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Perfluorinated carbon-chain copolymers with functional groups and cation exchange membranes based on them: synthesis, structure and properties

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ABSTRACT. The review is devoted to perfluorinated polymers with sulphonic and carboxylic acid groups and to cation exchange membranes based on them. The synthesis is described of copolymers of tetrafluoroethylene with perfluorovinyl ethers containing functional groups by radical copolymerisation in an organic medium and in aqueous emulsions. Special features of the copolymerisation and approaches to obtaining copolymers with set characteristics are discussed. Data are presented on the structure and physicochemical properties of the polymeric films. Attempts to form membranes from the polymers obtained, the means of strengthening them and methods for chemical modification are described. Data are correlated on the influence of structure and polymer composition and the nature of the functional groups on the electrochemical characteristics of membranes. Special features of the functioning of perfluorinated membranes in the process for making chlorine and alkali by the electrolysis of sodium chloride solution are considered.

The bibliography has 104 references.

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I. Introduction

Perfluorinated carbon-chain polymers occupy an important place in the wide range of carbon chain polymers. The presence of fluorine atoms in the main chain causes unique chemical stability and high thermal sturdiness for materials prepared from these polymers. The combination of such properties has aided wide application of perfluorinated polymers (PFP) [primarily polytetrafluoroethylene and copolymers of tetrafluoroethylene (TFE)] in various areas of science and technology.[1]

The creation of ion exchange materials based on copolymers of TFE with perfluorovinyl ethers (PFVE) containing functional groups has extended the areas of application of PFP still more. With the aid of cation exchange membranes (CEM) prepared from PFP a process has been established for obtaining alkali and chlorine by the electrolysis of concentrated aqueous solutions of sodium or potassium chloride (the so-called "chlorine–alkali" electrolysis) by membrane technology. This process has given the most powerful impulse to the development of cation exchange membranes from PFP, to the technology of preparing them, and also to the investigation of the structure and properties of such materials. The problem posed was therefore that of developing CEM with a high chemical stability and mechanical sturdiness, low electrical resistance and high selectivity.

The results of such developments are reflected in the large number of patents published in the seventies and eighties by several companies from the USA (Dupont) and Japan (Asahi Chemicals, Asahi Glass, etc.). The total energy consumption on obtaining chlorine and alkali in an electrolysis plant using CEM is 25–40% less than in traditional methods of electrolysis with mercury and diaphragms.[2] The replacement of mercury by membranes in plant is exceptionally important from the ecological point of view apart from anything else.

The use of perfluorinated CEM is not restricted solely to the chlorine–alkali electrolysis process. They are used in a whole range of electrochemical processes[3,4] and their sphere of application is widening precipitately.

The correlation of information enabling a linking of the special features of membrane function in various processes with the structure and properties of the polymers from which they were prepared and with the conditions of forming and modifying films of these polymers, will stimulate further development of new polymers and membranes and will enable the limits of their application in practice to be extended.

II. Synthesis and macromolecular characteristics of copolymers with functional groups

The creation of CEM both for chlorine–alkali electrolysis and for other processes is a complex problem. It comprises a series of necessary and inseparably linked steps. The first is the synthesis of suitable perfluorinated monomers with functional groups, the second is the development of conditions for the copolymerisation of TFE with these monomers, the third is the obtaining of membranes from the prepared polymers, including stages of making the films, strengthening them and modifying them chemically.

1. Selection of monomers

The synthesis of monomers for obtaining PFP with ion exchange groups is a vast self-contained area of organofluorine chemistry in which intensive investigations are being conducted continuously. Several tens of monomers have been patented but only a few of them are used in practice.

PFVE of the following general formula are used as monomers with functional groups and are copolymerised with TFE:

$$CF_2=CF-O-(CF_2-\underset{\displaystyle CF_3}{\underset{|}{CF}}-O)_m-(CF_2)_n-X$$

(A)

where usually m = 0 to 2, n = 1 to 4, X is SO_2F, SCH_2H_5, $COOCH_3$. The group X then changes to the ionic form SO_3^- or COO^- in the obtained copolymers.

The first PFVE of the indicated type was perfluoro-(4-methyl-3,6-dioxa-7-octene)sulphonyl fluoride (I):

$$CF_2=CF-O-CF_2-\underset{\displaystyle CF_3}{\underset{|}{CF}}-O-CF_2-CF_2-SO_2F$$

(I)

The sulphonic cation exchange membrane 'Nafion' was made based on its copolymers with TFE. Monomers developed later have also acquired great practical importance, e.g. methyl perfluoro-(5-oxa-6-hepten)oate (II),

$$CF_2=CF-O-CF_2-CF_2-CF_2-COOCH_3,$$

(II)

methyl perfluoro-(6-methyl-5,8-dioxa-9-decen)oate (III)

$$CF_2=CF-O-CF_2-\underset{\displaystyle CF_3}{\underset{|}{CF}}-O-CF_2-CF_2-CF_2-COOCH_3$$

(III)

perfluoro-(4-oxa-5-hexene)sulphonyl fluoride (IV)

$$CF_2=CF-O-CF_2-CF_2-CF_2-SO_2F,$$

(IV)

and perfluoro-(5-methyl-4,7-dioxa-8-nonene)sulphonyl fluoride (V):

$$CF_2=CF-O-CF_2-\underset{\displaystyle CF_3}{\underset{|}{CF}}-O-CF_2-CF_2-CF_2-SO_2F$$

(V)

The routes of synthesis of the main monomers have been published.[5]

In addition to those listed PFVE containing two carboxyl groups,[6] and perfluoroallyl ethers with functional groups[7] have been proposed in the patent literature. Several other monomers described in patents do not introduce any changes in principle into the composition and structure of the ion exchange materials based on them compared with polymers synthesised from compounds (I)–(V) and differ only in method of synthesis. For example it has been proposed to use PFVE for the synthesis of ion exchange materials which have formula (A) where X is a ketone of structure $-C(O)-CF_3$ or $-C(O)-CH_3$ [8] or X is ω-hydroperfluoropropylvinyl ether $CF_2=CF-O-CF_2-CF_2-CF_2H$.[9] The side groups of the units of these monomers were oxidised to carboxyl groups in the copolymers obtained with TFE.

The preparation of PFVE containing ionogenic groups for phosphonic acids has been described.[10] However the complexity of synthesising such monomers precludes discussion of their practical application at present. Finally PFVE have been patented[11] differing in the replacement of the CF_3 group in them by CF_2Cl which affords additional possibilities for modifying the obtained PFP.

As a third comonomer the use of PFVE containing no functional groups, e.g. $CF_2=CF-O-CF_2-CF_2-CF_2-CF_3$, has been recommended in the copolymerisation of functional PFVE with TFE. Their introduction improves the physico-mechanical properties of films.[12–14] The possibility of using ethylene or other olefins as a third comonomer has been mentioned.[15]

The method of strengthening the polymeric material of membranes by cross-linking by introducing perfluorinated compounds with two vinyl groups as comonomer with PFVE at the polymerisation stage has been discussed in many patents.[13,16–18] However this method has not been used in practice probably because of the difficulty of forming films from the cross-linked polymers and also because of the poor availability of monomers of that kind.

