethers is complicated owing to the necessity to ensure safe conditions for research because peroxides formed at the oxidation of fluoroolefins with oxygen are potentially explosive compounds.

Based on literature data and our own research, in the Center "Applied Chemistry" was studied the process of synthesis perfluoropolyethers from hexafluoroproplene as a raw material. The process is carried out in liquid phase

Table 1. Selected properties of perfluoropolyethers

Boiling Range, °C / 1 mm Hg	Vapor pressure, torr	Viscosity, cSt	Molecular mass	Freezing temperature
80–130	10^{-3}	5–15	1200	<–80
130–180	10^{-5}	50–90	1500	~–70
180–240	10^{-7}–10^{-8}	100–150	2500	~–50
>240	10^{-10}	400–700	5000	~–40
>320	10^{-14}	1000–1800	10 000	~–30

at low temperatures (–30°C and below) and the use of X-ray, or elemental fluorine.

Boiling point of hexafluoropropylene (CF_3–CF=CF_2) is –29.1 ° C. Density of liquid hexafluoropropylene at various temperatures is presented in Table 2.

SYNTHESIS OF PERFLUOROPOLYETHERS

The process of synthesis of the target "neutral" perfluoropolyethers includes the following steps:

– low-temperature liquid-phase oxidation of hexafluoropropylene initiated by X-ray or fluorine into perfluoropolyetherperoxides with fluoroanhydride end groups (–COF),

– stabilization of perfluoropolyetherperoxide by means of elimination of the peroxide groups in the chain and end group (–COF) which is achieved by processing the perfluoropolyetherperoxide with elemental fluorine or CoF_3, or other fluorinating agent,

– vacuum rectification of the stabilized perfluoropolyether with isolation of target fractions,

– finishing sorption purification of perfluoropolyethers.

Analysis showed that obtained by photochemical method perfluoropolyethers have "irregular" structure:

$$CF_2ClH \xrightarrow{H_2O,\ t} CF_2{=}CF_2$$

$$CF_2ClCH_3 \xrightarrow{H_2O,\ t} CF_2{=}CH_2$$

therewith the low-temperature properties of such perfluoropolyethers are better than those of the perfluoropolyethers with regular structure.

A STUDY OF THE PROCESS OF THE LIQUID PHASE PHOTOOXIDATION OF HEXAFLUOROPROPYLENE

The process was carried out in a quartz or metal reactor (stainless steel) at different temperatures (–20 to –40°C). The reactor (steel X18H10T) is a cylindrical cup with a screw top head that has quartz glass window. The reactor is equipped with a pocket for the thermocouple, a gopher crane, a jacket for temperature control. The source of radiation is a quartz high pressure mercury lamp DRT-400 powered by AC 220 V.

Hexafluoropropylene from a container is passed through a column with silica gel and molecular sieve (removing moisture and other impurities), and is condensed into the reactor. The reactor is cooled to a given temperature and then oxygen fed to it at the UV irradiation. After completion of the process the gaseous products of reaction are evacuated, the reactor is opened, and the reaction mass transfused to a special container for the subsequent stabilization and selection of target products by vacuum distillation.

Table 2. Hexafluoropropylene density at various temperatures

Temperature, °C	Density, g/cm^3
–40	1.565
–20	1.498
0	1.419
+20	1.332
+40	1.321
+60	1.105

The photo-oxidation is a complex chain reaction with the participation of three different types of radicals:

perfluoroalkyl ($R_F^{\cdot}$),

perfluoroalkoxyl ($R_FO^{\cdot}$), and

perfluoroperoxyl ($R_FOO^{\cdot}$).

The most important elementary reactions (5) are as follows:

$$RF_2O_2 + h\nu \xrightarrow{1} R_FO^{\cdot} \qquad \text{initiation}$$

$$RCOF + h\nu \xrightarrow{1} R_F^{\cdot}O + C^{\cdot}OF$$

$$R_FO + M \xrightarrow{2} R_FOM$$

$$R_F^{\cdot} + O_2 \xrightarrow{3} R_FO_2^{\cdot} \qquad \text{chain propagation}$$

$$R_FO_2^{\cdot} + M \xrightarrow{4} R_FOOM^{\cdot}$$

$$R_FO_2^{\cdot} + M \xrightarrow{4} R_FO^{\cdot} + MO^{\cdot}$$

$$2R_FO_2^{\cdot} \xrightarrow{5} 2R_FO^{\cdot} + O_2 \qquad \text{radical reactions}$$

$$-MO \xrightarrow{6} R_F^{\cdot} + A$$

$$2R_FO_2^{\cdot} \xrightarrow{7} 2R_{F2}O_2^{\cdot} + O_2$$

$$2\dot{C}OF \xrightarrow{7} (COF)_2,\ CO + COF_2 \qquad \text{chain truncation}$$

$$R_FO^{\cdot} + COF \xrightarrow{7} R_FOCOF$$

M = CF_3–CF=CF_2, R_F = CF_3, –M, R_F' = –OCF_2, –OCF(–CF_3), A = CF_2O, CF_3COF.

