

Thermal Degradation of Poly(phenylene Sulfide) and Perfluoropoly(phenylene Sulfide)*

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Synopsis

The thermal and oxidative degradation of poly(phenylene sulfide) and perfluoropoly(phenylene sulfide) have been studied by a weight-loss method. The products of breakdown in vacuum have also been analyzed. The poly(phenylene sulfide) is more thermally stable in inert and oxidizing atmospheres than the fully fluorinated analog. The breakdown products can be accounted for by chain scission and transfer reactions. The formation of a large proportion of residue implies that crosslinking reactions play an important part in the degradation.

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 comparison of the thermal and oxidative stability of perfluoroaromatic polymers with their unfluorinated analogues is of considerable interest. This paper compares the stability and mode of decomposition of poly(phenylene sulfide) and perfluoropoly(phenylene sulfide).

EXPERIMENTAL

Materials

The poly(phenylene sulfide) was a commercial sample obtained from the Dow Chemical Company. It was analyzed as follows: C 64.9%, H 3.8%, S 28.7%, Br 2.8%. Assuming that the bromine was present as endgroups, a chain of 51 units would give an analysis of C 65.2%, H 3.6%, S 28.4%, Br 2.8%.

Two samples of perfluoropoly(phenylene sulfide) were examined. The first (A) was provided by R. Stephens, of Birmingham University, and was made by the reaction of hexafluorobenzene with sodium sulfide in pyridine.¹ The agreement of the elemental analysis with that calculated for a linear

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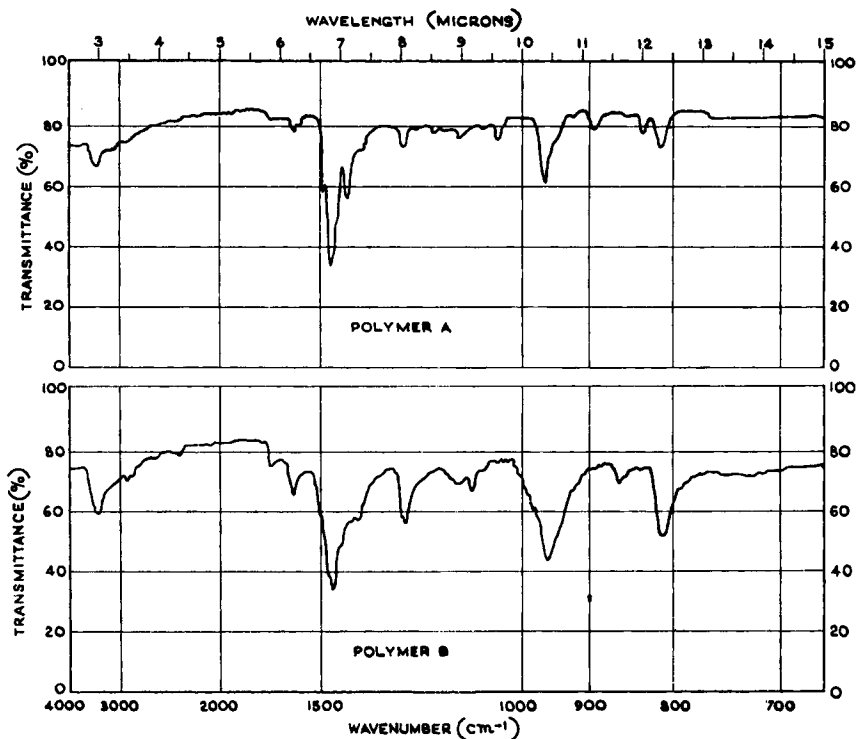


Fig. 1. Infrared spectra of perfluoropoly(phenylene sulfides).

polymer was poor (found, C 40.5%, H 0.5%, F 32.5%, S 24.6%; calculated for $[\text{C}_6\text{F}_4\text{S}]_n$, C 40.0%, F 42.2%, S 17.8%), indicating that the material was either heavily branched or crosslinked. The second sample (B) was prepared by heating potassium pentafluorophenoxide in a sealed glass tube at 240°C. for 3 hr., the product being refluxed with water for several hours, to remove soluble impurities. The elemental analysis of this sample was much closer to that for a linear polymer (found, C 39.6%, F 41.9%, S 18.1%). The infrared spectra of the two polymers are shown in Figure 1.