2. Special features of the radical copolymerisation of vinyl ethers with tetrafluoroethylene

Copolymers of PFVE and TFE are obtained by radical copolymerisation. Vinyl ethers, particularly when perfluorinated, have an extremely low reactivity on copolymerisation with TFE. The shape of the curve describing the dependence of copolymer composition on the composition of the monomeric mixture (Fig. 1) indicates that on copolymerisation (II) and (III) require to be in considerable excess in relation to TFE in order to obtain polymers with an appreciable content of PFVE units. The curves for the dependence of polymer composition on the composition of the monomer mixture when copolymerising TFE with PFVE (IV) or (V) have a similar shape.[20] The copolymerisation constants calculated by the Fineman–Ross method for ethers (II) and (III) were 0.14 and for TFE 7.0.[19] Close values for the copolymerisation constants were also obtained for sulphonyl fluoride monomer (V) and TFE, 0.08 and 8.0 respectively.[5] Calculation of the parameters of the Alfrey–Price equation gave values of Q (a parameter proportional to the degree of double bond conjugation with substituents) and of e (a parameter reflecting the excess charge of the monomer caused by the polarising influence of the substituents) for carboxyl-containing PFVE equal to 0.0057 and 1.08 while values for Q and e for TFE were 0.089 and 1.22 respectively.[21] Such appreciable differences in the size of parameter Q, i.e. in the activity of TFE and ether,

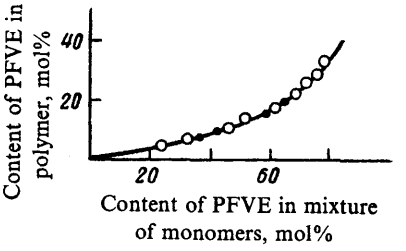


Figure 1. Dependence of copolymer composition on the composition of the mixture of monomers in the copolymerisation of PFVE (II) or (III) with TFE alone at 70 °C.[19]
○ Experimental data for PFVE (II), ● ditto for PFVE (III).

significantly complicate the synthetic process for copolymers of a given composition and demand careful observation of the experimental conditions, particularly the maintenance of a precise concentration ratio between the comonomers during the whole experiment.

Another special feature of the process of copolymerising PFVE with TFE, which is essentially reflected in the molecular weight (MW) and molecular weight distribution (MWD) of the obtained polymers, is linked with a fragmentation reaction of the radical of the terminal unit of a monomer ether:

$$\sim CF_2-\dot{C}F \longrightarrow \sim CF_2-\underset{\displaystyle O}{\overset{\displaystyle \|}{C}}-F + R_f-\dot{C}F_2 .$$
$$\quad\quad\quad

pressure limit indicated in patents is 0.7 MPa but mostly copolymerisation in an emulsion is carried out at a TFE pressure of 1.4–2.0 MPa.[17]

The most important advantage of emulsion copolymerisation over polymerisation in an organic medium is the possibility of conducting the process up to a high conversion of the ether monomer. At conversions above 45% polymerisation at constant TFE pressure does not provide consistency of composition for the obtained polymer. This consistency may be achieved only in a regime of an automatically regulated reduction in TFE pressure according to the reduction in PFVE concentration.[21]

It should be noted that the emulsion polymerisation process makes it possible to obtain copolymers with a higher MW and provides a better reproducibility of results compared with polymerisation in non-aqueous medium. However it presents exceptionally high requirements both in precision of maintaining technological parameters and in the purity of all components.

One of the requirements is the maintenance of the necessary pH value of the aqueous phase since the extent of hydrolysis of the ester groups on the functionalised monomer depends on it (Fig. 2). The appearance of carboxyl groups in the polymer as a result of hydrolysis leads to an abrupt worsening of its reprocessability by reason of an appreciable increase in pour point due to generated hydrogen bonds. Carboxyl groups may also be formed on hydrolysis of the terminal acyl fluoride groups resulting from rearrangement of the ether monomer radical as a result of the fragmentation reaction (1). Consequently, before reprocessing, copolymers obtained by the emulsion method are treated with methanol[28] with the aim of re-esterifying carboxyl groups.

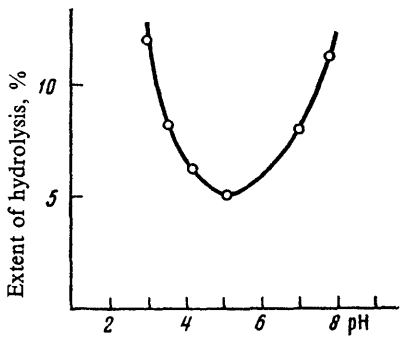


Figure 2. Influence of aqueous phase pH on the extent of hydrolysis of monomer (II) ester groups during emulsion copolymerisation.[21]

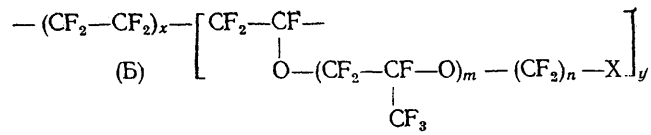
The regulation of copolymer MW is achieved by introducing aliphatic hydrocarbons or alcohols into the medium,[18] i.e. by methods traditional for obtaining fluoropolymers. Agents for chain transmission reduce the contribution of the fragmentation (1) of the growing radical. Stable hydride groups, viz.-CF_2H, are formed in place of terminal acid fluoride groups.[1]

On isolating the polymer obtained by emulsion polymerisation quantitative extraction of unreacted PFVE with freon CF_3CCl_3 from the latex has been proposed[21] followed by purification by distillation with addition of agents preventing thermal polymerisation. Treatment of the latex with freon has a second purpose, viz. removal from the copolymer of its lowest molecular portion.[29]

The emulsion copolymerisation of TFE and sulphonyl fluoride monomers has been patented very recently.[30–33]

5. Copolymer composition

The composition of copolymers used as materials for making perfluorinated CEM is expressed by the following formula:



where x and y are the molar fractions of TFE and PFVE units respectively. Due to the low reactivity of functionalised PFVE, units of it are distributed statistically in the copolymer on polymerisation and do not form blocks.

The ratio of TFE and PFVE units determines the whole complex of physicochemical, mechanical and electrochemical properties of the membranes prepared from the obtained copolymers. The molar proportion of the units of functionalised monomer in the copolymer may be varied over extremely wide limits from 5 to 30 mol.%.[18] The optimum content of PFVE with ionogenic groups in copolymers was from 8 to 15 mol.%. At a lower content membranes have high electrical resistance and low ion exchange capability. The preparation of films of such copolymers is difficult due to the high reprocessing temperature. Films of copolymers with a content of PFVE units bearing ion exchange groups greater than 20% swell excessively in solutions of electrolytes.

The homogeneity of macromolecules of the obtained copolymer is important. The content of ionogenic units in a copolymer must not deviate more than 0.3 mol.% in either direction for reproducibility of the electrochemical characteristics of membranes obtained from various batches of copolymer.[21]

If a non-ionogenic perfluoroalkylvinyl ether is introduced into the copolymer its molar proportion comprises from 2 to 20%.[18] It was shown in the same study that the molar ratio of units of ethylene or other olefin to TFE may be varied from 1:9 to 6:4.[18]

The terms "equivalent weight" (EW) and "exchange capacity" (EC) are used for the characterisation of the composition of copolymers of TFE and PFVE with ion exchange groups. The equivalent weight is the molecular weight of polymer corresponding to one ion exchange group and the exchange capacity is the quantity of milligram-equivalents of ion exchange groups contained in 1 g dry polymer. The exchange capacity of a copolymer is greater the greater the molar portion of monomer with ion exchange groups in it, and at equal molar proportions of such units the EC grows with the reduction in MW of the functionalised monomer. The equivalent weight and exchange capacity are inversely proportional, EC = 100/EW. The values of EW lie as a rule in the range 500–2000 and of EC 0.5–2.0 mg-eq/g.

6. Molecular weight and molecular weight distribution of copolymers

There are practically no data in the literature concerning the macromolecular characteristics of copolymers of the described type which is due, firstly, to the considerable methodological difficulties in determining them and secondly to the fact that not all the scientific results obtained in the industrial laboratories of companies are reflected in publications.[12]

Methodological difficulties are caused by the difficulty of obtaining solutions of copolymers which are suitable for MW determinations. Some results of MW determinations have been reported.[21] According to the report MW values of copolymers of (II) with TFE lie within the limits 10^5-10^6, however these data also were obtained by an indirect route. The copolymer of TFE with (II) is insoluble in accessible solvents but the copolymer of TFE with $CF_2=CF-O-(CF_2)_3-COOC_{10}H_{24}$ is soluble in chlorobenzotrifluoride. The MW of the copolymer containing decyl groups may therefore be measured by osmometry. The values of copolymer MW obtained in this way were extrapolated to the copolymer of (II) with TFE which was synthesised under analogous conditions and used in membrane preparation.