The oxidation reaction begins under the influence of ultraviolet light of the wavelengths shorter than 320 nm obtained using low pressure and medium pressure mercury lamps (DRT-400 type).

Hexafluoropropylene like other fluoroolefins, being free of impurities and oxidation products, as well as its mixture with oxygen does not absorb light with the wavenumber above 200 nm which results in a short induction period of the reaction. During the induction period a small quantity of the fluoroolefin is transformed into a compound such as CF_3COF or peroxide that absorb light. At the photolysis break O–O bonds of peroxides (reaction 1) and C–C bonds of acylfluoroides (reaction 1 [1]) with the formation of free radicals, initiating chain reaction between the olefin and oxygen (reactions 2–4).

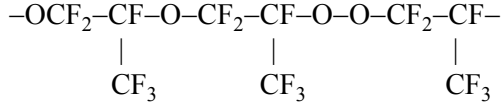
It is not excluded a possibility of another mechanism of emergence of active reaction centers through formation of donor-acceptor complexes of oxygen and hexafluoropropylene which absorption band can be shifted to long-wave region of the spectrum. Photolysis of these complexes can lead to the formation of active particles that can initiate the oxidation reactions.

It is know that perfluoroalkoxy radicals have a tendency even at low temperature of spontaneous decay at the C–C bond therefore the radical reactions (reaction 5 and 6) contribute significantly to the chain propagation.

According to experimental and available published data the most important reaction of the chain truncation is the reaction of peroxy radicals (reaction 7) [6]. A part of the fomed fluorinated peroxyradicals enters to recombination (reaction 5) giving two perfluoroalkoxyradicals continuing the chain.

It should be noted that the chain transfer reaction with the oxidation of hexafluoropropylene occurs as a result of disruption of C–C bonds which is responsible for the structure of terminal groups and the value of molecular weight of the formed perfluoropolyether.

On the basis of massspectral analysis and in accordance with the literature data [7] for the products of oxidation of hexafluoropropylene is accepted the following structure: it is a linear chain of perfluoroalkilene links C_3F_6 connected via oxygen atoms and partially via the bridge links:



Molecules are terminated by the end groups of two types: perfluoroalkoxyl (R_FO) and acyl fluoride (–COF).

Molecular mass of the produced compounds depends on the parameters of the process of hexafluoropropylene oxidation. At the oxidation at –30 to –40 ° C the molecular mass is within the range of 3000–4000.

The main reaction products formed at the low-temperature liquid-phase photochemical oxidation of hexafluoropropylene are polyetherperoxides, their composition depends on the conditions of the process. In a small amount are formed gaseous fluorocompounds COF_2, CF_3COF and hexafluoropropylene oxide.

The following dependence of the yield of the reaction products on the some parameters of the process are revealed.

– Effect of temperature on the rate of hexafluoropropylene oxidation.

In the temperature range –45 to +25 °C and oxygen pressure 7 atm the effective activation energy of fluorocompounds formation is shown in Table 3 (inflection point of logarithmic curves at –5°C).

At low temperatures (–35 to –5 °C) are formed in amount ~ 5% low-molecular compounds: COF_2, CF_3COF, and hexafluoropropylene oxide. More than 95% of hexafluoropropylene is transformed into oligomer with an average MW ~ 4000.

It is found that at higher temperature, up to –15 °C, the main product of the reaction is perfluoropolyetherperoxide, above –15°C increases yield of low-molecular compounds (COF_2, CF_3COF, etc.).

– Influence of oxygen pressure on the rate of hexafluoropropylene oxidation.

Studies of this dependence at temperatures –35°C and –15°C and pressures in the range of 0–13 atm showed that the rate of accumulation of polyetherperoxide grows

Table 3. Effective activation energy of formation of fluorocompounds

Compound	E_{eff}, kcal mol^{-1}	
	–45°C...–5°C	–5°C...25°C
Polyetherperoxide	4.43	0
Hexafluoropropylene oxide	3.05	12.6
CF_3COF	5.26	2.13
COF_2	1.52	3.75

proportionally to the pressure from 0 to 2 atm, at 2 atm and higher the rate does not depend on the pressure of oxygen.

