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Fluorine-containing Polyethers, polyesters, and polythia-compounds

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Methods of preparation and the influence of fluorine atoms on the principal physicochemical characteristics of fluorine-containing polyethers, polyesters, and polythia-compounds are reviewed. Heterochain and carbochain polyethers and polyesters and their possible regions of practical use in chemistry and technology are discussed. 197 references.

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I. INTRODUCTION

The development of atomic energy, chemical technology, radio electronics, high-altitude aviation and space-flight, and other important branches of technology requires the creation of new polymeric materials which can be used under extremely severe conditions. Here the material should not only withstand contact with various aggressive media but also retain a complex of physicochemical and strength characteristics in these media over a wide range of high and low temperatures. One of the promising directions for increasing the thermal and chemical stability of polymeric materials is the replacement of the hydrogen atoms in them by fluorine atoms. Here the maximal effect can be reached when completely fluorinated monomers are used for the preparation. However, in several instances a considerable improvement in physicochemical properties of the polymeric materials can be brought about by the introduction into their chain of individual fluorine atoms or small perfluorinated groups. Polymers in which the fluorine atoms are linked to carbon are of the greatest practical interest. Systems in which fluorine is bound to silicon, phosphorus, nitrogen, etc. usually are not very resistant to hydrolysis and are not of practical interest for the preparation of high-molecular-weight compounds.

Non-fluorinated polyethers, polyesters and polythia-compounds can be readily converted into rubbers, films, fibres, etc. However, their thermal and chemical stabilities are low, which restricts the range of practical use of these comparatively accessible and cheap materials. The preparation and study of the properties of fluorine-containing polyethers and polyesters have been dealt with in a large number of papers. Both completely fluorinated polyethers and polyesters and also polymers having chains containing various lengths of non-fluorinated substituted methylene groups are of interest.

The present review deals with methods of obtaining fluorine-containing polyethers, polyesters, and polythia-compounds which contain oxygen or sulphur atoms in the main or side polymeric chains. The contribution of the fluorine atoms to the change in physicochemical properties of these polymers in comparison with their non-fluorinated analogues is discussed. Without any pretence of a complete survey of the published material, the review nevertheless reflects sufficiently adequately the general state of the problem of fluorine-containing polyethers, polyesters, and polythia-compounds and makes orientation in this important part of polymer chemistry somewhat easier.

II. POLYETHERS

The $-CF_2-O-CH_2-$ grouping of low stability chemically[1,2] and therefore its introduction into polyether chains is undesirable. Completely fluorinated ethers of the $-CF_2-O-CF_2-$ type exhibit high thermal and chemical stability. The energy of the C–O–C bond in non-fluorinated ethers is ~90 kcal mole^{-1}, whereas for fluorinated ethers it is ~10 kcal mole^{-1} greater. If it is assumed that the energy of the C–C bond in polytetrafluoroethylene is also 90 kcal mole^{-1}, then evidently the introduction of oxygen atoms into a chain consisting of difluoromethylene groups does not reduce the thermal stability of the polymer, but confers upon it several new properties. Methods for the preparation of fluorine-containing polyethers and polythia-compounds are given below and some of their physicochemical properties are described.

A. Heterochain Polyethers and Polythia-compounds

1. Reaction of fluorine-containing alkenes with oxygen. At the beginning of this century, Swarts showed[3] that acyl halides are formed in the oxidation of fluorinated alkenes by oxygen. Subsequently[4,5] further investigation of this process disclosed a tendency of perfluoroalkene–oxygen systems to explode. In the oxidation of tetrafluoroethylene with molecular oxygen at atmospheric pressure[6] using ultraviolet radiation or X-rays as initiator or under the influence of elevated temperature, in addition to simple oxidation products (COF_2, CF_2-CF_2 (O), CF_2-CF_2 (CF_2), etc.) a polymer of composition $(-CF_2CF_2-O-O-)_X$ is formed. The latter is an unstable copolymer of tetrafluoroethylene and oxygen. It was suggested that the oxidation of tetrafluoroethylene proceeds by a chain mechanism[7]. In the absence of

initiators liquid tetrafluoroethylene copolymerises with oxygen at elevated pressure, forming an elastic product with 0.76 mole oxygen per mole tetrafluoroethylene[8]. In the presence of ozone the induction period of the reaction between oxygen and tetrafluoroethylene is shortened but the ozone does not affect the composition of the copolymer[9,10]. A study of the ^{19}F NMR spectra showed that the copolymer has a homogeneous structure $(-CF_2CF_2-O-O)_X$. Evidently, the oxidation of halogenated alkenes takes place analogously to copolymerisation[11], when one of the monomers is incapable of homopolymerisation. A study of the kinetics of oxidation of tetrafluoroethylene by molecular oxygen[12], under the influence of γ- or X-rays confirmed the suggestion of the formation of intermediate products of peroxide type. The reaction of tetrafluoroethylene with oxygen is an autoxidation of the alkene, which is accelerated in the presence of traces of ozone, and is evidently linked with the radical copolymerisation of alkenes with oxygen. Chain growth can be represented by the scheme[10]:

$$\ldots -CF_2^{\cdot} + O_2 \rightarrow \ldots CF_2-O-O^{\cdot} + CF_2=CF_2 \rightarrow \ldots CF_2-O-O-CF_2CF_2^{\cdot}$$

The formation of gaseous products—carbonyl fluoride and tetrafluoroethylene oxide—takes place in the decomposition of the copolymer:

$$\ldots -CF_2-O-O-CF_2CF_2-O^{\cdot} - \ldots -CF_2-O-O-CF_2^{\cdot} + COF_2$$

$$\ldots -CF_2-O-O-CF_2CF_2^{\cdot} - \ldots -CF_2-O^{\cdot} + \underset{\diagdown O \diagup}{CF-CF_2}.$$

The formation of a peroxide polymer with molecular weight up to 1000 as one of the main reaction products was also noted in the oxidation of chlorotrifluoroethylene[13]. The side-products isolated in this process[14] were COF_2, COFCl, $CF_2Cl-COCl$, and evidently

$$\underset{\diagdown O \diagup}{CF_2-CFCl} \text{ and } \begin{matrix} CF_2-CFCl \\ | \quad | \\ O-\!-O \end{matrix}[14].$$

When peroxide polymers are heated in an atmosphere of nitrogen the polymer $[-CF_2CF_2-O-]_X$ is formed, in addition to the gaseous products[8]; it exhibits high thermal and chemical stability. Poly(tetrafluorooxyethylene) is a crystalline and rather well orientated polymer with a spiral conformation of the macrochains[15].

Polyethers with a large number of successively linked difluoromethylene groups can be obtained in the common pyrolysis of the mercury salts of perfluorodicarboxylic acids[16]:

$$HgOOC-[CF_2]_n-O-[CF_2]_n-O-[CF_2]_n-COOHg + HgOOC-[CF_2]_y-COOHg \rightarrow \rightarrow [-O-[CF_2]_m-]_x$$

In the pyrolysis of this polymer up to 400°C there is partial cross-linking of its chain occurs. By heating iodides in the presence of mercury[17]:

$$O(CF_2CF_2I)_2 \xrightarrow[UV]{Hg} -[CF_2CF_2-O-CF_2CF_2-]_x$$

polyethers with $\bar{M}_n \simeq 40\,000$ were obtained. Their glass point is ~ -65°C, they withstand solvents and exhibit high thermal stability. Appreciable decomposition of these polyethers is observed above 500°C, which not only exceeds the decomposition temperature of non-fluorinated polyethers but even that of such a thermally stable polymer as poly(tetrafluoroethylene). As a result of the investigation of the thermal degradation of poly(tetrafluoroethylene oxide)[18] it was found that its maximal rate of decomposition is observed at 628°C, with the activation energy of the decomposition being 98 kcal mole^{-1}, whereas for poly(tetrafluoroethylene) these values are 568°C and 85 kcal mole^{-1} respectively. Evidently, the higher thermal stability of poly(tetrafluoroethylene oxide) is due to the greater stability of the radicals formed in the degradation.