As a result of the difficulty of determining MW directly for copolymers of PFVE with TFE the size of T_Q, linked with the melt viscosity, was introduced for assessing practically the MW of carboxyl-containing copolymers.[16] T_Q is the temperature at which the polymer melt flows at a rate of 100 mm^3/sec through a nozzle of diameter 1 mm and length 2 mm at a pressure of 3.0 MPa. A linear relationship was established between T_Q and log MW of the copolymer determined by the indirect method indicated above (Fig. 3). For polymers used for obtaining cation exchange membranes T_Q lies within the limits 180–300 °C.[17] Polymers with a lower T_Q, i.e. with a lower MW, do not give films with a sufficiently high mechanical strength and polymers with higher T_Q values are difficult to reprocess.

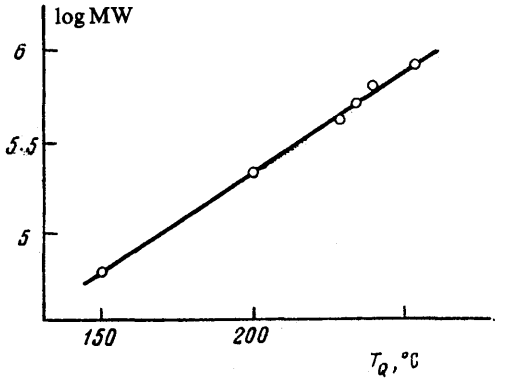


Figure 3. Relationship between T_Q of copolymers of (II) with TFE and their MW.[21]

There are no literature data on the MW of copolymers with sulphonyl fluoride or sulphide groups. It transpired that copolymers used for preparing membranes must possess high MW.[5,12] The required order of MW has been assessed[27] at the same value as in the case of carboxyl-containing polymers, i.e. 10^5-10^6.

There is even less information on the MWD of ion exchange PFP although this parameter may influence in a significant way the physico-mechanical and electrochemical properties of the membranes obtained from them. There are only hints that the synthesised PFP must have a narrow MWD. One of the purposes of MW regulators is to reduce the polydispersity of macromolecules.[18] The extraction of a copolymer with boiling freons under pressure enables removal of low molecular fractions and a narrowing of the MWD of a sample which improves the technological characteristics of the obtained membranes.[29]

III. Physicochemical properties of copolymers

The structure, physicochemical and electrochemical properties of perfluorinated CEM with sulphonyl groups based on copolymers of (I) with TFE (Nafion) have been investigated to a much greater extent than have the properties of other copolymers with carboxyl and sulphonyl groups developed later. The results of investigations of physicochemical properties of copolymers have been correlated.[34] Crystallinity, physico-mechanical properties and hydrophilicity exert an appreciable influence on the operating characteristics of CEM.

1. Crystallinity

The methods of investigating the supramolecular structure of the CEM Nafion (low-angle scattering of X-radiation and neutrons, IR spectroscopy, NMR) and the data obtained have been discussed.[35] A study has been devoted to the application of the X-ray diffraction method to the investigation of the structure of perfluorinated CEM with sulphonyl and carboxyl groups based on copolymers of TFE with (I).[36] Comparison of the results obtained for copolymers as sulphonic acids and for the same polymers in which the terminal $-CF_2SO_3H$ groups have been converted into carboxyl groups (Table 2) show that firstly the copolymers with sulphonyl groups with the same content of functionalised monomer units and identical length of side chain carrying the ion exchange group have a lower crystallinity than carboxyl containing copolymers. This may be linked with the stronger electrostatic repulsion of the sulphonyl groups characterised by a lower pK_a compared to carboxyl groups.[21] Secondly the degree of crystallinity of a copolymer falls with an increase in the content of PFVE units.

Table 2. Extent of crystallinity of copolymers of (I) and TFE as a function of their composition and type of ion exchange group.[36]

Composition		Extent of crystallinity (%) of copolymers with groups	
EW	(I), mol%	$-CF_2SO_3H$	$-COOH$
1100	13.3	12	18
1150	12.5	—	20
1200	11.7	19	23
1400	9.5	20	27
1500	8.7	22	28

Data on large-angle X-ray diffraction for copolymers of (II) with TFE also show a reduction in the degree of crystallinity with an increase in the proportion of ether monomer units.[37] Copolymers containing more than 20 mol.% monomer (II) are almost completely amorphous.

Crystallinity falls on hydrolysis of the nonionic ($-CF_2SO_2F$ or $-COOCH_3$) to the ionic form of the functional groups. The copolymers of (II) or (III) with TFE have a higher crystallinity as methyl esters than as sodium salts (Fig. 4).

Data on large-angle X-ray diffraction permit the conclusion that the crystal lattice of PFP with functional groups is, in essence, a crystal lattice of polytetrafluoroethylene with large disturbances of packing and is built of consecutive TFE units in the chains of the macromolecules.[21,38] This confirms the dependence of the degree of

crystallinity of copolymers on the proportion of TFE units in them recorded above. As analysis showed,[39] the copolymers are characterised at room temperature by larger intermolecular distances in the crystalline phase than polytetrafluoroethylene. It has been established[40] that these distances are reduced on increasing the EW of the copolymer, i.e. on reducing the PFVE portion, to a value close to 0.566 nm which is characteristic of the crystal lattice of polytetrafluoroethylene at room temperature.

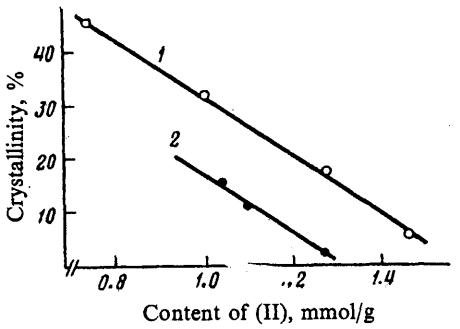


Figure 4. Relationship of crystallinity of copolymers of (II) with TFE on PFVE (II) content.[21]
1, Copolymers with $COOCH_3$ groups; *2*, copolymers with COONa groups.

Attempts to construct a model of the submicro structure of perfluorinated CEM based on the various experimental data, primarily on low-angle X-ray diffraction data, have arisen in the work of Gierke.[41] He has proposed a so-called cluster-channel model according to which hydrated ionogenic groups and counter ions form fairly voluminous (~5 nm in size) associates ("clusters"). Separate hydrated functional groups, forming "ion channels", participate in the transfer of ions and water molecules between such associates. This model has been developed subsequently.[42–44]

An alternative model of the submicro structure of perfluorinated CEM is based on representations of the comb-shaped structure of the copolymers comprising them.[45]

It was shown[46] that the structure of the sulphocation exchange membranes based on copolymers of (I) with TFE does not depend on the presence of low molecular polymer fractions. The latter are concentrated in the amorphous portion of the matrix from where they may be extracted with solvent (freon).

2. Physico-mechanical properties

The physico-mechanical properties of copolymers (viscosity, strength, elasticity) influence in an appreciable way both the processes of forming membranes based on them and on the operating characteristics of membranes.

The dependence of melting point of copolymers of (I) with TFE on content of TFE units proved to be linear (Fig. 5). Extrapolation of the line to 100% TFE content gave a value close to 326 °C, the melting point of polytetrafluoroethylene.

The viscosity of polymers is extremely sensitive to the presence of intermolecular bonds. The appearance in PFP molecules of carboxyl groups able to form hydrogen bonds sharply increases the temperature required for reprocessing and the melting point of such polymers becomes greater than their decomposition points.[21]

Physico-mechanical properties and their link with the supramolecular structure of polymers serving as material for Nafion membranes have been studied in detail.[47] Films of perfluorinated carboxyl-containing copolymers possess several better mechanical properties in comparison with the corresponding copolymers containing sulphonyl groups (Table 3).

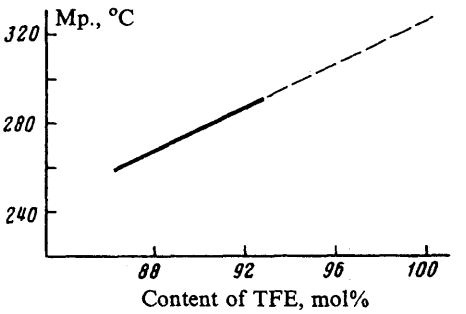


Figure 5. Relationship of melting point (Mp) of copolymers of (I) with TFE to TFE content according to differential scanning calorimetry data.[40]

Table 3. Mechanical properties of films of copolymers of (I) and TFE as a function of the type of ion exchange group.[5]

Property	Ion exchange group	
	$-CF_2SO_3H$	$-COOH$
Tensile strength, kg/cm²	224	236
Specific elongation at break, %	155	253
Modulus of tensile strength, kg/cm²	791	1560

Footnote. Ion exchange capacity of copolymer was 0.03 mg-eq/g, content of monomer (I) units was 0.3 mol.%. Measurements were conducted in aqueous medium at 25 °C.

