ELSEVIER

European Polymer Journal 36 (2000) 1035–1041

EUROPEAN
POLYMER
JOURNAL

Novel phosphonated perfluorocarbon polymers

Masaaki Yamabe*, Katsuyuki Akiyama, Yonezoh Akatsuka, Masao Kato

Research Center, Asahi Glass Company Limited, 1150 Hazawa-cho, Kanagawa-ku, Yokohama 221-8755, Japan

Received 6 August 1998; received in revised form 15 February 1999; accepted 20 May 1999

Abstract

The copolymerization or terpolymerization of dimethyl perfluoro(3-vinyloxypropyl)phosphonate with tetrafluoroethylene and perfluoro(propyl vinyl) ether yields new perfluorocarbon polymers bearing phosphono groups. A new method for the synthesis of perfluorovinyloxy-substituted perfluoroalkylphosphonic acid derivatives have been also developed by the transformation reactions of corresponding carboxylic esters, involving the facile formation of CF–P bonds by the reaction of perfluoroalkyl iodides with tetraethyl diphosphite. Some of the fundamental properties of these polymers are described. © 2000 Elsevier Science Ltd. All rights reserved.

1. Introduction

Two types of functional perfluorocarbon polymers, containing carboxylic [1] and sulfonic groups [2,3], respectively, have been developed and studied energetically for use, as membrane separators in a chlor-alkali process. Perfluorocarbons bearing phosphono groups were expected to show some distinctive performance as a third functionality with dibasic character. Inspite of such expectancy, suitable monomers with phosphono groups have not been synthesized because of the restriction of CF–P bond formation. One of the best known methods of forming these linkages is by Arbuzov reaction [4] between alkyl halides and trialkyl phosphites. This reaction generally proceeds by S_N2 attack of the phosphite on carbon to form very reactive quasiphosphonium intermediate, which undergoes dealkylation to afford alkylphosphonates. Another method is known as Michaelis–Becker reaction [5]. Dialkyl phosphite anion attacks on the carbon of alkyl halide to give alkylphosphonate by nucleophilic displacement. Thus, in hydrocarbon chemistry alkylphosphonates can be easily obtained from the corresponding alkyl halides.

Unfortunately these approaches can not be applied to perfluoroalkyl halides in general. Strongly electron-withdrawing perfluoroalkyl groups cause an electron-deficiency on the halogen atom of perfluoroalkyl halides. Consequently, the kind of nucleophiles discussed above would not attack on the carbon.

Exceptionally, some fluoroalkyl halides have been reported to afford these types of reaction products [6,7]. On the other hand, difluoromethylphosphonates have been prepared by the reaction of chlorodifluoromethane with sodium dialkyl phosphite [8], and free radical reaction of CF–P bond formation has been recorded [9–11].

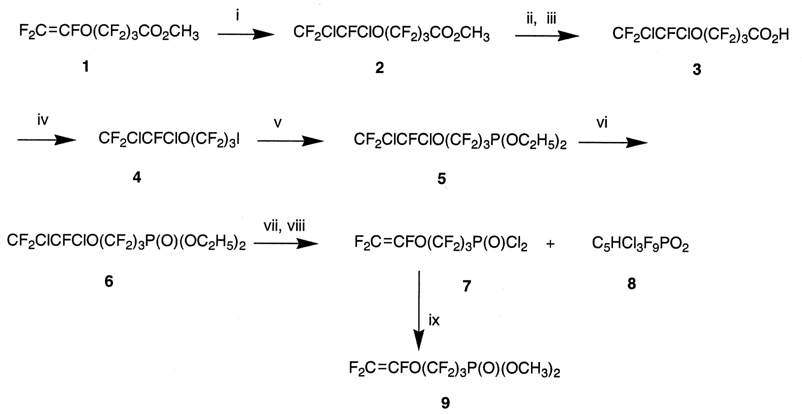
We have reported a general synthetic route to perfluoroalkylphosphonates from easily available perfluoroalkyl iodides [12]. In application of this synthetic route, perfluorophosphonic monomer **9** can be readily prepared as in Scheme 1 and copolymerized with tetrafluoroethylene or terpolymerized with a mixture of tetrafluoroethylene and perfluoro(propyl vinyl) ether to

---

* Corresponding author. Tel.: +81-3-3218-5862; fax: +81-3-3213-1318.