The polyesters based on perfluoropropene are of considerable interest and have already found practical application. The nature of the initiator employed has a considerable influence on the course of the reaction between oxygen and perfluoroethylene. With γ-rays, gaseous products are mainly formed[19], the bulk of which consists of COF_2 and CF_3-COF, and there is a small quantity of an explosive polymer with M = 120–330. A high yield of polymeric products could be obtained by using ultraviolet light as initiator. The oxygen in the copolymer depends on the reaction temperature and the wavelength of the radiation used[20]. In the photochemical copolymerisation of perfluoropropene and oxygen at −60°C the copolymer $[-CF_2-CF(CF_3)-O-]_X$ is formed, but with increase in the copolymerisation temperature the number of peroxide groups in the copolymer decreases[21]. On heating or further irradiation the proportion of oxygen in the copolymer drops. Copolymers of this type contain reactive terminal –COF groups. The stability of the polyether can be greatly increased by converting the terminal acyl fluoride groups into carboxyl groups followed by decarboxylation of the latter. Oligomers of composition $[-C_3F_6-O-]_X$ exhibit high thermal and chemical stability. They are unchanged on heating to 350°C. The structure of the elementary unit of the polymer,

$$\begin{matrix} (-CF-CF_2-O-) \\ | \\ CF_3 \end{matrix},$$

was deduced from the ^{19}F NMR spectra and chemically[22].

2. Polymerisation of oxides and thio-oxides of fluorine-containing alkenes. The polymerisation of oxides of fluorinated alkenes has been a more convenient method of making polyethers. It has allowed the process to be simplified and the formation of explosive peroxide polymers to be avoided. Oxides of the type

$$\underset{\diagdown O \diagup}{CF_3-CH-CH_2}$$

have been polymerised in the presence of catalysts of the Lewis acid type[23] with the formation of a thermally stable polyether with $M \simeq 230\,000$. Peroxide initiators and γ-rays do not bring about polymerisation of this monomer[23]. Oligoethers with $M = 1000-4000$ were obtained from 2,3-epoxy-1,1,1-trifluoro-propane in the presence of anionic or cationic catalysts[24,25]. The nature of the terminal groups of the polyether depends on the polymerisation catalyst employed. The use of aluminium chloride as a catalyst facilitates the formation of terminal hydroxyl groups whereas when alkaline catalysts or boron trifluoride are used double bonds are formed as terminal groups[24]. High-molecular-weight polyethers are also formed from other oxides in the presence of cationic catalysts, for example, from epoxy-2,2,3,3-tetrafluoro-1-vinylbutane[26,27].

Active carbon[28–30], alkali metal fluoride[29,31], or γ-rays[32] have been used as catalysts for the polymerisation of perfluorinated oxides. The polyethers from perfluoro(epoxypropane) have the composition:

$$F-[C_3F_6O-]_x-\underset{CF_3}{CF}-COF.$$

To increase the stability of this polyether [30] or of the copolymer of perfluoroepoxypropane with epoxytetrafluoroethylene [33], the terminal –COF groups are decarboxylated. To do this, the polyether with terminal functional groups is treated with elemental fluorine and if double bonds are present ultraviolet light is used, which leads to doubling of the molecular weight of the polyether. If the ammonium salts of these acids are decarboxylated the polyethers will also contain rather stable $-CF_2H$ terminal groups [34].

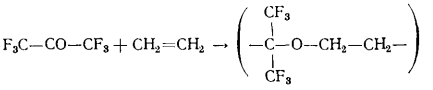
Fluorine-containing thio-oxides form homopolymers or copolymers in the presence of initiators of the radical type or under the action of ultraviolet radiation [35]. Fluorine-containing polythia-compounds exhibit increased fire resistance and chemical stability, and can also be used as plasticisers, for example, for poly(tetrafluoroethylene).

The polyethers from perfluoro(epoxypropane) exhibit extremely valuable properties [21] and are greatly superior to their non-fluorinated analogues. They are insoluble in various solvents, resistant to the action of oxidants such as O_2, O_3, and Cl_2 up to 250°C; stable to radiation, which distinguishes them favourably from poly(tetrafluoroethylene); incombustible, and of low toxicity. Liquid polyethers retain their viscosity over a wide range of temperatures and are used as lubricants. These polyethers withstand heating up to 410°C and low-molecular-weight polyethers can even be distilled at 490°C without decomposition. Films of fluorinated polyethers exhibit satisfactory mechanical strength and do not lose their elasticity at –80°C [36]. Attempts to use these polymers for obtaining rubbers were unsuccessful since no reliable methods for their vulcanisation have yet been discovered. The copolymerisation of perfluoroepoxyalkanes and perfluorodiepoxyalkanes (the preparation of the first representatives of fluorine-containing diepoxides and their polymers has been mentioned [37,38]), or the cross-linking of polyether macrochains at the stage of the decarboxylation of the terminal groups can probably be used for this purpose.

3. Copolymerisation of oxides and alkenes. Copolymers of fluorinated oxides and non-fluorinated alkenes are interesting. Perfluoroepoxyalkanes readily form block-copolymers with non-fluorinated vinyl monomers (styrene, butadiene, isoprene, methyl methacrylate, etc.) in the presence of alkali metals or their complexes with aromatic compounds [39]. Block-copolymers exhibit increased resistance to the action of organic solvents, increased impact strength, fire resistance, and low gas permeability. Fluorine-containing polyethers can also be obtained by the copolymerisation of non-fluorinated oxides, for example, ethylene oxide and highly fluorinated alkenes (perfluoropropene, chlorotrifluoroethylene) in the presence of peroxide initiators or on irradiating a mixture of monomers with ultraviolet light [40]. Copolymers soluble in organic solvents are formed thereby, and their composition and properties can be regulated readily by means of the composition of the initial mixture of monomers. Unlike poly(ethylene glycol), when exposed to the action of sulphuric acid at 150°C, the above copolymer is stable under these conditions.

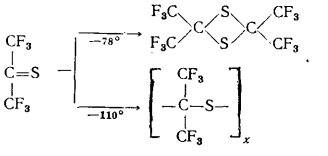
4. Polymerisation of ketones or thioketones and their copolymerisation with alkenes. The carbonyl groups of aldehydes and ketones are usually stable to the action of free radicals, although in some instances such reactions have been effected [41,42]. However, fluorinated ketones, the carbonyl group of which is under the inductive influence of electron-withdrawing perfluoroalkyl radicals, are capable of adding compounds of the R–H type at the carbonyl group under conditions for free-radical processes [43]. The carbonyl group of fluorinated ketones is reminiscent of the weakly polarised double bond of alkenes, which facilitates their participation in reactions which take place according to a free radical mechanism in comparison with non-fluorinated analogues. In the presence of t-butyl peroxide, hexafluoroacetone is capable of adding either simple low-molecular-weight substances (hydrocarbons, ethers, aldehydes, etc.) or high-molecular-weight compounds, for example, polyethylene [43]. It is noteworthy that fluorinated ketones are readily broken down into radicals under the influence of ultraviolet light. The least stable of them under these conditions is evidently hexafluorocyclobutanone. Even at room temperatures this loses the carbonyl group, being converted into perfluorocyclopropane [44]. At low temperatures hexafluorocyclobutanone polymerises in the presence of sodium acetate with the formation of a linear polyether.

