

Polyelectrolytes Prepared from Perfluoroalkylaryl Macromolecules

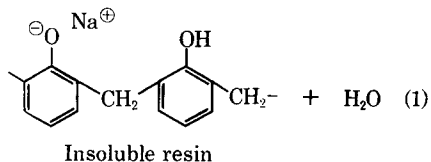
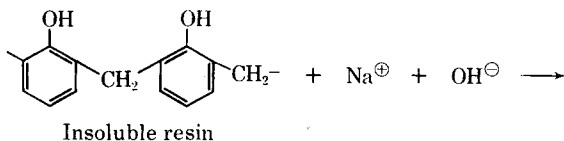
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Synopsis

The synthesis of a new generation of high-capacity oxidation-resistant ion-exchange resins and membranes is described which are sulfonic acid polyelectrolytes prepared from high molecular weight poly- α,β,β -trifluorostyrene. The difficult sulfonation of poly- α,β,β -trifluorostyrene is discussed in terms of the finding that this sulfonation must be effected upon an aromatic ring possessing a *meta*-directing substituent group. The oxidative stability of these new types of perfluoroalkyl aromatic sulfonic acid polyelectrolytes is both demonstrated and described with comparisons to their polystyrenesulfonic acid homologs. The difference in their oxidation-depolymerization stabilities is described in terms of benzylic carbon substituents.

INTRODUCTION

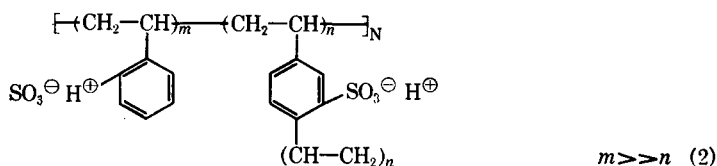
Synthetic polyelectrolytes or ion-exchange resins were first prepared and used three decades ago by Adams and Holmes,^{1,2} who reacted phenol with formaldehyde to form a crosslinked condensation polymer and then proceeded to use this resin as an ion exchanger for strongly basic solutions.



Since that time, functional groups with higher acid strength (or higher ionic strength cations) as well as groups of high basic strength (or high ionic strength anions) have been synthetically attached to the skeletons of crosslinked phenolformaldehyde polymers to make up a class of organic resins called either "condensation ion-exchange resins" or "condensation polyelectrolytes."

The following groups have been successfully substituted on the phenol-formaldehyde resin skeleton so as to serve as functional polyelectrolyte groups: $-\text{SO}_3^\ominus\text{H}^\oplus$, $-\text{COOH}$, $-\text{COO}^\ominus\text{M}^\oplus$, $-\text{CH}_2\text{SO}_3^\ominus\text{M}^\oplus$, $-\text{O}-\text{CH}_2-\text{COOH}$, $-\text{O}-\text{CH}_2-\text{COO}^\ominus\text{M}^\oplus$, $-\text{O}-\text{CH}_2-\text{PO}_3^\ominus=(\text{H}^\oplus)_2$, $-\text{O}-\text{CH}_2-\text{PO}_3^\ominus=(\text{M}^\oplus)_2$, $-\text{ASO}_3^\ominus=(\text{H}^\oplus)_2$, $-\text{ASO}_3^\ominus=(\text{M}^\oplus)_2$, $-\text{NR}_3^\oplus\text{A}^\ominus$, $-\text{SR}_2^\oplus\text{A}^\ominus$, $-\text{P}^\oplus\text{R}_3\text{A}^\ominus$, where $\text{M}^\oplus = \text{Na}^\oplus, \text{K}^\oplus, \text{NH}_4^\oplus, \text{Cs}^\oplus, \text{Rb}^\oplus, \text{Tl}^\oplus, \text{Ag}^\oplus$; $\text{A}^\ominus = \text{Cl}^\ominus, \text{Br}^\ominus, \text{I}^\ominus, \text{SCN}^\ominus, \text{N}_3^\ominus, \text{NO}_3^\ominus$.

In the years 1943 and 1944, G. D'Alelio³⁻¹⁴ invented a more heat-stable and synthetically controllable crosslinked polyelectrolyte type which to this day is used as the principle skeletal structure for nearly all functional group variations of ion exchange polyelectrolyte resins. This invention was an insoluble, infusible, sulfonic acid-substituted polystyrene-divinylbenzene resin, which provides the base structure for nearly all cationic ion-exchange resins manufactured and used at this time.



By merely varying the divinylbenzene content relative to styrene (i.e., 0.25 to 25 mole-% based on monostyrene), D'Alelio could produce ion-exchange polyelectrolytes (by sulfonation) having various degrees of swelling and thus a multiplicity of end uses.

Since the invention of polystyrene-divinylbenzene sulfonate polyelectrolytes, other groups have been successfully substituted onto these aromatic rings to give a series of cation or anion exchange resins: $-\text{PO}_3^\ominus=(\text{H}^\oplus)_2$, $-\text{PO}_3^\ominus=(\text{M}^\oplus)_2$, $-\text{ASO}_3^\ominus=(\text{H}^\oplus)_2$, $-\text{COOH}$, $-\text{COO}^\ominus(\text{M}^\oplus)$, $-\text{CH}_2-\text{NH}_3^\oplus\text{A}^\ominus$, $-\text{CH}_2-\overset{\oplus}{\text{N}}\text{R}_3\text{A}^\ominus$, $-\overset{\oplus}{\text{C}}\text{H}_2-\overset{\oplus}{\text{P}}\text{R}_3\text{A}^\ominus$, $-\overset{\oplus}{\text{N}}\text{R}_3\text{A}^\ominus$, where $\text{M}^\oplus = \text{Na}^\oplus, \text{K}^\oplus, \text{Rb}^\oplus, \text{Cs}^\oplus, \text{NH}_4^\oplus, \text{Tl}^\oplus, \text{Ag}^\oplus$; $\text{A}^\ominus = \text{Cl}^\ominus, \text{Br}^\ominus, \text{I}^\ominus, \text{SCN}^\ominus, \text{NO}_3^\ominus, \text{N}_3^\ominus$.

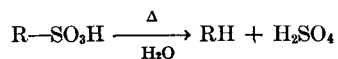
A review of all of the different anion and cation polyelectrolytes described briefly above can be found in Helfferich's works.^{15,16}

The ion-exchange resins heretofore described have received large industrial usage as bead-type exchangers for the purification of water, chemical separations, purification of food and drug solutions, recovery of valuable metals, and in heterogeneous catalysis; and recently in membrane form for uses in medicine, electrodialyses, and electrical power sources. While solution purification, metals extraction, and chemical separations find little need for oxidatively stable ion-exchange resins, ion-exchange membranes for use in medicine and especially those used for power sources (ion-exchange membrane hydrogen-oxygen fuel cell) are potentially or actually in need of polyelectrolyte resins having very high degrees of heat and oxidative environment stability. It is the principal purpose of this paper to describe the preparation and properties of a polyelectrolyte that is both

heat-resistant and oxidatively stable to peroxides and other active oxygen solutions. This water-insoluble polyelectrolyte, sulfonated poly- α,β,β -trifluorostyrene, is based on a perfluoroalkyl aromatic addition polymer which has been functionalized by specific ionic group substitution.

DISCUSSION

Both phenol-formaldehyde and polystyrene-divinylbenzenesulfonic acid resins have been examined for heat and oxidation stability. Such experiments, which will be described below, showed the resins to be heat-resistant up to 60–65°C. in the case of phenol-formaldehyde sulfonic acid resins and to 125°C. in the case of polystyrene-DVB-sulfonic acid resins. However, this refers to aqueous heat alone in the absence of any oxidation medium such as oxygen dissolved in water, oxidative potentials greater than 0.7 v., peroxide solutions, or other active aqueous oxidizing ions such as permanganate or persulfate.