The high mechanical properties of non-crosslinked perfluorinated copolymers are determined by the crystallites which are formed from sequences of TFE units belonging to different macromolecules. Such crystals with a characteristic spacing ~10 nm provide physical reinforcement to the perfluorinated matrix.[45] In this way the values of the intermolecular distances existing in the crystal at room temperature are achieved in crystals of pure polytetrafluoroethylene at enhanced temperature (200–220 °C).[48] The presence of ionic groups impedes a tighter packing of the indicated fragments in the copolymers. A third monomer, a non-ionogenic perfluoroalkylvinyl ether such as $CF_2 = CFO(CF_2)_3CF_3$, is introduced into the copolymers to reduce the wedging influence on crystals.[49] The relatively long perfluorinated radical in this comonomer causes

buffer zones containing ionogenic groups to form between the crystal and amorphous portions which improves the mechanical properties of membranes.

The form of the functional group proves to have a strong influence on the mechanical properties of functionalised PFP. Thus the strength of carboxyl-containing copolymers as sodium salts is greater than as methyl esters and this difference is increased significantly with an increase in temperature (Table 4). It is seen in Fig. 6, where the specific elongation at fixed tension is shown for these polymers, that at identical load the extension of films of copolymers with terminal $-COOCH_3$ groups is substantially greater than for films of copolymers having $-COONa$ as terminal groups.

Table 4. Tensile strength of films of copolymer of (II) and TFE in relation to temperature and the form of the functional groups.[37]

Temperature, °C	Tensile strength, kg/cm²	
	–COONa	$-COOCH_3$
25	320	250
50	250	40
90	230	7

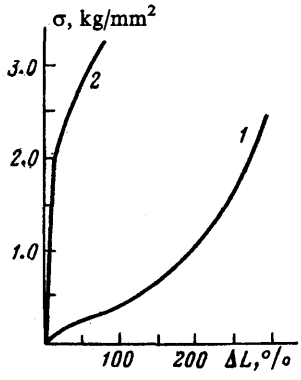


Figure 6. Relationship of stress (σ) and specific elongation (ΔL) for copolymers of TFE with (II) in the form of its *1*, methyl ester and *2*, sodium salt.[37]

Mechanical relaxation spectra permitting determination of phase transition temperatures have been studied for copolymers of (I) with TFE[47] and for copolymers of (II) and (III) with TFE.[50] The glass point of copolymers also depends primarily on the form of the functional group. It is increased substantially on going from copolymers with $-COOMe$ groups to copolymers with $-COOH$ groups and especially with $-COONa$ groups. The glass point falls with increasing content of the number of PFVE units in the copolymer. Thus copolymers of (II) with TFE with $-COOMe$ groups for which EC = 1.25 mg-eq/g has a glass point of 30–35 °C and the same copolymers with EC = 1.80 mg-eq/g only 14–21 °C. These same copolymers with COOH groups have glass points close to 70 °C and its reduction with growth of EC is less significant in this case.

3. Hydration of perfluoropolymers with ion exchange groups

The functional properties of perfluorinated CEM during chlorine–alkali electrolysis are determined to a significant degree by the amount of water absorbed by the membrane since the latter proved to be decisive in the selectivity of the CEM. In the case of a high degree of hydration a reversible migration of hydroxyl ions from the catholyte to the anolyte may occur together with transfer of sodium ions through the hydrated ion channels of the membrane. Water molecules are grouped in the membrane in amorphous regions near ionogenic groups so that the process of water molecule aggregation is determined by the types of ionogenic groups and counter ions (cations) and their interaction (Table 5). In this way the hydrophobic matrix also proves to influence the state of the water molecules in the membrane. IR spectroscopic data make it possible to draw conclusions about the presence of water molecules in perfluorinated CEM which enter hydrate coatings of ions ("bound water") and that found between them ("free water").[38]

The dependence of membrane water content on the type of ionogenic group has paramount importance. Since the electrical polarisability of the COO^- group is greater and of the SO_3^- less than that of a water molecule, COO^- anions (in contrast to SO_3^-) are able to displace water from the hydrated environment of cations.[51] As a result carboxyl containing perfluorinated CEM absorb a substantially lower quantity of water than do sulphonic cation exchange resins (Table 6).

Table 5. Equilibrium water content in copolymers of (I) and TFE with exchange capacity of 1100 for various forms of ion exchange groups.[36]

Ion exchange group	Water content	
	as% polymer dry weight	as number of molecules per ion exchange group
$-CF_2SO_3H$	32	19.6
$-CF_2SO_3Na$	27	16.9
$-CF_2SO_3Cs$	13	8.9
$-CF_2SO_3NHR$	3	2.0
$-COOH$	6	3.6

Table 6. Equilibrium water content in copolymers of (I) and TFE as a function of their composition and type of ion exchange group.[36]

Composition		Water content			
EW	(I), mol%	% polymer dry weight		number of molecules per ion exchange group	
		$-CF_2SO_3H$	–COOH	$-CF_2SO_3H$	–COOH
1100	13.3	32	6	19.6	3.6
1150	12.5	23	5	14.7	3.1
1200	11.7	20	4	13.3	2.6
1400	9.5	10	3	7.8	2.3
1500	8.7	8	4	6.7	3.0

The reduction in hydrophilicity of copolymers with increase in their EW is linked with the increase in content of hydrophobic TFE units participating in the establishment of the crystal structure.[5,36]

It is seen from Table 5 that sulphonamide groups formed on treating sulphonic cation exchange membranes with amines have a substantially lower degree of hydration (10-fold in comparison with the initial $-CF_2SO_3H$).

A reduction of the length of the side group in PFVE lowers the hydrophilicity of its copolymers with TFE.[52] Therefore copolymers of TFE and $CF_2 = CFOCF_2CF_2SO_2F$ with an EW 800–1300 in the $-CF_2SO_3H$ form contain from 11 to 18 water molecules per ion exchange group in the swollen state which is substantially less than for copolymers of TFE and (I).[53] Such a reduction in hydrophilicity causes a somewhat better selectivity of membranes in the electrolysis process. However copolymers containing $-OCF_2CF_2.SO_3H$ as side group have not been widely adopted due to the complexity of synthesis of the corresponding monomer and due to the occurrence of a cyclisation side reaction in the course of its copolymerisation with TFE.[54]

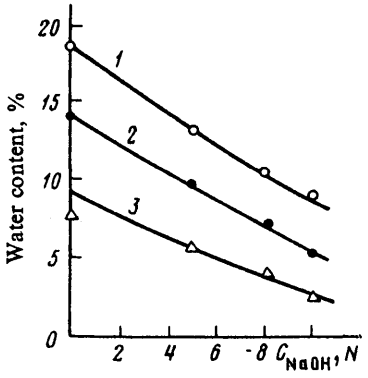


Figure 7. Water content of perfluorinated carboxyl-containing CEM based on modified copolymers of (I) and TFE with EW of: *1*, 1100; *2*, 1200; *3*, 1350 as a function of NaOH concentration.[5]

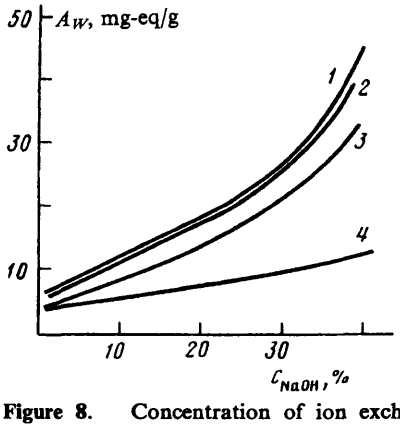


Figure 8. Concentration of ion exchange groups (in mg-eq per gram absorbed membrane water A_W) as a function of alkali concentration for copolymers of (II) and TFE with *1*, EC 1.23 mg-eq/g and *2*, EC 1.44 mg-eq/g, for copolymers of (III) and TFE with *3*, EC 1.21 mg-eq/g and for copolymers of (I) and TFE with *4*, EC 0.82 mg-eq/g.[37]

With an increase in alkali concentration the water content of the swollen polymer is reduced and this effect is strongly expressed for copolymers with a large EC (Fig. 7). Correspondingly with an increase in alkali concentration the effective concentration of ion exchange groups is increased (the mean distance between adjacent ion exchange groups is reduced) due to the reduction in membrane swelling and volume. This effect is displayed more strongly for carboxyl-containing membranes (Fig. 8).