E-mail address: masaaki-yamabe@om.agc.co.jp (M. Yamabe).

PII: S0014-3057(99)00158-5



Scheme 1.

give new perfluorocarbon polymers having phosphono groups. Some of the fundamental properties of these polymers were studied.

2. Experimental

Infrared (IR) spectra were recorded on a JASCO A-202 model spectrometer. Proton and ^{19}F nuclear magnetic resonance (NMR) spectra were measured on a Varian EM-390 instrument and a JEOL JNX-FX 100 spectrometer. Mass spectra (MS) were taken on a Hitachi RMU-6MG single-forcing instrument at an ionization potential of 20 eV. Quasi-molecular ions (QM) were also detected by chemical ionization (CI) method. Analytical gas–liquid chromatography (GLC) were carried out on a Hitachi Gas Chromatograph 163 model instrument, equipped with a thermal conductivity detector. The column used, was commercially available 4% KF-96 (4 mm × 2.5 m) on Chromosorb G (80–100 mesh). GLC peak integrals were obtained by Shimadzu Chromatopack C-RIA. Unless otherwise cited, yields were of distilled products of at least 95% purity by GLC analysis.

2.1. Monomer synthesis

*2.1.1. 1,2-Dichlro-1,2,2-trifluoroethyl 3-iodo-1,1,2,2,3,3-hexafluoropropyl ether (**4**)*

Gaseous chlorine was introduced into a solution of 3-(methoxycarbonyl)-1,1,2,2,3,3-hexafluoropropyl trifluorovinyl ether (**1**) [1] (39.2 g, 128 mmol) in 1,1,2-trichloro-1,2,2-trifluoroethane (R-113, 62 g) with stirring, while the reaction temperature was maintained at 0–5°C. After the starting vinyl ether was completely consumed, the solvent was removed under reduced pressure. Hydrolysis of the residual oil by aqueous sodium hydroxide and subsequent acidification with conc. HCl gave saturated carboxylic acid 3 (44.2 g, 122 mmol); IR (liquid film) 3400 and 1780 cm^{-1} (–COOH). A solution of 3 in R-113 (92 g), iodine (30.8 g, 243 mmol), and benzoyl peroxide (27.4 g, 113 mmol) was placed in a 200 ml hastelloy autoclave, and the reaction mixture was heated at 100°C for 1 h and 120°C for 3 h with vigorous stirring. After cooling, solidified benzoic acid was removed by filtration. Concentration of the filtrate and distillation of the residue through column gave compound **4** (41.8 g, 73% yield); bp 90°C/117 mmHg; IR (liquid film) 1230–1100 cm^{-1} (CF_2); MS m/z 444, 446, 448 (M^+); ^{19}F-NMR ($CDCl_3$) (relative to $CFCl_3$) $\delta = -59.5$ (2F, m, $-CF_2I$), -71.7 (2F, m, CF_2Cl), -77.0 (1F, m, CFCl), -79.9 to -84.0 (2F, AB, $J=144.0$ Hz, OCF_2), -117.5 (2F, m, CF_2).

*2.1.2. 3-(Diethoxyphosphinoyl)-1,1,2,2,3,3-hexafluoropropyl 1,2-dichoro-1,2,2-trifluoroethyl ether (**6**)*

A solution of ether **4** (41.8 g, 93.9 mmol) in R-113 (80 g) was placed into a 200 ml autoclave. Di-*t*-butyl peroxide (6.85 g, 46.9 mmol) and tetraethyl diphosphite (36.4 g, 141 mmol) were added and the resulting reaction mixture was heated at 100°C for 3 h and at 120°C for 2 h, with stirring. After cooling, the formation of phosphonite **5** was confirmed by ^{19}F- and ^{31}P-NMR spectroscopy, and GLC analysis. The reaction mixture was placed in a glass flask fitted with a dropping funnel. The flask was cooled to −10°C under nitrogen and a solution of *t*-butyl hydroperoxide (25.4 g, 282 mmol) in methanol (60 ml) was slowly added via the dropping funnel. After complete addition, the stirring was continued at 0°C for 30 min. The volatile materials were removed under reduced pressure and the residue was distilled through column to give ether **6** (17.5 g, 40% yield); bp 80°C/0.5 mmHg; IR (liquid film) 1295 (P=O), 1220–1100 (CF_2), and 1050 cm^{-1} (P–O–C); MS m/z 454, 456, 458(M^+); ^{19}F-NMR

