

The Thermal Degradation of Perfluoro Polymers

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Synopsis

A number of perfluoro polymers were heated at a constant rate of temperature rise in an atmosphere of nitrogen or air, and the volatile degradation products were passed into an aqueous solution, where the F^- ions produced were monitored with a fluoride ion-selective electrode. Compounds giving rise to F^- ions were formed in both nitrogen and air, but in larger amounts in the latter atmosphere. For the formation of appreciable quantities of F^- ions, temperatures greater than $500^\circ C$ were normally necessary.

INTRODUCTION

In an earlier paper¹ are given the results of a study of the thermal dehydrofluorination of hydrofluoro polymers. The technique used was to pass the volatile degradation products into an aqueous solution and to monitor the fluoride ion produced with a fluoride ion-specific electrode. It was found that with polymers containing both hydrofluoroalkylene groups and perfluoroaromatic rings in the main chain, the yield of fluoride ion was greater than that theoretically available from the hydrofluoroalkylene units alone. This was so in both inert and oxidizing atmospheres, and it indicated that species giving rise to fluoride ion were being formed from the perfluoroaromatic rings. Since this might lead to corrosion problems while using these polymers, and since the defluorination obviously played a part in the mechanism of decomposition at elevated temperatures, it was considered worthwhile to study the thermal defluorination of such perfluoro polymers as were readily available.

EXPERIMENTAL

Polymers Examined

Polytetrafluoroethylene, $\text{-(CF}_2\text{CF}_2\text{)}_n\text{-}$. Prepared by emulsion polymerization at $60^\circ C$ using a persulfate/borax recipe.² Found: C, 23.9%; F, 71.5%; H, 0.1%. Calcd: C, 24.0%; F, 76.0%.

Copolymer of Tetrafluoroethylene and Hexafluoropropylene, $\text{-(CF}_2\text{-CF}_2\text{)}_m\text{-(CF}_2\text{CF(CF}_2\text{))}_n\text{-}$. Commercial sample from du Pont Ltd. Pyrolysis-

gas chromatography indicated that it contained 16 mole-% of hexafluoropropylene.³

Perfluoropolyphenylenes, $+C_6F_4+_n$. A number of *p*-linked samples were prepared by decomposition of pentafluoromagnesium bromide in refluxing tetrahydrofuran.^{4,5} High molecular weight polymer (D.P. ~ 100)—Found: C, 47.2%; F, 50.1%; Br, 2.6%. Calcd: C, 48.7%; F, 51.3%. Low molecular weight polymer (D.P. 25)—Found: C, 48.1%; F, 51.9%. Model compound, perfluoro-*p*-quaterphenyl—Found: C, 45.4%; F, 53.7%. Calcd: C, 45.7%; F, 54.3%. Corresponding *m*-linked samples were prepared by reaction of 1,3-dibromotetrafluorobenzene with activated copper bronze in dimethylformamide.⁶ High molecular weight polymer (D.P. ~ 107)—Found: C, 48.6%; F, 50.7%; Br, 0.3%. Calcd: C, 48.7%; F, 51.3%. Low molecular weight polymer (D.P. ~ 20)—Found: C, 47.8%; F, 51.8%; Br, 0.4%. Model compound, perfluoro-*m*-quaterphenyl—Found: C, 46.1%; F, 54.1%. Calcd: C, 45.7%; F, 54.3%.

Perfluoropolyphenylene Sulfides, $+C_6F_4S+_n$. Two samples were examined, a linear polymer made by decomposition of potassium pentafluorothiophenoxide in a sealed glass tube at 240°C and a crosslinked material made by reaction of hexafluorobenzene with sodium sulfide in pyridine.⁷ Linear sample—Found: C, 39.6%; F, 41.9%; S, 18.1%. Calcd: C, 40.0%; F, 42.2%; S, 17.8%. Crosslinked sample—Found: C, 40.5%; H, 0.5%; F, 32.5%; S, 24.6%.