Thermogravimetric Studies

Weight-loss measurements in vacuum or under 200 mm. Hg pressure of oxygen were made on 8–10 mg. samples with sensitive quartz spring-balance assemblies, which have been fully described previously.² The experiments were carried out isothermally.

Pyrolysis Studies

The polymer samples (10–100 mg.) were pyrolyzed for 1 hr. at temperatures between 300 and 500°C. in sealed, evacuated, glass ampoules equipped with break seals. The volatile products were analyzed with an

A.E.I. Ltd. MS 2-H mass spectrometer with 70 v. electrons, a partial separation of the products being obtained by fractional evaporation into the mass spectrometer. For identification of molecular ions some spectra were obtained with low-energy electrons.

RESULTS AND DISCUSSION

Thermogravimetric Studies

Different types of weight-loss curve were obtained from the experiments in vacuum for the three polymer samples studied. These are illustrated in Figure 2. The poly(phenylene sulfide) broke down completely to volatile degradation products within the time scale of the experiment at the highest temperatures used. The curves were characterized by an initial slow rate of weight loss, akin to a stabilization effect, followed by a much faster rate of degradation. The perfluoropoly(phenylene sulfides) were completely different in behavior, sample A showing typical stabilization effects, whereas sample B degraded completely to volatiles, the rate of breakdown being essentially constant for a large part of the reaction. This reflects the difference between their initial crosslinked and linear states. The curves for poly(phenylene sulfide) and for sample B of the perfluoro polymers were amenable to kinetic analysis; the data derived are given in Table I.

Similarly, differences between the three polymer samples were observed on degrading them in an oxidizing atmosphere (Fig. 3). Once again, only the curves for poly(phenylene sulfide) and sample B of the perfluoro polymers could be analyzed; the results are included in Table I. The values for the overall activation energy for degradation of the perfluoro polymer are surprisingly low in comparison with those for polytetrafluoroethylene

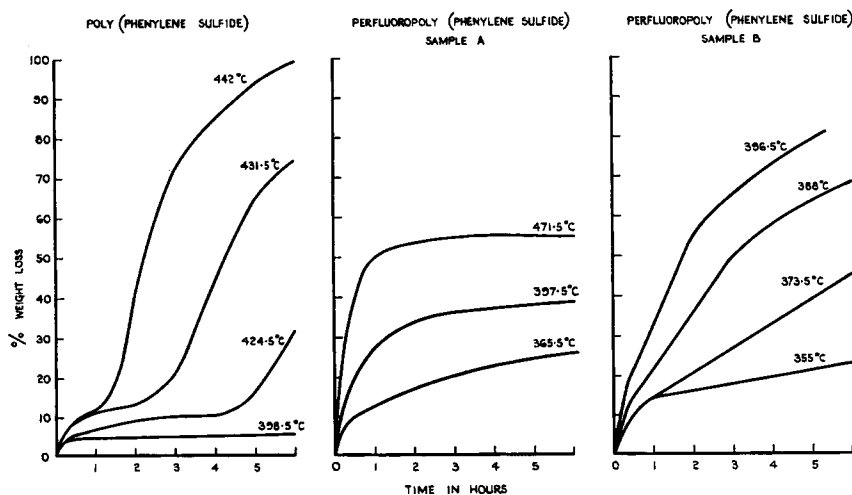


Fig. 2. Weight loss curves for polymers in vacuum.

but are comparable to values obtained for perfluoropolyphenylenes.³ The relative stabilities of the polymers in vacuum and oxygen are illustrated in Figure 4. From this it may be seen that all three polymer samples were

TABLE I
Kinetic Data for Degradation of Poly(phenylene Sulfide)
and Perfluoropoly(phenylene Sulfide)

| Atmosphere | Activ. energy, kcal./mole | Arrhenius factor, sec. ⁻¹ | Rate of wt. loss at 350°C., %/min. | Method of calc. |
|--|------------------------------|--|--|--------------------|
| Poly(phenylene sulfide) | | | | |
| Vacuum | 48 | 10 ¹⁴ | 0.005 | Max. rates |
| Oxygen | 37 | 10 ¹¹ | 0.009 | Zero-order |
| Perfluoropoly(phenylene sulfide), sample B | | | | |
| Vacuum | 54 | 10 ¹⁷ | 0.016 | Zero-order |
| Oxygen | 33 | 10 ¹⁰ | 0.048 | Zero-order |

little affected by oxidizing conditions but that the poly(phenylene sulfide) was appreciably more stable than either of the perfluoro poly(phenylene sulfides). This difference in stability is reflected in isoteniscope data on

