

## Thermal Degradation of Perfluoropolyphenylenes\*

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### Synopsis

The thermal degradation of *meta*- and *para*-linked perfluoropolyphenylenes *in vacuo* and in oxygen has been studied. Rates of breakdown were determined thermogravimetrically and products of breakdown in vacuum analyzed by using a mass spectrometer. The thermal stability *in vacuo* was comparable with that of polyphenylene, and that in oxygen was rather inferior to that of polytetrafluoroethylene. The higher molecular weight polymers gave as the main volatile degradation products silicon tetrafluoride and carbon dioxide, together with a carbonized residue containing virtually no fluorine.

### INTRODUCTION

Knowledge of the thermal stability and mechanism of decomposition of fully fluorinated polymers, especially of the aromatic type, is very limited. With the present development of the perfluoroaromatic field and the possible production of new types of polymers, a knowledge of the thermal and oxidative stability of perfluoropolyphenylenes is of considerable interest. The only results reported to date have been on low molecular weight polymers prepared by Ullman reactions with 1,4-dibromo- or 1,4-diiodotetrafluorobenzene.<sup>1</sup> These contained residual bromine or iodine and were apparently unaffected by heating *in vacuo* to 430°C.<sup>2</sup> Recently, perfluoro-*m*-polyphenylenes have been prepared by the Ullman reaction<sup>3</sup> and perfluoro-*p*-polyphenylenes<sup>4</sup> and related model compounds<sup>5</sup> by an alternative route. The thermal degradation of these polymers in inert and oxidizing atmospheres is reported here.

### EXPERIMENTAL

#### Materials

Perfluoro-*m*-polyphenylene (sample A) was prepared by reaction of 1,3-dibromotetrafluorobenzene with activated copper bronze in dimethylformamide. Two samples of perfluoro-*p*-polyphenylene were made. Decomposition of pentafluorophenylmagnesium bromide in refluxing tetrahydrofuran yielded polymer of apparently high molecular weight (up to

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15000, Mechrolab vapor-pressure osmometer), but with an uncertain distribution of linkages and containing a small quantity of bromine (sample B). If the decomposition was carried out in the presence of perfluorobiphenyl, polymer of lower molecular weight (up to 3700) but containing no residual bromine was formed even at room temperature (sample C). The production of perfluoro-*p*-terphenyl, -*p*-quaterphenyl, and -*p*-quinquephenyl by the latter route by use of excess perfluorobiphenyl indicated that the polymers were predominantly *para*-linked. The properties of the polymer samples are given in Table I.

TABLE I  
Properties of Perfluoropolyphenylene Samples

Sample	Elemental analysis			Solubility in THF, %	Degree of polymer- ization
	C, %	F, %	Br, %		
A	48.6	50.7	0.3	100	~107
B	47.2	50.1	2.6	90	~100
C	48.1	51.9	0	Insoluble	~25
Calculated for $(C_6F_4)_n$	48.7	51.3	—		

### Apparatus and Experimental Technique

Weight loss measurements *in vacuo* or in 200 mm Hg pressure of oxygen were made with a quartz spring balance assembly, which has been fully described previously.<sup>6</sup>

Analysis of the volatile products of degradation *in vacuo* were made either by condensing them in suitable traps and then submitting them to mass spectroscopic examination or by pyrolyzing the sample in evacuated, sealed glass or silica ampoules and then connecting these directly to the mass spectrometer inlet and fractionally evaporating the volatile components in. The mass spectrometer used was an AEI Ltd. MS2-H instrument, and the standard conditions were 70 V electrons, an accelerating voltage of 1975 V, and a sample reservoir temperature of 240°C.