4. Solutions and dispersions of copolymers

The problem of obtaining solutions of perfluorinated copolymers with functional groups is extremely important. Apart from the question of determining copolymer MW and MWD which was referred to above this problem has great value in applications. When solved it would be possible to form membranes by glazing from a solution. In addition the repair of membranes would be substantially simplified. Consequently much attention has been paid to the search for methods of dissolving perfluorinated copolymers. Publications have been devoted to the study of the solubility of copolymers of (I) with TFE and of the swelling of membranes based on these copolymers.[55,56]

Copolymers with CF_2SO_2F and $COOCH_3$ groups pass into solution with great difficulty. They dissolve successfully only in perhalogenated oligomers, perfluorinated kerosenes[57,58] and in perhalogenated compounds with polar groups, such as carboxyl and tertiary amino groups, at high temperatures of 170–220 °C.[58] On cooling these solutions the polymer separated in the form of a solid or gel. At room temperature stable solutions of such copolymers were obtained in saturated perhalogenated ethers simulating the structure of the ether unit of the polymeric chain.[59,60] However similar compounds are expensive and inaccessible.

Conversion of the functional groups ($COOCH_3$ or CH_2SO_2F) into the ionogenic form is alleviated by obtaining solutions of copolymers. Their ability to dissolve increases with an increasing content of ionogenic groups. Thus the hydrolysed copolymer of (I) and TFE containing 16 mol.% monomer (I) units (EW 970) dissolves in ethanol.[61] Copolymers of such type with EW 1100–1200 [11.7–13.3 mol.% of (I)] passed into solution on heating at 250 °C in water–alcohol mixtures under pressure.[61] After cooling to room temperature a 1% solution of copolymer was obtained. It was established that destruction of the polymer did not occur on solution under such forcing conditions. Concentrated (25% or more) solutions of carboxyl-containing copolymers with COOH groups were obtained at room temperature using a mixture of hydrophilic solvents (alcohols, glycols, acetone, methylpyrrolidone, etc.) with a small quantity of water (between 0.05 and 20%).[62] Polymers did not pass into solution in non-aqueous solvents nor on replacing COOH groups by CO_2Me.

Under certain conditions such as when making films, it is possible to use dispersions of polymers in hydrophilic solvents in place of solutions. A method of making such dispersions has been proposed and consists of replacing water in the emulsions obtained after polymerisation by a hydrophilic solvent.[63] Removal of water was effected either by centrifugation before introducing the solvent or after introducing solvent by freezing or by evaporation if the solvent used has a boiling point above that of water. Another method consists of treating the polymer with an aqueous alcoholic mixture at high temperature (180–300 °C) under pressure, the higher the water content in the mixture the higher must be the temperature.[64] The polymer concentration in the dispersion obtained in this way may amount to 2 to 18%.

IV. Membrane formation

The performance of perfluorinated CEM was established at each manufacturing stage including the step of making films from copolymers.

1. Single layer films

The making of films from perfluorinated copolymers is effected before conversion of their functional groups into an ionogenic form since otherwise the temperature required for processing is substantially increased and may reach the decomposition point of the polymer. Preparation of the films is effected by methods traditional for polyfluoroethylene resins. Extrusion at 180–220 °C, i.e. close to T_Q for carboxyl containing polymers, is usually used. Methods of hot pressing or rolling are rarely used.

The thickness of a membrane has almost no influence on its selectivity however to decrease resistance and the resultant energy losses it is desirable to reduce the thickness of a film. Here the mechanical strength proved to be the limiting factor.

The problem of mechanical strength is usually solved by introducing a reinforcing base into a film. Polytetrafluoroethylene fabric is used as such a base for reasons of chemical stability. The film thickness (usually 150–250 μm) must be sufficient such that the reinforcing fabric is encapsulated in the film without disturbing its integrity. The fabric is combined with the film by hot pressing. Such a reinforcement doubles the tensile strength of the membrane with a simultaneous 3- to 4-fold reduction in its ability to stretch (specific elongation at break).[65] Flakes of microporous polytetrafluoroethylene of thickness 13–75 μm and pore size 3–15 μm have been used in place of fabric.[66]

The presence of non-ion exchange strengthening material increases the electrical resistance of the membrane so that one of the problems is to reduce the volume fraction of such material in the membrane. The original method of reinforcing films was suggested in a patent.[67] The copolymer was mixed with a small amount (2–3%) of fibrilar polytetrafluoroethylene, extruded and the obtained film stretched, as a result of which the polytetrafluoroethylene forms an oriented structure confering high stability towards bending and punching to the membrane and the required mechanical strength.

The possibility of using chemical cross-linking for strengthening films has been indicated in several patents, however there are no data on the practical application of this method.

2. Multilayer membranes

The perfluorinated CEM used in the chlorine–alkali electrolysis process consist, as a rule, of two or more layers. There are three main methods of preparing multilayer films.

The first, the chemical modification of the surface layer of one prepared film, will be considered in detail in the next chapter. The second method is the lamination of two or several films. The advantage of the lamination method is that the layers of the ensuing membrane may be prepared separately and independently of one another and each of them may set desired characteristics. This explains the wide application of such a method. The disadvantage of laminated membranes is the risk of their separation during operation. Since one of the layers usually contains a copolymer with carboxyl groups and the other one with sulphonic acid groups, then to reduce the differences (in swelling ability for example) between these layers and to improve adhesion it is possible to introduce between them a layer of a mixture of such copolymers,[68] or to laminate films in one of which the sulphonate groups have been converted into carboxyls.[69] The problem of obtaining multilayer membranes stable towards separation remains, as before, a real one.

The third method of preparing multilayer films, viz. the application onto the surface of an initial film of a glazing from solution, has been used only recently in connection with the successful resolution of the problem of preparing sufficiently concentrated solutions of perfluorinated polymers with ionogenic groups. Thin layers of polymer, not exceeding 15–20 μm as a rule, are usually applied in this way.[68,70,71] Dispersions of polymers may be used in place of solutions, the methods of obtaining them have been discussed above. All three methods enumerated may be applied simultaneously for preparing multilayer membranes.[68]

The reinforcement of twin- or multilayer membranes is usually effected at the lamination stage, by packing the polyfluoroethylene between the two films. In membranes prepared without lamination the reinforcing material is introduced into the thickest layer by hot pressing.

With the aim of reducing the voltage in the electrolytic cell the distance between the electrodes and the membrane is minimised so that electrolysis occurs in the vicinity of the membrane surface. However at a distance of less than 1 mm between membrane and cathode it becomes difficult to remove bubbles of nascent hydrogen which have a tendency to stick to the membrane and lead to an increase in electrolysis voltage.[20] In order to prevent gas bubbles, primarily of hydrogen, sticking to the membrane on its cathode side, membranes for chlorine–alkali electrolysis have recently come to be prepared with rough surfaces. The beneficial effect of a rough membrane surface on the anode side on selectivity, because such a surface aids creation of a thicker diffusion layer, has been described.[72] Many methods of creating a rough surface on perfluorinated CEM have been patented.[15] Best results were given by incorporating fine particles of non-oxide ceramics, usually silicon carbide, into the surface layer on the cathode side and titanium dioxide or zirconium dioxide on the anode side.[68,73,74]

V. Chemical modification of membranes

The functional groups of the PFVE used are in the non-ionogenic form, viz. $-CF_2SO_2F$, $-CF_2SR$ or $-COOR$, at the stages of polymerisation and film formation. Conversion of them into an ionic form is usually brought about after membrane formation by hydrolysis with water or alcoholic alkali. The hydrolysis kinetics of copolymers with sulphonyl fluoride [copolymers of TFE with (I)][75] and with carboxyl groups [copolymers of TFE with $CF_2=CFO(CF_2)_5COOCH_3$][76] have been studied by IR spectroscopy. The energy of activation of the hydrolysis reaction has been determined and is 100 kJ mol^{-1} for copolymers with sulphonyl fluoride groups[75] and 105–140 kJ mol^{-1} for copolymers with carbomethoxy groups depending on the chemical nature of the alkali taken.[76] Moist morpholine was used in place of a solution of alkali for the hydrolysis of the copolymer of TFE with (I).[77] In this case the formation of sulphonamide groups simultaneously with hydrolysis was observed to a small extent.