In the presence of dissolved (H_2O) oxygen or, even worse, hydrogen peroxide solutions, phenol-formaldehyde and polystyrenesulfonic acid resins exhibit very poor chemical stability at 70°C. and measurable instability even at 25°C. The chemical stability described here is defined as resistance to chain scissions of the crosslinked polyelectrolyte skeletons and not to the loss of functional ionic groups (hydrolysis). Of course, chain scissions of even highly crosslinked polyelectrolytes lead to ultimate water solubility of the ion exchanger and contamination of its mobile aqueous phase. Despite being highly crosslinked, polyelectrolytes of both phenol-formaldehyde and polystyrene-divinylbenzenesulfonic acid resins are converted into water-soluble fragmentary polyelectrolytes in a matter of a few hours in the presence of hydrogen peroxide and in days, depending on the degree of crosslinking, in the presence of oxygen and/or ultraviolet light near the 3000 Å. region of wavelength.

A brief review of this instability toward an oxidizing medium will be given here. It will not exhaustively cover all of our oxidative stability studies, as this coverage is very extensive and definitely belongs in a separate dissertation, which will be published at a later date.

Since a phenol-formaldehyde sulfonic acid polyelectrolyte was found to be more oxidatively unstable, rate-wise, than a polyelectrolyte prepared from styrene and divinylbenzene, we will describe the oxidation instability of the latter, it being immediately obvious that a similar mechanism of benzylic oxidative degradation is operative in both cases but with a much faster rate for the phenol-formaldehyde sulfonic acid polyelectrolyte.

The following tests were devised and found effective in rating polyelectrolyte stability to oxidation and light instability: (a) effect of 3% hydrogen peroxide with 1 ppm ferrous ion in the temperature range 60–

TABLE I

Degree of Solubilization (Oxidative Scission Depolymerization) of Various Sulfonic Acid Polyelectrolytes in the Presence of Ferrous Ion-Catalyzed Hydrogen Peroxide at 70°C. for 24 hr. Exposure Times^a

Test	Polyelectrolyte	Weight poly- electro- lyte, g.	3% H ₂ O ₂ , ml.	Fe ⁺² , ppm	Solubiliza- tion (degrada- tion), %
1	Phenol-formaldehyde-sulfonic acid, IEC = 2.15 meq. H ⁺ /g. dry resin ^b	3	25	1	97.2
2	Polystyrene-1% divinylbenzene-sulfonic acid, IEC = 5.00-5.10 meq. H ⁺ /g. dry resin	3	25	1	62.4
3	Polystyrene-2% divinylbenzene-sulfonic acid, IEC = 5.00-5.10 meq./g.	3	25	1	46.5
4	Polystyrene-4% divinylbenzene-sulfonic acid, IEC = 5.00-5.10 meq./g.	3	25	1	25.8
5	Polystyrene-8% divinylbenzene-sulfonic acid, IEC = 5.00-5.10 meq./g.	3	25	1	10.6
6	Polystyrene-12% divinylbenzene-sulfonic acid, IEC = 5.00-5.10 meq./g.	3	25	1	6.4
7	Sulfone-crosslinked poly- α,β,β -trifluorostyrenesulfonic acid, IEC = 1.23 meq./g. ^c	3	25	1	0.0
8	Sulfone-crosslinked poly- α,β,β -trifluorostyrenesulfonic acid, IEC = 2.70 meq./g. ^c	3	25	1	0.0

^a DVB in per cent based on styrene during polymerization.

^b IEC = ion-exchange capacity.

^c The sulfone crosslinking has been measured by $-\text{SO}_2/-\text{SO}_3^{\ominus}\text{H}^+$ ratio and found to lie between 0.1 and 0.25%.

75°C.; (b) effect of ultraviolet light in the 3000 Å. wavelength region. These test methods are described in the experimental section.

Table I shows the effect of 3% hydrogen peroxide in the presence of 1 ppm ferrous ion at 70°C. upon styrene-divinylbenzenesulfonic acid polyelectrolytes of various degrees of crosslink density and upon poly- α,β,β -trifluorostyrene polyelectrolytes of varying acid strengths.

Figure 1 shows the effect of crosslink density on the resistance of polystyrene-divinylbenzenesulfonic acids towards oxidation scission degradation.

A most interesting finding from the above data is the fact that even though its crosslink density is very low; poly- α,β,β -trifluorostyrenesulfonic acid, regardless of its acid capacity, is not destroyed by this severe peroxygen degradation test. In fact, more severe oxidation tests with

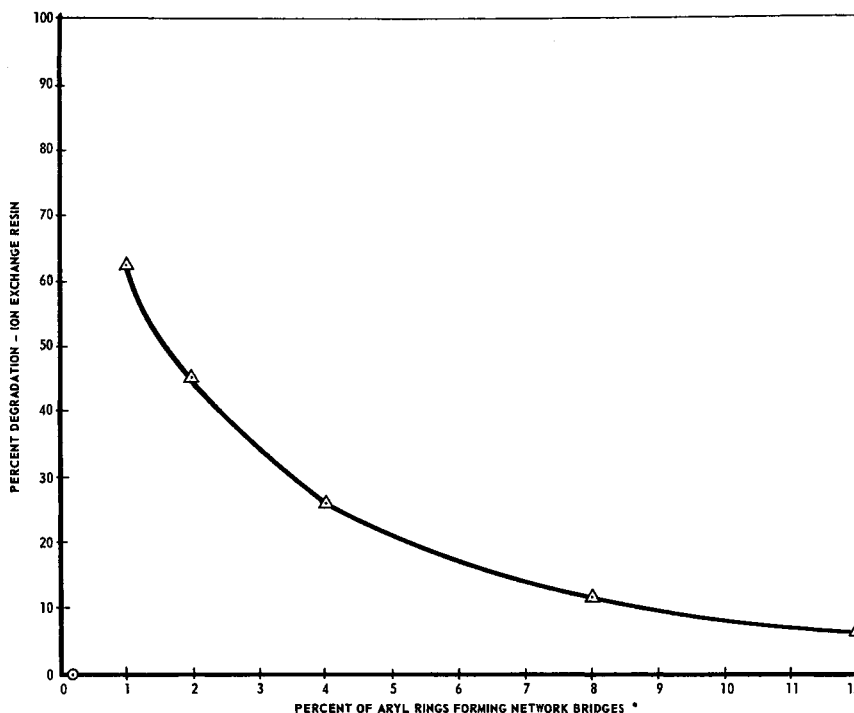


Fig. 1. Effect of 25 ml. of 3% H_2O_2 with 1 ppm Fe^{++} on 3 g. ion-exchange resin for 24 hr. at $70^\circ C.$: (Δ) polystyrene-divinylbenzenesulfonic acid.

fuming nitric acid at room temperature or 5% solutions of potassium persulfate and potassium permanganate at $60^\circ C.$ also failed to break down poly- α,β,β -trifluorostyrenesulfonic acid while doing total damage in the form of total solubilization of the phenol-formaldehyde and polystyrene-1% divinylbenzenesulfonic acids.