## RESULTS AND DISCUSSION

### Thermogravimetric Studies

Preliminary experiments were made in both vacuum and oxygen with the temperature rising at a rate of approximately 3°C/min in order to assess the relative thermal stability of the polymer samples. The results are shown in Figures 1 and 2. The perfluoropoly-*m*-phenylene (sample A) suffered no major breakdown *in vacuo* until a temperature of 600°C was reached. The perfluoropoly-*p*-phenylene (sample B), after an initial weight loss of some 10%, also began to break down at the same temperature. If sample B was heated at 400°C for 1 hr *in vacuo* before carrying out the experiment with the temperature rising, the initial weight loss was

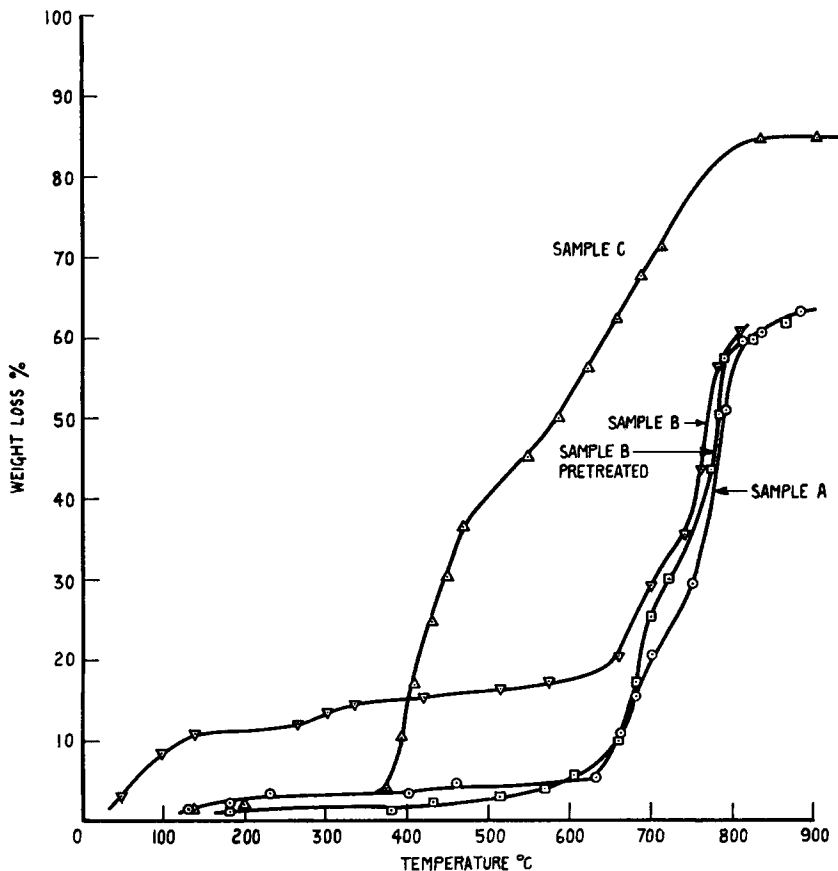


Fig. 1. Comparison of the thermal stability *in vacuo* of various perfluoropolyphenylenes.

absent, but the main degradation still commenced at 600°C. The pre-treatment caused no significant change in the elemental analysis. The thermal stability of the other perfluoropoly-*p*-phenylene (sample C) was much lower. The reason for this was probably associated with its much lower molecular weight, as with this type of material there is evidence<sup>2</sup> that molecules of up to 1700 molecular weight may volatilize unchanged in vacuum at temperatures above 400°C.

The polymers were considerably less stable in the presence of oxygen (Fig. 2), breakdown becoming rapid above 400°C.

Isothermal experiments *in vacuo* were characterized, as with polyphenylenes,<sup>7</sup> by a rapid initial loss in weight, the amount depending on the temperature, followed by stabilization (Fig. 3). This type of curve does not lend itself to kinetic analysis, so only one polymer sample was examined in any detail, in order to compare its stability with that of unfluorinated polyphenylenes. The results are summarized in Figure 4, a curve also being included for polytetrafluoroethylene. It can be seen that the per-

