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AROMATIC FLUORINE-CONTAINING POLYAMIDES*

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IT HAS been established that benzene decomposition starts at 600°, while in the case of hexafluorobenzene the same process begins at temperatures above 650° [1]. However, it has not yet been found possible to prepare perfluoroarylene polymers with decomposition temperatures higher than those of their unfluorinated analogues. The decomposition of perfluoropolyphenylenes [2], and of polytetrafluorophenylene oxides or sulphides [3] takes place at lower temperatures compared with their unfluorinated analogues. This is thought to be the result of phenolate or thiophenolate endgroups participating in further reactions with the fluorinated phenylene units of the macrochains of these polymers, upon heating. The heat-resistance of carboxyl groups attached to a fluorinated benzene ring is quite low [4]; for instance, the decarboxylation of pentafluorobenzoic acid takes place at 197°, while in the case of tetrafluoro-*m*-phenylenediamine the same process is observed at 203°. Fluorinated phenylenediamines, e.g. tetrafluoro-*m*-phenylenediamine or octafluorobenzidine, are stable monomers. However, the thermal and hydrolytic stability of polyamides based on the latter are not equal to those of their unfluorinated analogues [5, 6]. The functional groups responsible for polymer formation are attached directed to the fluorinated benzine rings in the monomers referred to above

If an attempt were made to separate the fluorinated ring from the functional groups in the original monomers by means of unfluorinated units, such as phenylene rings, it could well be that the difficulties referred to above might be overcome, and polymers possessing thermal stability and other properties close to those of their unfluorinated analogues might then be obtainable.

Accordingly we synthesized novel dicarboxylic acids, namely derivatives of diphenyl ethers of hydroquinone of tetrafluorohydroquinone. From dichlorides of these acids and different aromatic diamines we prepared a series of polyamides and investigated their thermal stability, hydrolytic stability, and certain other properties.

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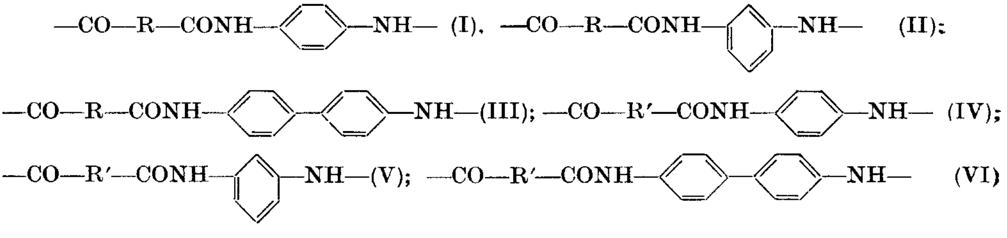
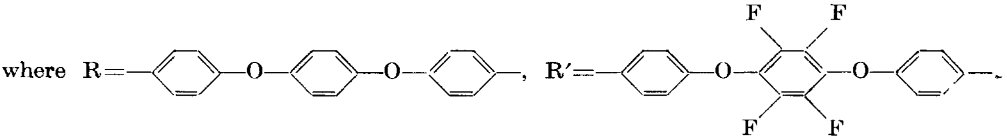
It should be noted that the above dicarboxylic acids and their dichlorides were, as expected, heat-resistant, and it was therefore possible to purify them by vacuum-distillation.

The following are the elementary units of the synthesized polyamides.





EXPERIMENTAL

Di-(p-carboxyphenyl) ether of tetrafluorohydroquinone 3·72 g of chromic anhydride was added, in small portions, whilst stirring, to a suspension of 2·8 g of di-(*p*-cresyl) ether of tetrafluorohydroquinone in 15 ml of acetic anhydride, 15 ml of its anhydride and 3·1 ml of sulphuric acid ($d = 1·82$) at 40–45°. Stirring was continued for 1 hr at 40–45°, after which the mixture was decanted into 200 ml of water The precipitate was filtered, washed with water, an dried Yield 2·7 g (82·6%), m p 368–370° (purification by vacuum-distillation).