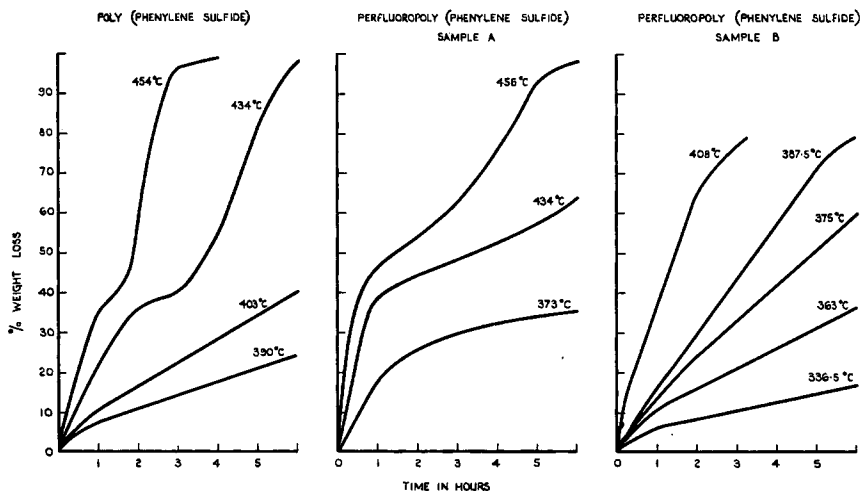


Fig. 3. Weight loss curves for polymers in oxygen.

model compounds, which show that the decomposition temperatures for compounds of the type $C_6F_5SC_6F_4SC_6F_3$ are approximately 40°C. lower than those for the unfluorinated analogs.⁴

Pyrolysis Studies

Pyrolysis of a sample of poly(phenylene sulfide) at 350°C. for 1 hr. gave relatively little volatile material. Trace amounts of SO₂, CO₂, and COS were detected, and by heating the residue to 275°C. low-intensity mass spectral peaks were obtained, corresponding to C₆H₅Br, C₆H₄Br₂, C₆H₅SC₆H₅, BrC₆H₄SC₆H₅, and BrC₆H₄SC₆H₄Br. The low-voltage spectra also indicated the presence of dibenzthiophene.

Raising the pyrolysis temperature to 460°C. resulted in a dark-green residue amounting to 72% of the original weight of sample. This shows that in the thermogravimetric experiments a large part of the weight loss must be due to material that is only volatile at the temperature of pyrolysis.