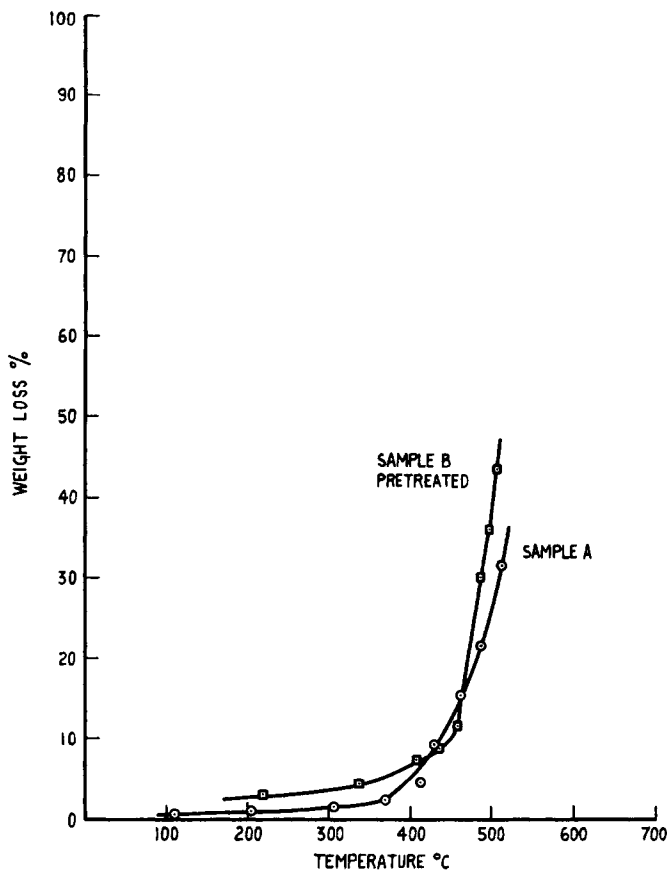


Fig. 2. Comparison of the thermal stabilities in oxygen of perfluoropoly-*m*-phenylene and perfluoropoly-*p*-phenylene.

fluoropoly-*p*-phenylene (sample B), as prepared, had a stability very similar to that of polymeta- and poly-*p*-phenylene.

That the pretreatment *in vacuo* at 400°C, besides removing the more volatile components of the polymer, also improved the stability of the residue was shown by the fact that heating the residue for 6 hr at 550°C resulted in a loss of weight of only 6%. From Figure 3 it can be seen that for the untreated polymer the difference in loss of weight between 6 hr at 397°C and 530°C was approximately 17%.

Isothermal weight loss curves in oxygen for the perfluoropoly-*p*-phenylene (sample B) before and after pretreatment are shown in Figures 5 and 6. The considerable increase in oxidative stability because of the pretreatment is evident. The first set of curves did not yield satisfactory results with any of the methods of kinetic analysis tried. The second set of curves was more amenable to analysis and it was possible to derive from them a value for the overall activation energy for breakdown. The results are given in Table

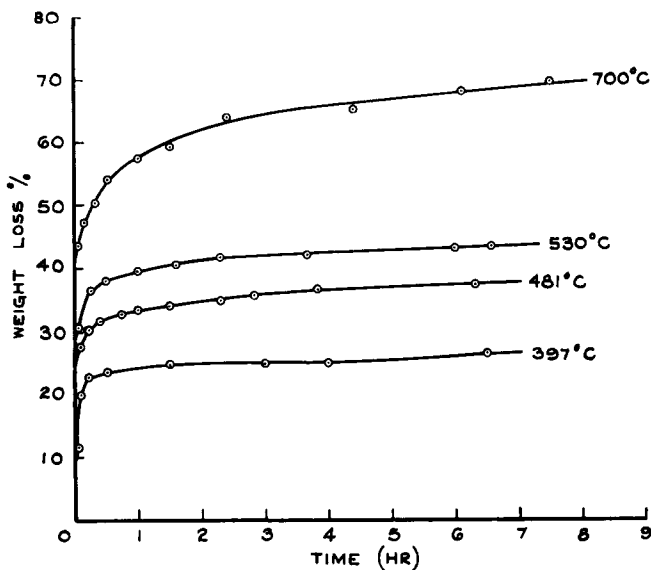


Fig. 3. Isothermal weight loss curves in vacuum for a perfluoropoly-*p*-phenylene (sample B).