Perfluoropolyppyridine, $+C_5NF_3+_n$. Prepared by heating the lithium derivative of bromo-2,3,5,6-tetrafluoropyridine in refluxing tetrahydrofuran. Found: C, 45.6%; F, 42.3%; N, 11.6%; H, 1.0%. Calcd: C, 45.8%; F, 43.5%; N, 10.7%. Results on this particular polymer have been reported previously,⁸ but some data are included here for comparison purposes.

Two oxymethylene-linked polymers, $+C_6F_4CF_2O+_n$ and $+C_6F_3-(CF_3)CF_2O+_n$, were prepared by decomposition in water of the potassium salt of the appropriate perfluoro-*p*-cresol.⁹ Found for $+C_6F_4CF_2O+_n$: C, 38.5%; F, 53.3%; H, 0.2%. Calcd: C, 39.3%; F, 53.3%. Found for $+C_6F_3(CF_3)CF_2O+_n$: C, 36.5%; F, 55.8%. Calcd: C, 36.3%; F, 57.6%.

Apparatus and Experimental Technique

The apparatus and experimental technique have been described in detail previously.¹⁰ Briefly, fluoride yield experiments were carried out on 5-mg samples in either a dry air or nitrogen flow of 50 ml/min and at a rate of temperature rise of 2°C/min. For convenience, a platinum sample boat was used for the majority of the polymers, but a number of experiments were made with one polymer using a calcium fluoride boat to check on any possible catalytic activity of the platinum.

Thermogravimetric measurements were made using a du Pont 950 thermogravimetric analyzer with sample size of 5 mg, gas flow of 50 ml/min, and temperature rise rate of 4°C/min.

RESULTS AND DISCUSSION

Reproducibility of Results

Good reproducibility of results had been obtained previously¹⁰ with hydrofluoroethylene polymers both in inert and oxidizing atmospheres. In the present study a number of check runs were made on poly(tetrafluoroethylene), and the results are given in Figure 1. As with the hydrofluoroethylene polymers, the reproducibility was rather better in a nitrogen atmosphere than in air. Similar results were obtained using either a platinum or a calcium fluoride boat, confirming that the platinum was not exerting a catalytic effect upon the breakdown reaction.

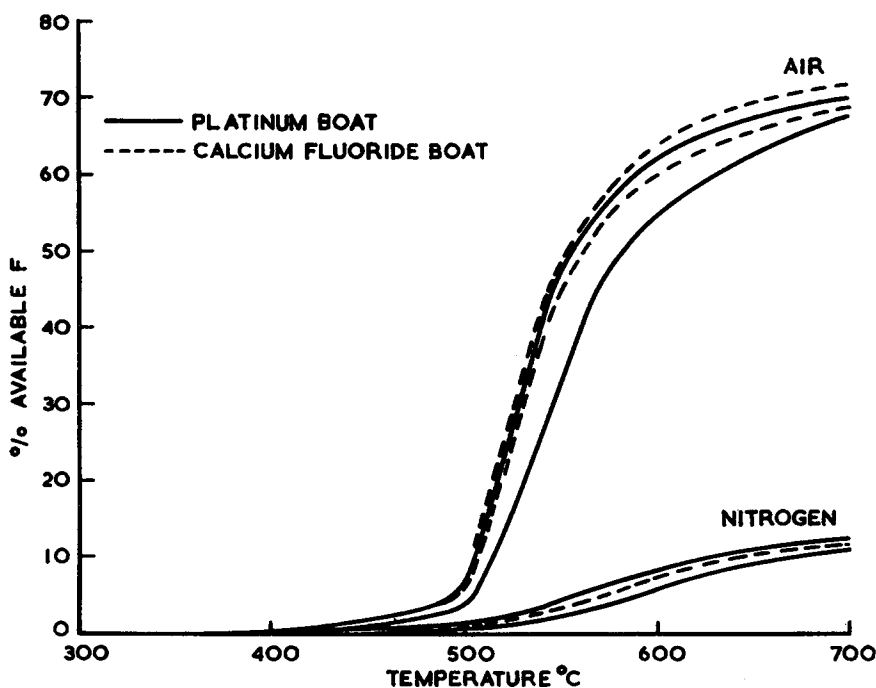


Fig. 1. Yield of F from poly(tetrafluoroethylene).

