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New perfluoropolymers bearing dialkylamino groups as side chains

Yoshio Hayakawa*, Haruhiko Fukaya, Eiji Hayashi, Masakazu Nishida and Takashi Abe
National Industrial Research Institute of Nagoya, Chemistry Department, Fluorine Chemistry Laboratory, Hirate-cho, Kita-ku, Nagoya 462, Japan

Nobuyuki Nose, Tetsuo Shimizu and Masayoshi Tatemoto
Daikin Industries Ltd, Nishi-Hitotsuya, Settsu, Osaka 566, Japan
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New perfluorovinyl monomers such as perfluorovinylamines, perfluoroallylamines and perfluorovinyl ethers bearing a dimethylamino, pyrrolidino, morpholino or piperidino group were subjected to copolymerization. Whereas perfluorovinylamines and perfluoroallylamines copolymerized only with vinylidene fluoride, the radical copolymerization of perfluorovinyl ethers and tetrafluoroethylene afforded copolymers that could be fabricated into films and had high thermal stability and gas permeability. These copolymers bearing cyclic amino groups as side chains were reacted with fuming sulfuric acid and then hydrolysed to give perfluoropolymers bearing carboxyl groups, which showed improved wettability.

(Keywords: perfluoropolymers; perfluorovinyl monomers; radical polymerization)

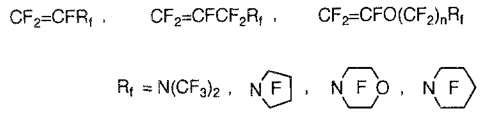
INTRODUCTION

Perfluoropolymers comprise a class of materials with unusual properties that may include high thermal stability, chemical and oxidative resistance, and low surface energy. Therefore they have been developed for commercial use. Perfluoropolymers that have dialkylamino groups, however, have not received much attention because of the lack of suitable monomers.

We previously synthesized perfluoro(3-dialkylaminopropionyl fluoride)s and perfluoro(3-dialkylaminoisobutyryl fluoride)s by electrochemical fluorination that had a dimethylamino, pyrrolidino, morpholino, piperidino, or other amino group[1,2]. Alkaline hydrolysis of the acyl fluorides and thermal decarboxylation of the resulting alkali-metal carboxylates afforded perfluorovinylamines and perfluoroallylamines[3,4]. Perfluorovinyl ethers with a dialkylamino group were also prepared by pyrolysing the adducts of the acyl fluorides and hexafluoropropene oxide[5] (*Scheme 1*).

The reactivity of perfluorovinylamines with some reagents have been investigated[6], but the polymerizability of these unsaturated compounds as monomers of little-known perfluoropolymers bearing bulky dialkylamino groups has not been studied. The only report of polymerization of a perfluorovinylamine is the copolymerization of N,N-bis(trifluoromethyl)trifluorovinylamine with ethylene or vinylidene fluoride in the presence of dinitrogen difluoride[7].

Preliminary experiments showed that perfluorovinylamines have little radical homopolymerizability. We therefore copolymerized these perfluoromonomers that have a dialkylamino group with some fluoromonomers and evaluated the properties of the copolymers formed, including their reactivity towards fuming sulfuric acid.



Scheme 1 The monomer structures

EXPERIMENTAL

Materials

Perfluorovinylamines and perfluoroallylamines that bear a dialkylamino group were prepared as described elsewhere[3,4].

Perfluoro(3-dimethylaminopropyl vinyl ether) was prepared as follows. A dry potassium salt of perfluoro(6-dimethylamino-2-methyl-3-oxahexanoyl fluoride) (90.6 g, 0.195 mol), which was prepared by the reaction of perfluoro(3-dimethylaminopropionyl fluoride) and hexafluoropropene oxide[5], was pyrolysed at 230 to 260°C under reduced pressure (13–14 mmHg). A mixture (83.0 g) containing ca. 75 wt% of perfluoro(3-dimethylaminopropyl vinyl ether) was collected by a cold trap kept at −78°C, and the vinyl ether (56.3 g, 72% yield) was isolated by fractional distillation over molecular sieves 13 ×.