At the higher reaction temperature the molecular weight of the formed perfluoropolyperoxide is shown to fall down (at a temperature of +25 ° C MW = 1000) and further increase in temperature increases yield of hexafluoropropylene oxide.

At the increase in intensity of UV light the molecular weight of the oligomer falls, approaching some constant value.

The reaction of hexafluoropropylene photooxidation with oxygen has a short induction period. At the accumulation of the formed in the reaction perfluoropolyetherperoxides the initiation is accelerated owing to the photolysis of the latter (light absorption coefficient for 250 nm is 2.0 l mol^{-1} s^{-1}).

As is known that the main disadvantages of the process of photochemical oxidation of fluoroolefinov are:

– low productivity of the process

– complex hardware design (sealed quartz tubes)

– low efficiency of sources of UV radiation (~ 90% is thermal infrared radiation), etc. With these shortcomings a more progressive seems the method of radical copolymerization of fluoroolefins with oxygen at the use of chemicals capable of homolytic dissociation at low temperature such as elemental fluorine [6].

Using ^{19}F NMR spectroscopy was established structure of the obtained by this method perfluoropolyethers from hexafluoropropylene:

$$R_FO(CF(CF_3)-CF_2O)_nCF(CF_3)-COF$$

where $R_F = CF_3–$, $(CF_3)_2CF–$.

A feature of the process at the initiation with fluorine is the fact that the structure of the formed compounds virtually does not include fluoroformiate and difluoromethylene oxyde groups that are mandatory at the photochemical oxidation.

It is anticipated that at the chemical initiation with fluorine the reaction of copolymerization of hexafluoropropylene and oxygen proceeds according to Scheme 1.

At the chemical initiation of the processes of hexafluoropropylene copolymerization with oxygen by fluorine the side product difluorofosgen (COF_2) is formed in much less amount, 0.01–0.2 mol per 1 mol of perfluoropolyether (by an order of magnitude less than in the photochemical process.

The peculiarity of the chemical initiation process is the lack of inhibitory effects of the reaction by-products: COF_2, CO, CO_2, CF_3COF, etc.

In contrast, in the photochemical oxidation of hexafluoropropylene with oxygen the side compounds whose concentration in the gas phase is over 30% fully inhibit the process of copolymerization.

The chemical initiation of copolymerization of hexafluoropropylene with oxygen requires strict maintenance of technological parameters: the full expenditure of initiator. Concentration of fluorine in the gas mixture (0.5–1.4%) is provided at the height of liquid column of hexafluoropropylene in the reactor not less than 200 mm. Breakthrough of fluorine can lead to spontaneous ignition and combustion of the monomer in the oxygen environment.

The choice of a method of synthesis of perfluoropolyethers in each specific case is defined by safety requirements to the process of copolymerization of hexafluoropropylene with oxygen, as well as the capabilities of hardware design.

The acyl fluoride group in the perfluorooligoethers obtained by copolymerization of hexafluoropropylene

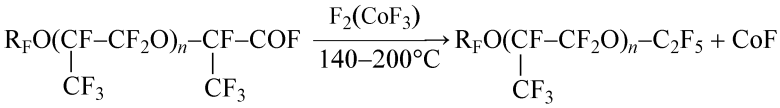
Scheme 1.

$$CF_3-CF=CF_2 \xrightarrow{F_2} CF_3-CF^*-CF_3 \xrightarrow{O_2} (CF_3)_2CFO^*$$

$$\xrightarrow{CF_3-CF=CF_2} (CF_3)_2CFO-CF(CF_3)-CF_2^* \rightarrow (CF_3)_2CFO-(CF(CF_3)-CF_2O)_n-CF(CF_3)-CF_2O^*$$

$$\rightarrow (CF_3)_2CFO-(CF(CF_3)-CF_2O)_n-CF(CF_3)-COF$$

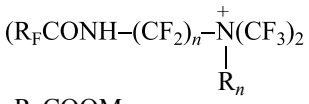
Scheme 2.



with oxygen is eliminated in the interaction with elemental fluorine, CoF_3 or other fluorinating reagent (Scheme 2).

This results in obtaining of neutral perfluoropolyethers.

Based on the perfluoropolyetheroacid fluorides is obtained a series of high-performance fluoro-surfactants: cationogenic, anionogenic, nonionic [7]



R_FCOOMe,
$R_FCOO(C_2H_4O)_nH$,

which are widely used as a component of foam-extinguishing agents for the burning petroleum products, additives for oils, lubricants, diesel fuels, which dramatically reduce friction and improve performance characteristics of various mechanisms.

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