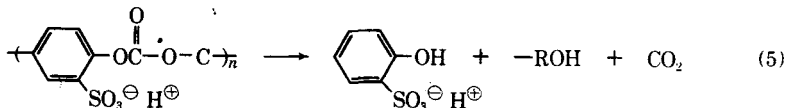
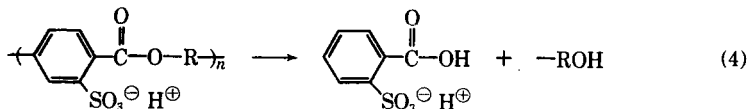
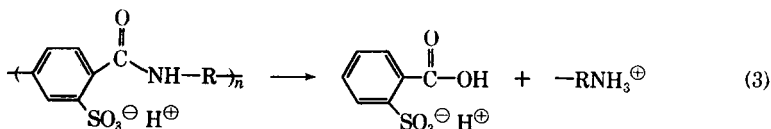
In a separate test, the effect of dissolved oxygen in water in the presence of ultraviolet light at 3000 A. upon several types of sulfonic acid polyelectrolytes was measured. Similar results were found as in the case of peroxide oxidation. These results are summarized in Table II.

The photochemical degradation test shows (Fig. 2) the effect of crosslink density upon solubilizing degradation. Again, α,β,β -trifluorostyrenesulfonic acid was found to be stable despite a very low crosslink density, (i.e., high water content compared to even 1% DVB-crosslinked polystyrene electrolytes).

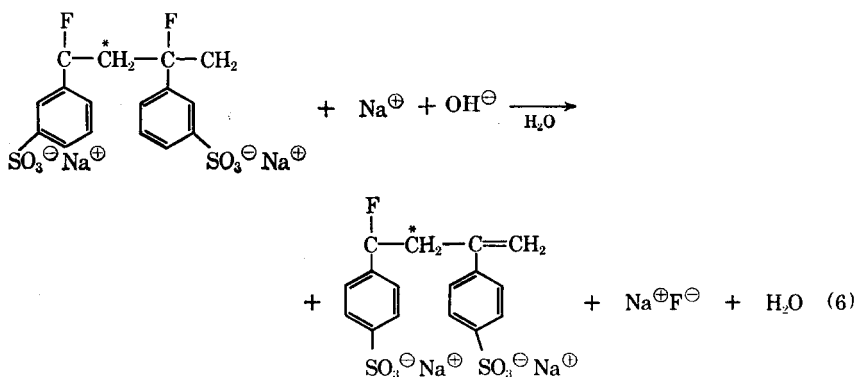
The above data show preliminary evidence that poly- α,β,β -trifluorostyrenesulfonic acid is a very stable molecule with regards to oxidation and ultraviolet irradiation. Its resistance to degradation despite the absence of a high crosslink density appears to suggest that its styrene-divinylbenzenesulfonic acid analogs are weak at the α - or benzylic carbon-

hydrogen bond (77 kcal./mole) whereas the α or benzylic carbon-fluorine bond (103 kcal./mole) of this new oxidatively stable compound is indeed quite resistant to oxidative damage.

Since the molecular structures of today's commercial ion-exchange polyelectrolytes are apparently oxidatively weak to attack at benzylic C—H sites, this paper describes the preparation of a polyelectrolyte system which will be devoid of benzyl C—H groups and, thus more resistant to oxidative depolymerization. This synthesis will be limited to the class of sulfonated hydrocarbon or halohydrocarbon since the synthetic use of polyesters, polycarbonates, or polyamides and the like is not feasible. This is because strong acid functional groups are likely to cause polymer degradation by simple hydrolysis.



The substitution of an oxidation-resistant fluorine group onto the α carbon of polystyrene is one possible solution to benzylic C—H instability but should the polyelectrolyte material ever be exposed to highly basic solutions, a different mode of degradation, i.e., dehydrohalogenation, would occur.



This would only serve to create a new allylic weak point at the asterisk-labeled carbon and thus set up a new type of oxidatively unstable system (i.e., allylic β -carbon-hydrogen scission).

In light of the above arguments, it was decided to synthesize polyelectrolytes based on fully fluorinated alkyl chains having alternate carbons substituted with benzenesulfonic acid. The easiest synthetic route to such a material was first to synthesize α,β,β -trifluorostyrene, polymerize it, introduce the sulfonic acid group onto the aromatic ring, and either complete the synthesis by crosslinking it to render it water-insoluble or to sulfonate partially only a certain fraction of its aromatic rings. All of these syntheses were completed and are described below, along with several reactivity

TABLE II
Degree of Solubilization of Various Sulfonic Acid Polyelectrolytes Under 48 hr. Irradiation with 3000 A. Ultraviolet Light (Mazda Sun Lamps) Placed 15 in. Away from Wet Polyelectrolytes

Test	Polyelectrolyte	Weight polyelectrolyte, g.	Weight water, g.	Solubilization (or degradation), %
1	Polystyrene-1% divinylbenzenesulfonic acid, IEC = 5.00-5.10 meq. H ⁺ /g. dry resin	5	25	65.6
2	Polystyrene-2% divinylbenzenesulfonic acid, IEC = 5.00-5.10 meq. H ⁺ /g. dry resin	5	25	41.7
3	Polystyrene-4% divinylbenzenesulfonic acid, IEC = 5.00-5.10 meq. H ⁺ /g. dry resin	5	25	24.6
4	Polystyrene-7% divinylbenzenesulfonic acid, IEC = 5.00-5.10 meq. H ⁺ /g. dry resin	5	25	19.0
5	Polystyrene-9% divinylbenzenesulfonic acid, IEC = 5.00-5.10 meq. H ⁺ /g. dry resin	5	25	16.4
6	Polystyrene-12% divinylbenzenesulfonic acid, IEC = 5.00-5.10 meq. H ⁺ /g. dry resin	5	25	14.2
7	Poly- α,β,β -trifluorostyrenesulfonic acid, sulfone-crosslinked, IEC = 2.70 meq. H ⁺ /g. dry resin	5	25	0.0

variances not found while making the more easily formed sulfonated polystyrenes.

The preparation of the monomer α,β,β -trifluorostyrene was first carried out by Cohen et al.,¹⁷ who reported its total synthesis. The polymerization of this monomer was described by Prober,¹⁸ who found that this perfluorinated derivative of styrene was quite reluctant to homopolymerize to a high molecular weight macromolecule; but instead preferred to dimerize, under free-radical bulk polymerization conditions, most probably

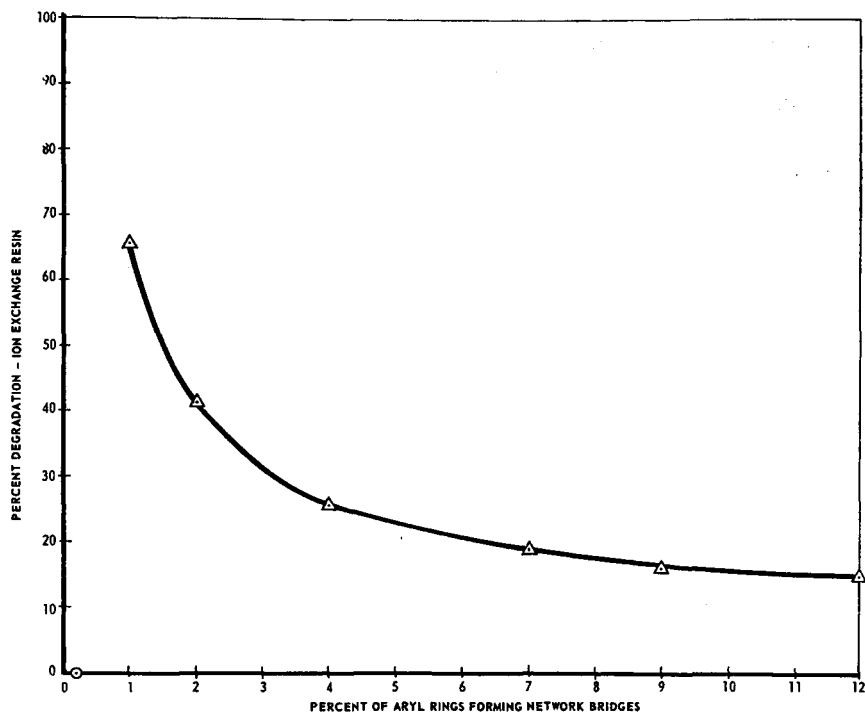
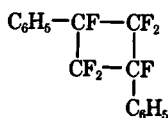