Perfluoro(3-dimethylaminopropyl vinyl ether) (**1**): b.p. 97.5–98.0°C; n_D^{20} 1.2813; d_4^{20} 1.7203. I.r. (gas): 1839 cm^{-1} ($\nu_{C=C}$). ^{19}F n.m.r. (**1**): −53.0 (A, m), −85.7 (D, m), −91.4 (B, m), −113.8 (F, dd), −122.1 (G, dd), −125.2 (C, m),

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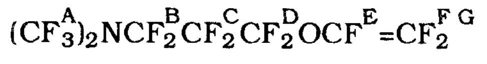
* To whom correspondence should be addressed

−135.8 (E, dd); $J_{EF} = 65.7$ Hz, $J_{EG} = 111.6$, $J_{FG} = 83.1$. M.s. m/z (relative intensity): 302 (3.6) $[M - OCF{=}CF_2]^+$, 214 (8.0) $[C_4F_8N]^+$, 202 (5.8) $[C_5F_{11}NO]^+$, 169 (10.4) $[C_3F_7]^+$, 131 (5.7) $[C_3F_3]^+$, 119 (6.2) $[C_2F_5]^+$, 114 (27.5) $[C_2F_4N]^+$, 100 (8.3) $[C_2F_4]^+$, 97 (4.2) $[OCF{=}CF_2]^+$, 81 (6.8) $[C_2F_3]^+$, 69 (100) $[CF_3]^+$, 50 (3.4) $[CF_2]^+$.



$(\overset{A}{CF_3})_2N\overset{B}{CF_2}\overset{C}{CF_2}\overset{D}{CF_2}O\overset{E}{CF}{=}\overset{F\ G}{CF_2}$

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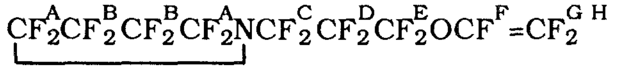
Similar procedures with the corresponding potassium salts afforded perfluoro(3-pyrrolidinopropyl vinyl ether) and perfluoro(2-morpholinoethyl vinyl ether) in 54% and 64% yields, respectively.

Perfluoro(3-pyrrolidinopropyl vinyl ether) (**2**): b.p. 127.0–127.5°C; n_D^{20} 1.2972; d_4^{20} 1.7708. I.r. (gas): 1840 cm^{-1} ($\nu_{C=C}$). ^{19}F n.m.r. (**2**): −85.3 (E, m), −91.0 (B, m), −93.3 (C, m), −113.9 (G, dd), −121.2 (H, dd), −126.5 (D, m), −133.2 (A, m), −135.8 (F, dd); $J_{FG} = 65.7$ Hz, $J_{FH} = 111.6$, $J_{GH} = 83.1$. M.s. m/z (relative intensity): 364 (13.7) $[M - OCF{=}CF_2]^+$, 264 (27.9) $[C_5F_{10}N]^+$, 214 (11.2) $[C_4F_8N]^+$, 176 (9.6) $[C_4F_6N]^+$, 169 (45.0) $[C_3F_7]^+$, 131 (14.8) $[C_3F_5]^+$, 119 (22.3) $[C_2F_5]^+$, 114 (16.2) $[C_2F_4N]^+$, 100 (25.4) $[C_2F_4]^+$, 97 (11.0) $[OCF{=}CF_2]^+$, 81 (11.1) $[C_2F_3]^+$, 69 (100) $[CF_3]^+$, 50 (6.1) $[CF_2]^+$.



