Synthesis of Poly-p-oxyperfluorobenzylene and Related Polymers. A Novel Synthesis of the Monomer 2,3,5,6-Tetrafluoro-4-trifluoromethylphenol*

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The synthesis and polymerization of 2,3,5,6-tetrafluoro-4-trifluoromethylphenol (heptafluoro-p-cresol) is described. The polymer, poly-p-oxyperfluorobenzylene (polyperfluoro-p-benzylene oxide), is probably formed through the perfluoro-p-quinonemethide intermediate obtained by the intramolecular loss of either hydrogen fluoride or a metal fluoride. The polymer has a structure analogous to that reported for the polymer derived from p-trifluoromethylphenol under similar conditions.

In the course of the synthesis of the monomer, heptafluoro-p-cresol, a novel synthetic method was discovered. The synthesis consists in the prior preparation of 1-t-butoxy-2,3,5,6-tetrafluoro-4-trifluoromethylbenzene and its subsequent thermal decomposition into the isobutylene and the desired cresol. Similarly, N-t-butyl-2,3,5,6-tetrafluoro-4-trifluoromethylaniline undergoes a similar liquid phase pyrolysis into isobutylene and 2,3,5,6-tetrafluoro-4-trifluoromethylaniline. However, during the course of this pyrolysis, practically all of the aniline undergoes polymerization with the concomitant loss of hydrogen fluoride. The polymer is formed by the same mechanism operative in the thermal polymerization of p-heptafluorocresol except that additional quantities of hydrogen fluoride can be eliminated from the $-\mathrm{NHCF_2}-$ segments of the polymer chain thereby introducing $-\mathrm{N}=\mathrm{CF}-$ units into the polymer backbone.

Other t-butyl derivatives were synthesized and their thermal decomposition studied. Several possible mechanisms for the decomposition of these t-butyl compounds are considered.

Key Words: 1-t-Butoxy-2,3,5,6-tetrafluoro-4-trifluoromethylbenzene, perfluoro-p-quinonemethide, polymerization, poly-p-oxyperfluorobenzylene, pyrolysis, 2,3,5,6-tetrafluoro-4-trifluoromethylphenol.
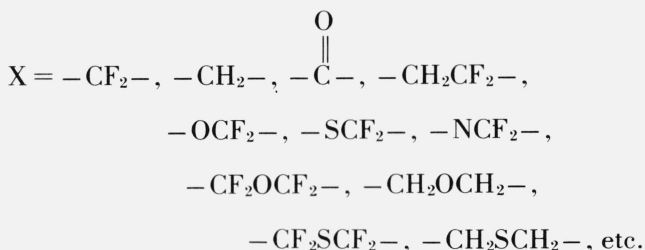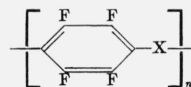
1. Introduction

The need for new polymers that display both good stability and elasticity at elevated temperatures is well known. Although, at present, there appear to be no theoretical reasons to suppose that this elusive combination of properties can not be realized in a polymer, general experience associates good thermal stability with stiff, high melting, and usually intractable materials.

For example, in an earlier phase of this work [1],[1] it was reported that although perfluorophenylene ether polymers exhibit rubbery characteristics above 90 °C, their thermal stability is not exceptional. Conversely, polymers of the type polyperfluorophenylene show good thermal stability (about 600 °C in vacuo) but poor elasticity [2–7].

Since the ether linkage between polyfluoroaromatic rings resulted in a lowering of the thermal stability of the polyfluorophenylene type polymer, it was thought that the introduction of a different linkage or swivel group into the polymer chain might result in an elastic phenylene polymer of superior thermal stability. Thus such groups as shown below might prove useful as links in polyperfluorophenylene type polymers.

$$X = -CF_2-,\ -CH_2-,\ -\overset{\overset{\displaystyle O}{\|}}{C}-,\ -CH_2CF_2-,$$

$$-OCF_2-,\ -SCF_2-,\ -NCF_2-,$$

$$-CF_2OCF_2-,\ -CH_2OCH_2-,$$

$$-CF_2SCF_2-,\ -CH_2SCH_2-, \text{etc.}$$

This paper will deal primarily with the synthesis of poly-p-oxyperfluorobenzylene (polyperfluoro-p-benzylene oxide), where X is $-OCF_2-$, and the requisite monomer, 2,3,5,6-tetrafluoro-4-trifluoromethylphenol (heptafluoro-p-cresol) [2]

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[1] Figures in brackets indicate the literature references at the end of this paper.