Fig. 2. Effect of O_2 and ultraviolet light (3000 A.) 15 in. from aqueous polyelectrolytes (48 hr.): (Δ) polystyrene-divinylbenzenesulfonic acid.

by a biradical mechanism, nearly quantitatively into 1,3-diphenylperfluorocyclobutane (I):



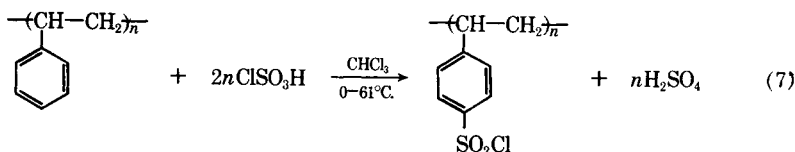
I

By keeping the free-radical initiator in very low concentration in the bulk phase (organic monomer phase), however, self-addition of monomer to a growing free-radical chain is favored, and a macromolecular species having a number-average molecular weight between 40,000 and 300,000 may be obtained. This can only be accomplished by emulsion polymerization techniques. Prober¹⁸ first prepared this polymer in high molecular weight by such a technique. Copolymers of α,β,β -trifluorostyrene with both styrene and with chlorotrifluoroethylene were described by Livingston et al.¹⁹

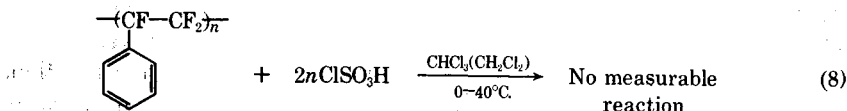
Sulfonation of Poly- α,β,β -Trifluorostyrene

The preparation of sulfonated polyelectrolytes from poly- α,β,β -trifluorostyrene was found to be a much more difficult task than that en-

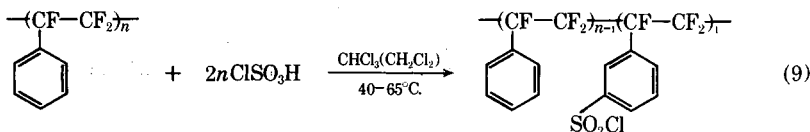
countered in the preparation of the corresponding polystyrene or polystyrene-divinylbenzene sulfonates. A solution of polystyrene in either chloroform or methylene chloride reacts instantly and quantitatively with chlorosulfonic acid to yield principally *para*-substituted sulfonyl chloride groups according to eq. (7).



Poly- α,β,β -trifluorostyrene fails to undergo the above type of reaction in the temperature range 0–40°C. and fails to react with even 30% oleum under any conditions.



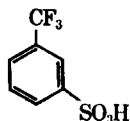
However, a very low degree of substituted product is obtained in the temperature range 40–65°C. according to eq. (9), where $10 < n < 13$. With



only an increase in the concentration of sulfonating reagent (ClSO_3H), however, polyelectrolytes of α,β,β -trifluorostyrene were obtained whose final degree of sulfonation was very dependent on the temperature of sulfonation.

When 0.9 mole of chlorosulfonic acid is added to 0.1 mole of poly- α,β,β -trifluorostyrene of $[\eta]_{\text{C}_6\text{H}_6} = 0.6-0.9$ in excess chloroform at 30°C. a brown residue precipitates from solution which, upon subsequent hydrolysis with water at 80°C., yields a water-insoluble, alcohol-insoluble, infusible, cross-linked poly- α,β,β -trifluorostyrenesulfonic acid resin. This resin was found to be crosslinked. Analysis shows the crosslinks to be sulfone linkages and infrared spectroscopy examination shows that the sulfonic acid groups have been substituted *meta* to the perfluorovinyl groups of the aromatic rings. This finding suggests a plausible explanation for the difficulty in obtaining the ease of reaction that one observes with the sulfonation of polystyrene. The sulfonation of an aromatic ring possessing an electron-withdrawing substituent is always many times more difficult than with an unsubstituted aromatic ring or one possessing one or more electron-donating groups. A detailed examination of the infrared spectra of freshly prepared membrane films of linear poly- α,β,β -trifluorostyrenesulfonic acid of $\text{IEC} = 1.27$ meq. H^+ /g. dry resin showed a very sharp and distinct ab-

sorption peak at exactly 700 cm.^{-1} and the total absence of any absorption peak at 750 cm.^{-1} . This can be true only of *meta*-substituted benzene molecules or 1,2,3-trisubstituted benzene molecules. This spectrum was confirmed by preparing *m*-methforylbenzenesulfonic acid by the direct sulfonation of methforylbenzene with hot 70% oleum and again finding the 700 cm.^{-1} absorption peak and the absence of the 750 cm.^{-1} peak with the pure compound (II).



II

The use of a large molar excess of chlorosulfonic acid in the presence of poly- α,β,β -trifluorostyrene in chloroform or methylene chloride does not succeed in giving mole for mole aromatic substitution. However, a step-wise series of temperature increases during different sulfonation reactions did indeed show an upgrade in the degree of substitution. In all cases, where a large excess of sulfonating reagent was used, the sulfone cross-linking appeared as a minor reaction although an extremely important

TABLE III
Effect of Temperature and Concentrations of Reactants on the
Preparation of Various Types of Poly- α,β,β -trifluorostyrenesulfonic Acid

Concentration Poly- α,β,β - trifluorostyrene mole/l. mer units ^a —CF ₂ —CF— C ₆ H ₅	Chloroform solvent		Temperature, °C.	Type of polyelectrolyte obtained (based on solubility) ^b
	Concentration of ClSO ₃ H, mole/l.	IEC, meq. H ⁺ /g. dry resin		
0.105	0.021	1.23	61	L
0.105	0.033	1.28	61	L
0.105	0.048	1.99	61	L
0.105	0.096	4.07	61	L
0.105	0.021	0.95	50	L
0.105	1.43	2.11	30	N
0.105	1.00	2.24	35	N
0.105	1.00	2.46	40	N
0.105	1.00	2.92	50	N
0.105	1.00	3.85	60	N
0.105	0.85	2.15	30	N
0.105	0.58	1.91	30	N
0.105	0.105	0.00	30	—
0.105	0.105	0.00	35	—
0.105	0.105	0.14	40	—
0.105	0.210	0.27	40	—

^a $[\eta]$ (benzene, 30°C.) = 0.6–1.4.

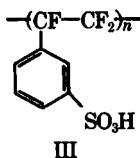
^b L = linear; N = network (sulfone).

one for the preparation of useful ion-exchange resins. Crosslinked resins are water-insoluble.