II, together with values derived for the other perfluoropolyphenylenes and also for polytetrafluoroethylene (PTFE), for comparison purposes. The overall activation energies for breakdown are surprisingly low in comparison with that for PTFE. It is manifest that the thermo-oxidative stability of the perfluoropolyphenylenes is less than that of polytetrafluoroethylene. This is further illustrated by the comparison of thermal stabilities in Figure 7. Two other points of interest arise from this graph. These are that the low and high molecular weight samples of perfluoropoly-*p*-phenylene (after pretreatment) have similar stabilities in oxygen, despite the great difference in their stabilities under inert conditions. The perfluoropoly-*m*-phenylene is somewhat less stable than the *para*-linked polymers, despite the apparent similarity shown by the rising temperature experiments (Fig. 2). This serves to illustrate the dangers of relying too heavily upon rising tempera-

TABLE II  
Kinetic Data for Thermal Degradation of Perfluoropolyphenylene Samples in Oxygen

Sample	Activation energy, kcal/mole	Arrhenius factor, sec <sup>-1</sup>	Rate of weight loss at 350°C, %/min
A	26	10 <sup>8</sup>	3.3 × 10 <sup>-2</sup>
B (preheated at 400°C <i>in vacuo</i> for 1 hr)	39	10 <sup>9</sup>	2.5 × 10 <sup>-3</sup>
C (preheated at 400°C <i>in vacuo</i> for 1 hr)	31	10 <sup>7</sup>	4.4 × 10 <sup>-3</sup>
PTFE	79	10 <sup>20</sup>	3.3 × 10 <sup>-6</sup>