[2] During the course of our investigation of the poly-p-oxyperfluorobenzylene polymer, V. C. R. McLoughlin and J. Thrower of the Royal Aircraft Establishment, Farnsborough, England informed us that they were engaged in closely related research. They have since published some of their results [8].

2. Historical Data

In 1947 R. G. Jones reported [9] that p-trifluoro-methylphenol, upon treatment with cold dilute alkali or a trace of hydrogen fluoride, forms a polymer of the structure shown at the right of the following equation,

$$n \, HO\text{---}\langle\ \rangle\text{---}CF_3 \xrightarrow[-HF]{\text{dilute alkali} \atop \text{or HF}} \left[\langle\ \rangle\text{---}OCF_2\right]_n$$
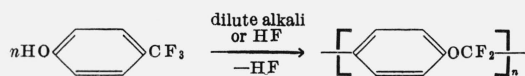
Similarly, o-trifluoromethylphenol is found to undergo facile polymerization under similar conditions to give an *ortho*-linked polymer as shown below,

$$n \overset{CF_3 \ OH}{\langle\ \rangle} \xrightarrow{-HF} \left[\overset{CF_2 \ O}{\langle\ \rangle}\right]_n$$
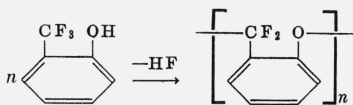
However, the m-trifluoromethylphenol, in contrast with the *ortho* and *para* isomers, is stable to aqueous alkali. No polymerization is evident even when the *meta* isomer is heated to 100 °C with 50 percent aqueous sodium hydroxide. The susceptibility of the *ortho* and *para* isomers of trifluoromethylphenol to polymerization by the elimination of a molecule of hydrogen or alkali fluoride seems to suggest the intermediacy in the reaction mechanism of such quasiquinoidal structures as shown below,

ortho quinoidal intermediate   *para* quinoidal intermediate
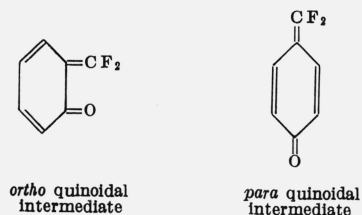
Since the *meta* isomer would be incapable of existing in a similar quinoidal form, its inability to undergo polymerization, at least by this mechanism, is explicable.

3. Synthesis of 2,3,5,6-Tetrafluoro-4-trifluoromethylphenol (Heptafluoro-p-cresol)

The facile polymerization of the *ortho* and *para* isomers of trifluoromethylphenol ($CF_3C_6H_4OH$), probably by means of a quasi-quinoidal intermediate, would seem to suggest that an analogous polymerization process would be followed by the *ortho* and *para* isomers of heptafluorocresol ($CF_3C_6F_4OH$).

Accordingly, in order to test this hypothesis and to prepare a *para*-linked polyoxyperfluorobenzylene polymer, a search was undertaken for a convenient synthesis of the monomer, 2,3,5,6 - tetrafluoro - 4 - trifluoromethylphenol (heptafluoro-p-cresol).

