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αββ-Trifluorostyrene and polymers based on it

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ABSTRACT. The literature data on the synthesis, properties, and applications of αββ-trifluorostyrene and the polymers based on it are surveyed. The characteristic features of the polymerisation and copolymerisation of αββ-trifluorostyrene, the methods of preparation of ion-exchange materials based on polytrifluorostyrene, and their characteristics and applications are examined.

Certain aspects of the effect of fluorine atoms in the vinyl group of αββ-trifluorostyrene on its reactivity and physicochemical properties are discussed. The applications of polytrifluorostyrene-based materials and their advantages are indicated.

The bibliography includes 136 references.

Contents

I. Introduction 575
II. Synthesis and properties of αββ-trifluorostyrene 575
III. Polytrifluorostyrene and αββ-trifluorostyrene copolymers 579
IV. Ion-exchange materials based on polytrifluorostyrene. Their synthesis and properties 582
V. Other aspects of the applications of polytrifluorostyrene 587

I. Introduction

Among the large series of fluorine-containing compounds capable of polymerising, αββ-trifluorostyrene (TFS) occupies a special position by virtue of the combination in its molecule of the perfluorinated vinyl group and the aromatic ring. As a result of this, TFS can be regarded both as a phenyl derivative of tetrafluoroethylene and as a styrene with a perfluorinated vinyl group. Such combination of properties is responsible for a number of characteristic features and for the differences between this monomer and its two analogues both in polymerisation and when they are involved in different chemical reactions.

The polymer obtained on polymerisation of TFS, namely polytrifluorostyrene (PTFS), belongs to the class of thermally and chemically stable materials: it contains a perfluorinated main chain, which is resistant to thermal oxidation, and phenyl substituents. In contrast to polytetrafluoroethylene and the majority of its derivatives, which do not dissolve in any solvent, PTFS is readily soluble in many organic compounds, which permits its processing in different solutions. The presence of the benzene ring in the PTFS molecule ensures the possibility of introducing into it various functional groups and the preparation on its basis of modified materials. This renders PTFS particularly promising for the development of various ion-exchange and other materials with enhanced thermal and chemical stability.

The combination in the TFS molecule of the electronegative fluorine atoms, the vinyl group, and the benzene ring makes it an extremely interesting object for the theoretical study of the effect of electronic structural factors on the reactivity of the unsaturated and aromatic components of this compound and on its physicochemical properties and also on the properties of the monomers based on it.

II. Synthesis and properties of αββ-trifluorostyrene

1. Methods of synthesis of αββ-trifluorostyrene

The first mentions of the synthesis of αββ-trifluorostyrene, a new fluorine-containing monomer, dates back to the end of the 1940s and the beginning of the 1950s when the study by Cohen, devoted to a multistage method of synthesis of this compound, was published.[1,2] The starting materials in this synthesis were the salts or the chlorides or chlorofluoro- or trifluoro-acetic acids:

$$CF_3COCl \xrightarrow[AlCl_3,CS_2]{C_6H_6} C_6H_5COCF_3 \xrightarrow{PCl_5} C_6H_5CCl_2CF_3 \xrightarrow{SbF_3} \rightarrow C_6H_5CFClCF_3 \xrightarrow[\text{abs. ethanol}]{Zn} C_6H_5CF{=}CF_2 .$$

The synthesis is based on the Friedal–Crafts reaction, which results in the formation of the corresponding trifluoroacetophenone or chlorodifluoroacetophenone. The overall yield of TFS does not exceed 30% and the main difficulty is the reaction involving the abstraction of ClF in the last stage of the process.

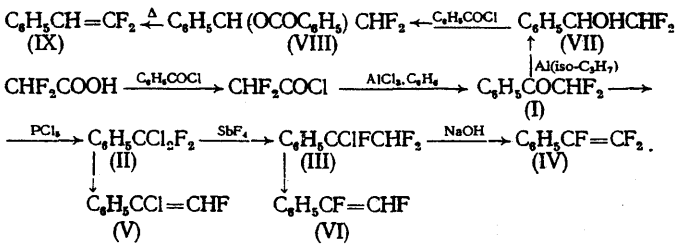
$$C_6H_5COCF_2Cl \rightarrow C_6H_5CCl_2CF_2Cl \rightarrow C_6H_5CFClCF_2Cl \rightarrow C_6H_5CF{=}CF_2 .$$

Table 1. Polymerisation of αββ-trifluorostyrene and its derivatives.[3]

Monomer	Initiator	c_{in}^{*}, %	Polymer, %	T_{soft}^{**}, °C
$C_6H_5CF{=}CF_2$	BP***	9.7	2.9	185–190
(TFS)	BF_3	1.2	0	—
$C_6H_5CH{=}CF_2$	BP	0.4	3.5	176–180
(ββ-DFS)	BF_3	0.4	2.4	127–130
$C_6H_5CF{=}CHF$	BP	0.7	2.7	—
	BF_3	30.0	2.8	225–230
$C_6H_5CCl{=}CHF$	BP	2.7	0	—
	BF_3	3.2	0	—

*c_{in} = initiator concentration.
**T_{soft} = softening temperature of the polymer.
***BP = benzoyl peroxide.

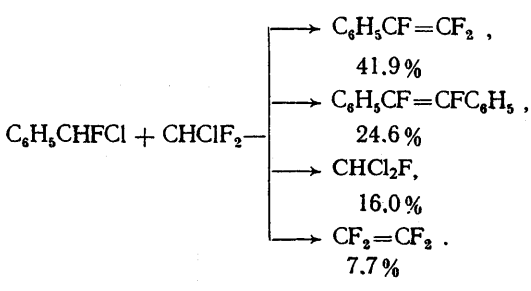
The synthesis of TFS in Prober's study,[3] also dating back to the 1950s, is a development and modification of the method described above. Together with TFS, its derivatives with chlorine and hydrogen atoms instead of fluorine in the vinyl group are obtained by this procedure. These processes can be represented schematically as follows:



All the monomers obtained, with the exception of the chlorine-containing compound (V), are capable of polymerising with formation of polymeric compounds. Table 1 presents data on the polymerisation of these monomers and on the softening temperatures of the polymers based on them.

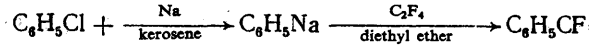
Prober also developed a direct method of synthesis of TFS from chlorotrifluoroethylene and benzene when they are jointly pyrolysed[4,5] in the temperature range 550–600 °C. There is an indication that this reaction can be accelerated by various acid compounds (for example BF_3) and substances with a high specific surface (activated charcoal, $PbMe_4$, etc.).[4] In this method, the reaction mixture is repeatedly circulated through a hot zone with successive enrichment of the mixture in TFS; the mixture is then distilled through a fractionating column with a large number of theoretical plates. A low yield of the final product (not exceeding 30%) and the large amount of side products, which are difficult to remove from TFS because of their ability to form azeotropic mixtures with the latter, must be included among the disadvantages of this procedure (as in the previous methods of synthesis).

Yet another method of the pyrolytic synthesis of TFS consists in the copyrolysis of C_6H_5CHFCl and $CHClF_2$ at 600–800 °C in a stream.[6] The gaseous products obtained are absorbed in scrubbers using water and are fractionated. For the initial proportions of 68.5 mol% of C_6H_5CHFCl and 31.5 mol% $CHClF_2$, the following mixture of products is obtained:

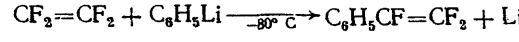


A change in the initial reactant ratio affords other proportions of the final products.

A procedure is also known for synthesising TFS by the reaction of solid PhNa with C_2F_4 in a heterogeneous liquid–solid system containing a solvent for C_2F_4.[7] The reaction is carried out in the presence of an excess of C_2F_4 (whose amount is 50–500%) at a pressure of $(0.7-14)\times10^5$ Pa and in the temperature range from −30 to −100 °C:



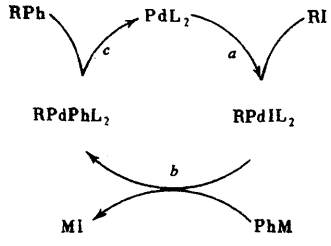
One of the most widely known methods of synthesis of TFS and its derivatives is Dixon's method in which it is obtained via organolithium compounds.[8,9–13]



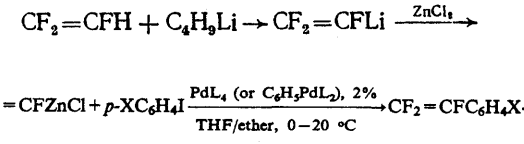
In this procedure, 1 mol of the organolithium compound under an inert atmosphere and in dry diethyl ether at −80 °C is added slowly to 1.2 mol of the fluoroalkene. The yield of TFS by this method also does not exceed 20–30%, since the main product is 1,2-difluorostilbene,[11–14] but the TFS obtained is much purer and its isolation is much simpler.