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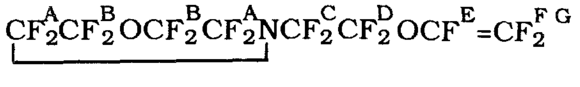
Perfluoro(2-morpholinoethyl vinyl ether) (**3**): b.p. 119.0–119.5°C; n_D^{20} 1.2967; d_4^{20} 1.7694. I.r. (gas): 1841 cm^{-1} ($\nu_{C=C}$). ^{19}F n.m.r. (**3**): −87.4 (A, m), −93.0 (B, m), −95.9 (C, p), −114.4 (F, dd), −122.7 (G, dd), −90.4 (D, m), −136.3 (E, dd); $J_{EF} = 65.8$ Hz, $J_{EG} = 111.6$, $J_{FG} = 83.4$. M.s. m/z (relative intensity): 427 (1.3) $[M]^+$, 330 (4.3) $[M - OCF{=}CF_2]^+$, 280 (3.8) $[M - CF_2OCF{=}CF_2]^+$, 192 (7.5) $[C_4F_6NO]^+$, 169 (4.4) $[C_3F_7]^+$, 164 (18.8) $[C_3F_6N]^+$, 119 (100) $[C_2F_5]^+$, 114 (33.8) $[C_2F_4N]^+$, 100 (26.7) $[C_2F_4]^+$, 97 (20.0) $[OCF{=}CF_2]^+$, 81 (5.3) $[C_2F_3]^+$, 69 (50.8) $[CF_3]^+$, 50 (7.5) $[CF_2]^+$.



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Solution polymerization

A perfluorovinyl monomer, a radical initiator and 1,1,2-trichlorotrifluoroethane as the solvent were placed in a 50 ml autoclave. After the mixture was degassed in a successive freeze–thaw cycle, the gaseous comonomer was added and then polymerization was carried out under heating. The polymer formed was collected by filtration, washed with methanol and dried *in vacuo*.

Emulsion polymerization

A perfluorovinyl ether, ammonium persulfate as the initiator, ammonium perfluoro(2,5-dimethyl-3,6-dioxanonanoate) (10 g) as the emulsifying agent and water (100 ml) were placed in a 200 ml autoclave. After the mixture was degassed in a successive freeze–thaw cycle, the gaseous comonomer was added under pressure. Polymerization was carried out with mechanical stirring at 400 rpm. During polymerization, the internal pressure of the vessel was kept between 5 and 6 kg cm^{-2} by charging the vessel with the comonomer. The resulting dispersed polymer was coagulated by cooling the mixture, then collected by decantation, washed with water and methanol and dried *in vacuo*, giving a white powdery polymer.

Chemical modification

Films of the copolymers were prepared by hot moulding. The copolymers were melted at 320°C then pressed at ca. 15 kg cm^{-2}.

The film (1.0 cm × 1.5 cm) or powder (2.0 g) of the copolymer was added to ca. 30% fuming sulfuric acid (30 g) in a 50 ml flask equipped with a condenser, after which the heterogeneous mixture was stirred magnetically, and refluxed (140–160°C). The copolymer film was removed, hydrolysed by washing it with water and dried *in vacuo*. The powdery sample was treated in a similar manner and fabricated into film by hot moulding. The modified polymer films were characterized by i.r. and x.p.s. To estimate the wettability of the films, the contact angles of water droplets on the polymer surface were measured.

Measurements

I.r. spectra were obtained with a Hitachi EPI-G3 spectrometer with a glass cell equipped with KBr windows and a Perkin-Elmer FT-IR-1760X. Mass spectra were taken with a Shimadzu GCMS-7000 instrument at 70 eV. ^{19}F n.m.r. spectra (84.67 MHz) were obtained with a Hitachi R-90F spectrometer using $CDCl_3$ as the solvent, and chemical shifts were defined as δ values relative to $CFCl_3$. Melting and decomposition temperatures of polymers were determined with a Seiko I & E DSC-20 differential scanning calorimeter and a TG-20 thermogravimeter. X.p.s. analysis was done with a Shimadzu ESCA-750. Oxygen and nitrogen permeabilities of the hot moulded films were measured at 25°C with a Yanako GTR-10, the upstream sides of the films being maintained at atmospheric pressure and the downstream sides at ca. 10^{-3} cmHg. The amount of gases permeated through the films was measured by gas chromatography, and the permeability coefficients were determined from the slopes of the time–permeate volume curves in the steady state.

