

## The Thermal Degradation of Perfluoropoly pyridine

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### Synopsis

The thermal degradation of perfluoropoly pyridine was studied in inert and oxidizing atmospheres by thermogravimetric techniques. Volatile products were analyzed mass-spectrometrically, and the yield of products giving rise to fluoride ion was also determined. The stability of the polymer on a weight loss basis is rather better than that of polytetrafluoroethylene in inert atmospheres, but rather worse in oxidizing atmospheres. The major breakdown route seems to involve removal of the fluorine from the heterocyclic nucleus by a mechanism as yet unknown.

### INTRODUCTION

Relatively little is known of the thermal stability of polymers composed solely of perfluoroaromatic or perfluoro heterocyclic groups, the only materials investigated to date being perfluoropolyphenylenes<sup>1,2</sup> and perfluoropolytolylene.<sup>3,4</sup> The perfluoropolyphenylenes as first made<sup>1</sup> were of relatively low molecular weight and contained bromine or iodine endgroups. They were examined by direct evaporation into a mass spectrometer,<sup>5</sup> and the results showed that little degradation took place, at least up to 430°C. The later materials<sup>2</sup> were of much higher molecular weight and could be made without residual halogen. Their thermal stability as determined thermogravimetrically was comparable with that of polyphenylene in vacuo and rather inferior to polytetrafluoroethylene in oxygen. The main volatile degradation products were silicon tetrafluoride and carbon dioxide, together with a carbonized residue containing virtually no fluorine. The perfluoropolytolylene were not studied in such detail, but the indications are that they behave similarly to the perfluoropolyphenylenes.

With the availability of samples of perfluoropoly pyridine, it was of interest to study their degradation to see how the results correlated with those described above. This paper describes the determination of thermal stability in air and in vacuum by thermogravimetry, an analysis of degradation products by mass spectrometry, and measurement of the fluorine loss from the polymer.

## EXPERIMENTAL

### Preparation of Polymers

Two polymers samples were provided by Dr. G. E. Wright of Durham University. These were prepared by the decomposition of lithio-2,3,5,6-tetrafluoropyridine (polymer A) or lithio-2,4,5,6-tetrafluoropyridine (polymer B) in refluxing tetrahydrofuran. This was essentially the same type of reaction that had been used previously for the preparation of the perfluoropolyphenylenes<sup>6-8</sup> and perfluoropolytolylene.<sup>3,4</sup> The polymers as supplied, had a poor elemental analysis, but this was rectified in the case of polymer A by a prolonged extraction with boiling water (found: C, 45.6%; F, 42.3%; N, 11.6%; H, 1.0%. Calcd for  $(C_5F_3N)_n$ : C, 45.8%; F, 43.5%; N, 10.7%). The figures for polymer B were still poor after extraction (found: C, 37.8%; F, 44.2%; N, 10.0%; H, 0.7%), and hence most experiments were done with polymer A.

### Thermogravimetric Analysis

Weight loss measurements under vacuum ( $10^{-1}$  torr), or in an air flow of 30 ml/min, were made both isothermally and at a constant rate of temperature rise ( $4^\circ\text{C}/\text{min}$ ) using a du Pont 950 thermogravimetric analyzer. Sample size was approximately 5 mg.

### Analysis of Degradation Products

Polymer samples (10–40 mg) were pyrolyzed in sealed, evacuated ( $1.33 \text{ mN}/\text{m}^2$ ) silica ampoules fitted with breakseals. These were connected directly to a mass spectrometer inlet, and the volatile components were fractionally evaporated in. The mass spectrometer used was an A.E.I. Ltd. MS2-H instrument, and the standard conditions were 70 eV electrons, an accelerating voltage of 1975 V, and a sample reservoir temperature of  $240^\circ\text{C}$ . Elemental analysis and infrared spectra determinations were carried out on some of the residues.