In order to obtain TFS derivatives with substituents in the benzene ring, substituted benzene derivatives were used as the initial organolithium compounds. The corresponding phenyl-lithium derivatives were obtained from them.[13]

Finally a method of synthesis of TFS and its derivatives in a high yield (≥87%) from trifluorovinyl derivatives of lead and zinc and iodobenzene derivatives in the presence of palladium complexes was described recently.[15,16] The method is based on cross-coupling reactions which are known to involve several stages: oxidative-reductive addition (a), transmetallation (b), and reductive elimination (c):[17]



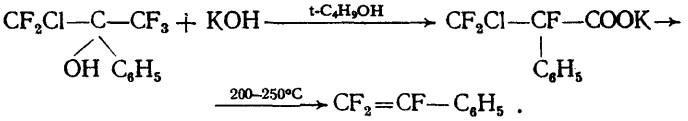
When applied to the synthesis of TFS and its derivatives, this process can be expressed by the general scheme



X=H, CH_3, CH_3O, Cl.

The catalytic reaction involving the coupling of CF_2 = CFZnCl to ArI can be represented as the successive interaction of $ArPdI(PPh_3)_2$ with CF_2 = CFZnCl (exchange reaction) leading to the formation of the complex $ArPd(CF=CF_2):(PPh_3)_2$, which is converted as a result of reductive elimination into the zerovalent palladium complex $Pd(PPh_3)_2$ and CF_2 = CFAr. After the oxidative addition of ArI, the initial complex $ArPdI(PPh_3)_2$ is regenerated.[16] These processes take place in solution in different solvents, the yield of the products increasing as a function of their nature in the following sequence: HMPA ≃ DMF > DMSO > THF > C_6H_6 > $C_2H_4Cl_2$.[15]

In addition, a procedure is known for the synthesis of highly pure TFS using chlorinated 2-phenylperfluoro-2-propanol, from which $CF_2ClCF(C_6H_5)COOK$ is obtained. The latter compound is decomposed at 200–250 °C and 20 mmHg. For example, the synthesis of 1-chloro-2-phenylperfluoro-2-propanol proceeds as follows:



When this method is used, TFS without any impurities is obtained.[18,19]

2. Physicochemical properties of αββ-trifluorostyrene

TFS is a colourless liquid with a specific smell. When stored in air, it gradually decomposes to benzoic acid with liberation of HF.[20] A cyclic dimer is formed readily. This will be described in detail below.

In order to characterise the monomer with the aid of spectroscopic data, one usually employs the UV absorption maximum at 240 nm,[27] the IR absorption band at 1752 cm^{-1} due to the C=C (vinyl) group,[9,27,28] the 1650 and 2000 cm^{-1} bands due to the ring-monosubstituted derivatives, the 690 and 755 cm^{-1} deformation vibration bands,[24] and the 1075 and 1175 cm^{-1} bands due to the CF and CF_2 groups.[24] Table 2 presents certain characteristics of TFS taken from different sources.

Table 2. Physicochemical characteristics of TFS and PTFS.

TFS			PTFS		
property	parameter	refs.	property	parameter	refs.
T_b	133–136 °C (at 760 mmHg)	[4]	T_{soft}	185–190 °C	[3, 21]*
T_b	68–70 °C (at 75 mmHg)	[2, 8]	$T_{g,exp}$	202 °C	[22, 23]**
T_m	−23–−22 °C	[2]	$T_{g,calc}$	204 °C	
Dielectric constant ε	2.56±0.05 in the range 10^2–10^{11} Hz	[24]	Tangent of electrical losses angle tan δ	0.0033–0.0043 at 10^2–10^8 Hz	[24]
Dipole moment μ	1.98 D	[21, 26]			

*Barb[21] used the method of the LSP-limit of the softening point.
**Brown[23] determined the glass point T_g using a scanning calorimeter.

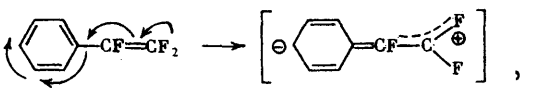
It is known that all non-aromatic fluoroethylene derivatives are coplanar, i.e. all the fluorine atoms lie in the same plane as the double bond.[25,26] On the other hand, the TFS molecule has a non-planar, non-coplanar structure. The *cis*-β-fluorine atom and the *ortho*-hydrogen atom of the benzene ring do not lie in the same plane because the distance between the centres of the hydrogen and fluorine atoms (1.6 Å) is smaller than the sum of their van der Waals radii.[25,26,29]

The results of geometrical calculations are confirmed satisfactorily by the dipole moment of TFS (1.98 D), which indicates the rotation of the trifluoroethylene group relative to the benzene ring and the absence of π-electron interaction between them, as a consequence of which the dipole moment of TFS is identical with those of other fluorinated alkenes, for example, 1,1,2-trifluorooct-1-ene (1.97 D).[25,26] Calculation of the dependence of the dipole moment on the angle between the planes of the benzene and perfluorinated groups showed that the angle in TFS is close to a right angle.[30,31]

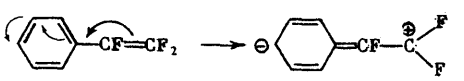
The breakdown of coplanarity in the TFS molecule is also indicated by UV absorption spectroscopic data for this compound. The study of the UV absorption spectra of mono-, di-, tri-, and tetra-substituted derivatives of TFS also lead to the conclusion that the conjugation between the perfluorinated vinyl group and the benzene ring breaks down, which indicates the non-coplanarity of these molecules.[30,31]

One can postulate on the basis of the foregoing that the nature of the effect of fluorine on the electronic structure of the C=C bond in fluorinated ethylenes and fluorinated styrenes is the same. However, analysis of different data permits the conclusion that the fluorine atoms are involved in the π-conjugation of the perfluorovinyl group with the benzene ring. This is demonstrated by the difference in the character of the sulphonation reactions of TFS and PTFS. Whereas the former compound is sulphonated directly with extreme difficulty and the process requires very severe conditions, PTFS can be sulphonated under relatively mild conditions (for example, with chlorosulphonic acid or SO_3 in dry hydrocarbon solvents at temperatures in the range 20–50 °C) (see Section IV).

The presence of conjugation leading to an increased reactivity of the C=C bond, which can be represented schematically by the formula

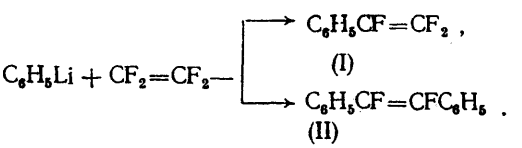


[Presumably intended scheme is:

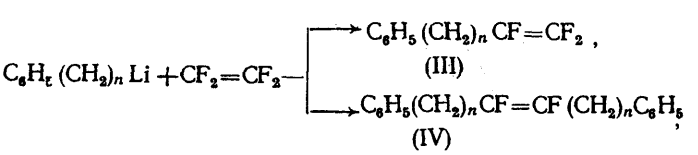


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is believed to be one of the causes of the low yield of TFS (I) in its synthesis via phenyllithium as a consequence of side reactions which result in the formation of a stilbene (II):[11–13]



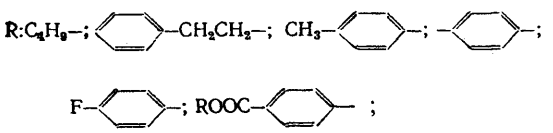
For example, this has been established when one or two methylene groups were introduced into $Ar(CH_2)_nLi$ or when polymethyl derivatives of phenyllithium $(CH_3)_nC_6H_5Li$, where $n > 1$ and CH_3 in in one or two *o*-positions, are used. Judging from the ratio of the products (III) and (IV) obtained by the reaction



when conjugation breaks down, the reactivity of the C=C bond in compound (III) falls, so that the compounds resemble the alkylfluoroethylenes AlkCF = CF_2.[14]

Data concerning the presence of conjugation between the perfluorinated vinyl group and the benzene ring in TFS have also been obtained by spectroscopic methods and have been interpreted on the basis of the available data for the effect of substituents on the electronic spectra and π-donor properties of benzene derivatives.[32]

Interesting data, associated with the presence of conjugation between different groups, have been obtained in the study of the structures, steric effects, the parameters δ and *j*, and other characteristics of TFS by the ^{19}F NMR method.[33–37] Analysis of the NMR spectra of a series of RCF = CF_2 derivatives showed that the change in the δ_{F_1} and δ_{F_2} (β-fluorine atoms) signals is associated with the inductive-resonance effect of the substituents. Thus the shifts of δ_{F_2} diminish in the following sequence:



δ_{F_2}: −7.0 −7.5 −16.3 −17.4 −17.7 −20.8.