RESULTS AND DISCUSSION

Radical copolymerization

Radical copolymerizations of perfluorovinylamines were done in 1,1,2-trichlorotrifluoroethane with diisopropyl peroxydicarbonate as the initiator. The results are shown in *Table 1*. Perfluoro(*N*-vinylmorpholine) (NVM) copolymerized with vinylidene fluoride (VdF); whereas, copolymerization of NVM with tetrafluoroethylene (TFE) or chlorotrifluoroethylene afforded a polymer in low yield, which did not contain NVM units. In the copolymerizations of NVM and VdF, an increase of

Table 1 Radical copolymerization of perfluorovinylamines (FVA) with tetrafluoroethylene (TFE), chlorotrifluoroethylene (CTFE) or vinylidene fluoride (VdF)[a]

	Feed				Polymer			
Run	FVA[b] (mmol)	Comonomer (mmol)	Time (h)	Yield[c] (%)	FVA (mol%)[d]	$\overline{M}_n$ ($\overline{M}_w/\overline{M}_n$)[e]	T_m (°C)	T_d (°C)
1	NVM 10	TFE 0.64	6	trace	0 (–)	–	326	390
2	NVM 10	CTFE 40	18	30	0 (–)	–	–	360
3	NVM 20	VdF 56	17	10	6 (5)	15000 (1.6)	140	360
4	NVM 50	VdF 50	18	3	– (28)	1000 (1.2)	–	–
5	NVPr 20	VdF 80	18	19	– (13)	5000 (2.6)	–	–
6	NVPp 20	VdF 80	17	8	7 (3)	10000 (1.6)	139	350

[a] Copolymerization was carried out in 1,1,2-trichlorotrifluoroethane (10 ml) at 25°C with di(3,5,6-trichlorooctafluorohexanoyl) peroxide (0.014 g, 0.020 mmol) as the initiator for run 1. The other runs were at 40°C with diisopropyl peroxydicarbonate (0.20 g, 1.0 mmol)
[b] NVM, perfluoro(*N*-vinylmorpholine); NVPr, perfluoro(*N*-vinylpyrrolidine); NVPp, perfluoro(*N*-vinylpiperidine)
[c] The weight of methanol-insoluble fraction was divided by the total monomer weight in the feed
[d] Determined by elemental analysis; values determined by ^{19}F n.m.r. in parentheses
[e] Estimated by g.p.c. with THF as the eluent and correlated to polystyrene standards

Table 2 Radical copolymerization of perfluoro(*N*-allylmorpholine) (NAM) with TFE or VdF[a]

	Feed				Polymer			
Run	NAM (mmol)	Comonomer (mmol)	Time (h)	Yield[b] (%)	NAM (mol%)[c]	$\overline{M}_n$ ($\overline{M}_w/\overline{M}_n$)[d]	T_m (°C)	T_d (°C)
1	10	TFE 90	46	52	3 (–)	–	324	220
2	10	VdF 80	23	60	7 (6)	36000 (1.8)	140	330
3	20	VdF 80	21	43	11 (10)	21000 (1.5)	80	300
4	30	VdF 70	49	33	15 (12)	24000 (1.4)	–	–

[a] Copolymerizations were carried out at 40°C in 1,1,2-trichlorotrifluoroethane (10 ml) with diisopropyl peroxydicarbonate (0.20 g, 1.0 mmol) as the initiator
[b] The weight of methanol-insoluble fraction was divided by the total monomer weight in the feed
[c] Determined by elemental analysis; values determined by ^{19}F n.m.r. in parentheses
[d] Estimated by g.p.c. with THF as the eluent and correlated to polystyrene standards

Table 3 Solution copolymerization of perfluoro(3-dimethylaminopropyl vinyl ether) (DmPVE) with TFE[a]

	Feed					Polymer		
Run	DmPVE (mmol)	TFE (mmol)	Temp. (°C)	Time (h)	Yield[b] (%)	DmPVE (mol%)[c]	T_m (°C)	T_d (°C)
1	10	90	40	18	69	11	313	430
2	20	80	20	6.5	45	16	314	350
3	25	75	20	5.5	50	20	314	350