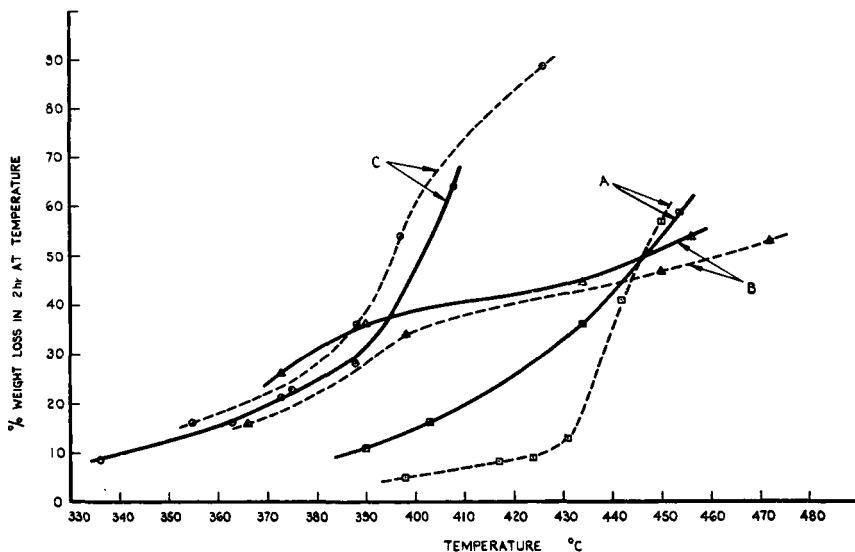


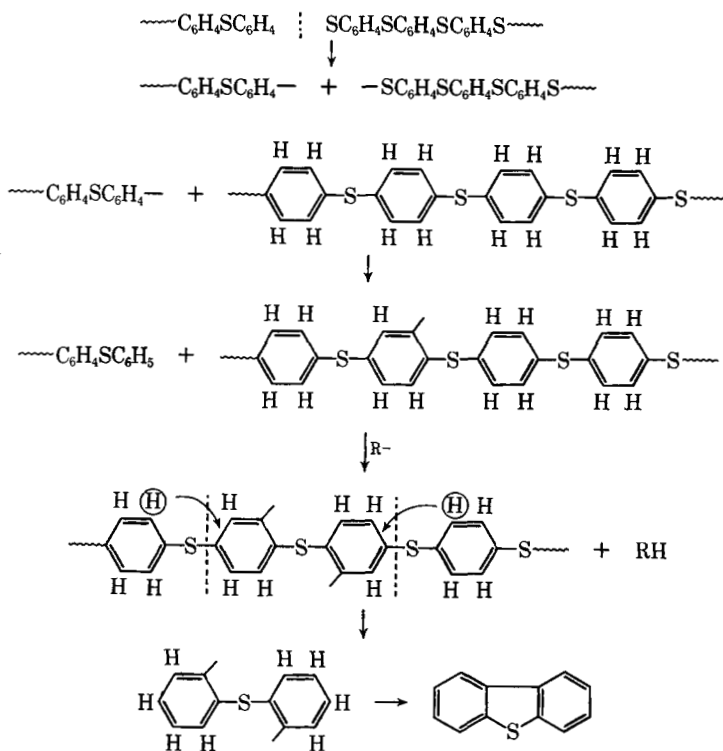
Fig. 4. Comparison of thermal stabilities of polymers (—) in vacuum and (---) in oxygen: (A) poly(phenylene sulfide); (B) perfluoropoly(phenylene sulfide), sample A; (C) perfluoropoly(phenylene sulfide), sample B.

The volatile products were essentially the same as those obtained at the lower temperature, although some hydrogen was also detected. From a comparison of the peak intensity of the m/e 2 peak with that for a known partial pressure of hydrogen it was estimated that the amount corresponded to 0.2% of the available hydrogen in the polymer. The principal volatile product on heating of the residue to 275°C. was dibenzthiophene.

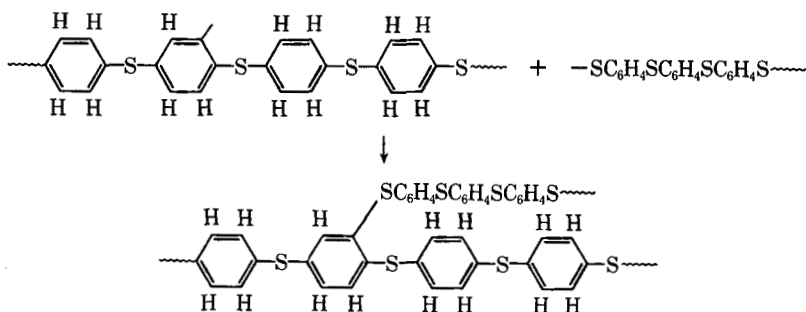
If the pyrolysis temperature was further raised to 500°C., the yield of hydrogen increased to 1.1% of that available. The charred residue also contained a white crystalline solid, which was isolated and identified as dibenzthiophene.

Formation of products of the type C₆H₅Br, BrC₆H₄SC₆H₅, or C₆H₅SC₆H₅ can easily be explained by chain-scission and transfer processes. The

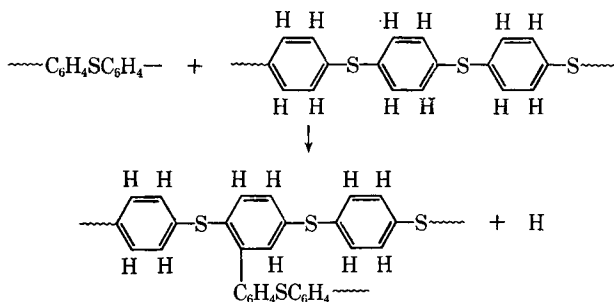
latter, leading to free-radical centers in the chain, could also account for the formation of dibenzthiophene:



Alternatively, the chain-transfer processes could lead to chain branching and crosslinking:



The dibenzthiophene might also be formed from diphenylene sulfide, $\text{C}_6\text{H}_5\text{SC}_6\text{H}_5$, since this has been reported to give dibenzthiophene on pyrolysis.⁵ This reaction would also account for the production of hydrogen. An alternative route for the formation of hydrogen involves a substitution reaction by a polymer radical rather than a transfer reaction:



Such reactions have been suggested to account for hydrogen evolution on irradiation of natural rubber⁶ or on tensile testing of it at -120°C .⁷

Pyrolysis of perfluoropoly(phenylene sulfide), sample A, at 350°C . also gave relatively little volatile material. There was a weight loss of 1% and trace amounts of SO_2 , CO_2 , COS , and SiF_4 were detected. Heating the residue to 250°C . produced no further products.