The successful synthesis of pentafluorophenol from hexafluorobenzene has been effected by several syn-

thetic methods [10–13]. However, early attempts, both here and elsewhere [14], at the synthesis of heptafluoro-p-cresol from octafluorotoluene by these same synthetic methods were for the most part unsuccessful. For example, when octafluorotoluene was heated under reflux with a 25 percent aqueous potassium hydroxide solution for 24 hr no cresol was obtained, but instead a complex mixture of solids, some polymeric, was formed. Apparently, both the nuclear and benzylic fluorine atoms are susceptible to attack by the hot alkaline solution. Furthermore, any initially formed *ortho* and/or *para* heptafluorocresol would undergo polymerization under the conditions of the reaction. Finally, the reaction is further complicated by the fact that the poly-p-oxyperfluorobenzylene polymer, unlike the analogous poly - p - oxy - α,α - difluorobenzylene polymer, is subject to hydrolytic degradation [8]. This method of synthesis therefore, was abandoned.

Less direct methods such as the cleavage of 1-ethoxy-2,3,5,6-tetrafluoro-4-trifluoromethylbenzene with various acidic and basic reagents failed to yield the desired heptafluoro-p-cresol [14]. Also, heating octafluorotoluene with an excess of potassium hydroxide in t-butanol or in a mixture of pyridine and ethylene glycol was reported to give a complex mixture of products but none of the desired cresol [14]. In our hands, the method of synthesis employing potassium hydroxide in t-butanol was partially successful.
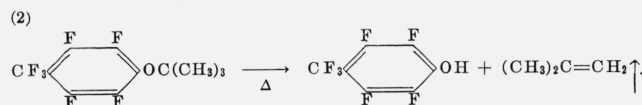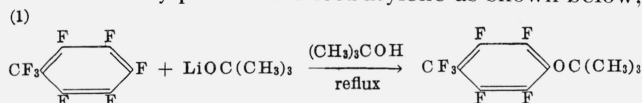
In addition to the formation of a polymeric solid (polyoxyperfluorobenzylene), a 57 percent yield of a liquid with a phenolic odor and boiling range of 140 to 155 °C was obtained. Vapor phase chromatographic analysis revealed the presence of three components with rather close retention times. One component comprised about 90 percent of the mixture. The two minor components were present in about equal quantities. Apparently all three of the possible isomers of heptafluorocresol had formed. The polymeric solid had arisen in all likelihood from the polymerization of the *ortho* and *para* isomers of heptafluorocresol. One of the minor components of the crude liquid product was shown to have the same retention time as an authentic sample of heptafluoro-p-cresol prepared by the novel synthetic method described below. Presumably, the other minor component is the *ortho* isomer. The major component, by a process of elimination, is then the *meta* isomer. However, although this structural assignment appears likely, it has not yet been confirmed by NMR analysis.

McLoughlin and Thrower [8] have studied this reaction more thoroughly and reported that under carefully controlled conditions (excess potassium hydroxide at 20 °C and long reaction times, or equivalent quantities of potassium hydroxide and octafluorotoluene at reflux temperature for short reaction times) a 70 percent yield of heptafluoro-p-cresol is obtained. The *para* cresol is purified by recrystallization of its ether soluble potassium salt using a solvent pair of ether/petroleum ether. The recrystallization procedure is necessary because of several contaminants

(heptafluoro-*o*-cresol and the *t*-butyl ethers of the cresols are mentioned as probable by-products of the reaction).

It was evident, therefore, that the standard methods available for the hydroxylation of polyfluoroaromatic compounds, when applied to octafluorotoluene, either gave polymeric solids and/or impure *para* cresol. A new synthetic reaction was needed that would lead to good yields of the pure *para* isomer of heptafluorocresol with a minimum of polymerization.

The procedure devised simply involves the prior synthesis of the highly branched ether, 1-*t*-butoxy-2,3,5,6-tetrafluoro-4-trifluoromethylbenzene and its subsequent thermal cleavage to 2,3,5,6-tetrafluoro-4-trifluoromethylphenol and isobutylene as shown below,

(1)

$$CF_3\text{—}C_6F_4\text{—}F + LiOC(CH_3)_3 \xrightarrow[\text{reflux}]{(CH_3)_3COH} CF_3\text{—}C_6F_4\text{—}OC(CH_3)_3$$