Chemical modification of polymeric films is also as a rule effected in addition to hydrolysis. The aim of such modification is to enhance the selectivity of membranes by preventing migration of hydrated hydroxyl ions along hydrophilic channels of the membrane from the catholyte to the anolyte. This was sought by creating on the cathode side of the membrane a thin (~2–10 μm) surface barrier layer with a relatively small moisture content.

1. Copolymers with sulphonyl fluoride groups

The first method proposed for modifying membranes of copolymers of TFE with (I) was treatment of their surface (before or after hydrolysis) with ammonia[78] or primary amines.[79] In this the formation of relatively hydrophobic sulphonamide groups (see Table 5) occurs in the surface layer of the film of thickness usually ~10 μm, by the following reaction:

$$R_f—SO_2F + RNH_2 \rightarrow R_f—SO_2—NHR + HF,$$

or, for a polymer previously hydrolysed and converted into the sulphonic acid form,

$$R_f—SO_3H + RNH_2 \rightarrow R_f—SO_2—NHR + H_2O.$$

The use of di- and polyamines permits subsequent cross-linking of the polymer on heating to 100–200 °C by the reactions:

$$R_fSO_2F + NH_2—R—NH_2 \rightarrow R_fSO_2—NH—R—NH_3^+F^-,$$

$$2R_fSO_2NHRNH_3^+F \xrightarrow{\text{heat}} R_fSO_2NHRNHRNHSO_2R_f + HF + NH_4F,$$

$$R_fSO_2NHRNH_3^+F^- + R_fSO_2F \xrightarrow{\text{heat}} R_fSO_2NHRNHSO_2R_f + HF.$$

The formation of a cross-linked structure increases the strength of polymeric films. The course of the indicated reactions has been investigated in detail by IR spectroscopy.[82] The sulphonamide groups resulting from amination have pK_a 8–9 and are completely ionised at pH > 10. In the process of electrolysing a NaCl solution this condition is known to be fulfilled for the aminated layer in the vicinity of the surface facing the cathode. However in electrolysis it is necessary to acidify the anolyte with hydrochloric acid for complete neutralisation of the hydroxyl ions penetrating there. As a result of the proton currents generated in the membrane by this the amino groups in the depth of the aminated layer may appear with a lower effective pH value. The electrical resistance of the membrane then increases sharply. For this reason the use of aminated membranes in chlorine–alkali electrolysis prevents acidification of the anolyte and as a result the chlorine obtained contains no less than 2% oxygen from oxidation of hydroxyl ions at the anode.[5] In addition the sulphonamide groups proved to be insufficiently stable chemically on contact with concentrated alkali.

A method of converting sulphonic acid into carboxyl groups proved to be far more promising from the point of view of improving the electrochemical characteristics of perfluorinated CEM.[5,83] The reaction of sulphonamide groups with anion radicals, for which complexes of sodium with aromatic hydrocarbons such as naphthalene serve as sources, has been proposed for such conversions.[84] Under the action of anion-radicals decomposition of sulphonamide groups occurs with elimination of sulphur dioxide but the generated primary fluorinated amines are unstable and immediately dehydrofluorinate to nitriles which are then subjected to hydrolysis:

$$\sim CF_2SO_2NH_2 \xrightarrow{\text{anion-radicals}} [\sim CF_2NH_2] \rightarrow \sim CF_2N \xrightarrow{\text{hydrolysis}} \sim COOH.$$

This laborious method is however not used in practice.

Many other methods of converting sulphonyl fluoride groups of perfluorinated copolymers into carboxyls have since been patented.[5,83] The most widespread is chemical modification through a sulphinic acid as follows:

$$\sim CF_2SO_2F \underset{(a)}{\rightarrow} \sim CF_2SO_3H \underset{(b)}{\rightarrow} \sim CF_2SO_2Cl \underset{(c)}{\rightarrow} \sim CF_2SO_2H \underset{(d)}{\rightarrow} \sim COOH \qquad (3)$$

The first step [step (*a*)] is usually hydrolysis of the sulphonyl fluoride. Then the $-SO_3H$ group is converted into the relatively more reactive, in comparison with sulphonyl fluoride, sulphonyl chloride by treatment of the polymer with a solution of PCl_5 in $POCl_3$ under fairly forcing conditions (temperature > 110 °C, treatment time > 20 h) [step (*b*)].[85] Step (*c*) proceeds under the action of a reducing agent. Some groups of reducing agents have been proposed, viz. metal hydrides and borohydrides, atomic hydrogen, organometallic compounds, lower valency transition metal salts, etc.[86] The reaction stops at the formation of sulphinic acid when using a weak reducing agent. When using a strong reducing agent and forcing conditions step (*d*), carboxyl group formation, is also effected straight away. We point out that in this case also conversion occurs through the intermediate step of sulphinic acid. A small quantity of sulphinic acid groups is present in the modified polymer and is then oxidised to sulphonate groups with sodium hypochlorite or hydrogen peroxide.[85] The detailed mechanism for step (*d*), the splitting off of two fluorine atoms from the terminal carbon atom under the action of a reducing agent and the formation of a carboxyl group, remains as yet unclear.

A whole series of modifications of the presented scheme exists in which the separate steps may be combined or brought about. Thus the sulphonyl fluoride has been reduced directly to CF_2SO_2H groups with hydrazine, the copolymer with sulphinic acid groups was then subjected to oxidation with molecular oxygen catalysed by variable valency metal ions.

Conversion of sulphonyl chloride to carboxyl groups may be carried out using an oxidising agent and not a reducing agent thus avoiding the sulphinic acid step,[88] for example with molecular oxygen in alcohol medium at high temperature (110–150 °C). Oxidation under forcing conditions, such as with nitrogen oxides or oxygen with UV irradiation at 140–150 °C or a mixture of oxygen and fluorine, permits a one-step process for converting sulphonic acid to carboxyl groups.[88,89]

One further route to obtain carboxyl groups may be represented by the following scheme:[5]

$$\sim CF_2SO_2Cl \xrightarrow[-SO_2]{X_2} \sim CF_2X \xrightarrow{\text{UV + oxidising agent}} \sim COOH, \qquad (4)$$

where X is iodine or bromine. In all cases the mechanism of the final step, in which two fluorine atoms are split off and a carboxyl group is generated, is unclear.

The advantage of the method of modifying functional groups by scheme (3) with reduction of sulphonyl chloride through the step of forming sulphinic acid is its high selectivity.[5] The use of concentrated hydriodic acid in glacial acetic acid as a reducing agent provides a smooth reduction in the proportion of carboxyl groups from 100% to zero in the surface layer of the modified film with a gradient of less than 12% in 1 μm.[85] The gradual change in content across the thickness of the film effectively increases the stability of the membrane towards separation. The kinetics of the chemical modification by the indicated method have been investigated by IR spectroscopy and the energies of activation of the individual steps of the process have been determined.[90]

The chemical modification of copolymers with alkyl sulphide groups (in place of sulphonyl fluoride) is not different in principle. These groups are readily converted by chlorine and oxygen to sulphonyl chloride or may be oxidised directly to sulphinic or sulphonic acid groups.[27]

It should be noted that in the course of converting a sulphonyl fluoride to a carboxyl group a reduction of one occurs in the

sequence of CF_2 units between the ion exchange group and the ether oxygen in the PFVE fragment. Thus from a copolymer of (I) with TFE a polymeric material with $-OCF_2CO_2H$ groups is formed. It has been shown that when only one CF_2 unit is present between the ether oxygen and the carboxyl group stable operation of membranes over an extended period in chlorine–alkali electrolysis is not provided.[5] The reason for this is as yet unclear. It may be connected either with the chemical stability of the terminal groups or with special features of the physical structure of the polymeric material.[5] This has served as a stimulus for the development of new sulphonyl fluoride monomers, including (IV) and (V). After their industrial manufacture was effected, copolymers of (I) with TFE have ceased to be used in practice for obtaining carboxyl-containing ion exchange materials employed in chlorine–alkali electrolysis. At the present time these copolymers are used in chlorine–alkali electrolysis but mainly as sulphonic acids for other purposes.