Alkenes are readily copolymerised with hexafluoroacetone in the presence of peroxide initiators [45,46]:



Such copolymers exhibit reduced combustibility and water-repellant properties and can be used as protective coatings on metals. The copolymer of ethylene and hexafluoroacetone is sufficiently thermostable. When the copolymer has 11% hexafluoroacetone its loss in weight at 400°C is 1.5%, that at 470°C is 8.7%. The copolymer is readily formed into films [45]. Not only alkenes can undergo copolymerisation with polyfluorinated ketones, but also several other substances which do not form homopolymers (CO, SO_2, etc.). Such copolymers can be used for protecting metals, as adhesives for sheet materials, and for increasing the elasticity of polymers [47]. Polymeric fluorinated ketones copolymerise with polyalkenes, polyethers or polyamides, in the presence of peroxide initiators, improving the fire-resistance, adhesion, and dye receptivity of the latter [48]. However, nothing has been published on the possibility of vulcanising these copolymers.

Fluorine-containing thioketones readily undergo polymerisation both in the presence of special catalysts (boron trifluoride–diethyl ether, dimethylformamide, benzthiols [49,50], aluminium or titanium isopropoxides [51]) and without them [52]. The course of the reaction is greatly affected by the temperature. In the presence of dimethylformamide a dimer is formed from hexafluoroacetone at –78°C, whereas at –110°C the sole product of the reaction is a polymer of linear structure:



Thioketones with 5–10 carbon atoms polymerise with difficulty, forming dimers or liquid products. With decrease in the number of carbon atoms in the thioketone the polymerisation is facilitated and solid, high-molecular-weight polymers with comparatively moderate melting

points are formed. The polymers of fluorinated thioketones are of low stability: their depolymerisation takes place at −78°C [51,53] or at room temperature [50]. However, in some instances their stability is high, which allows elastic films or fibres, resistant to the action of solvents, to be obtained from them [49,52].

Hexafluoroacetone readily forms addition compounds of 1:1 composition with alkenes having an allyl hydrogen atom [54], which made possible the modification of natural polyisoprene [54] and other polydienes, such as polybutadiene and neoprene [55], with hexafluoroacetone. After such treatment the fluorine content of the polymer is 43%.

5. Polymerisation of aldehydes and thioaldehydes. Fluorine-containing aldehydes of the R_f-COH type polymerise extremely readily both in the presence of various catalysts or initiators and without them. For this reason it has been impossible to determine the precise boiling point of thioacetaldehyde, as this polymerises during distillation [56,57]. The polyether formed as a result of the spontaneous polymerisation of the fluoral melts at ~50°C and depolymerises on heating. During a more detailed investigation of the conditions for the polymerisation of fluorinated aldehydes certain regularities were found [58]. In the polymerisation of the lower aldehydes peroxide initiators were more active than acid catalysts (H_2SO_4, Ac_2O). The higher fluorinated aldehydes polymerise more easily under the action of acid catalysts.

The structure of poly(fluoroaldehydes) is that of substituted poly(oxymethylenes) with terminal hydroxyl groups. Their thermal stability can be enhanced by replacing the terminal hydroxyl groups by halogen [59]:

$$HO-\underset{R_f}{CH}-\left[O-\underset{R_f}{CH}\right]_x OH + SOCl_2 \rightarrow Cl-\underset{R_f}{CH}-\left[O-\underset{R_f}{CH}\right]_x-Cl$$

Polyaldehydes containing fluorine and chlorine atoms, for example, poly(chlorodifluoroacetaldehyde), are less stable to the action of elevated temperatures than poly(perfluoroaldehydes) [60] and are depolymerised even at 180°C, forming the monomeric aldehyde.

Poly(fluoroaldehydes) can be used as coatings for metals. They are insoluble in organic solvents, oligophobic and hydrophobic, and do not decompose in contact with fuming nitric acid, or boiling alkalis, but break down in boiling sulphuric acid. Their depolymerisation was observed at 380−400°C, but other studies gave a considerably lower depolymerisation temperature [57,60].

Copolymers of formaldehyde and fluorinated aldehydes are very interesting. The copolymerisation of these monomers proceeds at low temperatures in the presence of quaternary ammonium salts [61]. After protection of the terminal hydroxyl groups a sufficiently stable polymer, which exhibits good mechanical properties in the temperature range from −78° to +200°C, is obtained.

Fluorine-containing polythia-compounds can be obtained readily by the polymerisation of such fluorine-containing thiocarbonyl compounds as thioaldehydes or thioacyl halides. In certain instances the polymerisation of these compounds proceeds spontaneously [62]. Thiocarbonyl fluoride is the simplest monomer which can be used for this purpose. It can be polymerised both by anionic [63,64] and by free-radical [65] mechanisms. Dimethylformamide [50,63], titanium or aluminium isopropoxides [63,64], and boron trifluoride−diethyl ether [50] have been used as catalysts for the polymerisation of thiocarbonyl compounds. Ultraviolet light [65,66] or organoboron compounds in conjunction with oxygen or oxidants [65] can be initiators of the free-radical polymerisation of fluorothiocarbonyl compounds.

Poly(thiocarbonyl fluoride) with $M = 2000-5000$ is formed even on storage of the monomer [50]. In the presence of catalytic amounts of dimethylformamide at −78°C thiocarbonyl fluoride is readily converted into a polymer of structure $[-CF_2-S-]_x$. The initiation of the anionic polymerisation of thiocarbonyl fluoride, chain growth, and chain breaking can be represented by the following scheme:

$$CF_2=S \xrightarrow{\text{solvent}} (CF=S)^+ + F^- + CF_2=S \rightarrow CF_3-S^-;$$
$$CF_3-S^- + CF_2=S \rightarrow CF_3-S-[CF_2-S]_x-CF_2-S^-;$$
$$CF_3-S-[CF_2-S-]_x CF_2-S^- \rightarrow CF_3-S-[CF_2-S]_x-CF=S + F^-.$$

This polythia-compound contains terminal thiocarbonyl groups −CF=S and a small number of −CF=O carbonyl groups, observable in the infrared spectrum of the polymer [50]. The value of the characteristic viscosity, measured for a 0.1% solution of the polymer in chloroform, varied from 3 to 6 [50,64], and the molecular weight, determined by an osmometric method, reached 300 000−400 000 [67]. Poly(thiocarbonyl fluoride) is an elastic and hard polymer, m.p. ~35°C, glass point −118°C, decomp. temp. 175°C. It can readily be formed into films (σ = 770 kgf cm^{-2}, ϵ = 90%). This polymer is stable to the short-time action of boiling nitric acid and boiling solutions of alkalis. Under the action of amines, poly(thiocarbonyl fluoride) is destroyed very rapidly [63]. Alkali brings about the slow destruction of this polythia-compound by acting on the terminal groups. The ability of the polymer to withstand high temperatures and alkalis can be considerably increased by conversion of the terminal thiocarbonyl groups into trifluoromethyl groups. To do this the polymer is treated with antimony(V) fluoride [50], after which the resistance of the polymer to the action of amines is also increased:

$$CF_3-S-[CF_2-S]_x-CF=S \xrightarrow{SbF_5} CF_3-S-[CF_2-S-]_x-CF_3$$

Another method of increasing the stability of this type of polythia-compound to the action of heat or amines is the copolymerisation of thiocarbonyl fluoride with certain halogenated thioacyl fluorides [63], for example, with CHFCl−CF=S. It is interesting to note that the homopolymers of thioacyl fluorides [51] are destroyed by alkalis even at room temperature [50].

The higher fluorinated thioaldehydes readily polymerise with the formation of liquid or solid high-molecular-weight compounds [68]. Crystalline polythia-compounds with branched fluorinated radical, which reduces their solubility in organic solvents, were obtained in the polymerisation of fluorinated thiobutyraldehyde [69]:

$$(CF_3)_2CF-CHS \rightarrow \underset{\underset{CF(CF_3)_2}{|}}{[-CH-S-]_x}$$

The decomposition temperature of this polymer is ~200°C.