(2)

$$CF_3\text{—}C_6F_4\text{—}OC(CH_3)_3 \xrightarrow{\Delta} CF_3\text{—}C_6F_4\text{—}OH + (CH_3)_2C{=}CH_2\uparrow.$$

The *t*-butyl ether of the *para* cresol was prepared by refluxing equivalent amounts of lithium *t*-butoxide and octafluorotoluene in a suitable solvent or diluent. Excess *t*-butanol serves this purpose quite well. After all the solvent is removed by careful distillation, the *t*-butyl ether is pyrolyzed either in the liquid phase or in the vapor phase. The overall yield of heptafluoro-*p*-cresol from octafluorotoluene is of the order of 70 to 75 percent. Vapor phase chromatographic analysis indicates that the product is a single substance (no trace of the other two possible isomers of the cresol was found). Both infrared and nuclear magnetic resonance analyses of the compound indicated that the hydroxyl group is *para* to the trifluoromethyl group.

The critical step in this synthesis is the initial preparation of the ether, 1-*t*-butoxy-2,3,5,6-tetrafluoro-4-trifluoromethylbenzene free of two other possible isomeric ethers.

Several factors seem to insure this result. One involves the nature of the substrate molecule, octafluorotoluene. It has been demonstrated that pentafluorophenyl derivatives of the type C_6F_5X undergo nucleophilic displacement reactions predominantly by substitution *para* to X, unless X is a very strong electron-attracting or repelling substituent [10, 15]. Electron-attracting groups, such as the trifluoromethyl group, also should enhance the reactivity of the substrate molecule toward nucleophilic attack. The enhancement of nucleophilic reactivity of octafluorotoluene, however, is slight and appears to be confined to the already activated *para* position rather than being distributed over both the *ortho* and *para* positions as expected [14]. This is borne out by the fact that with the exception of the hydroxylation reactions previously discussed [8], no *ortho* products have been observed in the reported nucleophilic reactions of octafluorotoluene [14]. This lack of *ortho* substitution may arise from the following considerations: (1) A charge repulsion between the highly dense electron cloud provided by the trifluoromethyl group and the attacking nucleophile, and (2) the steric hindrance created by the bulk of the nucleophile and the crowded condition of the *ortho* positions.

The nature of the nucleophile also is an important factor in assuring the formation of highly pure *para* *t*-butyl ether. In general, a more highly basic nucleophile will lead to a higher degree of *para* substitution than a less basic nucleophile. Attack at the *ortho* positions by a highly nucleophilic reagent is much less favored because of the increased charge repulsion existing between the trifluoromethyl group and the nucleophile. Thus, the *t*-butoxy anion should, by reason of its great nucleophilicity, prefer to attack the unhindered *para* position of octafluorotoluene. Even the less nucleophilic ethoxy anion is reported to give only *para* substitution [14]. Moreover, the large bulky nature of the *t*-butoxy anion would further hinder attack at the *ortho* positions.

As mentioned before, it had been found difficult to effect the successful cleavage of the ethoxy ether of heptafluoro-*p*-cresol by chemical means [14]. However, the relative instability of other *t*-butyl ethers to both heat and acid [16–18] suggested that the *t*-butyl ether of heptafluoro-*p*-cresol might possibly undergo facile cleavage to the desired cresol. Indeed, it was found that by either liquid phase or vapor pyrolysis the ether undergoes cleavage to give heptafluoro-*p*-cresol and isobutylene.

## 4. Mechanism of Ether Cleavage

The formation of heptafluoro-*p*-cresol from its *t*-butyl ether can be accounted for by several different mechanisms.

One possible mechanism is similar to that proposed for the thermal dehydrohalogenation of alkyl halides [19], whereby the decomposition is viewed as a unimolecular process involving a four-membered cyclic-transition state such as that shown below.