Addition Polymers

Comparative curves for poly(tetrafluoroethylene) (PTFE) and a copolymer of tetrafluoroethylene and hexafluoropropylene (FEP) in nitrogen or in air are shown in Figure 2, all curves being the average of at least two experiments. The behavior of the two polymers was very similar with a small but measurable yield of F^- in nitrogen and a much greater yield in air. In nitrogen, there was evidence of F^- production by breakdown of secondary products, the F^- yield at total weight loss being about 6% for poly(tetrafluoroethylene) and 4% for the copolymer, whereas the final total

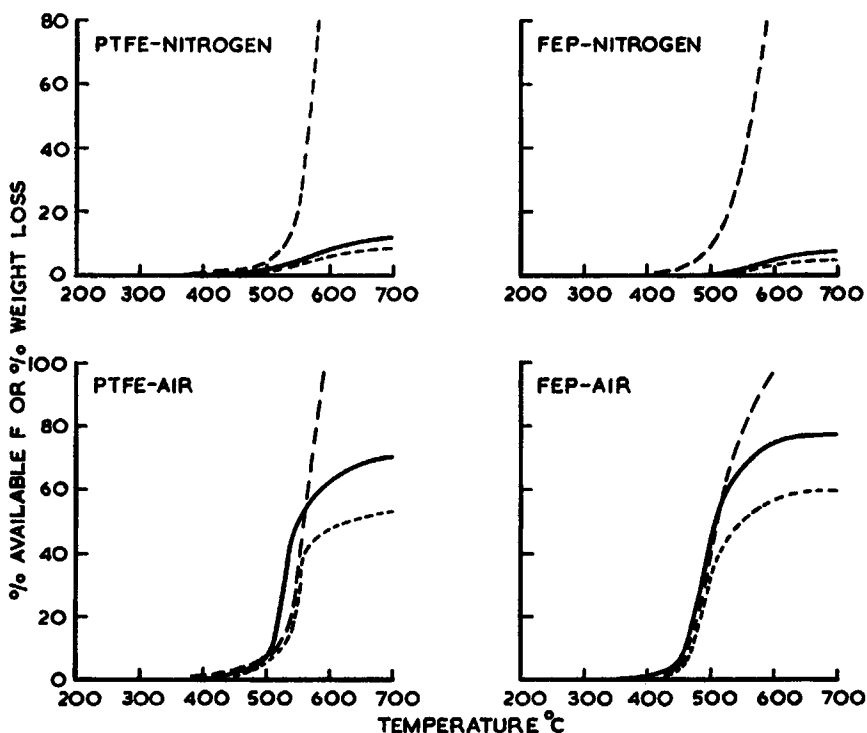


Fig. 2. Comparison of F yields from poly(tetrafluoroethylene) and a copolymer of tetrafluoroethylene and hexafluoropropylene: (—) F yield; (---) weight loss; (—) F yield as percentage weight loss.

yields measured were 11% and 7%, respectively. This arises because in the weight loss measurements only the total loss of volatiles from the sample crucible is measured. In the F yield experiments, primary degradation products may condense on cooler parts of the furnace tube and be further broken down, with yield of more F as the temperature there rises with the programmed heating cycle. In air, the copolymer was rather less stable both on the basis of weight loss and F⁻ yield. The two curves closely paralleled each other up to approximately 50% reaction.