Polymer samples (5 mg) were also pyrolyzed in a stream of nitrogen, or air, and the effluent gas was monitored for species giving rise to  $F^-$  ions in aqueous solution. The apparatus and experimental technique used for this and results on further perfluoro and hydrofluoro polymers will be fully described in subsequent papers, but essentially the method consisted of heating the sample contained in a platinum crucible in a calcium fluoride tube, with the temperature rising at a constant rate ( $2^\circ\text{C}/\text{min}$ ). The gas stream, which only came into contact with calcium fluoride or polytetrafluoroethylene, was passed into a buffer solution containing initially  $10^{-5}$  moles of  $F^-$  ion per litre, and the change in the  $F^-$  ion concentration was monitored by a fluoride electrode made by Orion Research Ltd. The output of the electrode was fed via a pH meter to the y-axis of an x-y recorder, the x-axis being connected to a thermocouple placed inside the furnace tube. In this way a plot was obtained of pF versus temperature,

which could be converted to a plot of the percentage of available  $F^-$  released versus temperature.

## RESULTS AND DISCUSSION

### Weight Loss Results

Weight loss results at a constant rate of temperature rise are shown in Figure 1 for both polymer samples. The results under vacuum were initially very similar for the two polymers, but at approximately  $700^\circ\text{C}$  and 40% weight loss, polymer B apparently underwent a very sudden decomposition. This may have been some form of decrepitation. In air, polymer B appeared the more stable, but the difference in the two curves was largely brought about by the presence of a 15% residue at high temperatures in the case of polymer B. This must have been inorganic in nature and presumably arose from metallic residues in the polymer. The sudden weight loss at  $700^\circ\text{C}$  under vacuum may also have been related to some interaction between the polymer and these residues.

Isothermal weight loss curves for polymer A under vacuum are shown in Figure 2 and in air in Figure 3. The results under vacuum were similar to those found previously for perfluoropolyphenylenes,<sup>2</sup> i.e., there was an initial rapid loss of weight followed by a much slower rate of breakdown, although the degree of stabilization was not as marked as with the perfluoropolyphenylenes. Taking the initial rates of degradation and assuming a pseudo-zero-order reaction, an overall activation energy of 83 kJ/mole was derived.

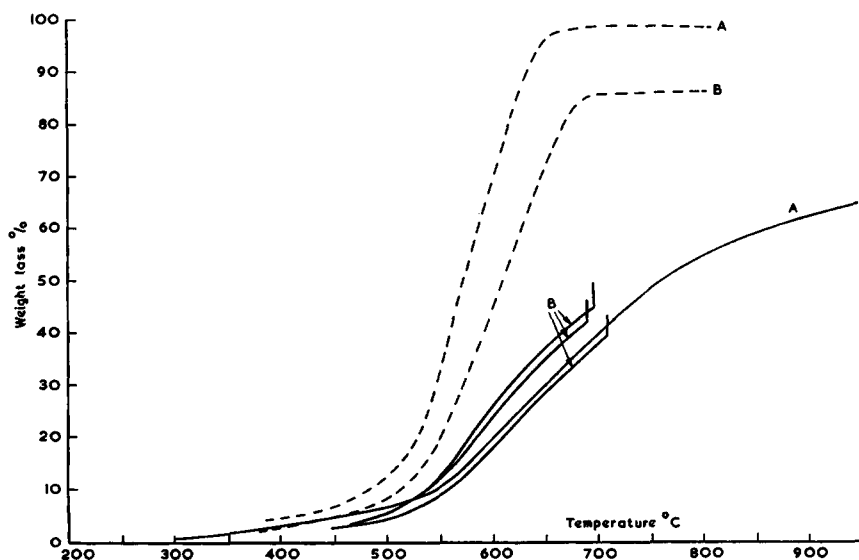


Fig. 1. Comparison of thermal stabilities under vacuum and in air of perfluoropoly-pyridines: (—) vacuum; (---) air.

The curves for degradation in air indicated a pseudo-zero-order reaction up to about 70% volatilization i.e., the rate of loss was constant with time. From these, the overall activation energy for breakdown is 113 kJ/mole. This value is compared in Table I with those for other perfluoro polymers degraded in oxygen.