Decomposition of Alkyl Halide

$$-\underset{|}{C}\underset{|}{\overset{H}{C}}\cdots\overset{\ddot{X}:}{} \longrightarrow -C{=}C- + H\ddot{X}:$$
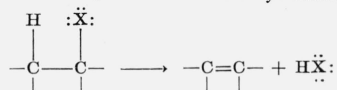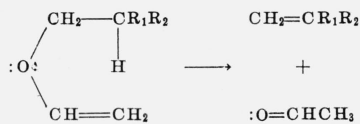
Decomposition of *t*-Butyl Ether
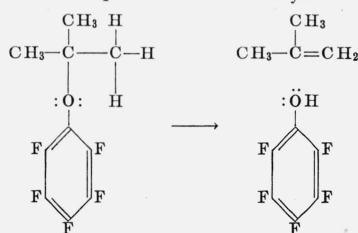
The thermal decomposition of alkyl vinyl ethers should bear at least a formal relationship to that of alkyl aryl ethers. One mechanism proposed for their thermal decomposition is unimolecular in nature and involves a six-membered cyclic transition state formed by a beta hydrogen of the alkyl group and the terminal carbon of the vinyl group [20].

Thermal Decomposition of Alkyl Vinyl Ether

$$CH_2\text{---}CR_1R_2 \qquad CH_2{=}CR_1R_2$$
$$:O\colon \qquad H \qquad \longrightarrow \qquad +$$
$$CH{=}\!\!=CH_2 \qquad :O{=}CHCH_3$$

Recently, W. J. Bailey and D. McKenzie [21] proposed an analogous mechanism to explain the thermal decomposition of phenetole into phenol and ethylene.

Thermal Decomposition of Alkyl Aryl Ether

(ortho)

(para)

stable enol form

unstable keto forms
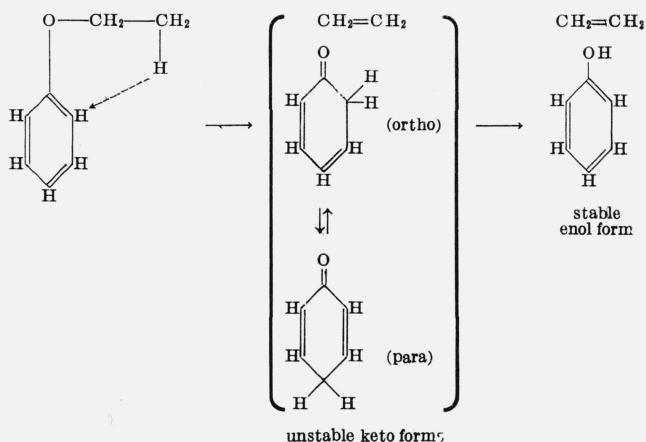
The transient cyclohexadienone intermediate, which can be viewed as the *ortho* and/or *para* tautomer of phenol, spontaneously reverts to the more stable enol form.

It seems likely that the same mechanism would be operative in the gas·phase pyrolysis of 1-*t*-butoxy-2,3,5,6-tetrafluoro-4-trifluoromethylbenzene. Thus the reaction would proceed as follows,

enol form

keto forms
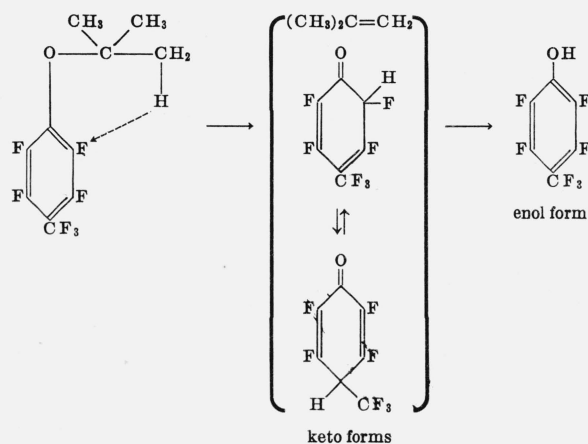
Although the isomerization of an *ortho* fluorine atom or the *para* trifluoromethyl group would seem to be possible, there is no evidence of the presence of either the hypofluorite, $CF_3C_6F_3HOF$, or of the ether, $C_6F_3HOCF_3$. The unfavorable energetics involved in the shifting to the oxygen either a fluorine atom or a trifluoromethyl group compared to that of shifting a hydrogen would seem to support these observations.