A series of copolymers of fluorinated thiocarbonyl compounds with other monomers has been obtained. Elastomers which do not crystallise at low temperatures are formed in the copolymerisation of thiocarbonyl fluoride with various alkenes [70] (ethylene, but-2-ene, styrene, butadiene, vinyl fluoride). These copolymers are more resistant to thermal destruction and are fabricated more readily. Copolymers of thiocarbonyl fluoride are extremely resistant to the action of concentrated nitric acid [66]. To reduce the tendency towards crystallisation of poly(thiocarbonyl fluoride) it was copolymerised with a thioacyl fluoride in the presence of catalytic amounts of aluminium or titanium alkoxides [71].

5. Aromatic polyethers and polythia-compounds. In the preparation of *p*-trifluoromethylphenol it was noted that in an alkaline medium in the cold it is converted into a polymer of structure $[-CF_2-C_6H_4-O-]_x$ [72]. Potassium perfluoro-*p*-tolyl oxide was more stable under these conditions; its polycondensation in the cold was very slow. At elevated temperatures a polyether with $M = 1500-3000$ is formed[73]:

$$CF_3-C_6F_4-OK \rightarrow [-CF_2-C_6F_4-O-]_x$$

Such a structure was attributed to the polyether from the ^{19}F NMR spectra. This polyether melts at ~100°C and starts to decompose at ~300°C.

A number of aromatic polyethers are of great interest. The tendency of perfluorinated aromatic compounds to undergo nucleophilic substitutions has been utilised for their preparation. When hexafluorobenzene is heated with alkalis, alkali metal pentafluorophenoxides are formed and on further heating they are converted into polyethers:

$$C_6F_5OK \rightarrow C_6F_5\ O-[C_6F_4-O-]_x-C_6F_4-OK$$

The softening temperature of poly(perfluoro-*p*-phenylene oxide) with $M \simeq 12\,000$ exceeds 100°C.[74]

Poly(perfluoro-*p*-phenylene sulphide), which melts at temperatures above 300°C, was obtained by the same scheme. Its structure is clearly shown by its desulphidation on Raney nickel, which gives only 1,2,4,5-tetrafluorobenzene (structural units) and a little pentafluorobenzene (terminal units).

However, the thermal stability of these polyethers and polythia-compounds was less than that of their non-fluorinated analogues. A similar relation was also noted in investigating the thermal destruction of the perfluoropolyphenylenes[75]. Evidently, the introduction of fluorinated phenyl nuclei into the chains of the polymers does not give a product more stable thermally than its non-fluorinated analogue. The presence of terminal hydroxyl or phenoxide groups should also facilitate subsequent processes which are accompanied by the release of alkali metal fluorides or of hydrogen fluoride.

B. Carbochain Polyethers and Polythia-compounds

There have been many publications, mainly patent specifications, describing polyethers obtained by the polymerisation of vinyl or allyl ethers and also of glycide ethers, that is, polyethers in which the oxygen atoms are in side-chains. Fluorine atoms were introduced into the alkyl (aryl) or vinyl part of these monomers or in both parts simultaneously.

1. Polymers and copolymers of fluoroalkyl vinyl or allyl ethers. This section will consider polymers made from monomers of structure $R_f-O-CH=CH_2$ or $R_f-CH_2-O-CH=CH_2$. The polymerisation of the non-fluorinated double bond of this type of monomer can be brought about by initiators of free-radical processes or catalysts of ionic type. The ability to polymerise under conditions of free-radical initiation depend on the structure of the original monomer. Perfluoroisopropyl allyl ethers[76] or $\alpha\alpha$-dihydroperfluoro-*n*-alkyl vinyl ethers[77] can be polymerised in the presence of benzoyl peroxide or ultraviolet light, whereas pentafluorophenyl vinyl ether does not polymerise[78] in the presence of free-radical initiators. It is noteworthy that the polymerisation of fluoroalkyl vinyl ethers has been studied insufficiently. There have been contradictory statements about the ability of peroxide initiators to bring about the polymerisation of some of these monomers[79]. In recent studies it has been noted[80] that the catalysts mentioned in earlier studies are either inactive generally or exhibit a very low activity.

In this respect fluoroalkyl vinyl ethers are reminiscent of their non-fluorinated analogues, which under the action of light or of initiators of the free-radical processes are slowly polymerised with the formation of low-molecular-weight products.

Catalysts of the Friedel–Crafts type are more effective for the polymerisation of fluoroalkyl vinyl ethers (as for their non-fluorinated analogues. Aluminium chloride[78], boron trifluoride–diethyl ether[77,80–82], or gaseous boron trifluoride[78,80] at low temperatures have been used as such catalysts. The polymerisation rate and the molecular weight of the polymer depend on the type of catalyst. Evidently, the most active is gaseous boron trifluoride; when this is used, trifluoroethyl vinyl ether is polymerised very rapidly with the formation of a high-molecular-weight product, whereas with boron trifluoride–diethyl ether the polymerisation is slow and a low-molecular-weight polyether is formed [80].

The presence of fluorinated substituents as side-chains confers a series of valuable properties upon the polymer: fire resistance, water- and oil-repellance, which enables it to be used as protective coatings for metals, cloth, paper, etc. An extremely interesting property of such polyethers, especially polyethers obtained from monomers with branched fluorinated radicals, is the extremely small critical surface tension for wetting. For example, for poly(heptafluoroisopropyl vinyl ether) $\gamma_w = 14.2$ dyne cm^{-1} [79]. It has been proposed to use a series of fluorine-containing polyethers as adhesives, like their non-fluorinated analogues[77].

Copolymers of fluoroalkyl vinyl ethers with various vinyl monomers are interesting. The copolymerisation can be carried out blockwise, in emulsion, or suspension in the presence of initiators of free-radical polymerisation[83]. Lauryl peroxide[84] or redox systems based on ammonium persulphate[85–87] have been used as polymerisation initiators. Usually, in the copolymer there is a smaller amount of the fluoroalkyl vinyl ether than there was in the monomer mixture[84]. The presence of polyfluoroalkoxide substituents in the copolymer chain increases the plasticity of the polymers. Copolymers of trifluoroethyl vinyl ether and tetrafluoroethylene can be fabricated into articles by the usual methods[85]. The introduction into the polyvinyl chloride chain of this same monomer increases its thermal and chemical stability which allows these copolymers to be used for protective coatings for metals[85]. Even small quantities of trifluoroethyl vinyl ether give its copolymers with vinyl chloride and other vinyl monomers increased thermal stability and improve their resistance to attack by solvents[84,86]. The use of these monomers for the preparation of special-purpose rubbers can be extremely promising. Copolymers of perfluorobutadiene and poly(fluoroalkyl vinyl ethers) compounded with carbon black are readily vulcanised with the formation plastics which withstand oil and petrol. Their resistance to oxygen at high temperatures is higher than that of rubbers based on copolymers of non-fluorinated butadiene and acrylonitrile[87]. Vinyl ethers, especially those which also contain other functional groups, for example, the ethylvinyl ether of 2-*N*-ethylperfluorooctanesulphonamide are used for the special treatment of fabrics to confer on the latter resistance to oil and water[88].