($CDCl_3$) (relative to $CFCl_3$) $\delta = -71.7$ (2F, m, CF_2Cl), -76.8 (1F, m, CFCl), -81.5–85.5 (2F, AB, $J = 145.0$ Hz, OCF_2), -122.5 (2F, d, $J_{F-P} = 89.8$ Hz, $CF_2P(O)$), -124.5 (2F, m, CF_2); ^1H-NMR ($CDCl_3$) $\delta = 1.42$ (6H, t, $J = 7.1$ Hz, CH_3), 4.38 (4H, dq, $J = 7.1$ Hz, $J_{F-H} = 7.6$ Hz, CH_2).

2.1.3. 3-(Dichlorophosphinoyl)-1,1,2,2,3,3-hexafluoropropyl 1,2,2-trifluorovinyl ether (7)

Compound **6** (17.5 g, 38 mmol) was added to a suspension of zinc dust (8 g, 122 mmol) and zinc chloride (800 mg, 5.87 mmol). Resulting reaction mixture was refluxed for 20 h. Ethanol was removed under reduced pressure and the residue was treated with phosphorus pentachloride (37.7 g, 181 mmol). The mixture was heated at 120°C for 5 h, during which time ethyl chloride was evolved and phosphoryl chloride was distilled over. The residue was distilled through column under reduced pressure to give ether **7** (8.1 g, 57.5% yield); bp 70°C/25 mmHg; IR (liquid film) 1840 ($CF_2{=}CFO$–), 1295 (P=O), 1200–1150 cm^{-1} (CF_2); MS m/z 364, 366, 368 (M^+), 267 ($M^+ - CF_2{=}CFO$–), 117 ($POCl_2$); ^{19}F-NMR ($CDCl_3$) (relative to $CFCl_3$) $\delta = -84.7$ (2F, m, –OCF_2–), -114.1 (1F, dd, $J = 65.9$ and 84.7 Hz, $C\underline{F}$ (*trans* to O)F(*cis* to O)=CF(O–)), -116.1 (2F, dt, $J_{F-P} = 113.5$ Hz, $J_{F-F} = 10.0$ Hz, –CF_2PCl_2), -121.6 (2F, m, CF_2), -121.9 (1F, ddt, $J = 84.7$, 112.1, and 5.9 Hz, CF(*trans* to O) $\underline{F}$ (*cis* to O)=CF(O–)), -135.8 (1F, ddt, $J = 112.1$, 65.9, and 5.9 Hz, $CF_2{=}C\underline{F}O$–). Small amount of saturated ether **8** was also obtained (5% yield on GLC); MS m/z 400, 402 (M^+).

2.1.4. 3-(Dimethoxyphosphinoyl)-1,1,2,2,3,3-hexafluoropropyl 1,2,2-trifluorovinyl ether (9)