A slightly different representation of the transient intermediate would be that of a quasi-zwitterionic intermediate, formed by the protonation of the π-electron system of the phenyl ring by a beta hydrogen, while the oxygen simultaneously is transformed into the phenoxide form as shown,
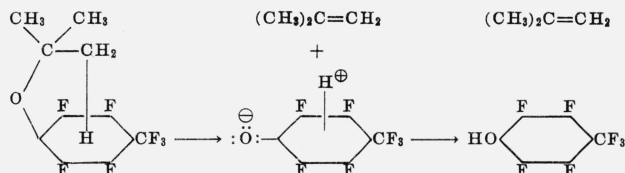
Such a species with disparate charges in close proximity would be expected to undergo instantaneous collapse to the stable cresol. The advantage of this type of representation is that it minimizes the disruption of the aromaticity of the benzene ring.

5. Polymerization of 2,3,5,6-Tetrafluoro-4-trifluoromethylphenol

The polymeric solid obtained from the reaction of potassium hydroxide and octafluorotoluene in *t*-butanol, as previously noted, arises from the polymerization of the potassium salts of the *ortho* and *para* isomers of heptafluorocresol. The polymer is a light-tan crystalline solid, which has a softening range of 65 to 70 °C. It is soluble in common organic solvents such as diethyl ether and acetone. Molecular weight determinations, as made by vapor phase osmometry (VPO), indicated a molecular weight range of 3000 to 4000.

When a pure sample of heptafluoro-*p*-cresol is heated with a 5 percent aqueous solution of sodium bicarbonate, a white solid soon begins to form. In one experiment the mixture was heated under reflux for 17 hr. A white crystalline solid was isolated. The molecular weight of the solid was of the same order of magnitude as that observed for the polymer obtained from the potassium hydroxide-*t*-butanol system. However, the softening range was somewhat higher, 70 to 75 °C. This discrepancy probably arises from the presence of *ortho* cresol units in the polymer obtained from the potassium hydroxide/*t*-butanol system.

The *para* cresol also undergoes polymerization by heating with a 1 percent aqueous potassium fluoride solution. After heating the mixture under reflux for 3 hr, a hard white solid was obtained with a softening range of 70 to 80 °C. The molecular weight (VPO), 4000 to 5000, was somewhat higher than that observed for the earlier polymer samples.

Still another method for the polymerization of the cresol is based on the technique discovered by Szwarc [22, 23] for the preparation of poly-p-xylylene. This method consists in the thermal dehydrogenation of the monomer, p-xylene, at high temperatures and at reduced pressures to an intermediate quinonedimethide, which on quenching undergoes spontaneous polymerization.
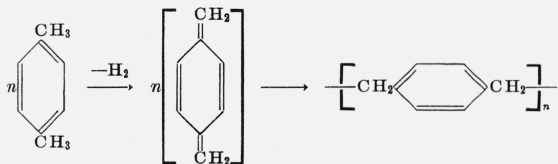
We were able to extend the application of this technique to the polymerization of both p-trifluoromethylphenol and heptafluoro-p-cresol by thermal dehydrofluorination under reduced pressure. The p-trifluoromethylphenol is simply passed through a quartz reactor tube heated in the vicinity of 900 to 950 °C and evacuated to a pressure of 1 to 5 mm. A tough slightly amber film is formed in the first trap held at room temperature. The polymer appears to be of higher molecular weight than that reported by Jones [9]. Infrared analysis of the film revealed little if any absorption in the hydroxyl region of the spectrum. The polymer also showed poor solubility in the common organic solvents (which may be indicative of high molecular weight and/or extensive cross-linking. Further study of the polymer is needed to establish which of these possible explanations is correct.