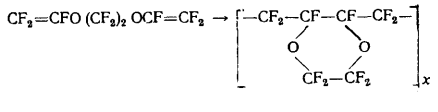
3. Polymers and copolymers of alkyl-perfluorovinyl and allyl ethers and sulphides. Unlike vinyl ethers with a non-fluorinated double bond, perfluorovinyl ethers are readily polymerised in the presence of initiators of free-radical processes. The following initiators were used for the polymerisation of these monomers: benzoyl peroxide[89], γ-radiation[90], or tetrafluorohydrazine[91]. Perfluorovinyl sulphides do not polymerise in the presence of benzoyl peroxide[89]. In the general case the ability of these monomers to polymerise decreases in the order[90]:

$$R_f{-}CH_2{-}O{-}CF{=}CF_2 > R_f{-}O{-}CF{=}CF_2 > R_f{-}S{-}CF_2{=}CF_2 .$$

The molecular weight of the polymers changes in the same order. It is noteworthy that the sulphides $R_f{-}S{-}CF{=}CF_2$ not only polymerise badly themselves but also inhibit the polymerisation of other vinyl monomers[90], probably because of capture of the electron by the vacant orbital of the sulphur atom. Polyethers of fluorine-containing allyl ethers were obtained from the corresponding monomers in the presence of persulphates[92]. They are used as adhesives for attaching halogenated polymers to metals.

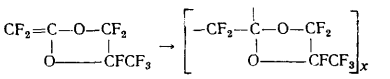
Alkyl- and polyfluoroalkyl-perfluorovinyl ethers are readily copolymerised with various vinyl monomers[93] to form liquid or solid copolymers[89]. High-melting copolymers of perfluoromethyl vinyl ether with tetrafluoroethylene can be converted into articles by the usual methods, for example, into stiff colourless and transparent films[90,91]. High-molecular-weight copolymers are formed when perfluoropropyl vinyl ether and tetrafluoroethylene are polymerised together[94,95]. The preparation of copolymers with various fluorine-containing alkenes is of interest for the production of elastomers with increased thermal stability and excellent resistance to frost. For example, a copolymer of vinylidene fluoride and perfluoroethyl vinyl ether, strengthened with magnesium oxide and hexamethylenediamine, retains its flexibility at $-25°C$ and its loss in weight after 200 h at 288°C totalled 10%[96]. Such materials were proposed for use for fuel cells and diaphragms working in contact with liquid fuel.

Perfluorinated bisvinyl ethers of the type $CF_2{=}CFO[CF_2]_n{-}OCF{=}CF_2$ are polymerised or copolymerised with fluorine-containing alkenes block-wise, in solution, or suspension in the presence of peroxide-type initiators. These monomers are interesting because their polymerisation can be effected at one vinyl group and then the fore-polymer obtained is converted into a cross-linked product by subsequent polymerisation in moulds[97]. In the polymerisation of such monomers ($n = 2$) in the presence of peroxides, for example, peroxides of the $(C_3F_6O_2)_x$ type[98], polyethers with rings in the chain are formed[99]:

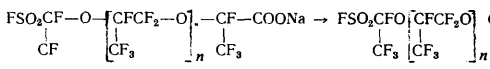


these exhibit high chemical stability and good electrical insulating properties. They are thermoplastic and can be extruded or cast under pressure. These polyethers withstand boiling nitric and sulphuric acids and boiling alkali solutions. Perfluorodivinyl ethers copolymerise with perfluoroalkyl vinyl ethers or perfluoroalkenes to give a fore-polymer. After additional polymerisation a rigid, chemically inert material is obtained[100].

The polymerisation of perfluoro-4-methyl-2-methylene-1,3-dioxolane in the presence of tetrafluorohydrazine gave a polymer with unusually high gas permeability[101], which allowed it to be used for the separation of many gases:

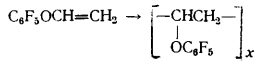


Perfluorovinyl ethers with several ether bonds are obtained by the pyrolysis of the alkali salts of carboxylic acids[102]:

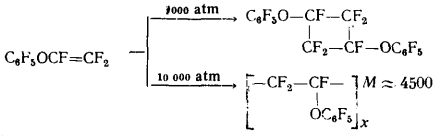


Polymers or copolymers of these vinyl ethers with vinylidene fluoride are plates or elastomers.

Of the fluorine-containing vinyl ethers, that with the least ability to polymerise is probably the phenyl vinyl ethers. Pentafluorophenyl vinyl ether[103] and its derivatives which contain a single hydrogen atom in the vinyl group[104] can be polymerised in the presence of Friedel-Crafts type catalysts. The molecular weights of these polymers are low (2300–17 000), and their melting points lie in the range 120–180°C.



Phenyl perfluorovinyl ethers[105] or perfluorophenyl vinyl ethers[106] are polymerised with difficulty even at 230°C after 10 days[107], the yield of polymers with characteristic viscosity 0.03 totalling 2–3%. However, on irradiation of these monomers with γ-rays at high temperatures a polyether soluble in perfluorobenzene and of increased thermal stability could be obtained in 6–7% yield. These monomers were polymerised by using high pressure (10 000 – 15 000 atm [106]) since at a pressure of 1000 atm dimers are formed exclusively:



3. Polymerisation and copolymerisation of glycide ethers. Fluoroalkyl glycide ethers became available monomers after the ability of perfluoroketones to react with alkali metal fluorides to form alkoxides of perfluoroalcohols had been observed. When the latter react with epichlorhydrin or epibromohydrin they are converted into the corresponding glycide ethers[109,110]. Glycide ethers based on hexafluoroacetone are polymerised in the presence of catalytic amounts of water and diethylzinc at $-70°C$ [109], whereupon a highly elastic polymer with $M \simeq 84\,000$, insoluble in ordinary and soluble in fluorinated solvents is formed[110]. The glass point and decomposition temperature of these polymers are $-43°$ and $+270°C$ respectively. When the glycide ethers are polymerised in the presence of boron trifluoride–diethyl ether, low-molecular-weight liquid products were isolated. Homopolymers and also copolymers of these monomers with the oxides of other alkenes are used for obtaining resins, coatings, adhesives, and also for special treatment of fabric to confer oil- and water-repelling properties upon it. For impregnation of overalls, glycide ethers of pyrans are also used[111], the polymerisation of which is effected in the presence of iron(III) chloride. Thermoreactive resins are obtained from glycide ethers, the molecules of which contain an additional vinyl group[112].

These resins were hardened by using amines, for example, diethylenetetramine. Perfluorinated epoxyalkenes of structure

$$CF_2=CF[CF_2]_n-CF-CF_2$$
$$\qquad\qquad\quad \backslash O /$$

are of considerable interest[113]. Monomers of this type can be polymerised or copolymerised with various fluorinated alkenes or their oxides to form polyethers capable of being hardened by polymerisation of the second functional group. These polymers have high thermal and chemical stability and can be used to obtain fibres, films, and moulded articles.

4. Modification of celluloses by fluoride-containing compounds. There have been descriptions of attempts to introduce fluorine atoms into cellulose or manufactured articles made on its basis. Attempts were made to introduce isolated fluorine atoms into cellulose by the action of the tosyl ethers of alkali metal fluorides upon it[114]. This method gives good results with several of the simplest esters of toluenesulphonic acids, but only small quantities of fluorine could be introduced into cellulose by this method. A method based on reactions of nucleophilic addition of alcohols to perfluoroalkenes, for example, to perfluoropropene, was more effective[115]. In alkaline medium cellulose reacts with perfluoropropene to form ethers of the $R-O-CF_2-CFH-CF_3$ type and a certain amount of ethers of the $R-O-CF_2-CF=CF_2$ type, products of the substitution of fluorine atoms in the allyl position. The ether bonds of such types were stable in acid and alkaline media, probably because of the increase in the hydrophobic nature of such fluorine-containing polymers. Up to 13% fluorine could be introduced into cellulose by this method and the polymer itself acquired water-repelling properties. Other fluorinating media can be used for introducing fluorine atoms, for example, sulphur tetrafluoride[116]. This fluorinating agent readily replaces hydroxyl, carbonyl, or carboxyl groups by fluorine atoms with the formation of C–F, CF_2, or CF_3 groupings respectively. This method is suitable for making paper or cardboard water-repellent.