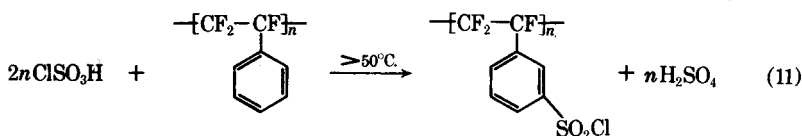
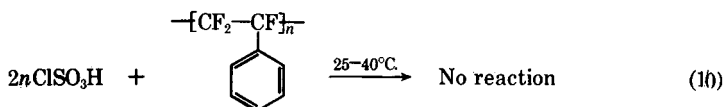
Table III shows range of degree of sulfonation of products obtained (measured in terms of ion-exchange capacity):

$$\text{Ion-exchange capacity (IEC)} = \frac{\text{meq. H}^+ \text{ (from } -\text{SO}_3\text{H group)}}{\text{g. dry resin}}$$

Fully sulfonated poly- α,β,β -trifluorostyrene (III) would have IEC = 4.20 meq. H⁺/g. dry resin.



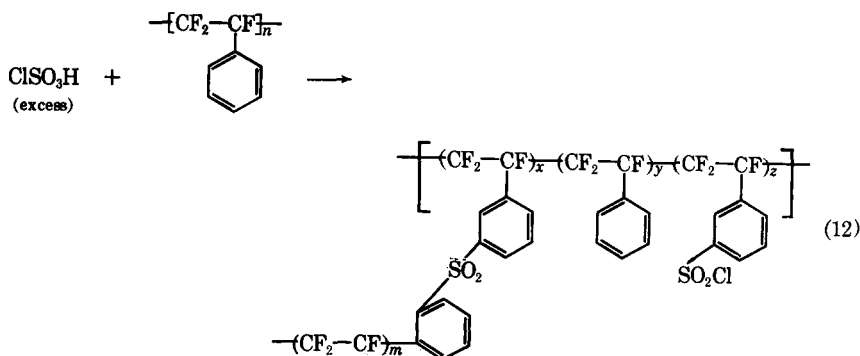
An examination of Table III shows that the reaction of poly- α,β,β -trifluorostyrene with a molar equivalent of chlorosulfonic acid fails to take place to any degree of significance until a temperature of 40–50°C. is maintained in the reaction system. Once this temperature range is attained, however, the reaction proceeds to completion even if the chlorosulfonic acid concentration is then reduced fivefold.



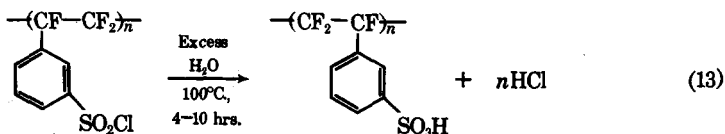
This reaction gives water-soluble (sometimes methanol-soluble and water-insoluble if ClSO₃H concentration is reduced) linear polymers of poly- α,β,β -trifluorostyrenesulfonic acid.

When a large excess of chlorosulfonic acid is present in its ratio to a mer unit of poly- α,β,β -trifluorostyrene, the sulfonation takes place but is temperature-dependent as to extent of substitution; of great importance is the fact that it produces networks by the creation of sulfone linkages between separate linear chains (eq. 12).

In the reaction (12) the ratios of unsubstituted mer unit, sulfone-crosslinked site, sulfonated mer unit, (x , y , and z) vary drastically depending upon reaction temperature. However, the sulfone crosslinking is totally dependent upon the excess of sulfonating reagent, and is not in any way dependent upon the temperature of the reaction.



After preparation of the sulfonyl chloride polymers of α,β,β -trifluorostyrene by use of excess ClSO_3H , these are easily converted to sulfonic acid polymers by boiling in distilled water for a period of 4–10 hr.



The linear sulfonic acid derivatives of poly- α,β,β -trifluorostyrene which are described in the first five rows of Table III were all soluble in methyl alcohol. That resin having $\text{IEC} = 4.07$ was both water- and methanol-soluble and is similar in properties to nearly fully sulfonated polystyrene-sulfonic acid ($\text{IEC} = 5.10$ meq. H^+ /g. dry resin). The other four partially sulfonated polymers were easily formed into useful ion-exchange products by either casting a membrane film from a 20% methanol solution or by forming pellets by spraying a 20% methanol solution of polymer into a benzene solution, which produces a fine, beadlike precipitate of the sulfonic acid resin. The preparation of useful ion-exchange materials from the sulfone-crosslinked network polymers was not as simple as with the linear polymers. These require special techniques of pressure forming whose detailed description is beyond the scope of this paper. However, a general description of this formation is given in the experimental section.

Chemical Properties of Sulfonic Acid Polyelectrolytes Prepared from Poly- α,β,β -trifluorostyrenesulfonic Acid

Two severe oxidation tests have been developed for assessing the oxidative stability of any organic polyelectrolyte. One tests the intrinsic viscosity lowering via oxidative chain scission of the linear water-soluble polyelectrolyte under consideration (model compound) in 3M sulfuric acid solution while the other tests the same resistance heterogeneously in the presence of 3% hydrogen peroxide with 1 ppm of ferrous ion present. These tests are described in the experimental section and the results of viscosity lowering are depicted in Table IV and those of peroxide degradation in Table I. Table IV shows the result of intrinsic viscosity lowering of

TABLE IV
Oxidative Viscosity Lowering of Water-Soluble Sulfonic
Acid Polyelectrolytes in $3M$ H_2SO_4 by the Action of Hydrogen and
Oxygen Gases at a Platinum Black Interface in Stirred Solutions

Polyelectrolyte species (in $3M$ H_2SO_4 , $c = 0.02M$)	Intrinsic viscosity (in $3M$ H_2SO_4 , $27.5^\circ C.$)	Time of oxidation, hr.
Polystyrenesulfonic acid (Orig. MW = 525,000; orig. IEC = 5.13 meq. H^+ /g. dry resin)	0.56	0
"	0.21	10
"	0.09	15
"	0.03	20
"	0.018	25
Poly- α,β,β -trifluorostyrenesulfonic acid (Orig. MW = 217,000; orig. IEC = 4.11 meq. H^+ /g. dry resin)	0.23	
"	0.26	10
"	0.22	15
"	0.24	20
"	0.25	25

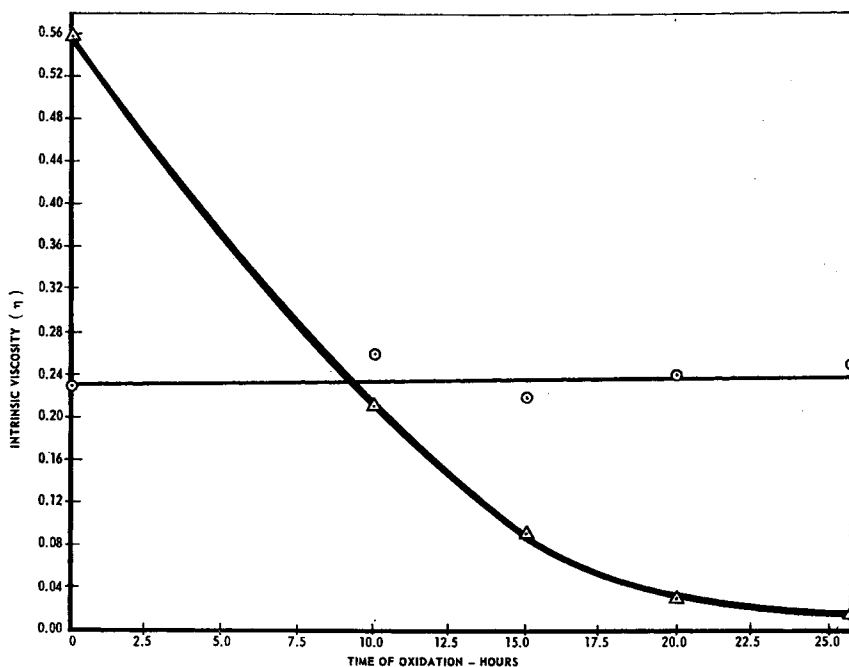


Fig. 3. Effect of H_2 and 5% O_2 in N_2 over a Pt black catalyst on the intrinsic viscosity of (Δ) linear polystyrenesulfonic acid and (\circ) linear poly- α,β,β -trifluorostyrenesulfonic acid in $3M$ H_2SO_4 at $27.5^\circ C.$

both water-soluble polystyrenesulfonic acid and water-soluble poly- α,β,β -trifluorostyrenesulfonic acid when a stream of hydrogen gas and a stream of 5% oxygen gas in nitrogen are bubbled at a rate of 15 bubbles/min. into a vigorously stirred solution of water-soluble sulfonic acid polyelectrolyte dissolved in 3*M* sulfuric acid. A screen of platinum black is suspended in the vigorously stirred polymer-acid-gas solution.