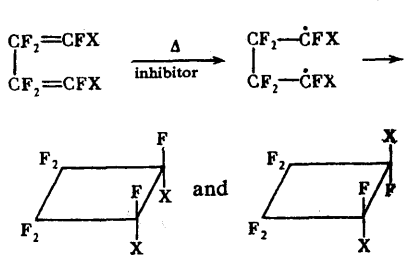
Comparison of the shifts δ_{F_2} for the compounds RCF = CF_2, where R = C_4H_9 or $C_6H_5CH_2CH_2$, with the remaining compounds shows that the greatest changes occur for the β-fluorine atoms (F_1 and F_2) as a result of the additional delocalisation of the π-electrons of the phenyl group associated with the conjugation effect.[14,35]

However, in certain chemical reactions of TFS conjugation is only weakly manifested. For example, the chlorination and bromination of $C_6H_5CF = CF_2$ afford $C_6H_5CFCl-CF_2Cl$ and $C_6H_5CFBr-CF_2Br$ respectively in 94–95% yields, i.e. the main process involves the ethylenic double bond, as for similar non-aromatic derivatives.[38]

αβ-Difluorostilbenes and their derivatives, which are obtained simultaneously with TFS and its derivatives in the synthesis via organolithium compounds, are also non-coplanar. The non-coplanarity of the structures of these compounds has been demonstrated by UV and ^{19}F NMR spectra; despite this, the conjugation effect does occur in molecules of this kind.[39]

3. Dimerisation of αββ-trifluorostyrene

Fluoroalkenes are known to exhibit a characteristic behaviour in polycentre reactions and, in contrast to the non-fluorinated monomers, they readily dimerise or react with other olefinic compounds, forming cyclobutanes by 1,2-addition.[40] The polarisation of the double bond does not affect their cyclodimerisation, which rules out an ionic mechanism. It has been suggested that the 1,2-addition reactions proceed via a two-step radical mechanism. A biradical, in which rotation about the C(1)–C(2) bond is possible, arises in the first stage:[40]



The coupling of fluoroalkenes in the first stage of the reaction proceeds in such a way that a radical centred on the carbon atom linked to the smallest number of fluorine atoms is produced. The "head to head" cyclodimerisation is not stereospecific and in the case of asymmetric fluoroalkenes leads to the formation of *cis*- and *trans*-isomers.

The tendency of TFS towards dimerisation is extremely pronounced. In all the early studies on the synthesis and polymerisation of TFS, it was already stated that this monomer readily dimerises.[3,24] Subsequently the dimerisation reaction and the dimer itself were investigated in fair detail.[29,41–48]

It is now regarded as generally recognised that TFS dimerises via a biradical two-step mechanism, illustrated schematically above. It has also been confirmed that this reaction is not stereospecific—the dimer is always formed as a mixture of *cis*- and *trans*-isomers. Their amounts in the mixture depend little on the process conditions and can be approximately equal.[29,42,48–51] In order to identify and establish the structures of these products, different methods have been used: spectroscopic, ^{19}F NMR, mass-spectrometric, chromatographic, etc. The results have been unambiguous.

From an analysis of NMR spectra, it has been suggested in recent years that the transition state in the dimerisation of TFS has symmetrical polarity and that the double bonds are polarised. A linear relation has been obtained between the Hammett constant σ and the ^{14}F NMR parameters and it has been suggested that the deformation of the π-electron clouds is caused by mutual repulsion and polarity.[41,46,47]

It has been demonstrated that heating of TFS in bulk or in hydrocarbon solvents in the absence of material initiators leads to the formation of dimeric products alone[29] and that this process is a second-order reaction: $V_{dim} = K_{dim}[M]^2$.[25,26,29] A relation has been derived for the determination of the dimerisation rate constant, which is $K = 1.5 \times 10^7 e^{-17652/RT}$.[49]

Table 3. The rate of dimerisation of TFS in bulk and in different solvents at 50 °C.[29]

System	TFS concentration, M	V^*_{dim}, % h^{-1}
In bulk (pH 6.0)	7.88	0.62
In bulk (pH 1.0)	7.88	0.64
Triethylamine (0.63 M)	7.28	0.66
Diethyl ether (0.22 M)	7.60	0.60
p-Benzoquinone (0.001 M)	7.60	0.65
In solution in cumene	3.06	0.72
In solution in toluene	2.84	0.76
In solution in toluene	6.27	0.70

*V_{dim} is the rate of dimerisation (adjusted to the TFS concentration in bulk).

The dimer is a mixture of a colourless oily liquid with a crystalline phase (the *trans*-isomer). The dimer completely freed from the monomer has no smell. On heating, one isomeric form of the dimer is converted into the other (*cis*–*trans* interconversion).

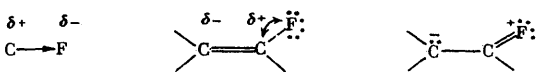
The dimer is extremely stable chemically but above 250 °C it decomposes back to the monomer: T_b = 120–121 °C at 6 mmHg, n_D^{20} = 1.4973;[3] n_D^{20} = 1.4954, d_4^{20} = 1.3884.[24] The rate of dimerisation of TFS depends only temperature[52] and the process is not inhibited or accelerated in the presence of various additives. Table 3 presents some results for the dimerisation of TFS in different systems.

III. Polytrifluorostyrene and αββ-trifluorostyrene copolymers

1. Polymerisation of αββ-trifluorostyrene

The presence of fluorine atoms in the TFS molecule leads to the specific behaviour of this monomer in polymerisation processes. We shall consider the causes of this behaviour.

The introduction of fluorine (the most electronegative element) atoms as substituents into the molecule of a saturated organic compound (at a carbon atom in the sp^3-state) usually leads to the appearance of a negative inductive effect ($-I_{eff}$). If the fluorine atom is linked to an sp^2-carbon atom of an unsaturated π-electron system, it exhibits the opposite effect, consisting in the repulsion of the π-electrons ($+I_{eff}$), which is due to the presence of three unshared electron pairs in the outer shell of the fluorine atom. A strong repulsion arises between the pairs of 2p electrons of the fluorine atoms and the pairs of $2p_\pi$ electrons at a neighbouring carbon atom. This effect, associated with the extremely strong influence on the reactivity of fluorine-containing monomers, is usually referred to as the "resonance-donor effect" or the R effect:[53]



$-I$ effect $+I$ effect $+R$ effect.

As a consequence of the $-I$ effect, the electronegative fluorine atom generates on the neighbouring carbon atoms an excess positive charge δ+. The pair of π electrons is then subject to the field of the positively charged carbon atoms which increases the Coulombic interaction of the π-electrons with the nuclei of these atoms. This alters their energy state and the symmetry of the distribution of electron density. As a result of this, the deformed cloud of π electrons becomes more extended along the C=C axis, binding more strongly the carbon nuclei.

For fluorinated styrenes, the change in the distribution of electron density on the C=C bond also entails a significant decrease in the conjugation of the π-electron double bond with the π electrons of the benzene ring (20%). The IR and Raman spectra of a series of fluorinated styrenes in the region of the C=C bond stretching vibrations indicate a greater strength of this bond compared with styrene.[54] Analysis of data on the copolymerisation of TFS with other monomers[55–57] shows unambiguously that TFS is more reactive than styrene.