These results may be compared with other published data. Kupel et al.¹¹ analyzed the breakdown products of PTFE and FEP in nitrogen and air, but unfortunately their results were tabulated in such a form that it is difficult to assess the relative amounts of the different products. The only molecular ions cited were those of carbon dioxide and tetrafluoroethylene, the abundance of the latter being low in nitrogen. Wall and Michaelsen¹² noted the absence of monomer and the presence of carbon dioxide, carbon monoxide, and silicon tetrafluoride when PTFE was pyrolyzed in oxygen. They attributed this to reaction of oxygen with polymeric free radicals and subsequent reaction of some of the oxygenated products with the glass of the reaction vessel. Such a mechanism is not possible with

the apparatus used in the present investigation, as the effluent gases come into contact with fully fluorinated materials only before they enter the aqueous solution. The results indicate, therefore, that the majority of the degradation products from pyrolyses of PTFE in air are compounds which react with water to give F^- ions. In this connection, it is of interest to note that Fenimore and Jones,¹³ in a study of the decomposition of burning PTFE in oxygen at 650°C , showed that elemental fluorine was present in the gaseous phase. Their calculations, in fact, indicated that F atoms would be a major flame species at equilibrium.

For pyrolysis under vacuum, there is ample evidence that the major breakdown products are the monomer for PTFE¹⁴⁻¹⁶ and the monomers for FEP.¹⁷ If the pressure is increased, the yield of monomer falls and that of a dimer increases proportionately.¹⁸ The production of up to 3 mole-% of SiF_4 on pyrolysis of PTFE under vacuum at 538°C has been noted,¹⁴ however, in agreement with the yield of F^- found in nitrogen in this investigation.

Condensation Polymers

Perfluoropolyphenylenes. Results for para-linked polymers are given in Figure 3 and for meta-linked materials in Figure 4. The pattern of behavior was the same for both linkages. The quaterphenyl model compounds effectively gave no yield of F^- in either nitrogen or air, as they both volatilized completely at relatively low temperatures. In nitrogen, there was a higher F^- yield with the higher molecular weight polymers, this being largely a function of improved thermal stability, as evidenced by the

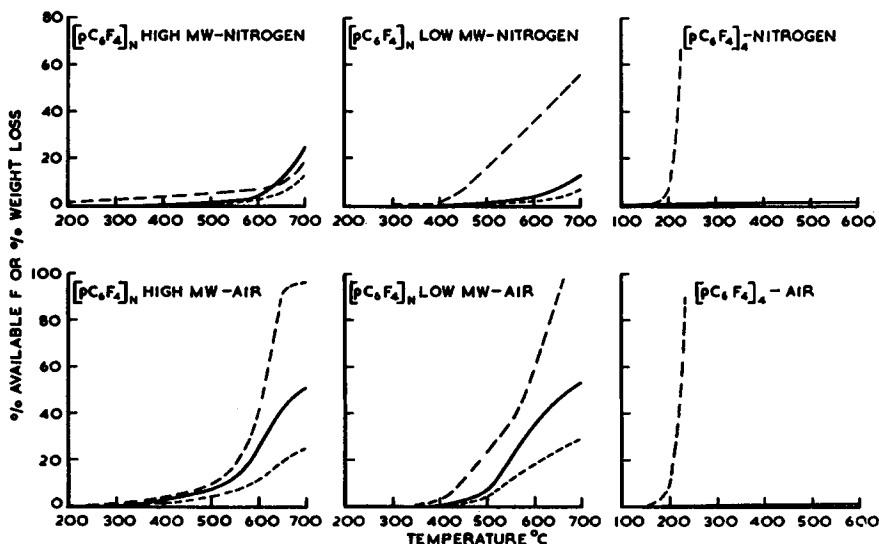


Fig. 3. Comparison of F yields from *p*-linked perfluoropolyphenylenes: (—) F yield; (---) weight loss; (—) F yield as percentage weight loss.

weight loss curves. This is in agreement with earlier work¹⁹ in which samples were pyrolyzed in evacuated silica ampoules, and it was found that the amount of fluorine contained in the pyrolysis residue depended upon the molecular weight of the starting material.