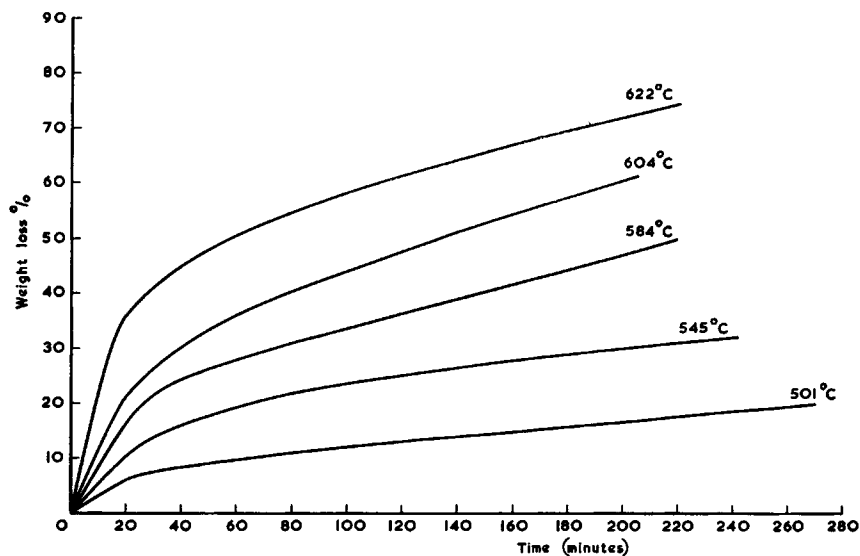


Fig. 2. Isothermal weight loss curves under vacuum for a perfluoropolyppyridine (sample A).

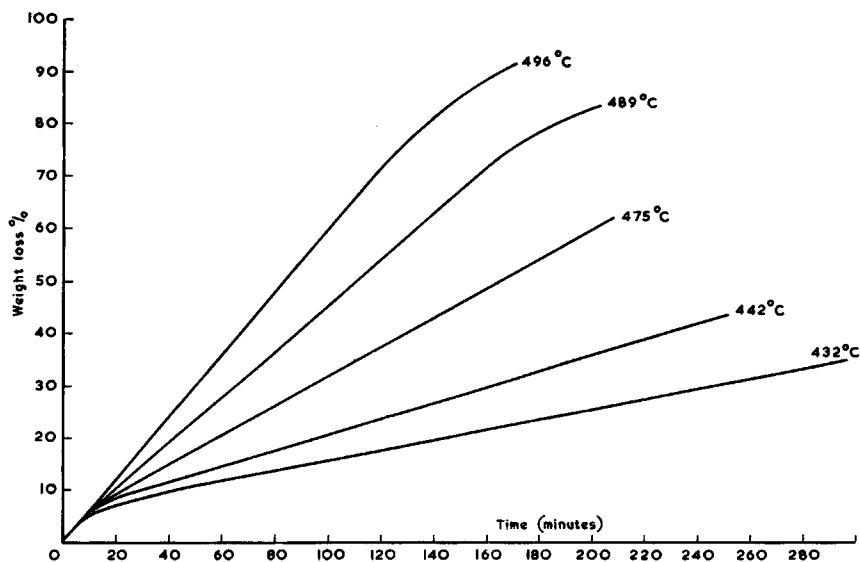


Fig. 3. Isothermal weight loss curves in air for a perfluoropolyppyridine (sample A).

TABLE I  
Kinetic Data for Thermal Degradation of Perfluoro Polymers

Polymer	Activation energy, kJ/mole	Arrhenius factor, sec <sup>-1</sup>	Rate of weight loss at 350°C %/min
Perfluoropolypyridine	113	10 <sup>6</sup>	4.2 × 10 <sup>-3</sup>
Perfluoro- <i>m</i> -polyphenylene	109	10 <sup>8</sup>	3.3 × 10 <sup>-2</sup>
Perfluoro- <i>p</i> -polyphenylene	130	10 <sup>7</sup>	4.4 × 10 <sup>-3</sup>
Perfluoropolyphenylene sulfide	138	10 <sup>10</sup>	4.8 × 10 <sup>-2</sup>
Polytetrafluoroethylene	331	10 <sup>20</sup>	3.3 × 10 <sup>-6</sup>

The generally low level of the overall activation energies for breakdown in oxidizing atmospheres of the perfluoro aromatic and heterocyclic polymers compared with the value for polytetrafluoroethylene should be noted.