As a consequence of the non-coplanarity of the TFS molecule, which was discussed in detail above, the effect of the polar factor for this compound is dominant and is hardly distorted by the effect of the conjugation with the benzene ring. Therefore the decrease in the reactivity of β-substituted fluoro-monomers is apparently caused precisely by the polar effect of the substituents.

The low reactivity of the TFS molecule and also the presence of fluorine atoms in it introduce definite characteristic features into the polymerisation of this monomer. The attempts to obtain the polymer by the traditional radical polymerisation in bulk and in solution, made in a number of studies, did not lead to the desired results.[3,29,58–60] The main reaction product under such conditions is a dimer, which consists of a mixture of isomers of diphenylperfluorocyclobutane, and a small amount of a low-molecular-weight polymer (oligomeric products with molecular weights in the range 1500–2000).[29] In such systems, the polymerisation of TFS involves the occurrence of two parallel and independent processes: dimerisation and oligomerisation.[29] The activation energy for the first process is then 58.58 kJ mol^{-1} and that for the second is 79.5–87.8 kJ mol^{-1} depending on the type of initiation.[29,52] When the process is carried out in solution, an increase in the dielectric constant of the medium leads to an increase in the molecular weight of the oligomer. Table 4 presents certain results for the polymerisation of TFS in different solvents.

Table 4. The rates of oligomerisation (V) of TFS in different solvents at 50 °C (AIBN*, 0.076 M).[29]

Solvent	ε	TFS concentration, M	$10^4 V$, mol litre^{-1} min^{-1}		Molecular weight
			Experimental	adjusted to concentration in bulk**	
In bulk	—	7.88	2.30	2.30	1 200
Cumene	2.23	3.06	0.94	2.42	1 100
Toluene	2.23	2.84	0.92	2.54	1 200
Toluene	2.23	6.27	2.23	2.27	1 170
Ethyl methyl ketone	18.0	4.88	3.36	5.26	2 000
N-Methylpyrrolidinone	31.0	3.14	2.02	5.05	4 300
Dimethylformamide	36.7	5.07	4.78	7.45	7 200
Sulpholan	44.0	4.23	10.72	20.17	10 000
Dimethyl sulphoxide	48.0	2.45	3.11	9.95	9 700

*AIBN = azobisisobutyrodinitrile—the initiator.
**The rate adjusted to the concentration in bulk on the assumption of a linear dependence of the rate of oligomerisation on the TFS concentration.

Nor can the high-molecular-weight polymer be obtained in an appreciable yield on polymerisation via ionic and ionic-coordination mechanisms in the presence of BF_3, $SnCl_4$, and Ziegler–Natta catalysts.[24,49,55,59,67]

A high-molecular-weight PTFS can be obtained only by emulsion polymerisation, which was first achieved by Prober in 1953.[3] The method of emulsion polymerisation still remains the only procedure for the synthesis of PTFS with a fairly high molecular weight and a high degree of conversion. Studies in this field can be divided into two groups: the study of the kinetics of the emulsion polymerisation of TFS in order to create a basis for the specific synthesis of PTFS[4,29,62,63] and the synthesis of PTFS with a specified set of properties.[3,24,55,59,60,64]

The first studies in this field already showed that the yield of the polymer and its molecular weight are affected to an appreciable extent by the nature of the emulsifying agent and its concentration

(the ratio of the phases comprising the aqueous solution of the emulsifying agent and the monomer) and also by the initiating system.[3,24,55,59] More detailed studies showed that a change (increase) in the rate of polymerisation and especially in the molecular weight on passing from the polymerisation of TFS in bulk to its polymerisation in emulsion has no analogues among other vinyl monomers. Thus for TFS the rate increases under these conditions by approximately a factor of 30 and the molecular weight increases by three orders of magnitude. Table 5 presents for comparison the corresponding data.[52] The polymerisation rate constant, activation energies, and pre-exponential factors for TFS and its *p*-methyl derivative using different polymerisation procedures were determined from the kinetic data. The data are presented in Table 6.[64] The ratio of the chain propagation and termination rate constants (k_p/k_t) for styrene proved to be greater by a factor of 4 than for TFS, while the chain propagation rate constant for styrene is greater by a factor of 400 than the value for TFS.

Table 5. Polymerisation of TFS under different conditions (0.5% BP relative to weight of monomer, 50 °C).[52]

Polymerisation conditions	Conversion, %	10^{-3} V, min^{-1}	M_n (ebullioscopic)
In bulk	12.0	2.1	1236
In bulk + 3.0 wt.% E-30	10.9	2.1	1200
TFS + water (phase ratio 1:7)	12.0	2.2	930
TFS in emulsion (phase ratio 1:7, 3.0 wt.% E-30)	24.0	63.0	$9\cdot10^{6}$*

*The molecular weight was determined by the light scattering method.

Table 6. Kinetic characteristics of the polymerisation of fluorostyrenes and their comparison with data for styrene.[64]

Polymerisation conditions, monomer	k_{60}, s^{-1}	E, kJ mol^{-1}	A, litre mol$^{1/2}$ s$^{1/2}$
TFS (in emulsion)	$4\cdot10^{-6}$	82.4	$3.5\cdot10^{7}$
p-Methyl-αββ-trifluorostyrene (in solution)	$0.9\cdot10^{-6}$	85.8	$2.6\cdot10^{7}$
p-Methyl-αββ-trifluorostyrene (in emulsion)	$2.6\cdot10^{-6}$	100.4	$1.3\cdot10^{6}$
Styrene (in solution)	$3.2\cdot10^{-6}$	88.7	$3.7\cdot10^{9}$
Styrene (in emulsion)	$16.0\cdot10^{-4}$	94.5	$6.0\cdot10^{11}$

However, one should note that the complete removal of HF from the reaction mixture makes it possible to obtain in bulk a polymer with a molecular weight of 30000 – 50000 at a system pH of 7.[29]

One of the distinctive features of the emulsion polymerisation of TFS is the marked dependence of the rate of the process and of the molecular weight of the polymer on the topochemistry of the initiation process. It has been established that only water-soluble initiators (of the type of persulphates) or oxidation-reduction systems whose components are soluble in different phases are capable of ensuring the maximum rates of reaction and the maximum molecular weights of the polymers obtained.[29,52,60,62,65]

Detailed study of the emulsion polymerisation of TFS made it possible to develop effective methods for the synthesis of this polymer in a form suitable for practical purposes.[29,52,62,65] It is noteworthy that TFS polymerises only when hydrocarbon emulsifying agents are used and that the best results are obtained in the presence of anionic emulsifying agents of the type of E-30 (sodium salt of $C_{15}-C_{16}$ alkanesulphonates) and their mixtures with non-ionic emulsifying agents of the type of hydroxyethylated alcohols.[29,52,60,62,65] The attempts to use for emulsion polymerisation of TFS fluorinated emulsifying agents—the salts of fluorocarboxylic acids which are widely employed in the polymerisation of many fluorine-containing monomers, did not yield positive results in the given instance.[66]

The emulsion system also affords fully cross-linked polymers when TFS is polymerised in the presence of polymeric peroxides.[63]

The attempt to obtain a high-molecular-weight PTFS in a high yield not in an emulsion system but by carrying out the process at a high pressure (up to 2000 MPa),[67] which likewise failed to give satisfactory results, should also be noted.