Found, % F 17·50; 17·55 $C_{20}H_{10}F_4O_6$ Calculated, % F 17·98

The dichloride was prepared from the acid and phosphorus pentachloride at 140–150°, then purified by vacuum-distillation, and the product used in the experiments had m p. 157–158° (from benzene)

Found, %: Cl 15·20; 15·32 $C_{20}H_8Cl_2F_4O_2$ Calculated, %. Cl 15·28.

Di-(p-carboxyphenyl) ether of hydroquinone To a solution of 10 g of di-(*p*-cresyl) ether of hydroquinone in 170 ml of pyridine and 84 ml of water were added, with stirring for 5 hr, 28·34 g of potassium permanganate, and the mixture was boiled for 1 hr, cooled, and after 100 ml of water had been added, acidified with hydrochloric acid The residue was dried, and crystallized Yield 11·27 g (94%), m.p. 313–315° (from iced acetic acid).

Found, % C 68·45, 68·53; H 3·92; 3·98. $C_{20}H_{16}O_6$ Calculated, % C 68·57; H 4·00

The dichloride was prepared from the acid and phosphorus pentachloride, and was purified by vacuum-distillation and the product used has m.p 207–209° (from benzene)

Found, % Cl 18·10; 18·20 $C_{20}H_{12}Cl_2O_4$ Calculated, % Cl 18·34

Synthesis of the polyamides. To a solution of 0·02 mole of diamine and 0·04 mole triethylamine in 75 ml of chloroform was added, at 8–10°, whilst stirring, a solution of 0·02 mole of the fluorine-containing acid dichloride in 75 ml of chloroform (in the investigation involving the unfluorinated acid dichloride a solution of the latter in 150 ml of chloroform was used), stirring at room temperature was continued for 3 hr The polyamide was then filtered off, washed to completely remove Cl ions, and vacuum-dried to constant weight.

The structure of the resulting polyamides was verified through the results of elementary analysis (for nitrogen in the case of polyamides I–III, and for fluorine in the case of polyamides IV–VI). The reduced viscosity was measured in sulphuric acid at 30° for polyamides I–VI (0·5 g/dl). The melting point of polyamides I–VI was determined in sealed capillaries. The hydrolytic stability (weight loss after heating a weighed portion of polymer containing a 20-fold excess of 10% aqueous caustic soda or 10% aqueous sulphuric acid) was determined by the weight method. The evolution of gas upon heating the polyamides was determined by the manometric method; the weight loss on heating the polymers in a vacuum, or in the presence of atmospheric oxygen, was determined on a MacBain balance. In all cases the heating rate was 3 deg/min. The curves in the Figures are based on the average results of three parallel experiments.

DISCUSSION OF RESULTS

The Table gives some properties of the polyamides synthesized under identical conditions. The yields of all the polymers are fairly high and are within limits of 74–89%. The reduced viscosity of the unfluorinated polyamides I–III, determined in concentrated sulphuric acid, is 0·4–0·48, while for polymers IV and V containing the fluorine atoms, it is slightly below 0·308–0·32. The viscosity of polymer VI could not be determined as it is insoluble in sulphuric acid. The different viscosities obtained for the fluorinated and unfluorinated polyamides are apparently unrelated to differences in the central unit of the dicarboxylic acid.

PROPERTIES OF THE SYNTHESIZED POLYAMIDES

Polyamide	Yield, %	η_{red}, dl/g	Weight loss (%) due to action of 10% NaOH	Weight loss (%) due to action of 10% H_2SO_4	Polyamide	Yield, %	η_{red}, dl/g	Weight loss (%) due to action of 10% NaOH	Weight loss (%) due to action of 10% H_2SO_4
I	89	0·48	2·5	1·0	IV	79	0·308	1·2	1·4
II	78	0·40	2·9	3·6	V	85	0·32	1·6	2·0
III	87	0·46	2·2	2·0	VI	74	—	1·3	2·2