2. Carboxyl-containing copolymers

Membranes of carboxyl-containing perfluorinated copolymers may be used without any preliminary chemical modification. A procedure for converting carboxyl groups of PFP into sulphonic acid groups has no practical application since the initial monomers with sulphonyl fluoride groups remain more accessible than those containing carboxyl groups.[90]

It is necessary to consider that the pK_a of carboxyl groups of polymeric perfluorocarboxylic acids is 1.9 and membranes of carboxyl-containing PFP may provide cation exchange only at a pH less than 3.[91] Therefore the possibility of adding hydrochloric acid to the anolyte is limited when using cation exchange membranes prepared only from carboxyl-containing polymers in the electrolysis of NaCl solution. Consequently in this case the chlorine obtained contains a certain amount of oxygen as when using membranes with sulphonamide groups. In addition chlorate ion accumulates in the anolyte and is extremely difficult to remove from the brine. Finally the evolution of oxygen at the anode reduces the life time of the latter. On the strength of the above mentioned factors monolayer membranes of carboxyl-containing copolymers are being superseded at the present time by multilayer membranes in which a layer of copolymer with sulphonyl groups possessing high acidity is facing towards the anode.

Polymeric perfluorocarboxylic acids are unstable towards the action of alkali of concentration above 40%.[16] The chemical mechanism of their decomposition under the action of alkali has not been described but it has been reported that sodium carbonate has been detected in the products of decomposition by concentrated sodium hydroxide and $-CF_2H$ groups are found in the polymer.[92] It has also been recorded that with a rise in temperature the alkali concentration sufficient for decomposition is reduced. This effect has been used for generating a surface layer, by short term treatment with concentrated NaOH solution, with a reduced concentration of carboxyl groups facing towards the cathode and consequently with a reduced moisture content. This may be carried out directly in the electrolyser.

3. Other procedures for chemical modification

A whole series of procedures for the chemical modification of perfluorinated CEM has been proposed in the patent literature. In some patents[13,93,94] it is recommended to impregnate membranes carrying sulphonyl groups on one side with carboxyl-containing monomers of various nature (carboxyl-containing dienes[93] or perfluoroacrylic acid[94]) in order to increase their selectivity. Polymerisation is then carried out afterwards. The proposed method[13] of copolymerising TFE simultaneously with other monomers carrying functional groups of a similar nature was ineffective since in this case a uniform material was obtained instead of a twin-layer membrane with a barrier layer.

Many attempts have been undertaken to use graft copolymerisation when obtaining and modifying perfluorinated CEM. The preparation of material for membranes by grafting monomers with ionogenic groups onto PFP, particularly polytetrafluoroethylene primarily by radiation grafting, is tempting in its simplicity. The grafting procedure has been patented.[95] However the most important disadvantage of this method is its non-selectivity. It was recorded[16] that copolymers prepared in this way did not possess the supramolecular structure which makes their use in membranes possible. Radiation grafting has been suggested for use only for modifying fabricated membranes. Thus the selectivity of perfluorinated sulphonic acid membranes is increased by grafting perfluorobutenoic acid on one side of their surface.

The introduction of the other halogens, chlorine, bromine and iodine into polymers as reactive groups in place of fluorine opens further possibilities for the chemical modification of membrane materials. They may be introduced, as indicated in Chapter II, at the monomer synthesis stage. However such a route is extremely laborious and furthermore the reactive groups may prove to have a negative influence on the polymerisation process, by playing a chain transfer role. Consequently it is expedient to carry out such chemical modifications on an already prepared polymer.

Thus a portion of the $-CF_2SO_2F$ groups in the copolymer (up to the stage of forming CH_2SO_2Cl groups) are replaced by $-CF_2I$ or $-CF_2Br$ and then initiation is carried out with peroxides grafting on carboxyl-containing monomers.[97] A similar result was desired when using the reaction of labile halogen atoms with radical initiators containing terminal carboxyl groups.[98] As a result the carboxyl-containing fragments of the initiator are linked with the polymer. Cross-linking of the polymer by the action of peroxide radical initiators at $-CF_2I$ and $-CF_2Br$ groups in place of grafting has been sought.[99] The preparation of a cross-linked structure in copolymers of (I) with TFE using di- and polyamines has been mentioned above.

All the methods enumerated in this section have not as yet been applied in practice to any extent.

VI. Electrochemical properties of membranes

The electrical resistance of membranes used in electrolysis processes must be as low as possible. The electrical conductivity of films and the quantity of water absorbed by them increase simultaneously with increasing content of ion exchange groups in the polymer but with growth in water content the selectivity of the membrane is reduced. The electrical conductivity and selectivity are in inverse relationship. Optimisation of these two parameters is the most important problem in the development of ion exchange membranes.

1. Film conductivity and composition

The dependence of the electrical conductivity of perfluorinated polymeric films on their composition is represented in Fig. 9. Films from carboxyl-containing copolymers have a lower electrical conductivity in comparison with films from copolymers with sulphonic acid groups at a given content of ion exchange groups in

the polymer. It is also evident that at constant EC some increase is observed in specific conductivity with increased comonomer molecular weight. This may be partially linked with the fall in copolymer crystallinity which shows up not only in the mechanical but also in the electrochemical properties of films.[12]

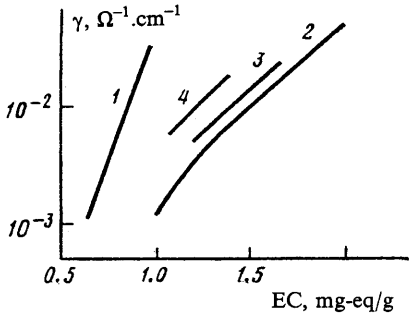


Figure 9. Dependence of electrical conductivity γ of polymeric films on their composition for copolymers of TFE *1*, with (I) in SO_3H form, *2*, with (II), *3*, with $CF_2 = CFO(CF_2)_4COOCH_3$ and *4*, with (III). Curves *2*–*4* in –COOH form.[37]

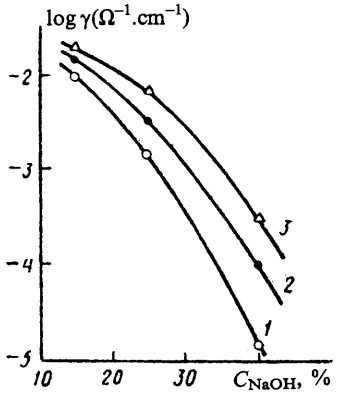


Figure 10. Dependence of electrical conductivity (γ) of carboxyl-containing membranes on NaOH concentration at temperatures of: *1*, 52; *2*, 72; *3*, 90 °C.[37]

The electrical conductivity of perfluorinated CEM depends markedly on the external conditions, viz. alkali concentration and temperature (Fig. 10). The activation energy for the transfer of Na^+ through a membrane of carboxyl-containing polymers at NaOH concentrations of 14, 25 and 40% were 16.4, 38.2 and 71.5 kJ/mol respectively.[37] Such an increase in activation energy with growth in alkali concentration is linked primarily with the reduction in membrane water content, mentioned in Chapter III, depending on the alkalinity of the medium as a result of which the diffusion coefficient of ions is sharply reduced.[38] The indicated effect supersedes the increase in electrical conductivity caused by the increase in mobile ions in the polymer as a result of the non-exchange absorption of electrolyte.