A mixture of ether **7** (8.1 g, 22.1 mmol) and R-113 (2.0 g) was slowly added to a solution of methanol (2.9 g, 91 mmol) in R-113 (9.0 g) at −10°C. After addition, the stirring was continued for 30 min. Excess methanol was removed by washing with water. Distillation under reduced pressure gave ether **9** (5.2 g, 14.6 mmol, 66% yield); bp 60°C/2 mmHg; IR (liquid film) 2960, 2870, 1840 ($CF_2{=}CFO$–), 1295 (P=O), 1180 (CF_2), 1040 cm^{-1} (P–O–P); MS m/z 356 (M^+), 259 (M^+ – $CF_2{=}CFO$–), 109 ($PO(OCH_3)_2$); ^{19}F-NMR ($CDCl_3$) (relative to $CFCl_3$) $\delta = -84.5$ (2F, m, –OCF_2–), -114.3 (1F, dd, $J = 64.9$ and 85.0 Hz, $C\underline{F}$(*trans* to O)F(*cis* to O)=CF(O–)), -121.8 (2F, dt, $J_{F-P} = 88.4$Hz, $J_{F-F} = 10.3$ Hz, –$CF_2P(O)$–), -122.3 (1F, ddt, $J = 85.0$, 111.3, and 5.9 Hz, CF(*trans* to O) $\underline{F}$(*cis* to O)=CF(O–)), -124.1 (2F, m, –CF_2–), -135.3 (1F, ddt, $J = 111.3$, 64.9, and 5.9 Hz, $CF_2 = C\underline{F}O$–); ^1H-NMR ($CDCl_3$) $\delta = 3.61$ (3H, d, $J_{P-H} = 11.0$ Hz, CH_3).

2.1.5. Polymerization

Tetrafluoroethylene was prepared by the pyrolysis of chlorodifluoromethane, followed by the low temperature distillation, and its purity was higher than 99.99%. Perfluoro(propyl vinyl) ether (PPVE) was commercially available.

2.1.6. Copolymerization

The 1,1,2-trichloro-1,2,2-trifluoroethane (R-113) (6.8 g) solution of **9** (M_2) (9.4 g) and 40 mg of 2,2′-azobisisobutyronitrile (AIBN) as a radical initiator in a stainless steel 100 ml autoclave equipped with a magnetically driven stirrer, was heated to 70°C followed by the addition of a preweighed amount of tetrafluoroethylene (TFE, M_1) (9.5 g) to the autoclave. The resulting mixture was stirred for 19 h until the pressure dropped by about 5 kg/cm^2, then cooled, and gaseous materials were vented off. 3.7 g of solid polymer was obtained after the conventional workup procedure. The structure of copolymer was confirmed by infrared (IR) spectroscopic data and elemental analysis. A volumetric flow rate (Q) at 175°C was obtained by capillary viscometry using a Shimadzu Flow-Tester (load, 30 kg/cm^2; diameter of capillary, 1 mm). Stress–strain curves were obtained for polymer films approximately 200 μm in thickness with a Toyo Balwin Tensilon at room temperature. The gauge length of test samples was about 9.5 mm, and the crosshead speed, 200 mm/min.

2.1.7. Terpolymerization

Terpolymerization of tetrafluoroethylene (TFE), the compound **9**, and PPVE was carried out in the same manner as described above.

The phosphonate ester type polymers were melted, processable and thin films were prepared by compression molding at 170–190°C.

3. Results and discussion

3.1. Synthesis of new perfluorovinyloxy-substituted phosphonic esters

We conducted the synthesis of new perfluorovinyloxy-substituted phosphonic esters by the transformation reactions of readily available 3-(methoxycarbonyl)-1,1,2,2,3,3-hexafluoropropyl trifluorovinyl ether (**1**) [13], involving the facile formation of CF–P linkage as shown in Scheme 1.

The trifluorovinyl ether moiety of **1** was protected for successive reaction steps by the addition of chlorine. The reaction proceeded almost quantitatively. Normal hydrolysis of ester moiety of the adduct **2** using sodium hydroxide in methanol and dilute hydrochloric acid, gave the saturated carboxylic acid **3**, which was further transformed into the iodide **4**. The Hunsdicker reaction is a useful method for the preparation of perfluoroalkyl iodides in general [14]. However, the silver salts of fluorinated carboxylic acids must be perfectly dried with difficulty for being highly hygroscopic. It was also recorded that some perfluoroalkanecarboxylic acids are decarboxylated by the reaction with benzoyl peroxide (BPO) [15]. By the latter peroxide method, facile decarboxylation of **3** occurred and the expected iodide **4** was obtained in 73% yield (Scheme 1).

Subsequently a new CF–P bond formation reaction was applied to the iodide **4** using tetraethyl diphosphite in the presence of di-*t*-butyl peroxide. The resultant phosphonite **5**[1] was oxidized by the treatment with *t*-butyl hydroperoxide in a mixture of R-113 and methanol to yield the phosphonate **6** in 60% yield on GLC.