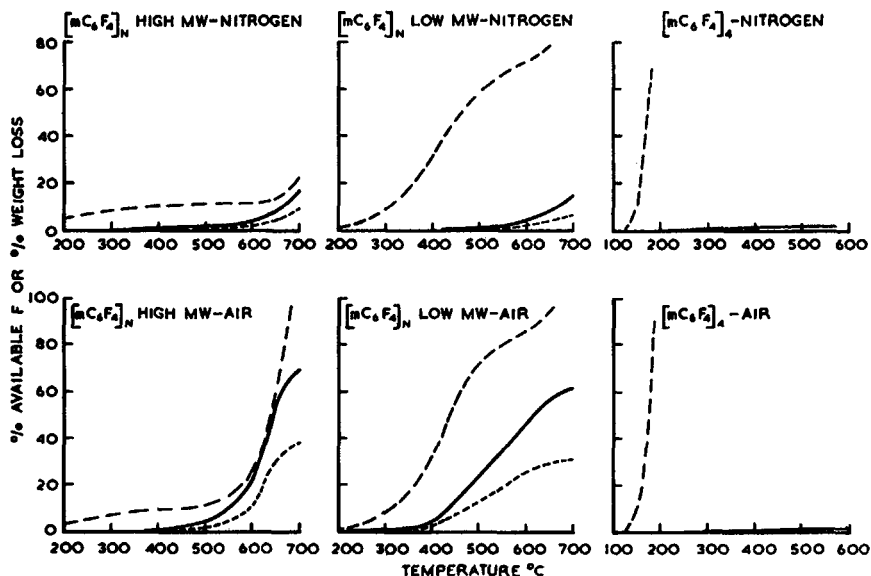


Fig. 4. Comparison of F yields from *m*-linked perfluoropolyphenylenes: (---) F yield; (—) weight loss; (- - -) F yield as percentage weight loss.

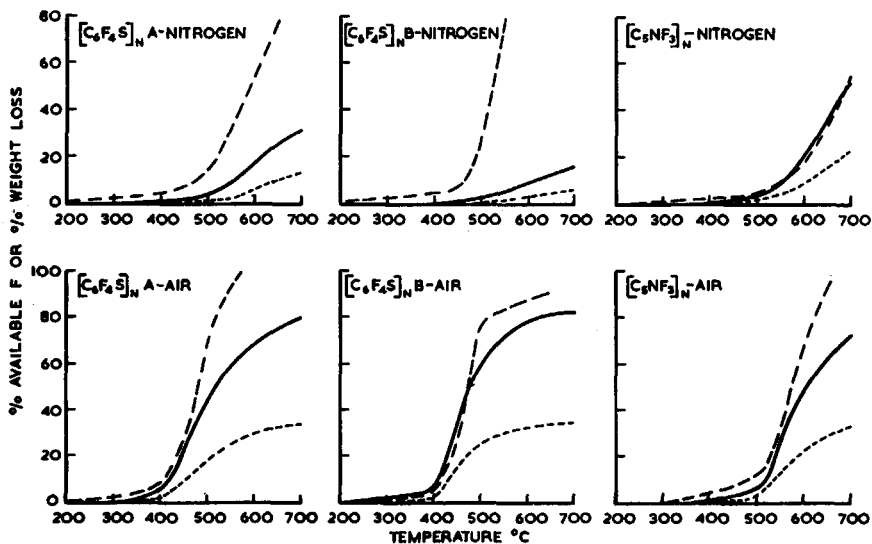


Fig. 5. Comparison of F yields from perfluoropolyphenylene sulfides and perfluoropyridine: (---) F yield; (—) weight loss; (- - -) F yield as percentage weight loss.