[a] Copolymerization was carried out in 1,1,2-trichlorotrifluoroethane (10 ml) at 40°C with diisopropyl peroxydicarbonate (0.20 g, 1.0 mmol) as the initiator for run 1 and with di(3,5,6-trichlorooctafluorohexanoyl) peroxide (0.72 g, 1.0 mmol) at 20°C for runs 2 and 3
[b] The weight of methanol-insoluble fraction was divided by the total monomer weight in the feed
[c] Determined by elemental analysis

NVM in the feed caused decreases in the yield and molecular weight of the copolymer formed, which suggested that the NVM radical at the propagating end of the polymer had little reactivity towards the monomers and thus NVM behaved as a polymerization retarder. For run 3 in *Table 1*, the monomer reactivity ratio of VdF estimated by the Mayo–Lewis equation is 5.2, when that of NVM is assumed to be 0. Perfluoro(*N*-vinylpyrrolidine) (NVPr) and perfluoro(*N*-vinylpiperidine) (NVPp) also copolymerized only with VdF. Because of less bulkiness of the cyclic amino group, NVPr had higher copolymerizability with VdF than did NVM and NVPp, which resulted in high yield, large incorporation of NVPr units in the copolymer and a low molecular weight of the copolymer.

Perfluoro(*N*-allylmorpholine) (NAM) was allowed to copolymerize with TFE or VdF under conditions similar to those used for the perfluorovinylamines. The results are shown in *Table 2*. NAM had higher copolymerizability than the perfluorovinylamines. The polymer formed from NAM and TFE contained 3% NAM units and it decomposed at 220°C; which was attributable to its low molecular weight. NAM and VdF gave copolymers, the NAM content in the copolymer varying with the NAM composition of the monomer feed. While the molecular weights of the copolymers changed little as

Table 4 Emulsion copolymerization of perfluorovinyl ethers (FVE) with TFE or VdF[a]

	Feed[b]				Polymer		
Run	FVE[c] (g)	Comonomer	Time (h)	Yield (g)	FVE (mol%)[d]	T_m (°C)	T_d (°C)
1	DmPVE 6.4	TFE	5.3	22.5	8	322	350
2	DmPVE 12.8	TFE	4.5	30.9	15	319	270
3	PrPVE 3.6	TFE	8.8	24.5	4	328	360
4	PrPVE 17.7	TFE	7.6	30.1	23	335	300
5	MEVE 7.4	TFE	4.3	28.2	10	317	350
6	MEVE 14.8	TFE	5.5	34.4	17	317	350
7	MEVE 3.7	VdF	21	12.9	6 (4)	167	340

[a] Copolymerizations were carried out at 65°C in water (100 ml) with ammonium persulfate (70 mg) as the initiator and ammonium perfluoro(2,5-dimethyl-3,6-dioxanonanoate) as the emulsifying agent (10 g)

[b] The gaseous comonomer was added to the emulsion throughout polymerization, the internal pressure of the reaction vessel being kept at 5–6 kg cm^{-2} by charging the vessel with the comonomer

[c] DmPVE, perfluoro(3-dimethylaminopropyl vinyl ether); PrPVE, perfluoro(3-pyrrolidinopropyl vinyl ether); MoEVE, perfluoro(2-morpholinoethyl vinyl ether)

[d] Determined by elemental analysis; values determined by ^{19}F n.m.r. in parentheses

the NAM content in the copolymers increased, their melting point decreased. The copolymer containing 15% NAM units was rubbery and had a glass transition temperature of −5 to −8°C.

Unlike the perfluorovinylamines and perfluoroallylamines, the perfluorovinyl ethers, which have the ether oxygen and two or three difluoromethylene units as a spacer between the vinyl and dialkylamino groups, are thought to have a good polymerizability, which is similar to that of perfluoro(n-alkyl vinyl ether). Perfluoro (3-dimethylaminopropyl vinyl ether) (DmPVE) copolymerized with TFE giving copolymers in good yields (*Table 3*). The perfluorovinyl ether was easily incorporated into the copolymers, and the vinyl ether content of the copolymers could be varied by changing the monomer composition in the feed.