Standard dechlorination with zinc dust in ethanol and successive chlorination with phosphorus pentachloride gave 3-(dichlorophosphinolyl)-1,1,2,2,3,3-hexafluoropropyl 1,2,2-trifluorovinyl ether (**7**) in 58% yield, accompanied by 5% of saturated by-product **8**[2].

Treatment of **7** with methanol afforded 3-(dimethoxyphosphinoyl)-1,1,2,2,3,3-hexafluoropropyl 1,2,2-trifluorovinyl ether (**9**) in 66% yield. Thus, new perfluorovinyloxy-substituted phosphonic esters was synthesized by the transformation reactions of functional groups from $CF_2=CFO(CF_2)_3CO_2CH_3$ in fairly good yield. The ^{19}F-NMR spectrum of **9** is shown in Fig. 1.

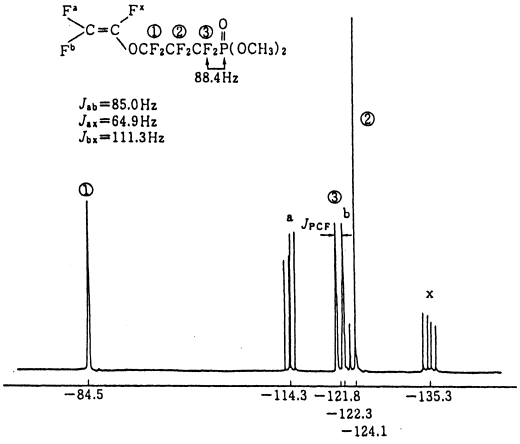


Fig. 1. ^{19}F-NMR spectrum (δ ppm, $CFCl_3$) of **9**: the fluorine atoms of vinyl ether group exhibit a typical ABX pattern, although a part of B are hidden by a doublet of CF_2 adjacent to phosphorus.

3.1.1. Copolymerization with tetrafluoroethylene (TFE)

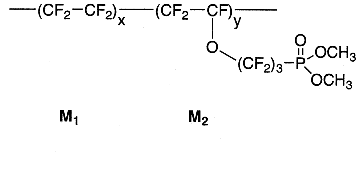
Copolymers having phosphono groups were obtained by copolymerizing TFE (M_1) with dimethyl perfluoro(3-vinyloxypropyl)phosphonate (M_2) (Scheme 2). The white solid polymer was obtained in a conversion lower than 25% based on the total charged monomers. The results are summarized in Table 1.

Charged monomers of various composition gave copolymers differing in phosphono group content which were determined by elemental analysis. The structure of each copolymer was confirmed by characteristic absorption bands in IR spectroscopy (ν_{CH} at 2980 and 2860 cm^{-1}, ν_{CF} at 1200–1150 cm^{-1}, ν_{POC} at 1053 cm^{-1}).

Generally the volumetric flow rate is considered to represent the melt flow behavior of a polymer, and is also used as a kind of index for molecular weight and the melt processability of the polymer. As shown in Table 1, copolymers with higher content of phosphono group have a greater volumetric flow rate as was indicated by capillary viscometry. For example, the copolymer with 1 mmol of phosphonic groups per gram of polymer had a volumetric flow rate (*Q*) of 50 at 175°C. On the contrary, *Q* of the copolymer having 1.13 mmol of phosphono groups was more than 1000.

All the obtained copolymers showed two kinds of decomposition temperatures, T_{d1} and T_{d2}, respectively, by thermogravimetric analysis (TGA). Typical TGA results are shown in Fig. 2. T_{d1} at 180°C probably represents the temperature at which decomposition of phosphonate residue to phosphonic acid takes place, and T_{d2} at 308°C may result in the cleavage of the CF_2–P linkage [16,17].

As described below, thin films of copolymer fabricated by melt processing did not possess sufficient flexibility. Thus, an attempt was made to obtain a more flexible perfluorophosphonic polymer by terpolymerization. It is well known that the flexibility of a perfluoropolymer increases or is improved by introducing perfluoro(alkyl vinyl) ether as a third component. Per-



Scheme 2.