2. Membrane selectivity

The selectivity of perfluorinated CEM has a key significance in their use. The efficiency of using electrical energy, i.e. the proportion of electric current consumed in obtaining the desired products (the so-called yield on current) and also their purity, depends primarily on membrane selectivity in the process of chlorine–alkali electrolysis.

The selectivity of perfluorinated CEM is determined by the degree of "reversible" migration of hydroxyl ions through the membrane from the catholyte into the anolyte which itself depends primarily on the concentration of non-exchange absorbed electrolyte in the membrane. This concentration is significantly lower in the less hydrophilic carboxyl-containing polymers than in copolymers with sulphonic groups particularly at high alkali concentrations (Fig. 11). Since the equilibrium Donnan concentration of hydroxyl ions in the membrane grows with increasing NaOH concentration, cation exchange membranes intended for obtaining electrolytically more concentrated alkali must have a higher density of fixed ionogenic groups. This dependence has been confirmed experimentally. Maximum yield on current is achieved for membranes of higher EC in the case of a higher concentration of alkali in the catholyte.[5,19,83] It has been recorded[16] that membranes of carboxyl-containing copolymers operate with the highest efficiency (yield on current 96–97%) when the concentration of carboxyl groups in the surface layer of the swollen membrane facing the cathode in relation to the water absorbed by it is equal to the alkali concentration in the catholyte. This may be explained by the fact that under such conditions the transfer of Na^+ ions from membrane to catholyte is not accompanied by a change in its degree of hydration. On the basis of this relationship membranes have been developed with various EC of the surface layer for obtaining alkali of various concentration.[93]

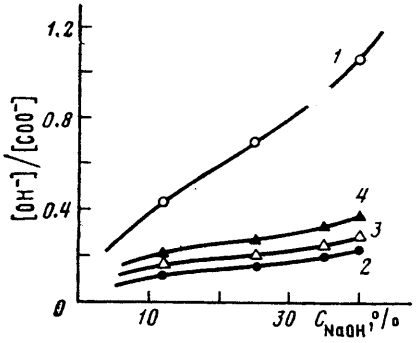


Figure 11. Dependence of hydroxyl ion concentration on alkali concentration at Donnan equilibrium in cation exchange membranes prepared from copolymers of: *1*, TFE and (I) with EC 0.82 mg-eq/g; *2*, TFE and (II) with EC 1.23 mg-eq/g; *3*, TFE and (II) with EC 1.44 mg-eq/g; *4*, copolymers of TFE and (III) with EC 1.21 mg-eq/g.[37]

It is evident from Fig. 11 that films of PFP with sulphonic groups may not possess high selectivity, particularly at high alkali concentrations, and require chemical modification to increase their selectivity or must be used in multilayer membranes having a barrier

layer of polymer with lower water content. The first attempt to prepare such membranes by laminating two layers of copolymers of (I) with TFE having different EC, such as with EM 1100 and 1500,[101] where the second of these layers fulfills a barrier role, was unsuccessful. The selectivity of such membranes was inadequate for their use in industry.[12] Later the analogous method of combining two films of different EC was used to increase the selectivity of membranes prepared from copolymers with carboxyl groups.[102] However as a rule polymer layers bear ionogenic groups of different types in multilayer membranes prepared both by chemical modification and by the lamination method.

Methods of chemical modification of films of ion exchange PFP have been considered in Chapter V. As already mentioned the route to increasing the selectivity of sulphonic cation exchange membranes, by carboxylation of a thin surface layer facing the cathode when fixed in an electrolytic cell, has displaced the method of aminating the surface of these membranes because of the inadequate chemical stability of sulphonamide groups, the increased electrical resistance of the aminated membranes and the difficulties of using them which are linked with the high pK_a of sulphonamide groups. The placing of a barrier layer of carboxyl groups on the surface of the sulphonic cation exchange membrane sharply increases its selectivity without an appreciable increase in electrical resistance. It is shown in Fig. 12 that a barrier layer of thickness 6–8 μm provides optimum selectivity and a further increase in the thickness of this layer did not increase further the yield on current. However the term "thickness of carboxylated layer" remains incompletely defined.[5,83] It is unclear what extent of conversion of sulphonic acid into carboxyl groups is applied as the border of this layer.

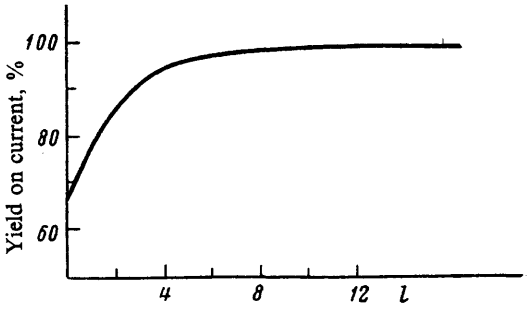


Figure 12. Influence of thickness (l) of carboxylated layer of sulphonic cation exchange membranes on yield on current when using them in the electrolysis of NaCl.[5]

All the highly selective perfluorinated CEM developed recently have a multilayer structure.[68,70,71] Their basic layer, having high EC and consequently low resistance, may be prepared from copolymers both with sulphonic acid[70] and with carboxyl groups.[68,71] In the latter case an additional layer of polymer with sulphonic groups possessing high acidity is placed on the side facing the anode. A relatively thin (10–40 μm) barrier layer of carboxyl-containing copolymer with reduced EC is placed close to the cathode. In membranes intended for preparing alkali of concentrations greater than 40% a further thin layer (~6–20 μm) of polymer with sulphonic groups was created on the side facing towards the cathode in order to protect the carboxyl-containing polymer of the barrier layer from decomposition by the concentrated alkali. It has been applied from a solution but chemical modification procedures may also be used for this purpose.[71] Across such a surface layer a fall of hydroxyl ion concentration occurs to values safe for the carboxyl-containing polymer. It is possible to introduce one more layer to improve the adhesion between layers of polymers of different chemical nature on lamination.[68] The membranes obtained in this way combined high selectivity, low electrical resistance, chemical strength and stability towards film separation.

VII. Conclusion

Great success has been achieved in the last fifteen years in the area of developing perfluorinated CEM as a result of which the industrial process for obtaining alkali and chlorine by membrane technology has been successfully put into practice. At the present time the efforts of many investigators have as usual been concentrated on improving the individual steps of this technology, on simplifying and making more economical the methods of synthesis of monomers used in the manufacture of membrane materials, on the development of methods of obtaining polymers with the desired characteristics by copolymerisation and polymer-like conversion reactions and also on the further development of procedures for fabricating membranes capable of working for an extended time with high efficiency under drastic conditions, on giving them a surface structure providing minimum energy losses during electrolysis, and optimising the parameters of membrane–electrode assemblies, etc. The synthesis of new functionalised perfluorinated monomers remains an urgent problem.

Expansion of the manufacture of perfluorinated cation exchange polymeric materials permits substantially the extension of investigations of their structure and physicochemical properties and, based on this, finding new areas for applying them.

Membranes of PFP with sulphonic groups having strongly acidic properties and providing a high proton mobility were already applied long before chlorine–alkali electrolysis as solid electrolytes in hydrogen–oxygen and hydrogen–halogen fuel cells. With the growth of hydrogen power the use of perfluorinated membranes in the electrolysis of water, where they are able to provide high current density and process efficiency, is extremely promising.[3] One more region for the application of perfluorinated sulphonic cation exchange membranes is that of ion selective electrodes.[4] A review[35] has been devoted to the use of perfluorinated sulphonic cation exchange polymers and 'Nafion' membranes based on them as catalysts. Possessing high acidity they may successfully replace traditional acid catalysts in such processes as hydration, esterification and the alkylation of benzene and its homologues. The use of catalysts based on ion exchange PFP containing metal ions has been considered in a review.[103] There have been communications on the use of perfluorinated CEM for drying gases[4] and for gas distribution.[104]

The uniqueness of the properties of cation exchange PFP and the intensity with which they are being investigated makes it possible to predict with confidence further extension of their spheres of application and an increase in their role in chemical technology.

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