2. Physicochemical properties of PTFS and its structure

The PTFS obtained by emulsion polymerisation is a white powder (d_4^{20} = 1.4903 g cm^{-3}) readily soluble in organic solvents—benzene, diethyl ether, acetone, ethyl methyl ketone, tetrahydrofuran, ethylene chloride, etc.—and also in aprotic solvents. Transparent films can be obtained from solutions, their strength amounting to 100 MPa but their relative elongation does not then exceed several per cent. The brittleness of the films greatly limits the application of this polymer, although its high thermal and chemical stability combined with its ability to undergo modification by the introduction of various groups into the phenyl units makes this polymer extremely promising for the preparation of functional polymeric materials. PTFS is an amorphous polymer, but the X-ray diffraction pattern of an extended specimen reveals a weak tendency towards texture formation. The reflections corresponding to 2.35 and 4.66 Å are concentrated along the meridian. Such a picture for an extended specimen indicates a definite degree of orientation but does not confirm the presence of a crystalline phase. The orientation of the extended specimens is also demonstrated by the high degree of double refraction in crossed polarisers.[24]

It has been suggested that the PTFS molecules have the form of a distorted C–C–C zig-zag. The attempt to construct a model on the basis of this hypothesis demonstrated that, as a consequence of steric hindrance, isotactic disposition of the benzene rings is impossible. The molecule can exist only in the syndiotactic version.[29] The NMR study of the structure of the *p*-methyl-αββ-trifluorostyrene homopolymer showed, however, the presence of non-equivalent CF groups of three types, which it has been suggested refer to the isotactic, syndiotactic, and heterotactic sections of the polymer chain.[68]

It has also been established that vitreous PTFS has different mechanical properties depending on the formation conditions of the specimens (from the melt or from solution), similarly to what has been observed for crystalline polymers.[69] It has been noted that certain important properties of the polymers (for example, their brittleness) depend on the supermolecular structure formation which

develops very slowly. This plays an especially notable role for the sulphonated PTFS, in which the formation of structural elements leads to an appreciable improvement of the strength characteristics but develops extremely slowly. The introduction of small amounts (up to 4%) of certain low-molecular-weight additives (for example, dibutyl phthalate) greatly accelerates the structure formation and leads to the strengthening of the polymer.[69] A change in the structure occurs also at low temperatures (in the range 4.2–300 K and for 1–2 Hz).[70]

Light scattering and viscometric studies of PTFS solutions showed that this polymer has chains with an enhanced rigidity and occupies an intermediate position between flexible chain and rigid chain polymers.[71] The increased skeletal rigidity of the PTFS chains is probably induced by the appreciable retardation of the internal rotation caused both by the increasing steric hindrance to their rotation owing to the large van der Waals radius of fluorine and by the dipole–dipole interaction of the polar C–F bonds. It is noteworthy that the comparatively high rigidity of the PTFS molecules (greater by a factor of four than that of styrene) is not caused by a secondary structure but is due to the true skeletal rigidity of its single-stranded chain.[29]

PTFS is an infusible polymer and cannot be worked in the molten state. Certain data on the softening temperature as well as the dielectric characteristics of PTFS films are presented in Table 2. PTFS has low dielectric losses over a wide frequency range[24] and some of its copolymers are polymeric dielectrics with an enhanced thermal stability.[72] However, the thermal stability of PTFS is appreciably lower than that of polytetrafluoroethylene (PTFE),[73] although in terms of its decomposition products (the yield of the pure monomer) PTFS is closest to PTFE. Thus the yield of the pure monomer on thermal degradation of PTFE, PTFS, poly(chlorotrifluoroethylene), poly(trifluoroethylene), poly(vinyl fluoride), and poly(vinylidene fluoride) is respectively M > 95, 75, 28, <1, <1.[74] According to mass-spectrometric data, the content of the monomer in the degradation products is 73.6%, while 26.4% corresponds to heavy fragments with an average molecular weight of 458.

On irradiation of PTFS with ^{60}Co γ-rays at a dose of 10^{22} eV g^{-1}, the radiation-chemical yield $G_{\text{cross-link}}$ does not exceed one, which indicates an appreciable radiation stability of the polymer, similar to that of the usual styrene.[75]

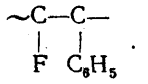
During recent decades, TFS together with other monomers and compounds which are difficult to polymerise has been polymerised in plasma. Films with improved thermal stability and containing oxygen were obtained on its surface.[76,77] The rate of formation of polymer films in a discharge plasma is 54 Å s^{-1} for TFS against 132 Å s^{-1} for styrene.[77]

3. Copolymerisation of αββ-trifluorostyrene

As already mentioned, the introduction of fluorine atoms into the vinyl group of styrene leads to specific features in the polymerisation of TFS. The copolymerisation reaction of this monomer is of interest from the standpoint of the effect of the fluorine atoms on the reactivity of TFS. It too constitutes a method of synthesis of new polymeric materials based on it and is a procedure for the modification of PTFS.

Data on the radical copolymerisation of fluorostyrenes confirm that the effect of fluorine atoms on the conjugation energy in these compounds is low. Systematic studies on the effect of the location of fluorine atoms on the reactivity of these monomers have made it possible to arrange fluorostyrenes in terms of their increasing reactivity in the following sequence:[57] ββ-difluorostyrene < β-fluorostyrene < αβ-difluorostyrene < TFS < pentafluorostyrene < 2,4-difluorostyrene < *p*-fluorostyrene.

The decrease in the reactivity of β-substituted fluoro-monomers can be attributed only to the polar effect of the substituents, since the effect of fluorine on the conjugation energy in the monomer is very insignificant and may be neglected. Being an electron acceptor, the fluorine in the β-position diminishes the electron density on the double bond and the monomer plays the role of an electron-donating partner in copolymerisation reactions. However, the decrease in the reactivity of the monomer is not compensated, as for the α-substituted monomers, by the increase in the reactivity of the radical, because the substituent in the radical formed is separated from the radical centre by the aliphatic C–C chain:[57]



As a result of all these factors, the constant for the copolymerisation of β-substituted styrenes [M_2] is low or even zero.

Table 7 illustrates the effect of the β-substitution of fluorine atoms on the parameters of the copolymerisation of styrene with fluorostyrenes. Thus, in the copolymerisation of styrene with *p*-fluorostyrene, the copolymerisation constants are very similar for both monomers, which is evidently caused by the weak inductive effect of the fluorine in the aromatic ring on the double bond. In the case of the styrene–2,4-difluorostyrene pair, there is some enrichment of the copolymer in styrene. The conjugation in the molecule of 2,4-difluorostyrene partly compensates for the polar effect of the fluorine atoms and the constants therefore differ insignificantly. Pentafluorostyrene enters into the polymer chain much less effectively. This is apparently caused by the steric hindrance due to the presence of the cumbersome perfluorovinyl groups and/or the effect of the polar factor.

Table 7. Copolymerisation of styrene with fluorinated styrenes.[57]

Monomer	r_1	r_2	Q	e
p-Fluorostyrene	0.7	0.9	0.83	−0.12
2,4-Difluorostyrene	1.05	0.75	0.65	−0.32
Pentafluorostyrene	1.53	0.62	0.22	0.52
β-Fluorostyrene	5.96	0.01	0	—
ββ-Difluorostyrene	10.4	0	0	—
αβ-Difluorostyrene	2.44	0.04	0.1	0.94
TFS	3.5	0.15	0.15	—

Remarks. r_1 and r_2 are copolymerisation constants, Q is a quantity characterising the reactivity of the monomer, and e is the polar factor.

In the case of β-fluorostyrene, the reactivity of the monomer diminishes very greatly. This is a result of the polar effect of the fluorine atom and not of steric hindrance. In the copolymerisation of ββ-difluorostyrene, the polar effect is manifested even more sharply and the homopolymerisation of styrene actually takes place.

The introduction of a fluorine atom into the α-position in β-fluorostyrene activates the monomer. Thus αβ-difluorostyrene and TFS are more reactive in copolymerisation than ββ-difluorostyrene or β-fluorostyrene.[55]

Table 7 presents quantities characterising the copolymerisation of styrene with these fluorine-containing compounds.[57] Attempts to obtain copolymers of TFS with other monomers containing, and not containing, fluorine atoms have been made since the 1950s. The aims of these studies were various. The task in most of them was the synthesis of new chain materials with improved thermal and chemical stabilities, modification (improvement of physicomechanical properties of PTFS), and the introduction of functional groups into the copolymers in order to obtain mainly ion-exchange materials. Quite a few studies have also been devoted to theoretical aspects of problems of the reactivity of the monomers, as already pointed out.