The data in Table IV shows that poly- α,β,β -trifluorostyrenesulfonic acid is unaffected by this oxidation. Testing of both solutions with TiO^{++} showed the presence of quantities of hydrogen peroxide by the direct combination of H_2 and O_2 on the platinum black surface.

Results in Table IV show that poly-styrenesulfonic acid is easily degraded oxidatively by these tests and the extent of degradation is proportional to the time. This is shown in Figure 3. The above tests failed to show any degradation of poly- α,β,β -trifluorostyrenesulfonic acid which had been lightly crosslinked (high water content compared to even 1% crosslinked polystyrenesulfonic acid) by sulfone groups within the range of experimental error.

Experimental results for direct peroxide degradation in the presence of 1 ppm Fe^{+2} are given in Table I.

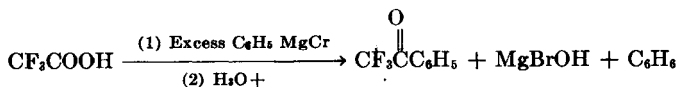
EXPERIMENTAL

α,α,α -Trifluoroacetophenone

This was prepared by the method of Cohen,¹⁸ except that a modified Grignard reaction was used to prepare α,α,α -trifluoroacetophenone rather than the more difficult Friedel-Crafts synthesis utilizing trifluoroacetyl chloride coupling to benzene in the presence of aluminum chloride.

Trifluoroacetic acid, 114 g. (Baker and Adamson Div. Allied Chemical), was added to 500 ml. of diethyl ether (Mallinckrodt Co.) in a 2-liter three-necked flask equipped with a reflux condenser, addition funnel, thermometer, and a magnetic stirring bar. This equipment was set up over a magnetic stirrer and the acid was stirred until homogeneous with the ether solvent. With vigorous stirring, exactly 1 liter of a 3*M* solution of phenylmagnesium bromide in ether (Arapahoe Chemical Co) was added dropwise over a 4 hr. period. There was a 4°C. in temperature during the course of the reaction. After final addition of the phenylmagnesium bromide, the contents of the reaction vessel turned light pink; the mixture was further stirred for 1/2 hr. The reaction mixture was transferred to a 4 liter beaker containing 1 liter of a 4*N* hydrochloric acid solution and was stirred with a glass rod for 10 min. The contents were transferred to a 3 liter separatory funnel and the layers separated, the acid layer being extracted three times with 100 ml. fresh ether and the ether layer extracted three times with 50 ml. distilled water. The organic layer with ether extactions was transferred to a 3-liter Erlenmeyer flask, three dry boiling chips added, and both ether and benzene evaporated from the reaction products on a steam bath until

no further volume change in solution was noted. This Grignard reaction involves principally only ketonization, as the reaction of phenylmagnesium bromide with an α,α,α -trifluoroketone is unfavorable.



The reaction products were transferred to a 500-ml. three-necked flask set into a heating mantle and equipped with a packed helice distillation column attached to a distilling head (with thermometer) and vacuum pump, capillary, and glass stopper. After setting and stabilizing a pressure of 37 mm. within the distillation system, exactly 126.1 g. of a product boiling at 66–67°C. was collected as a middle run. This fraction was ascertained to be α,α,α -trifluoroacetophenone by elemental analysis.

ANAL. Calcd. C, 55.17%; H, 2.90%; F, 32.76%. Found: C, 54.95%; H, 2.78%; F, 32.59%.

The overall yield of this reaction was found to be 72.3%.

α,α -Dichloro- β,β,β -trifluoroethylbenzene

Previously prepared trifluoroacetophenone (139.2 g., 0.8 mole) from two runs was combined with 208.5 g. (1 mole) of commercial phosphorus pentachloride (B & A Division, Allied Chemical Co.) and the contents heated in a 500-ml. three-necked flask equipped with heating mantle, thermometer glass stopper, and reflux condenser. The reactants were heated to reflux whence reaction took place, causing the reaction mixture to turn bright red. The reaction mixture was refluxed for 21 hr.; the excess PCl_5 was reduced with excess acetone in increments, and the excess acetone evaporated on a steam bath. The crude contents were placed in a 500-ml. round-bottomed flask attached to a vacuum apparatus and the phosphorous oxychloride boiled off at 1 atm. (b.p. 106–109°C.). The yield was = 121.3 g. (close to the theoretical amount expected). The α,α -dichloro- β,β,β -trifluoroethylbenzene was distilled over at 37 mm. pressure in the boiling range 88–89°C.; yield 149.4 g. (81.9%).

α -Chloro- α -fluoro- β,β,β -trifluoroethylbenzene

α,α -Dichloro- β,β,β -trifluoroethylbenzene (137.4 g., mole), 36.0 g. (0.2 mole) of antimony trifluoride (B & A Division, Allied Chemical Co.), and 3.2 g. (0.02 mole) of bromine were placed into a 500-ml. three-necked flask equipped with a heating mantle, magnetic stirrer, N_2 inlet capillary, and takeoff distilling head. After passing nitrogen through this mixture for 30 min., the contents were heated at reflux with stirring for 120 min. at which time the reactants turned to a purplish black tarry mixture. During this period, the distillation head was keyed to act as a reflux condenser. After cooling to 27°C., vacuum (100 mm.) was applied and 46.8 g. of

α -chloro- α -fluoro- β,β,β -trifluoroethylenebenzene was obtained in the boiling range 85–6°C. This was 36.6% of theory.

α,β,β -Trifluorostyrene

α -Chloro- α -fluoro- β,β,β -trifluoroethylbenzene (42.2 g., 0.2 mole) was added to a 1-liter round-bottomed flask which was equipped with a reflux condenser, heating mantle, and magnetic stirrer. To the flask was added 200 ml. of absolute ethyl alcohol (USI, National Distillers Co.), 12.8 g. (0.2 mole) of finely divided zinc powder (Fisher Scientific Co., U.S.P. grade), and 1.35 g. (0.01 mole) of anhydrous zinc chloride (Fisher Scientific Co.). This mixture was refluxed for 16 hr., cooled, filtered through a sintered glass funnel, and the residue washed three times with 50 ml. of warm absolute ethanol. The filtrate was transferred to a 500 ml Ehrlenmeyer flask and the ethyl alcohol removed on a steam bath. The residue was transferred to a 100-ml. three-necked flask equipped with a nitrogen inlet tube, distilling head, glass stopper, and heating mantle. The distilling head was equipped with a 100-ml. one-necked receiver which was immersed in a Dry Ice-acetone bath and a vacuum of 69 mm. Hg was applied. The temperature was raised, and a fraction weighing 2.27 g. was collected in a boiling range of 27–59°C. The vacuum and heat were removed, and a new 100 ml receiver was attached to the distilling head and immersed in a Dry Ice-acetone bath. Vacuum was again applied under a minute nitrogen stream at 69 mm. Hg and the temperature again increased. A fraction boiling at 69–72°C was collected, 25.8 g. (80.8% yield).