The thermal stabilities of perfluoropolypyridine under vacuum and in air are compared with those of perfluoropolyphenylene and polytetrafluoroethylene in Figure 4. It can be seen that polytetrafluoroethylene is somewhat more stable than the other polymers in an oxidizing atmosphere, but that the ring-containing polymers are superior, at least as far as weight loss is concerned, in an inert environment.

### Mass-Spectrometric Results

Samples of both polymers were pyrolyzed under vacuum in silica ampoules at 600°C. The products (volatile up to 300°C) identified by mass spectrometry were CO<sub>2</sub>, CO, and SiF<sub>4</sub>, no other products being detected. When the pyrolysis was carried out in a porcelain dish or a perforated platinum cylinder, the same volatiles were obtained. The pyrolysis residues were extensively charred, and their infrared spectra were poorly defined.

In the case of polymer A, the relative composition of the gaseous products was determined. The results for three differing sample weights are shown in Table II.

The figure for SiF<sub>4</sub> was calculated assuming that it represented the difference between the total volatiles (100%) and the sum of the CO<sub>2</sub> and CO percentages. The residues from the second and third experiments contained, in each case, 39% less fluorine than the original polymer. In two further experiments, 75.5 mg polymer was pyrolyzed at 600°C for 2 hr, and 175 mg polymer at 600°C for 16 hr. The residues contained 37% and 39%

TABLE II  
Composition of Volatile Products from Thermal Degradation of Perfluoropolypyridine

Weight of polymer, mg	Temperature, °C	Time, hr	CO <sub>2</sub> , mole-%	CO, mole-%	SiF <sub>4</sub> , mole-%
18.8	600	1	49	17	34
23.0	600	2	42	23	35
95.9	600	1	51	14	35

less fluorine, respectively, than the initial sample. Very similar figures, i.e., reduction in fluorine contents of 37% and 32%, were obtained on pyrolyzing samples of polymer B for 1 and 16 hr at 600°C. From these values it would appear that the bulk of the degradation occurs in the first 1–2 hr at 600°C. Very similar results to these had been obtained previously with the perfluoropolyphenylenes.<sup>2</sup>

No low molecular weight oligomers were available for examination, and so perfluoropyridine itself was pyrolyzed at 600°C for 16 hr in a sealed ampoule. The walls of the vessel became discolored and covered with a thin film of dark-brown material, which was involatile up to 300°C. The bulk of the perfluoropyridine (64.2%) was recovered unchanged, this being estimated from the intensity of the molecular-ion peak ( $m/e$  169) using the

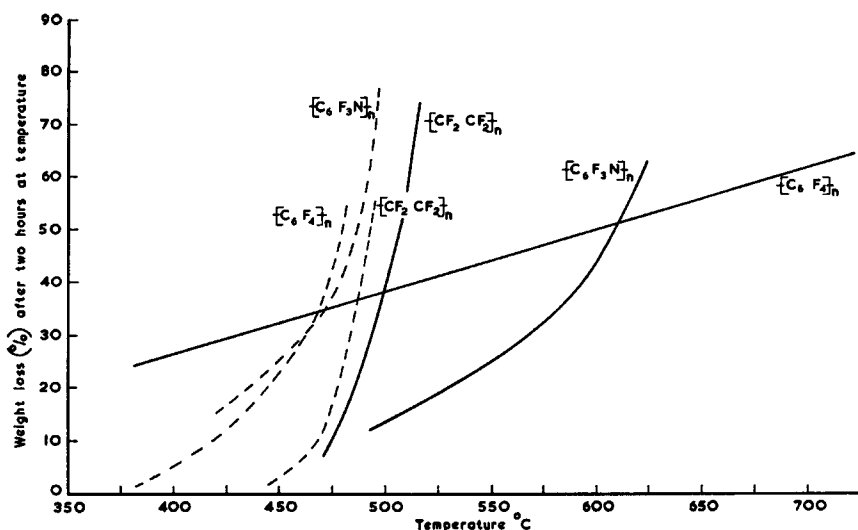


Fig. 4. Comparison of thermal stabilities of perfluoropolyphenylene, perfluoropyridine, and polytetrafluoroethylene: (—) vacuum; (---) air.