We know from data in the literature that oxygen atoms are poor intermediaries in regard to passing on the mutual effects of substituents located in different diphenyl ether rings [7] Therefore the effects of the fluorinated or unfluorinated phenylene rings on the reactivity of the acid chloride groups should not differ to any great extent. The rather lower viscosities of polymers IV and V compared with I and II cannot be taken yet as signs of lower molecular weight. In a previous investigation [8] it was shown, taking as examples fluorinated polyurethanes prepared from trifluoromethylphenylenediisocyanates, that with identical intrinsic viscosities the molecular weight of the fluorinated polyurethane was higher than that of the polyurethane prepared from toluenediisocyanate In a study of polyurethanes prepared from phenylenediisocyanates containing fluorinated or unfluorinated alkoxyl substituents it was found that with equal viscosities the molecular weights of the fluorinated polymers were five times higher than those of their unfluorinated analogues [9].

The hydrolytic stability of polyamides I–VI is fairly high. After the polyamides had been boiled with an acid or alkali the weight loss was found to be 1–3·6%. The stability of the fluorinated polymers in alkaline medium is slightly higher than that of their unfluorinated analogues The weight loss in alkaline medium is 1·2–1·6 for the fluorinated polymers compared with 2·2–2·9 wt % for their unfluorinated analogues The hydrolytic stability of polymers IV–VI is much superior to that of aromatic polyamides synthesized from tetrafluoro-*m*-phenylenediamine [5] or octafluorobenzidine [6], for which the weight loss amounts to 14–94%, under the same conditions

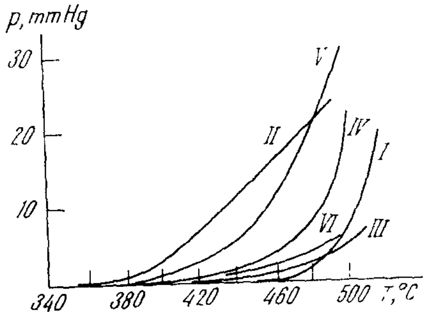


FIG. 1 Magnitude of gas evolution of polymers I–VI vs temperature.

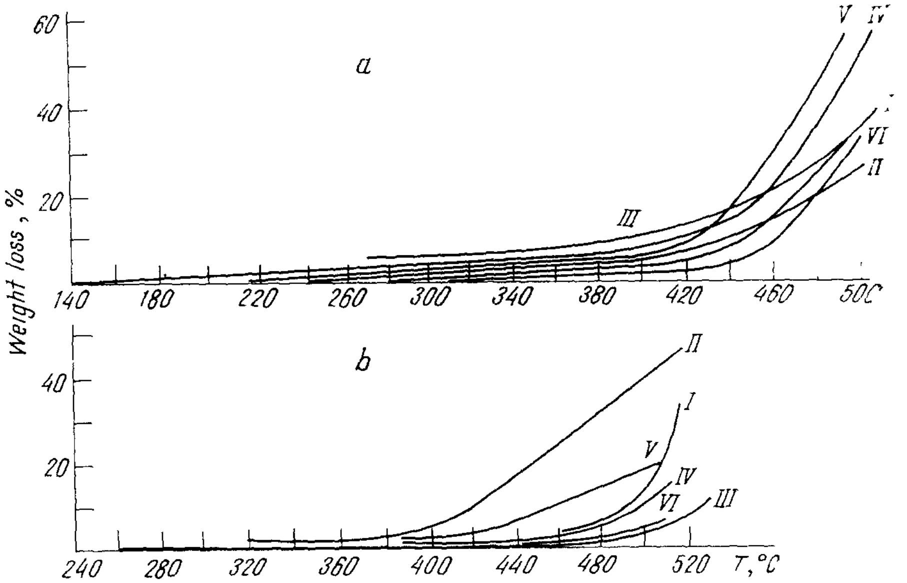


FIG. 2. TGA curves of polyamides I–VI on heating *in vacuo* (*a*) and in air (*b*)