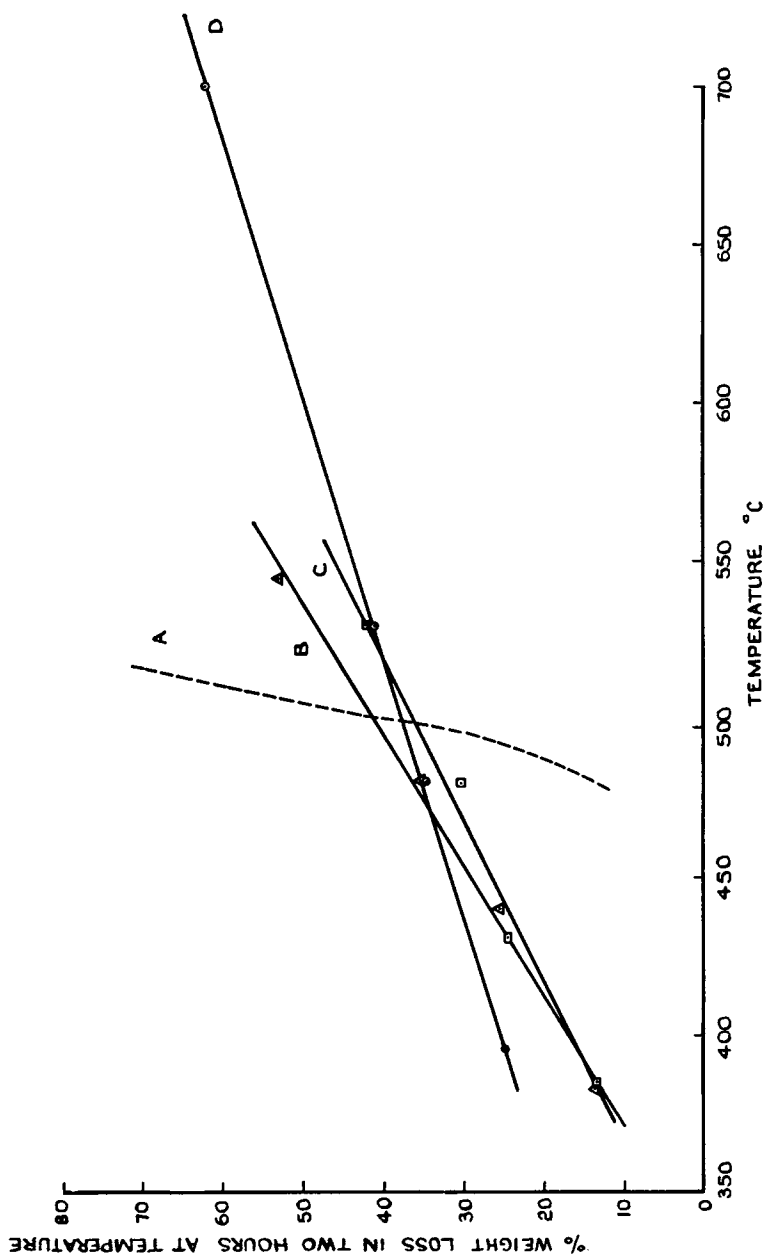


Fig. 4. Comparison of thermal stabilities of polyphenylenes and a perfluoropoly-*p*-phenylene *in vacuo*: (A) polytetrafluoroethylene; (B) poly-*m*-phenylene; (C) poly-*p*-phenylene; (D) perfluoropoly-*p*-phenylene (sample B).

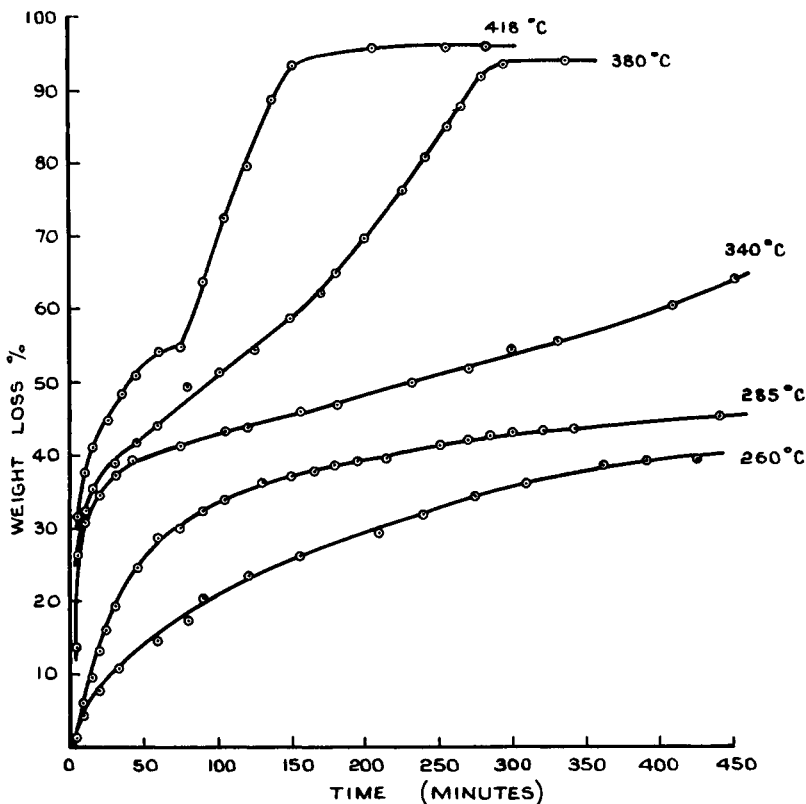


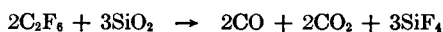
Fig. 5. Isothermal weight loss curves in 200 mm pressure of oxygen for a perfluoropoly-*p*-phenylene (sample B).

ture experiments (dynamic thermogravimetric analysis) for thermal stability comparisons.

### Mass Spectral Results

Preliminary experiments showed that temperatures higher than 500°C would be required to give reasonable amounts of volatile degradation products for analysis. Accordingly, all the results recorded below are for experiments carried out in evacuated, sealed, silica ampoules.

A 23.8-mg portion of perfluoropoly-*m*-phenylene (sample A) was heated at 700°C for 1 hr. A heavily charred residue was obtained, and a white deposit formed on the tube walls. The volatile products consisted almost entirely of silicon tetrafluoride and carbon dioxide, together with trace amounts of C<sub>6</sub>F<sub>6</sub> and C<sub>6</sub>F<sub>5</sub>H. Elemental analysis of the residue showed that it contained no fluorine. White and Rice<sup>8</sup> have reported that if hexafluoroethane is heated in a silica vessel between 800 and 840°C, a reaction occurs between the two with production of carbon monoxide, carbon dioxide, and silicon tetrafluoride.