By analogy with the formation of poly-p-xylylene from p-xylene, the poly-p-oxy-α,α-difluorobenzylene polymer should form in a similar fashion.
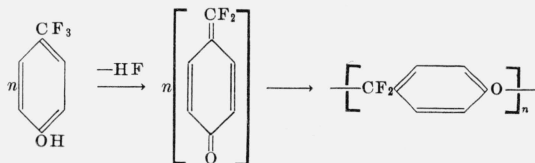
The heptafluoro-p-cresol, under similar conditions, also forms a polymer. However, the film produced in the first trap does not appear to be as tough as that which formed from the thermal polymerization of p-trifluoromethylphenol. An attempt to remove the film intact by prying it away from the glass trap resulted in its conversion to yellow waxy solid which softened at 110 to 120 °C.

6. Mechanism of Polymerization

The synthesis of the polymer, polyperfluorophenylene ether, proceeds via a nucleophilic attack of a growing phenoxide anion at nuclear carbon-fluorine position of a polyfluoroaromatic moiety capable of continuing the condensation process [1]. The same mechanism might be expected to apply to the polym-

erization of heptafluoro-p-cresol in solvent systems. However, the rather mild conditions that can be employed to effect polymerization would seem to argue for a different mechanism [8]. As in the case of the polymer derived from p-trifluoromethylphenol, $CF_3C_6H_4OH$, the polymerization proceeds by some reaction involving the phenoxide anion and the trifluoromethyl group. A likely mechanistic path is the formation of a p-quionoidal intermediate by chemical dehydrofluorination. The p-quinoidal intermediate, p-quinonedifluoromethide, is then the actual monomer which gives rise to the poly-p-oxy-α,α-difluorobenzylene polymer (see above). Additional support for the intermediacy of a p-quinoid transition state would seem to be offered by the successful polymerization of both p-trifluoromethylphenol and heptafluoro-p-cresol by thermal dehydrofluorination. However, further study is needed to ascertain conclusively that the same intermediate is involved in the two polymerization processes.

7. Thermal Stability

The thermal volatilization of several samples of poly-p-oxyperfluorobenzylene was investigated. Table 1 summarizes a typical experiment in which the polymer (a white crystalline solid, mp 70 to 75 °C, mol wt 4000 to 5000 as determined by vapor phase osmometry) was heated in vacuo successively for 1 hr at the indicated temperatures.

The results of this preliminary thermal analysis of the polymer would seem to suggest only a moderate order of thermal stability for poly-p-oxyperfluorobenzylene. However, since the polymer sample has a molecular weight of the order of 4000 to 5000, the possibility of some loss in weight through the evaporation of certain low molecular weight fractions must be considered in the evaluation of the results of this thermal analysis.

TABLE 1. *Thermal volatilization of poly-p-oxyperfluorobenzylene*

Wt	% Wt lost		Treatment	
	Incremental	Total	Time (hr)	Temp °C
18.35	0	0	0	
17.50	4.6	4.6	1	110
13.30	22.8	27.4	1	250
2.00	61.5	88.9	1	350

In their investigations, McLoughlin and Thrower [8] attempted to increase the molecular weight of a sample of poly-p-oxyperfluorobenzylene (prepared from a hot aqueous solution of the potassium salt of heptafluoro-p-cresol) by first treating the polymer with cold dilute alkali and then heating in vacuo the alkali-treated polymer to a temperature of over 200 °C. The original polymer was a pale amber brittle solid, mp 90 to 100 °C, with a reported molecular weight of 1500 to 3000.

The new polymer which displays rudimentary elastomeric properties above 120 °C, was found to undergo a rapid loss of weight above 300 °C in vacuo. Since the molecular weight of the new polymer was not given, the thermal stability reported for poly-p-oxyperfluorobenzylene should be considered only tentative. A more accurate determination of the thermal properties of poly-p-oxyperfluorobenzylene awaits the preparation of a truly high molecular weight polymer.