Several perfluorovinyl ethers were copolymerized with TFE by emulsion polymerization. The results are shown in *Table 4*. All the perfluorovinyl ethers afforded copolymers with TFE in good yields. Perfluoro(3-pyrrolidinopropyl vinyl ether) (PrPVE) required a longer polymerization time than DmPVE and perfluoro(2-morpholinoethyl vinyl ether) (MEVE) to yield a certain amount of copolymer. The copolymers had high melting points, but their decomposition temperatures were lower than that of poly[TFE-*co*-perfluoro(propyl vinyl ether)] (430°C) prepared under similar polymerization conditions. Cleavage of C–N bonds might occur at the initial stage of the thermal decomposition of copolymers. Copolymers with large vinyl ether contents started to decompose at temperatures lower than their melting points. While the copolymers were insoluble in all the solvents used, they could be fabricated into transparent films by hot moulding.

Gas permeability

Polytetrafluoroethylene (PTFE) has very low gas permeability owing to its high crystallinity, and TFE copolymers usually have higher gas permeability than PTFE[8]. The gas permeabilities of the copolymers that consisted of perfluorovinyl ether bearing a dialkylamino group and TFE were evaluated. As *Table 5* shows, their oxygen and nitrogen permeabilities were higher than those of the common TFE copolymers, and the copolymers with morpholine rings had slightly larger permeability coefficients than those with dimethylamino groups. The gas permeability of the copolymers was barely enhanced with vinyl ether content of the copolymers.

Table 5 Gas permeability of copolymers of perfluorovinyl ethers and tetrafluoroethylene[a]

Polymer[b]	Vinyl ether content (%)	P_{O_2}[c]	P_{N_2}[c]
DmPVE-*co*-TFE	4	6.9	2.5
MEVE-*co*-TFE	4	7.5	2.9
MEVE-*co*-TFE	10	7.6	2.7
FEB	–	4.9	1.6
ETFE	–	0.53	0.18
PFA	–	4.2	1.2

[a] Measured at 25°C

[b] DmPVE, perfluoro(3-dimethylaminopropyl vinyl ether); MEVE, perfluoro(2-morpholinoethyl vinyl ether); FEP, poly(tetrafluoroethylene-*co*-hexafluoropropylene); ETFE, poly(ethylene-*co*-tetrafluoroethylene); PFA, poly[tetrafluoroethylene-*co*-perfluoro(propyl vinyl ether)]

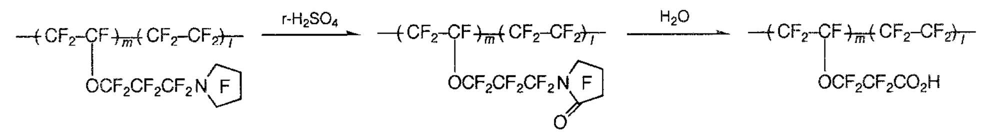
[c] Gas permeability coefficient in 10^{-10} cm^3(STP) cm cm^{-2} s^{-1} cmHg^{-1} (i.e. Barrers)

Chemical modification

The introduction of ionic groups to the surface or bulk of a fluoropolymer is thought to be significant. The enhanced hydrophilicity produced by ionic groups improves the wettability and adhesive properties of the polymer surface[9,10], and a fluoropolymer with ionic groups can be used as an ion-exchange resin, e.g. Nafion® (refs. 11, 12).

Some fluoro-tertiary amines react with sulfur trioxide to give α-fluorosulfonyloxyamines, which can be hydrolysed to give oxo or hydroxy derivatives[13]. Further, when fuming sulfuric acid is used as a sulfur trioxide source, perfluoro(*N*-alkyl cyclic amine)s are converted exclusively to perfluorolactams in one step[14].