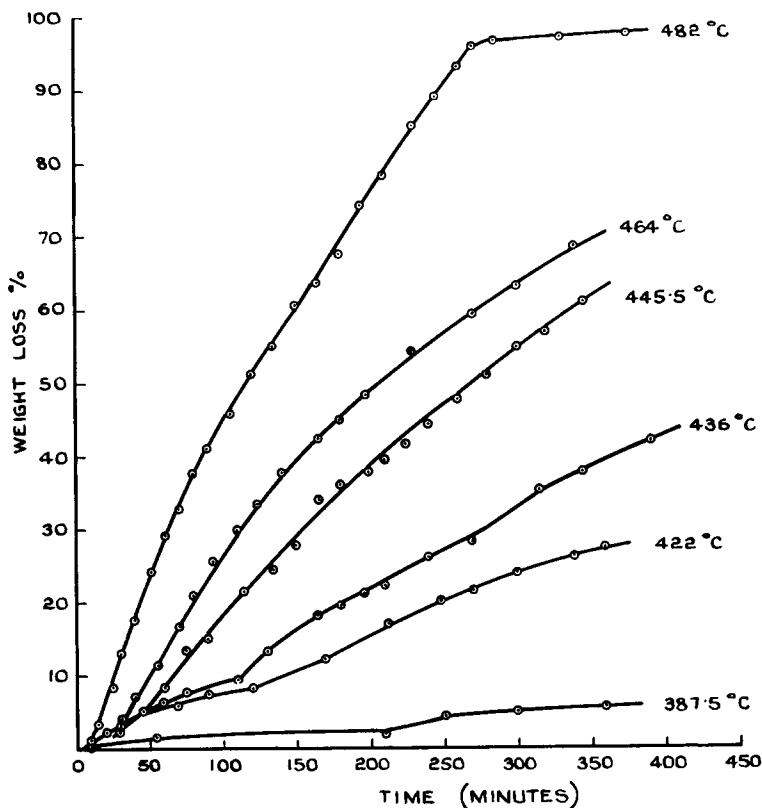


Fig. 6. Isothermal weight loss curves in 200 mm pressure of oxygen for a perfluoropoly-*p*-phenylene (sample B after heating at 400°C *in vacuo* for 1 hr).

To check if such a reaction were occurring directly with the polymer, a sample was placed inside a platinum vessel with a perforated cap and the whole heated in a silica ampoule for 1 hr at 700°C. Once again, a white deposit formed on the tube walls, and the major volatile products were silicon tetrafluoride and carbon dioxide, together with trace amounts of  $C_6F_5C_6F_4C_6F_5$  and  $C_6F_5(C_6F_4)_2C_6F_5$ . The charred residue contained approximately 1.6% fluorine.

For comparison purposes, a similar experiment was carried out with perfluoro-*m*-terphenyl. In this case, 44% of the original material was recovered unchanged. The principal volatile degradation products were  $C_6F_5C_6F_5$  and  $C_6F_6$ , together with some  $C_6F_5(C_6F_4)_2C_6F_5$ ,  $SiF_4$ , and  $CO_2$ . The sample as used contained about 0.6%  $C_6F_5(C_6F_4)_2C_6F_5$ , but after pyrolysis the proportion had risen to 3.6%.

Similar results to those with sample A were obtained using the perfluoropoly-*p*-phenylene (Sample B) i.e. the only degradation products volatile up to 305°C were silicon tetrafluoride and carbon dioxide, and analysis of the residue showed that it contained less than 1% fluorine.