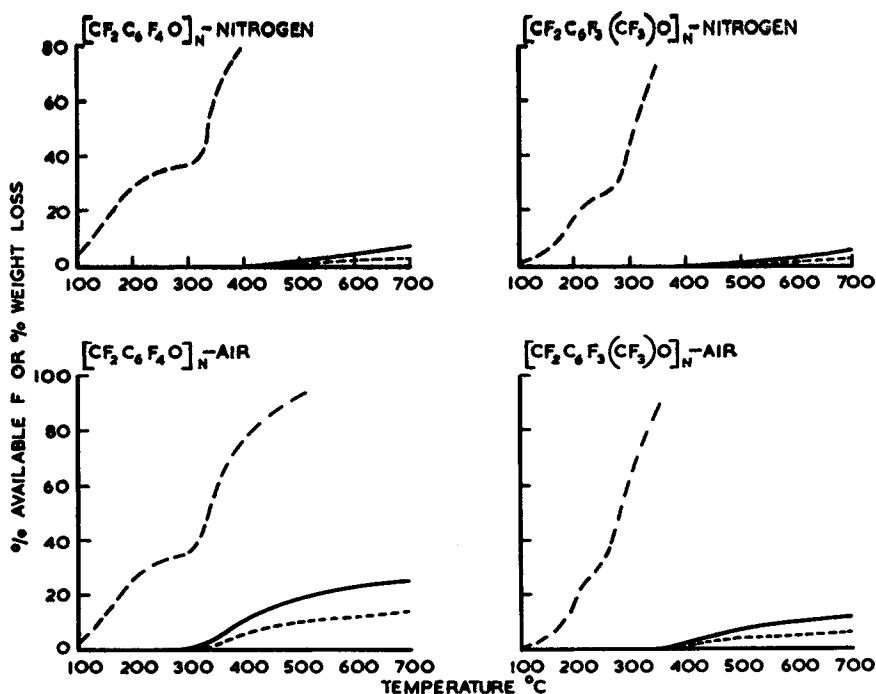


Fig. 6. Comparison of F yields from OCF_2 -linked polymers: (---) F yield; (—) weight loss; (· · ·) F yield as percentage weight loss.

In air, the meta-linked polymers gave a rather higher final yield of F^- (60–70%) than the para-linked polymers (50–60%). With the higher molecular weight materials, the F^- yield curve and the weight loss curve were very close to each other over the major part of the reaction.

Perfluoropolyphenylene Sulfides and Perfluoropolyppyridine. Results for these polymers are shown in Figure 5. The crosslinked phenylene sulfide polymer gave a higher final F^- yield in nitrogen (32%) than the linear polymer (16%), but in air there was little difference between them (yield approximately 80%). The results again are in agreement with earlier findings²⁰ from sealed ampoule experiments.

The perfluoropolyppyridine gave the highest yield of F^- in nitrogen of any of the polymers studied. This is presumably a function of the presence of the nitrogen atom in the ring, and it would be of interest to examine any other heterocyclic ring systems that are available to see if the effect is general. In air, however, there is little difference between perfluoropolyppyridine and the other perfluoroaromatics tested.

Polymers Linked by OCF_2 Units. These polymers had a relatively poor thermal stability, and any F^- detected in nitrogen arose from further breakdown of degradation products (Fig. 6). This was also true for the $[\text{C}_6\text{F}_3(\text{CF}_3)\text{CF}_2\text{O}]$ polymer in air, but with the $[\text{C}_6\text{F}_4\text{CF}_2\text{O}]$ polymer, which broke down in two clearly defined stages (see weight loss curve) some F^- (approximately 20%) was obtained in the second stage.

Overall Comparison of Results

Summaries of the results obtained in nitrogen and in air are given in Tables I and II, respectively. These tables include the following data: the temperatures for initial weight loss and 1% weight loss derived from a single experiment; the temperature for initial F⁻ ion detection (this was the lower of the figures obtained in two experiments, because of the variability of the initial pF reading); the temperature for 1% yield of F⁻ ions (average of at least two results); and the final total yield of F⁻ ions (again the average of at least two results). The final yield figure may include some F⁻ ion arising from secondary breakdown of degradation products.

In nitrogen, all the materials studied, with the exception of the quaterphenyls and the OCF₂-linked polymers, gave rise to some F⁻ ions during their primary breakdown. The amounts were normally small, a few per cent, with the exceptions of perfluoropyridine and the crosslinked sample of perfluoropolyphenylene sulfide. In most cases, F⁻ was first detected at relatively low temperatures (approximately 200°C), but the temperatures for 1% F⁻ yield were much closer to 500°C, the average for all results being 467°C. The inference is that the F⁻ ions arise from compounds which are only produced in abundance from perfluoropolymers at temperatures greater than 500°C, and hence that high yields cannot be expected from polymers unless they are reasonably thermally stable to those temperatures.