---

[1] The characteristic coupling constant ($J_{F\text{–}P}$) for CF–P was 81.0 Hz. Mass spectrum showed the molecular peak at 438 m/z.

[2] Although some free acids may be formed during dechlorination reaction, they can be readily converted to acid chlorides by PCl_5. The structure of **8** is assumed as $CF_2ClCFHO(CF_2)_3P(O)Cl_2$ by mass and IR spectra.

Table 1
Copolymerization with TFE (M_1), dimethyl perfluoro(3-vinyloxypropyl)phosphonate (M_2)

Composition of charged monomers M_1/M_2 (molar ratio)	Conversion (%)	Moles of phosphonic group per gram of copolymer ($\times 10^3$)	Volumetric flow rate Q (mm^3/s)	T_d (°C)[a] (T_{d1}/T_{d2})
83.0/17.0	24	1.00	50	184/310
80.0/20.0	23	1.06	180	178/270
77.7/22.3	25	1.13	> 1000	180/308
72.0/28.0	12	1.29	> 2000	–

[a] Decomposition temperature.

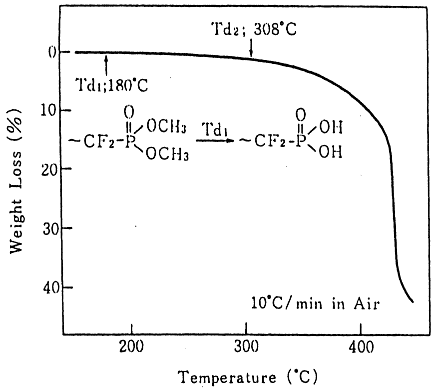
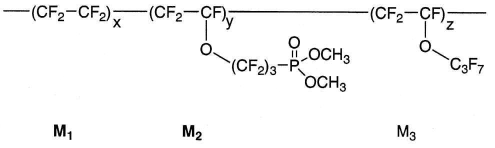


Fig. 2. Thermogravimetric analysis (TGA) of a typical perfluorophosphonic ester polymer.

fluoro(propyl vinyl) ether (PPVE) was selected as a termonomer.

3.1.2. Terpolymerization with TFE and PPVE

Radical terpolymerizations were conducted in an R-113 solution in the same manner as copolymerizations and in bulk at 70°C with AIBN as radical initiator. PPVE (M_3) concentrations ranged from 7.0 to 13.2 mol% (Scheme 3). Terpolymers differing in phosphono group content were obtained; this content depended on the composition of charged monomers and was determined by elemental analysis. A characteristic absorption band at 990 cm^{-1} in the IR spectrum of each terpolymer indicated the presence of PPVE. The terpolymer showed almost the same melt flow and thermal decomposition behavior as the copolymer. The results are presented in Table 2.


$$-(CF_2-CF_2)_x-(CF_2-\underset{\underset{O-(CF_2)_3-P(=O)(OCH_3)_2}{|}}{CF})_y-(CF_2-\underset{\underset{O-C_3F_7}{|}}{CF})_z-$$

Scheme 3.

3.1.3. Tensile properties

The tensile properties of the representative copolymer and terpolymer are summarized in Table 3. The stress–strain curves are shown in Fig. 3. Copolymer A broke down at a 2.1 kg/cm^2 tensile strength and 30% elongation, while the terpolymer B at the same tensile strength and 110% elongation. These results indicated that the flexibility of the perfluorophosphonic polymer was improved by the introduction of perfluoro(propyl vinyl) ether as a third component to the copolymer.

3.1.4. Acidification of copolymers and terpolymers

To evaluate the characteristic properties of a perfluorophosphonic acid polymer as an ion exchange resin or membrane, we attempted the transformation of phosphonic ester groups to phosphono groups in the polymer. When the phosphonate polymer was trea-

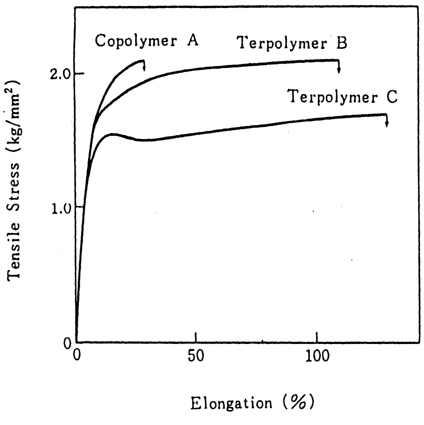


Fig. 3. Stress–strain curves for perfluorophosphonic ester polymers.