III. POLYESTERS

Nonfluorinated polyesters are readily formed in reactions between dicarboxylic acids and diols or polyols. In several instances re-esterification between the dimethyl or other diethers of dicarboxylic acids and diols has been used successfully. In certain instances (mainly in working with diols with increased acidic properties, for example, with various bisphenols) acyl halides of dicarboxylic acids are used. Polyesters are interesting for obtaining fibres, films, etc. or are intermediates for further syntheses, for example, for obtaining polyurethanes, etc.

In comparison with carboxylic acids their fluorinated analogues are stronger. The dissociation constant of acetic acid is 1.8×10^{-5}, whereas that for trifluoroacetic acid is several orders of magnitude greater (5.9×10^{-1}). This strengthening of the acidic properties is due to the inductive influence of the electron-withdrawing fluorinated radical. A similar effect of fluorinated radicals is seen in the acidic properties of fluorine-containing alcohols. Alcohols with the $-CF_2OH$ grouping are unknown. Alcohols with $-CF_2CH_2OH$ groups are completely stable. They are obtained in the telomerisation of tetrafluoroethylene and methanol (monohydric alcohols) or in the reduction of diesters of perfluorodicarboxylic acids (diols). The acidic properties of 1,1-dihydroperfluoro-alcohols are comparable with those for phenols. Therefore the direct esterification of such alcohols is difficult. To obtain esters under such conditions the anhydrides or acyl halides of fluorinated or non-fluorinated carboxylic acids are used.

The polyethers obtained from dicarboxylic acids and diols and also the polyesters made by the polymerisation of unsaturated esters are of practical interest. Both types of fluorine-containing polyester will be considered below.

A. Heterochain Polyesters

The available aliphatic fluorine-containing dicarboxylic acids at present are perfluoroadipic and perfluoroglutaric acids. They are obtained by the oxidation of dichlorooctafluorocyclohexene or dichlorohexafluorocyclopentene respectively. The electrochemical fluorination of dicarboxylic acids to perfluorodicarboxylic acids is extremely promising. Despite the comparatively low yields of valuable products (up to 20%) the electrochemical fluorination is simple and allows the process to be effected in a single stage. The preparation of the higher perfluorodicarboxylic acids is extremely difficult, which hinders the investigation of these products as monomers at present. Dimethyl or diethyl perfluorodicarboxylates are readily reduced to $\alpha\alpha\omega\omega$-tetrahydroperfluoroglycols of the type $HOCH_2[CF_2]_nCH_2OH$. Diols with $n = 3$ and 4 were used to obtain polyesters.

1. Polyesters from dicarboxylic acids and diols. Fluorine-containing polyesters have been studied in sufficient detail for some of them to be put into industrial production, whereas poly(thioesters) have hardly been investigated at all. The preparation of poly(thioesters) from the anhydrides of perfluorodicarboxylic acids and of non-fluorinated dithiols have been mentioned in the literature, but the properties of the polymers were not given[117].

Fluorine-containing polyesters can be obtained by all the methods employed for the preparation of their non-fluorinated analogues. However, high molecular weights could not always be attained. Polyesters with moderate molecular weights are readily formed from the anhydrides of perfluorodicarboxylic acids and fluorinated diols[118]. High-molecular-weight polyesters also could not be obtained by heating the disilver salts of perfluorodicarboxylic acids with $\alpha\omega$-polymethylene di-iodides[119] or by the esterification of non-fluorinated diols with perfluorodicarboxylic acids[119].

Best results were obtained on using the bisacyl chlorides of perfluorodicarboxylic acids. When the latter were heated with fluorinated diols polyethers with molecular weights up to 17 000 could be obtained[120]. Polyethers with even higher molecular weights are formed on using bis(acyl chlorides) of non-fluorinated dicarboxylic acids[121]. Polyesters can be obtained by re-esterification between the dimethyl esters of non-fluorinated dicarboxylic acids and fluorinated diols. Alkali metal alkoxides, metal oxides, and strong acids have been used as catalysts for the re-esterification[122]. The second stage (polycondensation) takes place at 200–300°C in the presence of catalytic amounts of oxides of Sb, Bi, Ti, or Mg.

Aliphatic or aromatic dicarboxylic acids can be used as the acidic constituent. Aliphatic dicarboxylic acids form low-melting or liquid polyesters[117-120], which exhibit high thermal stability and elasticity at low temperatures. Their glass points lie in the range from −30° to −57°C. Such polyesters are capable of being cross-linked at the stage of their preparation with polyols (glycerol)[120], or at the stage of subsequent retreatment with peroxides or calcium carbonate[121], or by other functional groups, for example, hydroxyl groups, found in the dicarboxylic acid molecule[122]. One of the most valuable polyesters of this type is poly(hexafluoropentamethyleneadipate). The oil- and petrol-resistant rubbers from this polyester, which exhibit good low-temperature characteristics, are produced on an industrial scale[123,124]. They can be used at temperatures from −72° to +150°C. Despite the fact that their mechanical properties are not outstanding (σ = 160 kgf cm^{-2}, ϵ = 120−230%), these rubbers have found practical application in the aviation industry.

Attempts have been made to increase the thermal stability of aliphatic polyethers by using terephthalic acid in place of part of the adipic acid. The resistance of low-molecular-weight polyesters ($M \simeq 1800-2700$) to heating was improved to some extent by replacing 30% of the adipic acid by terephthalic. The other properties of the polyesters changed insignificantly[125]. A further increase in the proportion of terephthalic acid leads to an increase in the melting points of the mixed polyester and a deterioration in its low-temperature characteristics[126]. Polyesters based on terephthalic acid and fluorinated diols are plastics themselves; they are readily soluble in organic solvents and are used as heat-resistant protective coatings or as cast resins[127].

In certain instances, when both the acid and diol are fluorinated, it is desirable to introduce a certain proportion of non-fluorinated diol or non-fluorinated hydroxy-acid into the polyester. These additions favour an increase in the molecular weights of the polyesters[128].

All the aliphatic fluorine-containing polyesters undergo hydrolysis to a considerable extent. Their hydrolytic stability is considerably less than that of their non-fluorinated analogues.

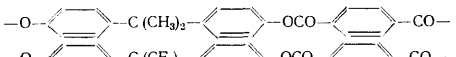
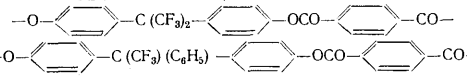
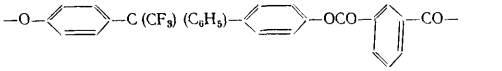
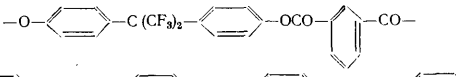
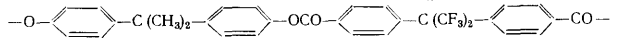
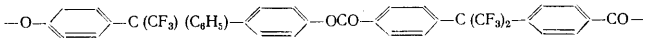
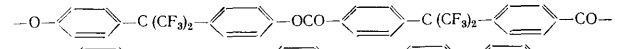
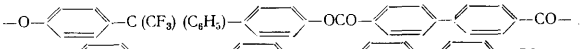
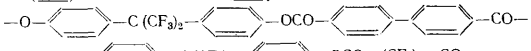
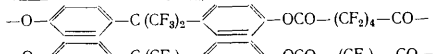
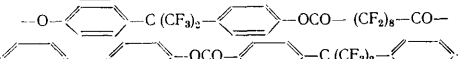
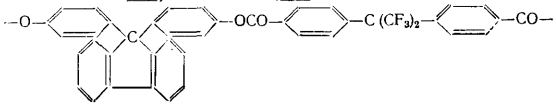
2. Polyesters from fluorinated aromatic dicarboxylic acids. Nothing has been published about polyesters obtained from aromatic dicarboxylic acids having fluorinated phenyl nuclei. Only the use of fluorophthalic anhydride for the preparation of glyptal resins has been described[129]. Evidently, the use of fluorinated aromatic dicarboxylic acids for the preparation of polyesters does not lead to an increase in their thermal and hydrolytic stabilities. The fluorine atoms, like those of any other halogen, will be comparatively easily displaced by nucleophilic agents under the influence of electron-withdrawing carboxyl groups even during the preparation of polyesters at 150−200°C. Furthermore, fluorinated aromatic acids themselves are readily decarboxylated on heating. Pentafluorobenzoic acid starts to decompose even at 190°C, and tetrafluoroisophthalic acid is decarboxylated at 203°C [130].