The copolymerisation reactions of TFS with styrene, its derivatives, and methyl methacrylate under various conditions have been studied in greatest detail.[24,29,55,56–72,78–85] The properties of the copolymers and their molecular weights were varied within wide limits, which determined to a large extent the properties of the materials obtained. Table 8 presents certain data for such copolymers.[78]

Table 8. Copolymerisation of αββ-trifluorostyrene and its derivatives.[78]

Copolymer	Copolymerisation time, h	Yield of copolymer, %	Composition of copolymer, mol%		[η]* (in benzene)
			M_1	M_2	
TFS [M_1]–styrene [M_2]	8	74	28.53	71.47	2.7
	7	70	39.77	60.23	2.8
	8	60	48.53	51.47	1.8
	8	40	53.75	46.24	0.9
TFS [M_1]–2,5-dimethylstyrene [M_2]	4	90	50.53	49.17	1.1
	4	50	60.77	39.23	0.6
TFS [M_1]–methyl methacrylate [M_2]	6	—	43.29	56.71	0.4
	11	41	53.88	46.22	0.2
m-Methyl-αββ-TFS [M_1]–styrene [M_2]	2.5	40	46.27	53.73	0.5
o-Methyl-αββ-TFS [M_1]–styrene [M_2]	33	11	50.41	49.59	0.5
p-Methyl-αββ-TFS [M_1]–styrene [M_2]	7	55	46.97	53.03	2.0
	7	64	36.77	63.23	1.4

*[η] is the intrinsic viscosity measured in benzene.

Comparison of the thermal stabilities of different copolymers of TFS with styrene and its derivatives showed that the highest thermal stability (190 °C) is exhibited by TFS–2,5-dimethylstyrene copolymers.[72,79] Certain other characteristics of copolymers based on TFS have also been determined.[79,86]

Attempts have likewise been made to obtain ternary TFS–styrene–diene copolymers.[82,84,85,87,88]

Among other monomers which copolymerise with TFS and its derivatives, the greatest interest attaches to monomers based on acrylic and methacrylic acids and their derivatives.[78,88–94]

The copolymerisation of TFS with divinylbenzene, leading to the formation of cross-linked insoluble polymers, has been carried out mainly in order to obtain on subsequent sulphonation ion-exchange materials with improved thermal and chemical stabilities.[88,95–99] This is described in greater detail below.

The attempt to obtain a peroxide oligomer by the copolymerisation of TFS with a redox initiating system containing diene or vinyl units is also noteworthy. Such oligomers are used to vulcanise rubbers in order to obtain chemically stable vulcanised materials.[100]

Among all the possible TFS copolymers, its copolymer with tetrafluoroethylene would be of greatest interest. Such a copolymer would possess unique properties—high chemical and thermal stabilities since it would have a fully fluorinated main chain, effective physicomechanical properties as a result of the introduction of flexible TFE units, and the ability to dissolve owing to the presence of phenyl groups. However, it is extremely difficult to achieve such copolymerisation for a number of reasons, although in principle, it should be possible. Hitherto, there have been only isolated mentions of the synthesis of such copolymers.[101,102] The copolymer is obtained, for example, by emulsion polymerisation with radical initiation in the presence of dodecylamine hydrochloride or sodium lauryl sulphate in an autoclave. Table 9 presents the characteristics of this copolymer obtained by the emulsion method.[102]

As can be seen from the results in Table 9, the rate of copolymerisation of TFS with TFE and the yield of the copolymers are extremely low. Depending on the composition of the initial mixtures and the excess of TFE, their content of TFE:TFS units can vary from 2:95 mol% to 95:5 mol%. The copolymers obtained have low molecular weights, are soluble, and form fairly satisfactory films.

IV. Ion-exchange materials based on polytrifluorostyrene. Their synthesis and properties

The presence in each monomer unit of PTFS of a benzene ring makes possible the introduction into the latter of different functional groups with retention of the main perfluorinated chain. The introduction of ionogenic groups (sulphonic and carboxylic acid groups, phosphorus-containing groups, amino-groups, and certain others), which lead to the formation of valuable ion-exchange materials with improved resistance to corrosive influences, is most promising in this respect. The commonest method for the introduction of such groups is sulphonation of PTFS, which affords ion-exchange materials with good electrochemical characteristics.

1. Homogeneous cation-exchange membranes

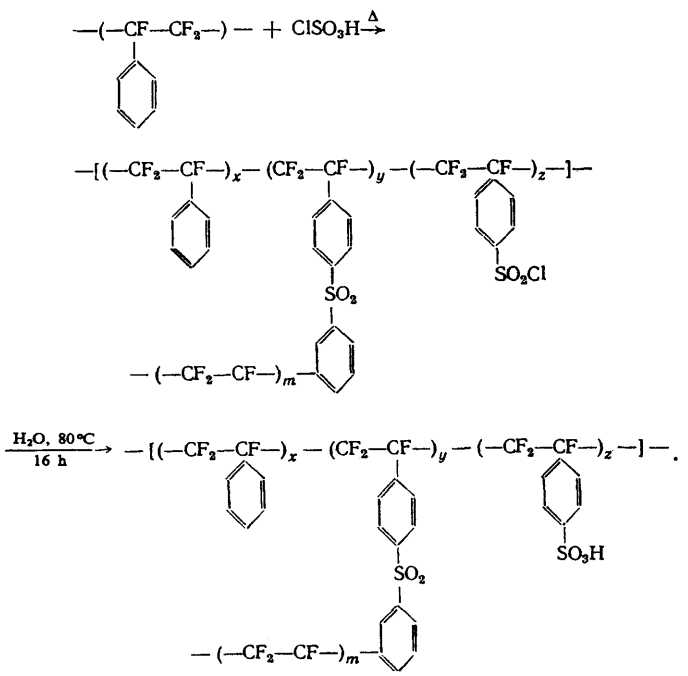
Numerous studies have been devoted to the sulphonation of PTFS in order to obtain cation-exchange materials with improved resistance to the action of corrosive media.[59,103–112] The sulphonation is usually carried out with chlorosulphonic acid or SO_3 in a dry halogen-containing solvent (usually chloroform) in the presence of an excess of the sulphonating agent. This results in the

Table 9. Copolymerisation of αββ-trifluorostyrene with tetrafluoroethylene.[102]

Recipe and copolymerisation conditions	Composition of copolymer, TFS:TFE, %	Characteristics of copolymer			
		viscosity [η]	T_g, °C	T_{decomp}, °C	elemental composition, %
TFS—16 g TFE—11.5 g $(NH_4)_2S_2O_8$—0.1 g $NaHSO_3$—0.05 g $C_{12}H_{25}NH_2.HCl$—1.45 g Water—50 ml Temperature—40 °C Duration—24 h Yield—2.2 g	90.7:9.3	0.35 dl g^{-1} [determined at 35 °C in ethyl methyl ketone (EMK)]	186 (Perkin–Elmer differential calorimeter)	361 (onset weight loss)	F—39.65 C—58.52 H—3.13
TFS—16 g TFE—250 g $FeSO_4.7H_2O$—2.4 g 50 ml of 3% H_2O_2 Ascorbic acid—12 g Water—500 ml Temperature—0–5 °C Duration—24 h Yield—3 g	64:36	0.15 dl g^{-1} (determined at 35 °C in EMK)	—	—	F—46.1 C—51.3 H—2.05

Remarks. The copolymers obtained are soluble in acetone, from solutions in which transparent flexible films can be cast.

formation of a polymer with different degrees of sulphonation and having both linear and cross-linked structures.



Depending on the sulphonation conditions and the presence of an excess of the sulphonating agent, the ratio of the linear and cross-linked sulphonated PTFS can be various.

There also exists a method for the synthesis of PTFS which is fully linear with a controllable number of sulpho-groups and which is in addition soluble in different solvents. The method reduces to sulphonation in solution with constant removal of the solvent whilst maintaining a constant concentration of the sulphonating agent.[113] In this way, it is possible to obtain sulphonated PTFS ranging from a water-soluble polymer [in the presence of a high content of sulphur-groups (>30 mol%)] to a polymer soluble in different hydrocarbon solvents (when the content of sulphur-groups is <10 mol%) and which can be worked in such solvents. The films obtained from the sulphonated PTFS can be used as ion-exchange membranes with high exchange capacity (>1 mequiv./g of polymer) and a low specific resistance. However, such films have low strength characteristics and are very brittle in the dry state.