If the pyrolysis temperature was raised to 450°C ., the main gaseous products were CO_2 and SiF_4 with smaller amounts of SO_2 and COS . Heating the residue, which amounted to 92% by weight of the sample, to 250°C . resulted in low-intensity peaks corresponding to compounds such as $\text{C}_6\text{F}_5\text{SC}_6\text{F}_5$, $\text{C}_6\text{F}_5\text{SC}_6\text{F}_4\text{Cl}$, $\text{HC}_6\text{F}_4\text{SC}_6\text{F}_4\text{SC}_6\text{F}_4\text{H}$, $\text{HC}_6\text{F}_4\text{SC}_6\text{F}_4\text{SC}_6\text{F}_5$, $\text{C}_6\text{F}_5\text{SC}_6\text{F}_4\text{SC}_6\text{F}_5$, and $\text{ClC}_6\text{F}_4\text{SC}_6\text{F}_4\text{SC}_6\text{F}_5$. The presence of chlorine in some of the compounds showed that the preparative route, which included an acidification with 16*N* hydrochloric acid, resulted in the incorporation of chlorine in the polymer.

At 500°C ., the residue amounted to 73% of the weight taken, and appreciable quantities of CO_2 and SiF_4 were produced. On heating the residue to 275°C . the most intense mass spectral peak observed corresponded to $\text{C}_6\text{F}_4\text{SC}_6\text{F}_4$. This experiment was repeated with the polymer sample enclosed in a perforated platinum cylinder, to avoid direct contact with the glass ampoule, but the products obtained were qualitatively the same.

Pyrolysis of sample B at 500°C . also gave similar results, although chlorine-containing species were, of course, absent. Analysis of the residue showed that it contained 18% less fluorine than the original polymer.

Formation of the low molecular weight fluorocarbons can be attributed to chain-breaking and transfer processes. The latter processes could also lead to extensive branching and crosslinking in the material, accounting for the large amount of residue. At the highest pyrolysis temperature used there are indications of the formation of perfluorodibenzthiophene, presumably by routes similar to those leading to the formation of dibenzthiophene from poly(phenylene sulfide). The principal gaseous products were SiF_4 and CO_2 . The fact that the formation of these was largely unaffected when the polymer was pyrolyzed in a platinum container makes direct reaction between the polymer and the glass ampoule unlikely. It is more probable that they arise in a reaction of low molecular weight degradation

products with the glass. Such a reaction has been reported for hexafluoroethane:⁸



Some support for this is given by the fact that the pyrolysis of 1,4-bis-(pentafluorophenylthio)tetrafluorobenzene, $\text{C}_6\text{F}_5\text{SC}_6\text{F}_4\text{SC}_6\text{F}_5$, or 4,4'-bis-(pentafluorophenylthio)octafluorobiphenyl, $\text{C}_6\text{F}_5\text{SC}_6\text{F}_4\text{C}_6\text{F}_4\text{SC}_6\text{F}_5$, in glass at 500°C. yielded SiF_4 as the major constituent of the gaseous degradation products, although these amounted to less than 2% of the original sample weight. The principal pyrolysis products were bis(pentafluorophenyl)-sulfide, $\text{C}_6\text{F}_5\text{SC}_6\text{F}_5$, and an involatile polymeric residue.

CONCLUSIONS

Poly(phenylene sulfide) is more thermally stable in either inert or oxidizing conditions than the perfluoropoly(phenylene sulfide) samples examined. This might have been predicted from the behavior of related model compounds. There is little difference in the stability of the perfluoro polymers between inert and oxidizing atmospheres.

In a closed system poly(phenylene sulfide) breaks down by chain-scission and transfer reactions, yielding largely an involatile residue plus some low molecular weight chain fragments. Some hydrogen and dibenzthiophene are also produced.

The behavior of the perfluoro polymers is very similar to that of poly(phenylene sulfide), but SiF_4 is also formed by the reaction of breakdown products with the glass ampoule. This is supported by work on model compounds.

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