experimentally determined sensitivity factor for perfluoropyridine. The major gaseous decomposition products were CO and CO<sub>2</sub>, together with a very small amount of SiF<sub>4</sub>. The mass spectrum of the products that were volatile at 250°C contained peaks of moderate intensity at  $m/e$  151 (most probably C<sub>5</sub>NF<sub>4</sub>H) and  $m/e$  166. Low intensity peaks were also present up to  $m/e$  300.

In a subsidiary experiment 20  $\mu$ l. (31.4 mg) of perfluoropyridine were pyrolyzed at 600°C for 50 hr. The film produced weighed 7.6 mg, i.e., a yield of 24.2%.

Production of higher molecular weight residues has also been observed in the pyrolysis of other perfluoro aromatic compounds, e.g., perfluoro-*m*-terphenyl,<sup>2</sup> perfluoro-*p*-quaterphenyl,<sup>2</sup> 1,4-bis(pentafluorophenylthio)tetrafluorobenzene,<sup>9</sup> and 4,4'-bis(pentafluorophenylthio)octafluorobiphenyl.<sup>9</sup>

**Determination of Fluoride Ion Yield**

The mass-spectrometric and elemental analysis data cited above indicated that the most important breakdown route for perfluoropolypyridine involved the removal of fluorine from the polymer. Accordingly, experi-

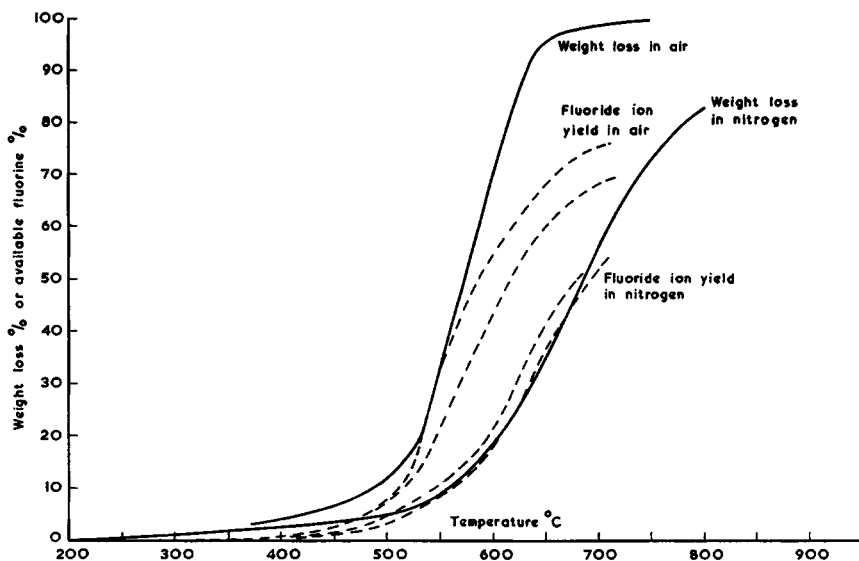


Fig. 5. Comparison of weight loss and fluoride ion yield curves.