Copolymers with cyclic amino groups were allowed to react with fuming sulfuric acid, then hydrolysed in order to introduce carboxyl groups (*Scheme 2*). The powdery poly(PrPVE-*co*-TFE)s and the films of poly(MEVE-*co*-TFE) reacted heterogeneously with fuming sulfuric acid



Scheme 2 Reaction of poly(PrPVE-*co*-TFE) with fuming sulfuric acid followed by hydrolysis

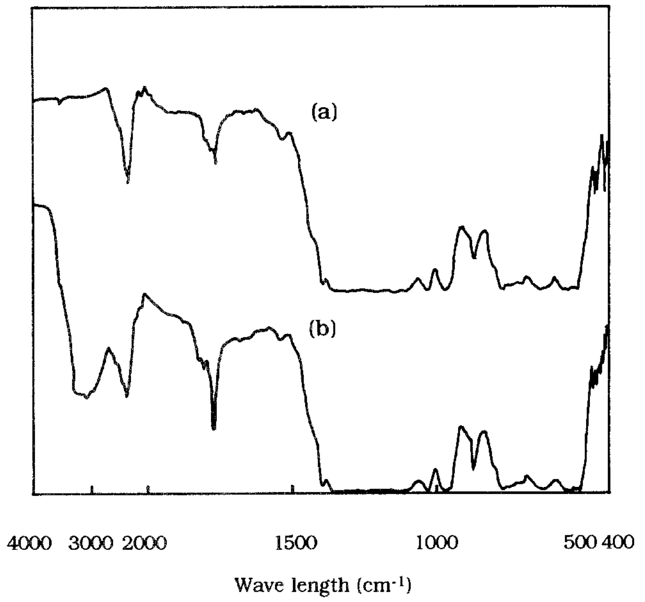


Figure 1 Infra-red spectra of poly(PrPVE-*co*-TFE) (23 mol% PrPVE) treated with fuming sulfuric acid: (a) before treatment; (b) after 7 h of treatment

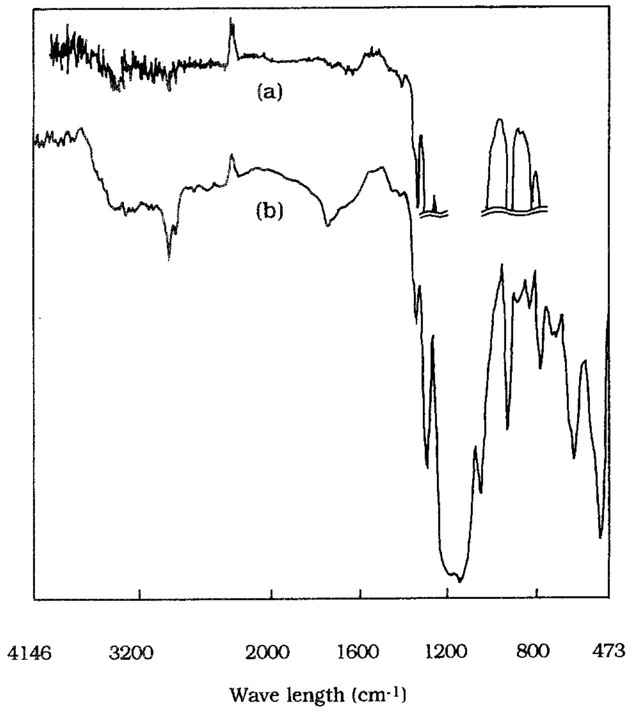


Figure 2 Infra-red spectra (a.t.r. method) of poly(MEVE-*co*-TFE) (10 mol% MEVE) treated with fuming sulfuric acid: (a) before treatment; (b) after 23 h of treatment