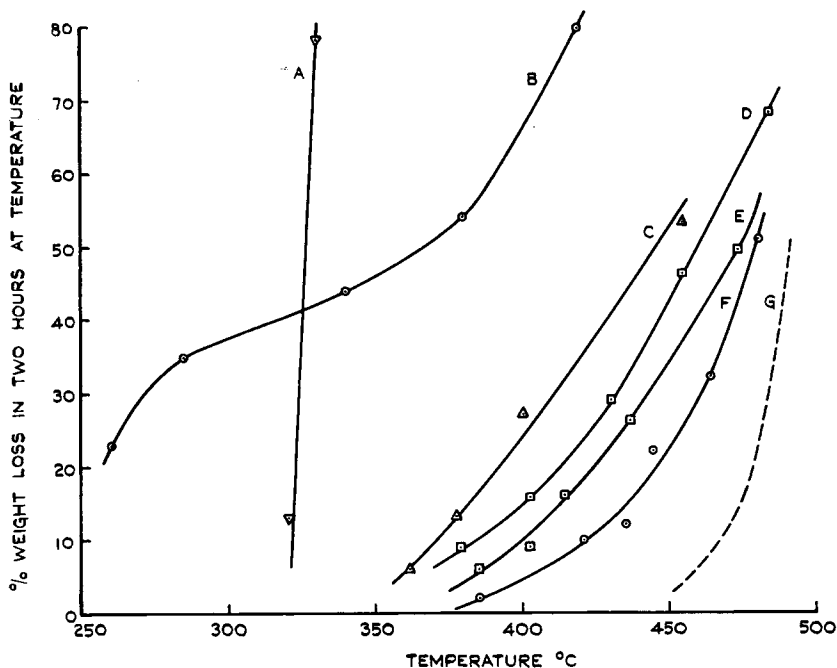


Fig. 7. Comparison of thermal stabilities of a polyphenylene and various perfluoropolyphenylenes in 200 mm pressure of oxygen: (A) poly-*m*-phenylene; (B) perfluoropoly-*p*-phenylene (sample B); (C) perfluoropoly-*m*-phenylene (sample A); (D) perfluoropoly-*p*-phenylene (sample C); (E) perfluoropoly-*p*-phenylene (sample C after pretreatment); (F) perfluoropoly-*p*-phenylene (sample B after pretreatment); (G) polytetrafluoroethylene.

If, however, the model compound perfluoro-*p*-terphenyl was used, the bulk of the material was recovered unchanged after 1 hr at 700°C, and the only volatile products were small amounts of  $C_6F_6$ ,  $C_6F_5C_6F_5$ , and  $C_6F_5-(C_6F_4)_2C_6F_5$ . Further evidence for the formation of higher molecular weight material on pyrolysis of these model compounds was obtained from isoteniscope examination of perfluoro-*p*-quaterphenyl. The decomposition temperature  $T_D$  (temperature for a rate of pressure increase of 0.84 mm Hg/min) was 392°C, compared with 426°C for *p*-quaterphenyl. Examination of the residue from the isoteniscope experiment showed the presence of 2% of an insoluble compound, whose infrared spectrum indicated that it was of higher molecular weight than the starting material.

Sample C (perfluoropoly-*p*-phenylene, DP 25) on pyrolysis at 700°C also gave a charred residue, but no white deposit formed on the sides of the tubes. The main volatile degradation products were again silicon tetrafluoride and carbon dioxide with trace amounts of  $C_6F_6$  and  $C_6F_5H$ . Elemental analysis of the residue, however, showed that it contained 33% fluorine. A repetition of this experiment gave a residue containing 41% fluorine.

To check if this apparent dependence of fluorine content of the residue upon molecular weight of the original polymer also occurred with the *meta* linked material, pyrolyses were carried out on polymers of approximate degrees of polymerization of 60 and 20. The residue from the former contained no detectable fluorine, and that from the latter 16% fluorine. On this basis it would appear that fluorine stripping is easier from the *meta* linked polymer.

### CONCLUSIONS

In inert atmospheres there is little difference between the thermal stabilities of perfluoropolyphenylenes and unfluorinated polyphenylene. In oxidizing atmospheres the perfluoro polymers are rather less stable than polytetrafluoroethylene and have a much lower overall activation energy for breakdown. The mechanism of breakdown *in vacuo* seems to be related to molecular weight. With low molecular weight model compounds the products of breakdown can be explained by scission of the inter-ring bonds, whereas as the molecular weight rises, silicon tetrafluoride and carbon dioxide become the main volatile products, and the carbonized residue contains lower amounts of fluorine. At degrees of polymerization greater than 60, the residue contains virtually no fluorine. This is not due to direct reaction between the polymer and the silica container, as the same results are obtained in platinum.

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