Table 10 presents the sulphonation conditions (concentration of the sulphonating agent, its excess, and reaction time and temperature) and the characteristics of homogeneous ion-exchange membranes based on sulphonated PTFS for a large number of specimens sulphonated to different extents.[103] It follows from the analysis of the data presented that a low concentration of the sulphonating agent (<0.1 M) and a ratio of the sulphonating agent and the phenyl groups below the stoichiometric value ensure the formation of a non-cross-linked sulphonated PTFS with a fairly high degree of sulphonation (up to the presence of a sulpho-group in each benzene ring) and an exchange capacity >1. With increase in the concentration of the sulphonating agent to a value close to 1 M and above and when its excess relative to the phenyl groups is by a factor of several units, the sulphonation process affords a cross-linked product insoluble in all solvents and characterised by an approximately uniform exchange capacity (Table 10). This shows that it is undesirable to increase the excess of the sulphonating agent, although this permits a reduction of the process temperature. It

Table 10. Preparation and properties of sulphonated polytrifluorostyrene and homogeneous ion-exchange membranes based on it (PTFS with a molecular weight of 125000 was used).[103]

Preparation and properties	1	2	3	4	5	6	7	8	9	10	11	12
Sulphonating agent, molar concentration	0.021	0.048	0.096	0.021	0.04	0.86	1.42	1.0	1.0	1.0	0.85	1.14
Reaction time, h	3	3	3	3	3	4	4	4	4	4	12	4
Temperature, °C	60	60	60	50	60	30	30	40	50	60	30	30
Sulphonating agent: phenyl groups molar ratio	0.2	0.45	0.92	0.2	0.25	8.2	14.1	9.8	9.8	9.8	8.2	11.1
Gravimetric exchange capacity, mequiv/g of polymer	1.23	1.98	4.07	0.95	0.87	2.05	2.11	2.46	2.92	3.35	2.15	2.28
Solubility:												
Methanol	+	+	+	+	+	—	—	—	—	—	—	—
Ethanol	+	+	+	+	+	—	—	—	—	—	—	—
Isopropyl alcohol	+	+	—	+	+	—	—	—	—	—	—	—
Butanol	+	+	—	+	+	—	—	—	—	—	—	—
Acetone	+	+	+	+	+	—	—	—	—	—	—	—
Formamide	+	+	—	+	+	—	—	—	—	—	—	—
Dimethylformamide	+	+	—	+	+	—	—	—	—	—	—	—
Dioxan	+	+	—	+	+	—	—	—	—	—	—	—
Benzene, chloroform, hexane	—	—	—	—	—	—	—	—	—	—	—	—
Water	*	*	+	*	*	*	*	*	*	*	*	*

*Insoluble in water but swells.

Table 11. Properties of heterogeneous membranes based on sulphonated polytrifluorostyrene and a second polymer without ionogenic groups in its composition.[103]

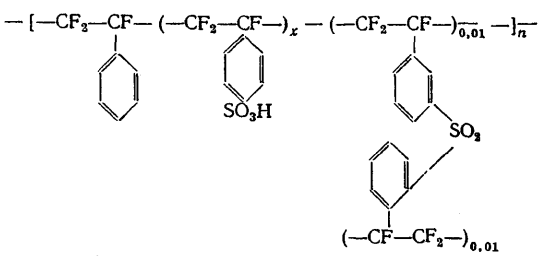
Characteristics and type of polymer	1	2	3	4	5	6	7	8	9	10	11	12
Gravimetric exchange capacity, mequiv/g of polymer	0.8	0.9	1.2	0.9	0.6	0.85	1.33	0.7	0.79	0.4	0.9	0.73
Resistance:												
H^+, Ω cm	28	42	—	—	—	25	18.5	21.9	13	—	—	70
K^+, Ω cm	—	3.01	23	—	5.54	—	—	—	—	7.0	4.2	—
Ion-exchange polymer, wt.%	20	50	67	50	67	35	50	30	33	50	50	50
Type of inert polymer, wt.%												
Kynar	80	50	33	—	—	—	35	—	—	—	—	—
Viton A-HV	—	—	—	50	33	—	—	—	—	—	—	—
CTFE–VF copolymer	—	—	—	—	—	65	15	—	—	—	—	—
Kel-F 810	—	—	—	—	—	—	—	70	—	—	—	—
Chlorosulphonated polystyrene	—	—	—	—	—	—	—	—	67	—	—	—
Poly(vinyl chloride)	—	—	—	—	—	—	—	—	—	50	—	—
Poly(vinylidene chloride)	—	—	—	—	—	—	—	—	—	—	50	—
Butadiene–styrene copolymer	—	—	—	—	—	—	—	—	—	—	—	50

follows from the data presented that all the parameters affect to some extent the characteristics of the sulphonated PTFS and hence the method of synthesis of ion-exchange materials from it.

2. Heterogeneous cation-exchange membranes

Heterogeneous membranes with good electrochemical parameters and better, compared with homogeneous membranes, physicochemical characteristics are also obtained from sulphonated PTFS. Such membranes are prepared either by mixing solutions of the corresponding polymers or by blending solid powdered polymers

with subsequent manufacture of the membranes from them.[103] These membranes are characterised by lower exchange capacities compared with the homogeneous membranes as a consequence of their appreciable content of an inert polymer but are more promising both in view of their improved physicomechanical properties and by virtue of the possibility of using different inert polymers depending on the operating conditions. Blends of polymers can also be used as neutral components of membranes of this kind; in such cases the heterogeneous membranes are obtained by blending three and more polymers.[104] The ionogenic component in the heterogeneous membranes is cross-linked sulphonated PTFS having the following structure:



$x = 2.3$.

Table 11 presents examples of different compositions of heterogeneous membranes and some of their electrochemical characteristics.[103]

Table 12. Surface modification of heterogeneous ion-exchange membranes based on sulphonated PTFS.[110]

Solutions of reactants (parts by weight)	Reaction conditions		ρ, Ω cm²	Transport number	Current yield, %	Concentration of NaCl in 5 M NaOH, M
	T, °C	time, h				
Naphthalene (30) $AlCl_3$ (10) CS_2 (60)	30	16	6.2	0.87	92	0.002
Xylene (30) $TiCl_4$ (10) CCl_4 (60)	30	8	6.3	0.87	91	0.004
Fluorene (20) $SnCl_4$ (5) CCl_4 (75)	30	16	6.2	0.87	90	0.005
Benzene (40) $AlCl_3$ (15) CCl_4 (45)	30	8	6.5	0.87	91	0.003
Without treatment	—	—	6.0	0.84	77	0.03

Like the best ion-exchange membranes available at present, which are based on a material of the Nafion type, the homogeneous and heterogeneous ion-exchange membranes obtained from sulphonated PTFS are designed for use under severe conditions (mainly in chlorine electrolysis in electrolytic cells). In terms of their electrochemical properties, these membranes are indistinguishable or differ little from the corresponding membranes based on the Nafion type material but are appreciably inferior to them as regards mechanical properties.

In order to improve certain electrochemical parameters, such membranes are subjected to surface modification which can be readily carried out using the Friedel–Crafts reaction by introducing various groups into the benzene rings of PTFS. Table 12 presents the changes in the current yield and in the selectivity of the membranes obtained by blending 30 parts by weight of the sulphonated and cross-linked PTFS with 70 parts by weight of a fine poly(vinylidene fluoride) powder (Kynar) using a blending and pressing procedure.[110]

3. Grafted cation-exchange membranes prepared using sulphonated polytrifluorostyrene

Membranes based on sulphonated PTFS, which have good thermal and chemical stabilities, are particularly valuable ion-exchange materials which are resistant to corrosive influences. However, such membranes, especially homogeneous ones, are characterised by inferior physiochemical parameters compared with membranes of the Nafion type. One of the most promising procedures for overcoming these disadvantages proved to be the grafting of TFS onto different films (usually fluorine-containing polymers) with subsequent sulphonation of the resulting graft copolymers or by introducing other ionogenic groups into their benzene rings.[99,101,114–125] The grafting is carried out as a rule by a radiation method.