Table 2
Terpolymerization with TFE (M_1), dimethyl perfluoro(3-vinyloxypropyl)phosphonate (M_2), and PPVE (M_3)

Composition of charged monomers $M_1/M_2/M_3$ (molar ratio)	Conversion (%)	Moles of phosphonic group per gram of terpolymer ($\times 10^3$)	Volumetric flow rate *Q* (mm^3/s)	T_d (°C)[a] T_{d1}/T_{d2}
73.7/13.2/13.2[a]	12	0.72	50	184/294
77.4/15.1/7.5[a]	24	0.89	24	181/312
80.7/11.0/8.3[b]	22	0.95	28	–
79.0/14.0/7.0[b]	20	1.18	ca. 500	–

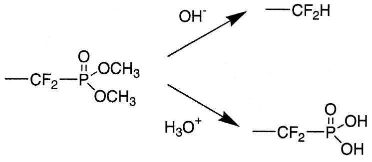
[a] Solution polymerization.
[b] Bulk polymerization.

Table 3
Tensile properties of the perfluorophosphonic polymer

Polymer	Molar ratio of M_1, M_2 and M_3[a]	Moles of phosphonic group per gram of polymer ($\times 10^3$)	Tensile strength (kg/mm^2)	Elongation (%)
A	80.4/19.6/0.0	0.98	2.1	30
B	77.4/15.1/7.5	0.89	2.1	110
C	73.7/13.2/13.2	0.72	1.6	130

[a] Composition of charged monomers in polymerization: M_1, TEF; M_2, $CF_2{=}CFO(CF_2)_3P(O)(OCH_3)_2$; M_3, PPVE.

ted with base, a complete cleavage of the CF_2–P bond and formation of $-CF_2H$ were observed as confirmed by characteristic absorption bands in IR spectroscopy (ν_{C-H} at 1020 and 830 cm^{-1}). The quantitative transformation of phosphonic ester polymer into phosphonic acid polymer was carried out by acid hydrolysis (Scheme 4).



Scheme 4.

The copolymers and the terpolymers were treated with a mixture of 1M (1M = 1 mol dm^{-3}) hydrochloric acid and acetic acid for 24–48 h at 90°C. The conversion was confirmed by IR spectroscopy, based on the disappearance of the characteristic absorption at 1050 cm^{-1} due to the presence of ester group (P–O–C). Table 4 shows some of the experimental results which indicate that the phosphono group content was almost the same as the initial phosphonate group content in the polymer. The ion exchange capacity of the polymers was about twice the value of the content of

Table 4
Acid hydrolysis of copolymers and terpolyers

Initial content of phosphonic esters groups ($mol\cdot 10^3/g\cdot$dry polymer)[a]	Content of phosphonic acid groups ($mol\cdot 10^3/g\cdot$dry polymer)[a]	Ion exchange capacity (meq/g·dry polymer)[b]
1.09	1.08	1.95
0.87	0.8	1.63
0.67	0.7	1.44

[a] Determined by elemental analysis.
[b] Determined by titration.

Table 5
Electric conductivity of perfluorinated cation exchange membranes in 1N-hydrochloric acid

Cation exchange membrane	Functional group (relative activity)	Ion exchange capacity (meq/g·dry polymer)	Electric conductivity[a] ($\Omega^{-1}\cdot cm^{-1}$)
Phosphonic acid type	$-CF_2-P(O)(OH)_2$ (10)	1.44 1.95 2.05	3.5×10^{-3} 2.7×10^{-2} 7.0×10^{-2}
Carboxylic acid type	$-CF_2-COOH$ (1)	1.44	3.4×10^{-5}
Sulfonic acid type	$-CF_2-SO_3H$ (430)	0.91	9.0×10^{-2}

[a] Calculated from membrane resistance measure at 25°C using Pt/Pt electrodes.