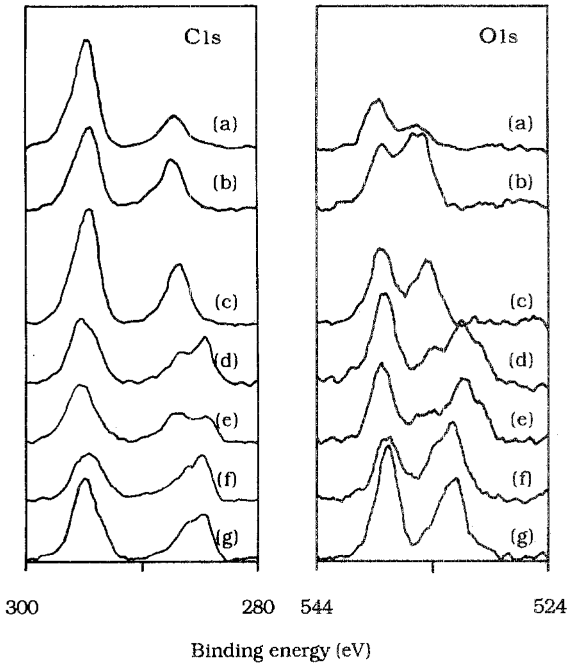


Figure 3 C 1s and O 1s core-level spectra of poly(PrPVE-*co*-TFE) (23 mol% PrPVE) and poly(MEVE-*co*-TFE) (10 mol% MEVE) treated with fuming sulfuric acid: (a) poly(PrPVE-*co*-TFE), before treatment; (b) poly(PrPVE-*co*-TFE), after 7 h of treatment; (c) poly(MEVE-*co*-TFE), before treatment; (d) one side of the poly(MEVE-*co*-TFE) film and (e) the other after 7 h of treatment; (f) and (g) opposite sides of poly(MEVE-*co*-TFE) after 23 h of treatment

then with water. After the reaction, the powdery samples were fabricated into films by hot moulding.

The i.r. spectra of these treated copolymers showed absorption peaks corresponding to the carbonyl and hydroxy groups (*Figures 1* and *2*). Incorporation of carboxyl groups into the copolymers was also confirmed by x.p.s. analysis (*Figure 3*). In the poly(PrPVE-*co*-TFE) film fabricated after the reaction, the O 1s peak at 534–536 eV was enlarged, but the C 1s, F 1s and N 1s spectra showed little change. In the poly(MEVE-*co*-TFE) that was treated in film form, a C 1s peak present at 284 eV was attributable to the carbonyl carbon, and an O 1s peak at 530–533 eV differed from the peak for the oxygen of the morpholine ring (535 eV).

Quantitative details about the reactions and structures of the resulting polymers are not clear because of the heterogeneity in the reaction of polymers with fuming sulfuric acid, and the difficulty in determining to what extent hydrolysis was complete. The completely hydrolysed structure is shown in *Scheme 2*.

The contact angles of water droplets on the surfaces of the modified polymers were measured to estimate the wettability of the polymers. Results are shown in *Table 6*. All the polymers showed a decrease in contact angle after the reaction. The poly(PrPVE-*co*-TFE)s, which had been treated in powder form, showed the most rapid reduction. The wettability of poly(PrPVE-*co*-TFE) with a large PrPVE content was enhanced markedly after treatment for 7 h. The poly(MEVE-*co*-TFE)s, which had been treated in film form, gave different values for the opposite sides of the film. This is because of the

Table 6 Contact angles of water droplets on poly(perfluorovinyl ether-*co*-tetrafluoroethylene)s before and after the reaction with fuming sulfuric acid[a]

		Contact angle (deg)			
Polymer[b]	Vinyl ether content (%)	0 h[c]	7 h	15 h	23 h
PrPVE-*co*-TFE	4	92	84	–	–
PrPVE-*co*-TFE	23	83	58	–	–
MEVE-*co*-TFE	10	91	90/87[d]	91/88	91/86
MEVE-*co*-TFE	17	94	92/88	–	96/86

[a] Powdery poly(PrPVE-*co*-TFE)s and films of poly(MEVE-*co*-TFE) were allowed to react with fuming sulfuric acid

[b] PrPVE, perfluoro(3-pyrrolidinopropyl vinyl ether); MEVE, perfluoro(3-morpholinoethyl vinyl ether)

[c] Reaction time

[d] Values for both sides of the film

heterogeneous reaction conditions, under which the films did not dip below the liquid surface of the fuming sulfuric acid.

CONCLUSIONS

The polymerization of perfluorovinyl ethers bearing dialkylamino groups and TFE afforded copolymers. Perfluorovinylamines and perfluoroallylamines, however, copolymerized with VdF but not with TFE.

The copolymers of perfluorovinyl ethers and TFE had higher gas permeabilities than the common TFE copolymers. They also reacted with fuming sulfuric acid, hydrolysis of the reacting copolymers giving the films enhanced wettability.

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