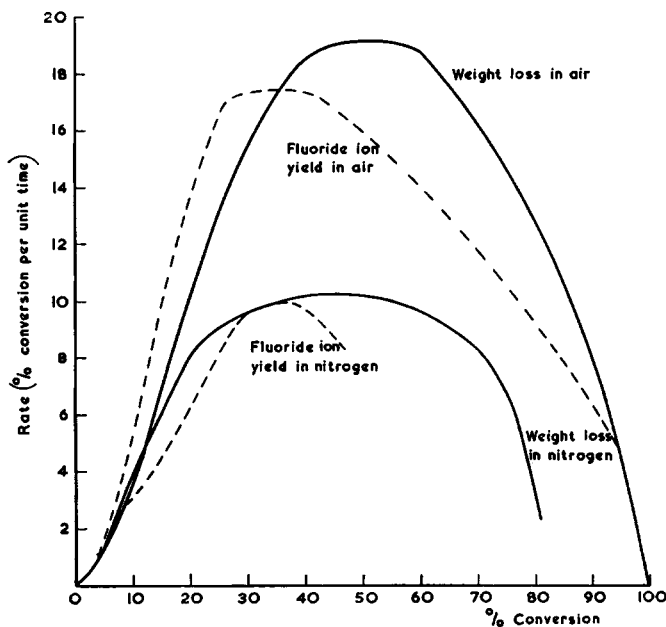


Fig. 6. Comparison of rates of weight loss and fluoride ion yield.

ments were carried out to determine the amount of the available fluorine, which was released when the polymer was heated in air or nitrogen. It must be emphasized that the technique used measured  $F^-$  ion concentrations and hence only monitored breakdown products, which gave rise to this species when dissolved in aqueous solution. The results for duplicate experiments are illustrated in Figure 5. The temperatures at which fluoride ion was first detected were very little different for oxidizing and non-oxidizing atmospheres (286°, 288°, and 291°, 311°C, respectively), but the total  $F^-$  yield by 700°C was appreciably greater in air than in nitrogen. It should be remembered that the total weight losses were also very different in the two cases, and hence the weight loss curves are also shown in Figure 5. In air, the fluoride yield amounted to approximately 34% of the total weight lost from 15–98% degradation, whereas in nitrogen the fluoride yield was 48% of the total weight loss from 5–63% breakdown. The relationship between weight loss and fluoride yield is shown in a different way in Figure 6, where the rates of weight loss and fluoride yield are plotted as a function of the percentage conversion. The results under vacuum and in nitrogen are consistent with the formation of a carbonaceous residue. The fluorine evolution results in nitrogen are also consistent with the results found in the sealed ampoule experiments.

### Possible Breakdown Routes

Three possible breakdown routes occurring either singly or in combination can be visualized for the thermal degradation of perfluoropolypyridine in an inert atmosphere: (i) scission of inter-ring bonds with production of lower molecular weight material of the same structure, including perfluoropyridine; (ii) scission of ring bonds with formation of low molecular weight fluorocarbons; (iii) scission of carbon-fluorine bonds with formation of elemental fluorine and fused ring carbonaceous structures.

The analytical data do not support routes (i) or (ii), although it might be postulated that low molecular weight volatile products react with the silica ampoules at elevated temperatures to give CO, CO<sub>2</sub>, and SiF<sub>4</sub>. Such a reaction has been shown<sup>10</sup> to occur with hexafluoroethane at 800–840°C. Perfluoropyridine does not react in this manner to anywhere near the required extent at 600°C, and, in any case, the fluoride yield results derived in the absence of silica cannot be explained by either reactions (i) or (ii). The available evidence would therefore suggest that reaction (iii) is preferred, although it seems highly unlikely on energetic grounds. Experiments are in progress to attempt to resolve this, i.e., attempts are being made to trap out fluorine if present, as the reaction seems to be a general one for perfluoro aromatic and perfluoro heterocyclic polymers.

### CONCLUSIONS

On a weight loss basis, perfluoropolypyridine is more stable in an inert atmosphere than polytetrafluoroethylene (PTFE), but this is largely be-



cause PTFE degrades completely to volatiles, whereas perfluoropolypyr-  
idine forms a carbonaceous residue. In oxidizing atmospheres, PTFE is  
the more stable polymer. The major breakdown route of perfluoropoly-  
pyridine is one involving removal of the fluorine from the ring, the yield  
of fluoride ion obtained being approximately 70% of the theoretical in air  
and 50% of the theoretical in nitrogen up to 700°C.

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