Films made up of polyethylene, polytetrafluoroethylene, poly(chlorotrifluoroethylene), the ethylene–TFE copolymer, the propene–TFE copolymer, poly(chloroethylene), the hexafluoropropene–vinylidene fluoride copolymer, the heptafluoropropene–TFE copolymer, the copolymer of TFE and perfluorinated vinyl ethers (Nafion), and other materials are used as inert supports. The irradiation dose is 1–30 Mrad. The films are irradiated in air and in oxygen or inert media. This results in the formation of radicals whose lifetime in an inert atmosphere is up to two weeks at 0 °C, up to seven days at 10 °C, and 2–3 days at room temperature.[118,119] In order to obtain graft TFS polymers on different supports, the irradiated films are placed in TFS or its solutions in chloroform, tetrachloroethane, CCl_4, Freon 113, or benzene and are kept there at a temperature of 10–90 °C for 1–50 h. The degree of grafting is 10–50%. The characteristics of such membranes are quite good and are comparable with those of ion exchange membranes based on Nafion. Comparative data for ion-exchange membranes based on the ethylene–TFE copolymer on which TFS has been grafted with subsequent sulphonation and for Nafion 120 membranes[119] are presented below.

Membrane	Exchange capacity, mequiv g^{-1}	ρ, in 0.5 M KCl, Ω cm²	Extensibility	Transport number, 0.5 M KCl/1 M KCl
With grafted TFS	0.61	1.71	3.4—4.5	0.94
Based on Nafion	0.83	1.48	4.0	0.93

Such membranes can be used as diaphragms for any purposes (the electrolysis of water, NaCl, and the Glauber salt, low-temperature dialysis, etc.). The methods employed provide for the irradiation of only the initial films, while TFS is not irradiated. They are economical and readily applied. Table 13 presents the characteristics of certain cation-exchange membranes obtained by grafting TFS onto different 100 μm supports with subsequent sulphonation in the

course of 40 min with chlorosulphonic acid in CCl_4 or tetrachloroethylene at 40 and 135 °C respectively.[119]

Table 13. Cation-exchange membranes obtained from different polymers by the radiation grafting of TFS and subsequent sulphonation.[119]

Support	Degree of grafting, %	Degree of sulphonation, %	Characteristics of membrane			Resistance to action of oxidant (weight loss)
			exchange capacity, mequiv. g^{-1}	ρ, Ω cm^2	transport number, 0.5 M KCl/1 M KCl	
Polyethylene (low density)	23	95	1.5	1.4	0.9	15
Poly(vinylidene fluoride)	20	60	0.6	3.2	0.93	10
TFE–ethylene copolymer	21	90	1.0	—	—	3
TFE–ethylene copolymer	16	80	0.7	3.5	0.93	3
Polytetrafluoroethylene	—	—	—	4.0	0.93	1

*Treatment with 3% H_2O_2 containing 4 p.p.m. of Mohr's salt at 70 °C for 24 h.

There is also a radiation method for grafting TFS onto inert films by irradiating the latter in a solution of the monomer. In this case, the degree of grafting for identical doses is regulated by the TF concentration in solution in different solvents and depends on the nature of the latter. Table 14 present data for the grafting of TFS onto the TFE–hexafluoropropene (HFP) copolymer in different solvents.[115] TFS was grafted onto a film which was placed in the form of a roll into the corresponding TFS solution, the chamber was evacuated or filled with an inert gas, and the temperature was kept at a level such that the solvent did not evaporate.

Table 14. Degree of radiation grafting of TFS at a dose of 2.59 Mrad.[115]

TFS concentration, %	Benzene, %	Degree of grafting, %	TFS concentration, %	Methylene chloride, %	Degree of grafting, %
10	90	1.4	10	90	2.5
30	70	8.2	30	70	9.7
50	50	14.3	50	50	17.6
70	30	24.0	70	30	27.1

4. Anion-exchange and other membranes prepared using grafted αββ-trifluorostyrene

Films with grafted TFS can be used after the appropriate treatment not only as cation-exchange membranes with sulphonic and carboxylic acid or phosphorus-containing groups but also as anion-exchange membranes after appropriate amination or as neutral membranes.[119]

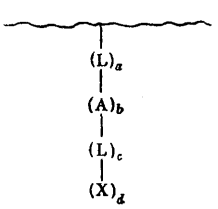
Anion-exchange membranes obtained by the radiation grafting of TFS onto different supports with subsequent chloromethylation and the preparation of quaternised aminated derivatives are of great interest. The reagents used for this purpose are CH_3OCH_2Cl, paraformaldehyde $(CH_2O)_3$, and HCl with which the grafted films are treated in the presence of $AlCl_3$ or $ZnCl_2$ as catalysts at 40 to 80 °C. The films are then treated with 5–50% aqueous solution of trimethylamine, triethylamine, or 2-hydroxyethyl(dimethyl)amine. Such anion-exchange membranes have good electrochemical parameters and an improved resistance to hydrolysis. The relevant data are presented in Table 15.[119]

Table 15. Anion-exchange membranes prepared from different polymers with radiation grafted TFS and subsequent chloromethylation and amination.[119]

Support	Degree of grafting, %	Degree of chloromethylation, %	Characteristics of membranes			Resistance to hydrolysis*
			exchange capacity, mequiv.g^{-1}	ρ, Ω cm^2	transport number, 0.5 M KCl/1 M KCl	
Polyethylene (low density)	23	80	0.86	4.2	0.92	without changes
Poly(vinylidene fluoride)	20	78	0.75	5.0	0.93	ditto
TFE–ethylene copolymer	18	80	0.70	4.8	0.94	»
Polytetrafluoroethylene	18	80	0.71	6.0	0.93	»

*Hydrolysis in distilled water at 95 °C for six days.

An interesting method of synthesising ion-exchange materials involves radiation cografting of a mixture of vinyl monomers and dicarboxylic acids onto a perfluorinated base. TFS can also be used as the vinyl monomer. Such ion-exchange materials can be represented schematically as the main perfluorinated chain with grafted side groups of the type[126]



where $a \geqslant 1$, $b \geqslant 0$, $c = 0.1$ or above, and $d \geqslant 1$, L represents the vinyl monomer residue, A represents active groups (dicarboxylic acids or their derivatives), and X is the polymer chain, capable of being terminated, or a fluorinated hydrocarbon polymer.

Insoluble cation-exchange resins with different exchange capacities have been obtained by copolymerising TFS with divinylbenzene and then sulphonated.[95,97,103,109]

V. Other aspects of the applications of polytrifluorostyrene

Together with the well known applications of PTFS as ion-exchange materials resistant to the action of corrosive media, this polymer is used for a number of other purposes. The use of PTFS for the preparation of an ultrafine fibrous filtering material FSPF (fluorostyrene Petryanov filter) proved to be the most promising application. This material is capable of withstanding repeated sterilisation with hot steam up to a temperature of 150 °C without change in filtration efficiency (99.99% with respect to an oil mist) and in physicomechanical parameters. The FSPF material is designed for use in bacterial filters sterilised by hot steam whose purpose is to free air from microorganisms in the microbiological, medical, and food industries and in health service establishments.[127–129]

Sulphonated PTFS can be employed as a catalyst in the synthesis of esters from neoalkylpolyols and aliphatic acids, its use greatly improving the properties of the products synthesised and simplifying their isolation from the reaction masses.[130] PTFS sulphonated to different extents can be used also in highly sensitive elements for a gravimetric hygrometer[131] and as a complex-forming material with a high selectivity in the separation of certain mixtures.[132]

The PTFS base material FC-430 is introduced in small amounts into compositions for the protection of films against electrochemical corrosion.[133]

PTFS-based materials with effective adhesion and antistatic properties are also employed to coat the grains of a photographic material.[134]

It has recently been reported that polymeric optical fibres, with excellent optical properties and a high capacity for the transmission of light have been prepared using PTFS.[135] PTFS is employed as their core. The losses in light transmission in such fibres are 130 dB km^{-1} (at 660 nm), 280 dB km^{-1} (at 780 nm), and 440 dB km^{-1} (at 850 nm).

PTFS has found recently an extremely interesting new application in the formation of negative electronic resistors with a high sensitivity, high chemical and thermal stabilities and a satisfactory resistance to dry etching.[136] In order to obtain such coatings, a solution of PTFS in chlorobenzene is deposited onto a silicon plate. On irradiation with a stream of fast electrons and subsequent treatment, coatings having a surface relief with a high resolving capacity, good adhesion, and a high resistance to dry etching are obtained.

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