Analysis of this material showed it to be α,β,β -trifluorostyrene.

ANAL. Calcd.: C, 60.77%; H, 3.16%; F, 36.07%; Found: C, 61.15%; H, 3.01%; F, 35.63%.

Polymerization of α,β,β -Trifluorostyrene

By the radical emulsion method Prober¹⁹ using dodecylamine hydrochloride, 100 g. of the monomer was converted into 75.4 g. of poly- α,β,β -trifluorostyrene having an intrinsic viscosity in benzene at 30°C. of 0.68 dl./g.

α,β,β -Trifluorostyrene (100 g. 0.63 mole) was placed in a 1-liter three-necked flask equipped with a gas inlet tube, air condenser equipped with a gas outlet tube, thermometer, and a magnetic stirrer. To this was added 600 ml. of distilled water containing 11.6 g. of freshly prepared dodecylamine hydrochloride. This mixture was stirred while bringing the temperature to $60 \pm 1^\circ\text{C}$. The system was then purged for 1 hr. with nitrogen gas, and 0.44 g. of potassium persulfate (Fisher Scientific Co.) was added. The polymerization is carried out with stirring for 60–72 hr. The reaction mixture was cooled to room temperature and then poured into a 4 liter beaker. Ice was then added (300 g.) followed by 50 g. of solid sodium chloride (Fisher Scientific Co.). After breaking of the emulsion, (about 30 min.), solid polymer was filtered from the aqueous phase. The

poly- α,β,β -trifluorostyrene was purified by dissolution in 1 liter of chloroform and precipitation by addition of 2 liters of methyl alcohol. The poly- α,β,β -trifluorostyrene was filtered, washed three times with 100 ml. cold methanol, and dried overnight at room temperature. The yield was 75.4 g. (75.4%) of poly- α,β,β -trifluorostyrene, intrinsic viscosity in benzene at $30 \pm 0.1^\circ\text{C}$. = 0.68 dl./g.

Sulfonation of Poly- α,β,β -trifluorostyrene

Linear, Methanol-Soluble, Water-Insoluble, Partially Sulfonated Poly- α,β,β -trifluorostyrene. Poly- α,β,β -trifluorostyrene (10 g., 0.063 mole) was added to 600 ml. of spectroquality grade chloroform (Fisher Scientific Co.) in a 2-liter three-necked glass resin kettle equipped with a Teflon stirrer, addition funnel, heating mantle, and reflux condenser and stirred until completely dissolved.

After neutralizing the 0.75% ethyl alcohol stabilizer in the chloroform solution by the addition of 11.4 g. of chlorosulfonic acid, 1.5 g. of chlorosulfonic acid (0.013 mole, 0.2 molecules per polymer phenyl group) and 10 ml. of chloroform were added by an additional funnel. The solution was heated to reflux (61.5°C .) and refluxed for a 3 hr. period followed by cooling to 27°C . At this point in cooling, a gelatinous precipitate appeared in the reaction mixture which settled to the bottom of the kettle. The tan chloroform solution was decanted away from the precipitate, and the latter taken up in 200 ml. of methyl alcohol. The solution of crude poly- α,β,β -trifluorostyrenesulfonic acid was boiled in its methanol solution and then evaporated to dryness to yield a tan polymer. This polymer was washed three times with 1 liter distilled water, dried overnight at 50°C ., ball-milled, and tested for functional group content. The yield was 11.3 g. of a material with IEC = 1.23 meq. H^+ /g. dry resin (theoretical IEC = 1.49 meq. H^+ /g. dry resin).

Sulfone-Crosslinked, Insoluble, Infusible, Poly- α,β,β -Trifluorostyrenesulfonic Acid. Exactly 10 g. (0.003 mole) of poly- α,β,β -trifluorostyrene ($[\eta] = 0.68$ dl./g. in benzene at 30°C .) was dissolved in 550 ml. of spectroquality grade chloroform (Fisher Scientific Co.) in a 2 liter resin kettle equipped with a Teflon stirrer, addition funnel, water bath heater, and reflux condenser. To the addition funnel were added 60 g. (8.2 molecules per phenyl group) of chlorosulfonic acid (Matheson, Coleman, and Bell) in 50 ml. of chloroform. The external water bath was brought to a temperature of $30 \pm 1^\circ\text{C}$. and the chlorosulfonic acid solution added over a 10 min. period to the rapidly stirred reaction mixture. The reaction solution turned a brown-red color after 5 min. and a large ball of precipitate formed around the stirrer after 8 min. The reaction mixture was stirred for 4 hr. after final addition of chlorosulfonic acid. The stirrer was removed from the resin kettle and the brown polymer cut from the stirrer blade and placed in a 4 liter beaker containing 1 liter of methyl alcohol. This polymer was heated in methanol for 2 hr.; the solid changed to a light tan color. The polymer was not soluble in methanol. The resin was cut

up and washed in distilled water until free of chloride and sulfate ions, then dried overnight at 50°C. before ball-milling into a fine tan powder. The yield was 12.0 g. of material having IEC = 2.05 meq. H⁺/g. dry resin (theoretical IEC = 4.20 meq. H⁺/g. dry resin); 13.82% S (theoretical 13.44% S).

Preparation of Membranes from Partially Sulfonated Poly- α,β,β -trifluorostyrene

On a laboratory rubber mill with rollers preheated to 50°C. was added 5.8 g. Kel-F 3700 elastomer (3-M Co.), 5.8 g. polyvinylidene fluoride (Pennsalt Chemical Co.), and 10.0 g. triethyl phosphate (Matheson, Coleman, and Bell). These were masticated for 10 min. until homogeneous and tacky. To this were added 8.4 g. of crosslinked, partially sulfonated poly- α,β,β -trifluorostyrene of any convenient IEC range between 1.00 and 3.00 Meq. H⁺/g. of dry resin and another 10.0 g of triethyl phosphate. The entire mixture was masticated for 30 min., the mill rollers being kept at 50–60°C. The preformed sheet was removed.

The preformed sheet was placed between sheets of Polyethylene terephthalate film (Mylar, E. I. du Pont de Nemours) sandwiched between two steel plates and a 4 mil shim. The stack was placed in a preheated press (140 ± 5°C.) which was heated without pressure for 2 min. A pressure of 40–60 tons was then applied for 7 min. and then the entire package was released, cooled, and removed. The membrane was then placed in a distilled water bath for 1 hr. at room temperature to effect partial leaching of the water-soluble triethyl phosphate, replaced in a fresh distilled water bath for a minimum of 6 hr., then heated to 65 ± 5°C. for a period of 30 min. These water treatments completed removal of triethyl phosphate and gave an ion-exchange membrane of good strength. This membrane was moved and stored in a sealed polyethylene bag with 5 ml. of distilled water.

The resistivity (1 kc.) of such homogeneous ion exchange membranes ranged from 20 to 100 ohm-cm., depending upon the IEC of the polymeric material.

The tensile strength of such an ion-exchange membrane ranged from 750 to 2000 psi (at 2 in./min. failure speed).

The equilibrium (soak) water content (wet basis) was 10–55%.