There is also considerable interest in aromatic dicarboxylic acids in which the fluorine atoms are not in the phenyl nuclei but in the side-chains. The acids of this type are devoid of the above drawbacks. Their thermal and chemical stabilities should be close to those for benzoic and terephthalic acids. The recently synthesised dicarboxylic acids of the type $HOOC-C_6H_4[CF_2]_n-C_6H_4COOH$ [131,132] and acids of the type $HOOC-C_6H_4-C(CF_3)_2-C_6H_4COOH$ can be regarded as promising monomers for the preparation of fluorine-containing polyesters. The latter acids have already been used for the preparation of polyesters[133]. The diols were aliphatic fluorinated diols or bisphenols of aromatic or aliphatic−aromatic series. The bis(acyl chlorides) of the dicarboxylic acids and bisphenols form polyesters (polyarylates) under interphase polycondensation conditions[134]. Table 1 gives certain properties of the fluorine-containing polyarylates with those their non-fluorinated analogues for comparison. As Table 1 shows, the replacement of methyl groups at the central atom of the bisphenol by trifluoromethyl groups leads to some increase in the thermal stability of the polyesters. Fluorine-containing polyarylates exhibit greater elasticity than their non-fluorinated analogues and are readily converted into films with satisfactory strength characteristics. Their breaking strength reaches 700−1000 kgf cm^{-2} and the elongation is 30−70%. Polyesters made from bisphenols fluorinated in the aromatic nucleus decompose at ~300°C [140].

A detailed study of the kinetic features of the thermal degradation of polyesters based on adipic, fumaric, or terephthalic acid and octafluorohexane-1,6-diol was made at 260−420°C. The replacement of part of the adipic acid by isophthalic acid in the preparation of the polyesters, or the use of fumaric acid, did not lead to an improvement in the thermal stability of the polyester[141]. A considerable increase in the thermal stability was noted for polyesters based on terephthalic acid. The release of volatile degradation products was observed here at 360−380°C, whereas polyesters from aliphatic acids released gaseous products at much lower temperatures (220−260°C). It is interesting to note that the hydrogen fluoride or silicon tetrafluoride formed in the reaction of the latter with glass were not observed in the degradation products[142]. The temperature for the start of the degradation of the fluorine-containing polyester based on terephthalic acid exceeds these values for poly(chlorotrifluoroethylene) and copolymers of vinylidene fluoride with chlorotrifluoroethylene or perfluoropropene and also for poly(ethylene terephthalate) for which degradation in nitrogen atmosphere was observed even at 280−320°C. A similar series of relations was also found for the degradation of fluorine-containing polyesters in the presence of oxygen[143], but the temperatures at which the polymer loses 25% of its weight in oxygen atmosphere is lower than for the same temperatures in a vacuum.

3. Polyesters based on carbonic acid (polycarbonates). Non-fluorinated polycarbonates have found application for the production of fibres, films, etc. There have been few studies of fluorinated polycarbonates. Aliphatic fluorine-containing polycarbonates were made from octafluorohexane-1,6-diol and octafluorohexamethylenebis(chloroformate) in the presence of an acceptor of hydrogen chloride[144]. This polycarbonate has a lower melting point than its non-fluorinated analogue, but it is 7−8 times more resistant to heating and hydrolyses somewhat more slowly in acid medium than the same non-fluorinated polycarbonate. Mixed polycarbonates of hexafluoropentane-1,5-diol and 2,2-bis-(*p*-hydroxyphenyl)-propane exhibit high chemical stability, good dielectric and water-repellant properties, and low coefficients of friction[145]. Polycarbonates from fluorinated aromatic bisphenols are obtained by interfacial polycondensation. Some improvement in the physicochemical characteristics of polycarbonate can be brought about by the introduction of individual fluorine atoms into the aromatic nuclei of the

Table 1. Thermal characteristics of fluorine-containing polyesters.

Structural unit of the polyester	T_{decomp}, °C	T, start of decompn. in nitrogen, °C	T for 20% weight loss in nitrogen, °C	References
	350	397	462	135
	261.350	438	512	134, 135, 136
	290.310	446	482	134, 135, 137
	260.300	—	—	134, 137
	240.290	—	—	134, 137
	280.300	424	484	135
	300	—	—	138
	280	424	484	135
	320	—	—	139
	400	—	—	139
	120	—	—	134
	80	—	—	134
	340	458	484	135

bisphenol. For example, the replacement of hydrogen atoms by fluorine in the *ortho*-position to the hydroxyl group of 2,2-bis(*p*-hydroxyphenyl)propane improves its Vik heat resistance from 164–166° to 170–175°C, and appreciably increases its volume resistivity in comparison with its non-fluorinated analogue[146,147]. However, the mechanical characteristics of the polymers and their melting points are almost unchanged, although the flame resistance of the fluorinated polycarbonates is improved.

The melting point of a polycarbonate can be raised considerably by substituting fluorine for the hydrogens of the methyl groups in the bisphenol molecule. The polycarbonate based on 2,2-bis(*p*-hydroxyphenyl)-1,1,3,3-tetrafluoro-1,3-dichloropropane melts at 295–315°C [147], whereas the melting point of crystallites of its non-fluorinated analogue is 263°C [147]. Polycarbonates of this type are distinguished by increased heat resistance and low steam permeability.

B. Carbochain polyesters

Methods of preparation and certain physicochemical properties of fluorine-containing polyesters in which the ester grouping is found in the side-chain of the polymer will be considered in this section. Polyesters of this type are of great practical interest. The starting monomers for certain types of carbochain polyesters are now available on an industrial scale. Their polymerisation, further treatment, and vulcanisation is carried out by the usual equipment of the synthetic rubber industry. Oil- and petrol-resistant rubbers with good frost resistance are processed on an industrial scale.

1. Polymers and copolymers of acrylic and methacrylic acids. Non-fluorinated esters of acylic or methacryllic acids are readily polymerised with other vinyl monomers in the presence of initiators of free-radical type. Esters of fluorinated acrylic acid polymerise badly under these conditions. Yakubovich and coworkers[148] explain such a sudden decrease in the activity of these monomers by the presence of a double bond conjugated with a carbonyl group in molecules of the type $CF_2=CF-COOR$, which leads to the formation of radicals of low activity and hinders the homopolymerisation of these esters. In the presence of other non-fluorinated vinyl monomers the esters of perfluoroacrylic acid form copolymers with high molecular weights. The introduction of fluorine atoms into the methyl group of methacryllic acid has little effect on the reactivity of the monomers but somewhat reduces the decomposition temperature of these polymers in comparison with their non-fluorinated analogues[149].