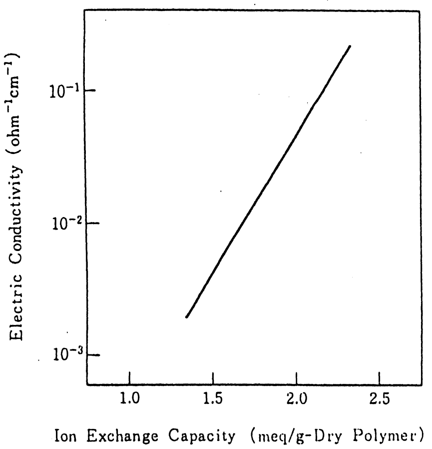


Fig. 4. Electric conductivity of perfluorophosphonic acid membranes against ion exchange capacity in 1M-hydrochloric acid at 25°C.

the phosphono groups. The content of phosphonic ester and acid group was determined by elemental analysis of the amount of phosphorus present in the polymer, and the ion exchange capacity was measured by titration. These results show that the perfluorophosphonic acid polymer can be easily obtained by acid hydrolysis of the phosphonate polymer without any decomposition of the phosphono groups.

3.1.5. Electric conductivity

Conductivity is a fundamental and important electrochemical property by which a polymer can be evaluated as an ion exchange membrane. The electric conductivity of the polymer was calculated from the electric resistance of prefluorophosphonic acid membranes having different ion exchange capacities. The membrane of a perfluorophosphonic acid polymer was obtained by acid hydrolysis of the phosphonate polymer film cast by melt-processing, as described above. Measurement of membrane resistance by AC was carried out in 1M-hydrochloric acid at 25°C using a cell with Pt/Pt electrodes. The electric conductivity of a perfluorophosphonic acid type membrane is shown against ion exchange capacity in Fig. 4.

Table 5 summarizes the electric conductivity of three types of prefluorinated cation exchange membranes in 1M-hydrochloric acid. The conductivity of the perfluorophosphonic acid membrane in acidic media was close to that of perfluorosulfonic acid, even though the acidity of phosphonic acid is somewhat closer to that of carboxylic acid than sulfonic acid. The relative acidity of perfluorinated carboxylic, sulfonic, and phosphonic acid is also shown in Table 5.

References

[1] Ukihashi H. Chem Tech 1980;10:118.
[2] Edwards PD. Soda to Enso 1979;30:45.
[3] Banks RE, Smart BE, Tatlow JC. Organofluorine chemistry: Principles and commercial applications. New York: Plenum Press, 1994.
[4] Harvey RG, LeSombre ER. In: Grayson M, Griffith EJ, editors. Topics in phosphorus chemistry, vol. 1. New York: Interscience, 1964. p. 58.
[5] Michaelis A, Becker T. Chem Ber 1897;30:1003.
[6] Burton DJ, Flynn RM. J Fluorine Chem 1977;10:329.
[7] Burton DJ, Flynn RM. Synthesis 1979;615.
[8] Soborovskii LZ, Baiva NF. Zur Obshchei Khim 1959;29:1144.
[9] Bennett FW, Emeléus HJ, Haszeldine RN. J Chem Soc 1953:1565.
[10] Emeléus HJ, Smith JS. J Chem Soc 1959:375.
[11] Brecht H. Ger. P. 2,110,769, 1972.
[12] Kato M, Yamabe M. J Chem Soc, Chem Commun 1981:1173. Recently, synthesis of fluorinated phosphonates via photochemical and thermal reactions has been reported; Nair HK, Burton DJ. J Am Chem Soc 1997;119:9137.
[13] Ukihashi H. Chemtech 1980;118.
[14] Hudlicky M. In: Chemistry of organic fluorine compounds. New York: Wiley, 1976. p. 225.
[15] Silbert LS. J Am Oil Chem 1969;46:615.
[16] Harris JF, Jr, McCane DI. U.S. Patent 3,180,895, 1965.
[17] Brace NO. J Org Chem 1961;26:3197.