Oxidative Degradation of Polyelectrolytes With Hydrogen Peroxide (3%) in the Presence of 1 ppm Ferrous Ion

A 3.00 g. portion of Polyelectrolyte sample of known acid content was placed into a 125 ml. Ehrlenmeyer flask equipped with a TFE stirring bar which had been previously boiled in 1% NaOH solution and then thoroughly rinsed with distilled water. Exactly 25 ml. of 3% hydrogen peroxide (Fisher Scientific Co.) previously heated to 65°C. was added to the Ehrlenmeyer flask containing the dry resin. The flask containing resin

plus 3% hydrogen peroxide was heated on a hot plate with magnetic stirring to $70 \pm 1^\circ\text{C}$. temperature, and exactly 0.25 ml. of a stock solution of freshly prepared (under N_2) ferrous ammonium sulfate hydrate (Fisher Scientific Co.) was added. (The stock solution of 1 ppm ferrous ion was made by dissolving exactly 0.7 g. $\text{Fe}(\text{NH}_4)_2(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ in 1 liter of distilled water.) Aliquots (usually 1 ml.) of the 3% H_2O_2 solution were taken at given times with correction for amount peroxide extracted, and the acid dissolved into solution from resin titrated against bromocresol purple indicator or potentiometrically.

Oxidative Degradation of Water-Soluble Polyelectrolytes with Hydrogen and 5% Oxygen in Nitrogen Over Platinum Black

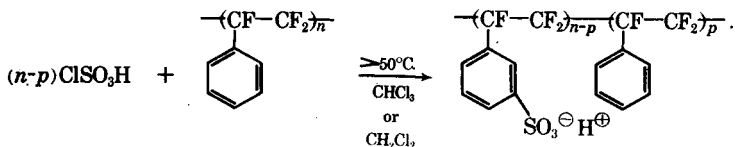
First, a screen of platinum gauze was dipped into a bath of chloroplatinic acid then immersed in a reactive sulfuric acid solution of sodium borohydride until a black surface is developed.

3M H_2SO_4 (100 ml.) was poured into a 500-ml. three-necked flask equipped with two gas inlet ports, a thermometer, and a magnetic stirrer. Platinum black gauze prepared previously was wrapped around the stem of the thermometer and immersed into the 3M sulfuric acid solution after exactly 0.002 mole (based on the known mer unit of the polyelectrolyte sample) dissolved in the acid. Immediately, 5 ml. of solution was withdrawn and its relative viscosity at 30°C . measured versus 3M H_2SO_4 at four dilutions. Both hydrogen and 5% oxygen (in N_2) gases were metered into the reaction vessel with stirring at exactly 15 bubbles/min. Samples of acid solution of dissolved polyelectrolyte were withdrawn at various time intervals and the intrinsic viscosity determined from relative viscosities.

SUMMARY AND CONCLUSIONS

By careful adjustment of reaction conditions of concentration and temperature, it has been possible to prepare a multiplicity of equivalent weights (different ion exchange capacity) of both linear and crosslinked poly- α,β,β -trifluorostyrenesulfonic acids.

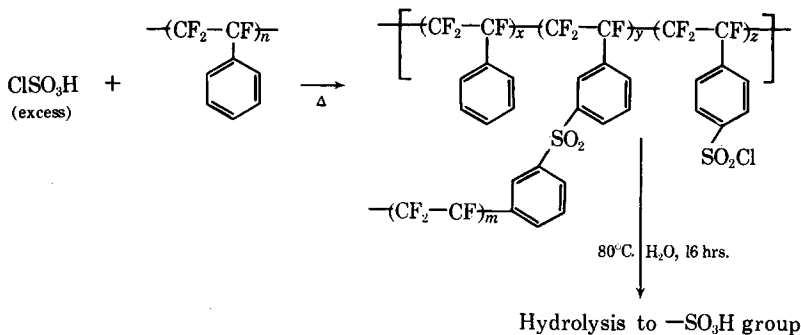
Linear poly- α,β,β -trifluorostyrenesulfonic acid may be prepared by a direct combination reaction:



provided that the number of moles of chlorosulfonic acid does not exceed the number of aromatic rings available for reaction and a temperature of 50°C . or higher is maintained in the presence of an excess of solvent. These polyelectrolytes are both water- and methanol-soluble if p is small but only methanol-soluble if p is in the range of $1/3$ - $1/2n$. These resins are easily

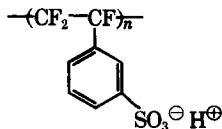
cast into ion-exchange membranes of useful form from 20% methanol solutions. They can also be blown (spray-dried) into useful ion-exchange powders.

Sulfone-crosslinked poly- α,β,β -trifluorostyrenesulfonic acid may be prepared according to the reaction sequence:



where x , y , and z vary according to the exact temperature of the first reaction step and a very large concentration ($>3:1$) of chlorosulfonic acid is used on a mole basis to each aromatic ring present. These crosslinked resins are difficultly molded by the aid of a phosphate plasticizer into useful ion-exchange membranes of any desired thickness.

The extreme difficulty in sulfonating poly- α,β,β -trifluorostyrene was found to be caused by the *meta*-directing influence of the perfluorinated polyalkyl group attached to the aromatic ring:



Unlike polymers of polystyrenesulfonic acid or the more useful cross-linked polystyrene-divinylbenzenesulfonic acids, poly- α,β,β -trifluorostyrenesulfonic acid has been found to be totally resistant to oxidative modes of degradation which cause drastic oxidative depolymerization of the polystyrene and polystyrene-divinylbenzenesulfonic acids. These tests include destruction by 3% hydrogen peroxide in the presence of trace quantities of ferrous ion at 70°C., the action of mixed hydrogen and oxygen over a platinum catalyst at room temperature, the action of 3000 Å. ultraviolet light in the presence of aqueous O_2 , and the action of up to 5% solutions of potassium permanganate or ammonium persulfate at 60°C.

It is concluded that the substitution of a fluorine atom in place of the benzylic hydrogen atom of polystyrene gives the added C-X bond strength required to resist the above oxidations.

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Résumé

La synthèse d'une nouvelle génération de résines échangeuses d'ions de capacité élevée et résistant à l'oxydation de même que de membranes correspondantes est décrite; ce sont des polyélectrolytes acide sulphonique préparées au départ de poly- α,β,β -trifluorostyrène de poids moléculaire élevé. La sulfonation difficile du poly- α,β,β -trifluorostyrène est discutée sur la base des résultats que cette sulfonation doit être effectuée sur un noyau aromatique possédant des groupes substituants orientant en *meta*. La stabilité à l'oxydation de ces nouveaux types de polyélectrolytes sulfoniques aromatiques perfluorés est à la fois démontrée et décrite par comparaison avec leurs homologues acide polystyrènesulfonique correspondants. La différence dans leur stabilité oxydation-dépolymérisation est décrite sur la base de substituants carbonés benzyliques.

Zusammenfassung

Die Synthese einer neuen Generation von oxydationsbeständigen Ionenaustauscherharzen hoher Kapazität, nämlich von Sulfonsäure-Polyelektrolyten aus hochmolekularem Poly- α,β,β -trifluorstyrol, wird beschrieben. Die schwierige Sulfonierung von Poly- α,β,β -trifluorstyrol wird anhand des Befundes diskutiert, dass diese Sulfonierung an einem aromatischen Ring mit einem *meta*-dirigierenden Substituenten ausgeführt werden muss. Die Oxydationsbeständigkeit dieses neuen Typs perfluoralkyl-aromatischer Sulfonsäure-Polyelektrolyte wird gezeigt und im Vergleich zu den Polystyrolsulfonsäure-Homologen beschrieben. Der Unterschied in ihrer Oxydations-Depolymerisationsbeständigkeit wird an den Benzylkohlenstoff-Substituenten diskutiert.

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