TABLE I
Summary of Results in Nitrogen

Polymer structure	Temperature, °C, for				Final total yield of F, %
	Initial weight loss	1% weight loss	Initial F yield	1% F yield	
[CF ₂ CF ₂]					
Platinum boat	350	432	289	510	11.6
Calcium fluoride boat			190	518	11.2
[CF ₂ CF ₂ /CF ₃ CFCF ₂]	400	457	293	530	6.6
[<i>p</i> -C ₆ F ₄]					
High molecular weight	330	376	271	504	22.9
Low molecular weight	350	393	337	512	12.8
<i>p</i> -C ₆ F ₃ C ₆ F ₄ C ₆ F ₄ C ₆ F ₅	150	175	—	>700	—
[<i>m</i> -C ₆ F ₄]					
High molecular weight	150	162	160	403	16.7
Low molecular weight	120	144	212	502	13.7
<i>m</i> -C ₆ F ₃ C ₆ F ₄ C ₆ F ₄ C ₆ F ₅	120	126	—	>700	—
[C ₆ F ₄ S]					
Crosslinked	200	315	180	374	31.3
Linear	170	215	212	467	16.1
[C ₅ NF ₃]	150	280	291	355	56.9
[C ₆ F ₄ CF ₂ O]	40	60	168	437	7.0
[C ₆ F ₃ (CF ₂)CF ₂ O]	100	128	198	486	5.1

TABLE II
Summary of Results in Air

Polymer structure	Temperature, °C, for				Final total yield of F, %
	Initial weight loss	1% weight loss	Initial F yield	1% F yield	
[CF ₂ CF ₂]					
Platinum boat	300	392	236	433	68.2
Calcium fluoride boat			239	359	70.7
[CF ₂ CF ₂ /CF ₃ CF ₂ CF ₂]	400	424	298	429	78.4
[<i>p</i> -C ₆ F ₄]					
High molecular weight	280	344	180	354	50.7
Low molecular weight	300	384	337	462	54.6
<i>p</i> -C ₆ F ₅ C ₆ F ₄ C ₆ F ₄ C ₆ F ₅	150	164	198	587	2.0
[<i>m</i> -C ₆ F ₄]					
High molecular weight	120	163	142	402	70.0
Low molecular weight	140	186	122	368	61.3
<i>m</i> -C ₆ F ₅ C ₆ F ₄ C ₆ F ₄ C ₆ F ₅	110	124	70	579	1.7
[C ₆ F ₄ S]					
Crosslinked	200	243	154	334	79.4
Linear	160	270	191	364	82.5
[C ₅ NF ₂]	180	290	286	410	72.6
[C ₆ F ₄ CF ₂ O]	50	75	182	310	25.2
[C ₆ F ₃ (CF ₃)CF ₂ O]	100	122	163	372	12.9

In air, the yields of F⁻ were much greater than in nitrogen, amounting to 50–70% of that theoretically available. This was because of the formation of species such as CF₂O, which gave F⁻ ions when dissolved in water. The temperatures for initial yield and 1% yield of F⁻ were also reduced, being 30–50°C below the comparable figures in nitrogen.

CONCLUSIONS

The formation of breakdown products which when dissolved in water give F⁻ ions has been shown to occur for the majority of the perfluoropolymers examined, both in inert and oxidizing atmospheres. The final total yields of F⁻ are, however, considerably different in the two atmospheres—an average of 17% for nitrogen and 60% for air. The process in nitrogen is one involving fairly high energies as the rate of F⁻ production is low until temperatures greater than 500°C have been reached. Very slight amounts of F⁻ have been detected at temperatures lower than 200°C, so there may be possible corrosion hazards with some of these materials.

Further work is necessary to ascertain precisely what are the primary breakdown products that give rise to the F⁻ ions.

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