It was desired to investigate the behaviour of polyamides I–VI upon heating these materials. Figure 1 shows the evolution of gas in relation to temperature. The presence of fluorine atoms in the dicarboxylic acid molecule has very little effect on the gas evolution compared with the unfluorinated polyamides. The pressure change on heating the polymers up to 400, 460 and 480° was 0·5, 1 and 2·5 mmHg for polyamide III, compared with 1·2 and 3·5 mmHg for polymer IV. Similar results were obtained for the remaining pairs of polyamides (I and IV or II and V). In all cases, however, the gas evolution was slightly higher for the fluorinated polymers than for the unfluorinated ones. The polymers containing *p*-phenylene units (polyamides I and IV) have better heat-stability than those containing *m*-phenylene units (polyamides II and V).

Figure 2*a* shows the relation of weight loss to temperature for polyamides I–VI. The weight loss for all the fluorinated polyamides is lower than than for their unfluorinated analogues. Polyamides I and IV containing *p*-phenylene units have better heat-resistance than polymers II and V.

The slight difference between the magnitude of the evolution of volatile products and the weight losses for the fluorinated and unfluorinated polyamides may be due to the participation of terminal amine groups and fluorinated benzene rings in nucleophilic reactions. Certainly, on heating polyamide VI up to 200°, gaseous products of an acid character were liberated, and resulted in a change in the red colour. Even when the unfluorinated polyamide III was heated up to 400° no gaseous products giving rise to a change in the Congo red colour were detected. The fluorine ion was found in the alkaline solution by which the gaseous products of the reaction were absorbed.

It should be noted that hexafluorobenzene and its derivatives are inclined to nucleophilic substitution reactions, while electrophilic substitution reactions are characteristic for benzene. For example, the action of ammonia on hexafluorobenzene at 100–150° [10] leads to the formation of pentafluoroaniline, tetrafluoro-*m*-phenylenediamine, and products of more advanced substitution. The heating of fluorinated polyamides IV–VI also leads to reactions of nucleophilic substitution involving the participation of amine endgroups with consequent evolution of hydrogen fluoride, seeing that the resulting secondary aromatic amines, being of lower basicity, do not bind hydrogen fluoride at elevated temperatures.

The conclusion that it is, in fact, amine endgroups, and not amide groups of the polyamides, that participate in the nucleophilic substitution reactions is confirmed by the relatively slight difference in the gas evolution observed for the fluorinated and unfluorinated polyamides in the region of 250–400°. The difference in the pressure change in the system is in this case 0·5–1 mmHg.

Figure 2*b* shows the weight loss during heating for polyamides I–VI in the presence of atmospheric oxygen. The weight loss of polyamides I–VI under conditions of thermooxidative degradation depends to a considerable extent on their structure. In the case of the polymers based on *m*- or *p*-phenylenediamine the introduction of fluorine atoms into the dicarboxylic acid unit lowers their stability compared with the unfluorinated polyamides.

The opposite was found true in the case of polymers III and VI: the fluorinated polyamide VI is more stable than its unfluorinated analogue III.

Thus the decreasing order of stability of polyamides I–VI towards vacuum heating was found to be as follows VI>III>IV>I>V>II (for a case where the weight loss is equal to 5%). The reduction in the stability of the polyamides under conditions of thermooxidative degradation was found to be in the order VI>I>II>V>IV>III

The fluorinated polyamide VI had the highest thermal stability among the polymers synthesized in this investigation

CONCLUSIONS

High-melting polyamides based on di-(*p*-carboxyphenyl) ethers of hydroquinone and tetrafluorohydroquinone and aromatic diamines have been synthesized, and some of their properties investigated It has been found that in some cases the thermal and hydrolytic stability of the polyamides was improved by the presence of tetrafluoro-*p*-phenylene rings not directly attached to the amide groups.

Translated by R. J. A. HENDRY

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