There is great interest in polymers obtained from esters of acrylic acid and fluorinated alcohols. These monomers readily polymerise spontaneously[150] or in the presence of various initiators: the light of an incandescent lamp[151], benzoyl peroxide[150,152,153], the lauryl[150] or acetyl[150] radicals, azoisobutyronitrile[150], ultraviolet light[150,154], high-energy electrons[155], hydrogen peroxide[152], aqueous solutions of potassium[151,152,156,157] or sodium[151,158,159] persulphate in the presence of various emulsifiers. The polymerisation of 1,1-dihydroperfluoroalkyl acrylates can be effected blockwise, in solution, or in emulsion[160]. Emulsion polymerisation is the most convenient method of polymerisation of such monomers. The molecular weight of the homopolymers reaches 10 000 000. The low-temperature properties, and also their resistance to swelling, depend considerably on the structure of the monomers. The glass points of the fluorine-containing polyesters are higher than those of their non-fluorinated analogues. The glass points in the polyfluoroalkylacrylates depend on the number of difluoromethylene groups in the alcohol residue.

They fall gradually and reach a minimum for the polymer with an alcohol residue with 6 carbon atoms. The polymer with 8 carbon atoms in this residue is already crystalline. It is interesting to note that in the series of non-fluorinated acrylates crystallisation is observed only for those polymers, the alcohol residues of which consist of 14 or more carbon atoms[161]. Nothing has been published on the minimal glass point for non-fluorinated acrylates, but the values for the brittle points[162] suggest that it will be for the polymer with an alcohol residue with 8 carbon atoms. The segment length for 1,1-dihydroperfluorobutyl acrylate, polymerised in the presence of potassium persulphate, has been found to be 15 carbon atoms[163]. This exceeds the values for other elastomers (seven carbon atoms for polyisobutene, eleven for polystyrene), but could not be connected with the glass point.

The frost resistance of fluoroalkyl acrylates was increased by the introduction of an ether bond into the chain of the alcohol residue.[164,165] Side-radicals with an ether bond increase the flexibility of the polymeric chain, playing the part of a plasticiser.

The resistance of these polymers to swelling in organic solvents also depends on the number of fluorine atoms in the alcohol residue and is rather high for a large degree of fluorination of the latter.

The most valuable polymers are those from 1,1-dihydroperfluorobutyl acrylate which have been named 1F4, or polyFBA [166-168], and the polymers from 3-(perfluoromethoxy)-1,1,-dihydroperfluoropropyl acrylate, called 1F2. These polymers were vulcanised by all the methods used for the vulcanisation of polyester rubbers. When the salts, oxides, or hydroxides of bivalent metals are used as vulcanising agent, these polyesters acquire increased mechanical strength. The use of magnesium oxide has maximal effect. In the vulcanisation of fluoroacrylate polyesters by polyamines[165,169,170] the vulcanisate acquires a resistance to the action of high temperatures, mineral acids, and oxygen. The vulcanisation of polyesters by the above agents evidently proceeds by the formation of salt bridges between the carboxyl groups which appear as a result of the hydrolysis of ester groups, and by bivalent metals owing to the formation of amide bridges. Strongly alkaline agents, for example, sodium silicate[165,169], can bring about ester condensation, which also leads to cross-linking of the macro-chain of the polyester.

Certain properties of 1F4 and 1F2 resins are given in Table 2.

Fluorinated rubber of grade 1F4 exhibits high resistance to the action of organic solvents of various classes (aliphatic and aromatic hydrocarbons, chlorinated hydrocarbons, ketones, etc.) which allows them to be used in the chemical industry[171] as coatings, and as liquids in aeroplane hydraulic systems[170]. They can be used at temperatures up to 200°C [168] in fuel and lubricant systems, that is, where copolymers of butadiene and acrylonitrile are unsuitable[166]. 1F2 rubber, which has better frost resistance, can be used in the same branches of technology[172].

A large number of publications, mainly patent specifications, deal with the production of copolymers of 1,1-dihydroperfluoroalkyl acrylates with various vinyl monomers. To obtain copolymers with dienes, block copolymerisation is not very suitable since the polymerisation is complicated by a Diels–Alder condensation[173]. The latter can be avoided by carrying out the copolymerisation in emulsion and in the absence of oxygen. Copolymers with butadiene exhibit increased frost resistance[158,174] (glass point = −75°C), but tend to swell[167]. They are readily vulcanised by the agents listed above, and also by sulphur[151,165,169].

Methods of making copolymers of 1,1-dihydroperfluoroalkyl acrylates with ethyl acrylate[154,175], acrylamide[153], acrylonitrile[153,157], methacrylamide[152], ethylene[176], and trifluoroethyl vinyl ether[159]. The presence in the copolymer of fluorinated groupings confers noninflammibility on the polymer[177], and the joint presence of fluorine and chlorine allows the polymers also to be used as adhesives[178]. Copolymers with methacrylyl chloride are used for the chemical modification of wool[179] and copolymers with butadiene and acrylic acid have been proposed for use as regulators of the combustion of rocket fuel[180].

Elastomeric properties are also exhibited by copolymers of allyl esters of fluorine-containing acids[181]. Polyesters with branched fluorinated radicals[182] and also polyesters the alcohol residues of which contain ester[183], amide[184], or sulphamide[185] groups have been proposed for use for the protection of cloth or leather from the action of solvents, dyes, oil, etc.

Table 2. Properties of resins from polyesters 1F4 and 1F2.

Property	Resins from	
	1F4	1F2
Tensile strength, kgf cm^{-2}	84	70
Stress at 300% extension, kgf cm^{-2}	71	47
Relative elongation, %	360	400
Recoil elasticity	6	12
Frost resistance after Dzhimen, T_{10}, °C	−7	−30
Brittleness temp., °C	−13	−40
Swelling, %		
in benzene	17	15
in acetone	26	19
in 7 : 3 iso-octane : toluene mixture	91	64

Fluorine-containing polyacrylates or polymethacrylates exhibit good water-, oil-, and dirt-repelling properties[186]. The investigation of polymers with fluorinated radicals of various lengths showed that groupings in which the number of fluorinated carbon atoms is less than 5 do not give rise to an oil-repelling effect, whereas increasing the number of these atoms to 8 gives the polyesters superlative oil repellance[187]. On replacing even a single fluorine atom in the ω position by hydrogen, the oil repellence effect disappears completely and the surface tension rises sharply. Thus for polyacrylates with perfluoroalkyl substituents, in the composition of which there are eight carbon atoms[188], γ_S is ~11 dyn cm^{-1}, which is comparable with values of γ_S for perfluorohexan-1-oic acid (8.6 dyn cm^{-1}) and perfluoro-octan-1-oic acid (7.9 dyn cm^{-1}). In investigating copolymers of fluoroalkyl acrylates with non-fluorinated vinyl monomers γ_S increases in proportion to the number of the latter introduced[189]. If the second monomer contains fluorine atoms, then γ_S decreases. Evidently, lateral fluorinated substituents are orientated vertically (in relation to the polymer chain) and packed densely, like the packing in the molecular layers of perfluorocarboxylic acids. The capability for orientation and close packing in the surface layer depends on the length of the fluorinated parts of the chain and on the structure and dimensions of the side-chains as a whole.

The influence of the lateral fluorinated substituents on the formation of ordered (syndiotactic) structure was noted in the investigation of polymers, synthesised from esters of methacrylic acid and fluorinated monohydric alcohols[190]. Polymethacrylic acid obtained after the hydrolysis of such polyesters is found in syndiotactic form. The vinyl esters of fluorocarboxylic acids are readily polymerised by a radical mechanism, and the poly(vinyl alcohol) obtained as a result of hydrolysis contains ~80% syndiotactic diads[190-193].

The value of γ_S is somewhat increased on replacing a linear fluorinated radical by a branched one[194] in those instances when the latter is separated from the chain by several methylene groups but the oil-repelling properties of the polymer disappear[195]. When the branched radical is directly connected with acrylic acid, the γ_S is less[196]. Such polyesters have been suggested for use to give wool oil- and water-repelling properties[197].

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