8. Synthesis of Related Monomers and Polymers

In order to study the scope of the synthetic method developed for the synthesis of heptafluoro-p-cresol, a similar synthetic approach was employed for the preparation of such known compounds as pentafluorophenol, pentafluoroaniline, 2,3,5,6-tetrafluoro-4-trifluoromethylaniline and 2,3,5,6-tetrafluoro-4-trifluoromethylthiophenol. The method of synthesis may be generalized as follows:
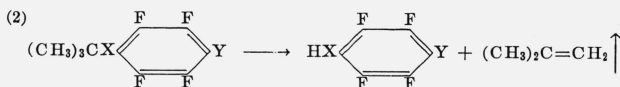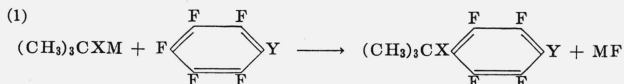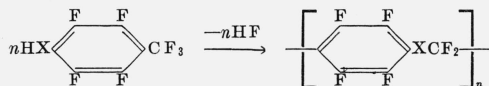

$$X = -O-, \ -S-, \ -NH-, \ \text{etc.}$$
$$Y = F, \ CF_3, \ \text{etc.}$$
$$M = H, \ Li, \ \text{etc.}$$

In general, derivatives of perfluorotoluene $(Y = CF_3)$ can undergo subsequent polymerization by an elimination reaction of the type shown,

8.1. Attempted Synthesis of 2,3,5,6-Tetrafluoro-4-trifluoromethylaniline

An attempt was made to prepare 2,3,5,6-tetrafluoro-4-trifluoromethylaniline by the scheme outlined above. Octafluorotoluene and excess t-butylamine undergo reaction under relatively mild conditions (25 to 50 °C) to give the expected N-t-butyl derivative of heptafluoro-p-toluidine. Unfortunately, after the excess t-butylamine was removed, distillation at atmospheric pressure of the yellow liquid led to a vigorous decomposition of the pot residue. A copious evolution of isobutylene and hydrogen fluoride occurred as the temperature of the pot residue was gradually increased. Tatlow and co-workers [14] reported a boiling point of 180 °C for 2,3,5,6-tetrafluoro-4-trifluoromethylaniline. However, from our distillation only a few drops of the aniline were obtained. Most of the product consisted of a brownish-red polymeric mass. Apparently the temperature of

the pot had reached the decomposition point of the heptafluoro-p-toluidine. Apparently the solid material is the poly-p-aminoperfluorobenzylene polymer. It was soluble in most organic solvents. On standing, further emission of hydrogen fluoride gas was evident. The solid had a wide softening range (80 to 135 °C). The polymerization would appear to follow the scheme indicated below,
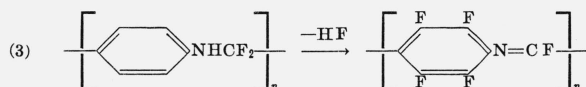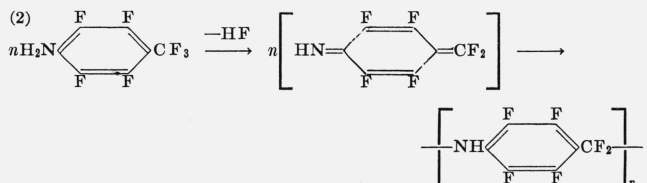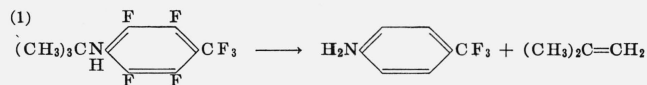
The secondary dehydrofluorination (reaction 3) is not unexpected since the juxtaposition of a $-NH_2$ or $> NH$ group next to a carbon carrying fluorine atoms is known to be an unstable arrangement of atoms.

Not necessarily all of the basic units need undergo this intramolecular secondary dehydrofluorination. Intermolecular secondary dehydrofluorination is also a possibility. However, since the great bulk of the polymer is soluble, this cross-linking reaction would appear to be at minimum.

8.2. Synthesis of Pentafluorophenol and Pentafluoroaniline

As expected, hexafluorobenzene undergoes a similar reaction with lithium t-butoxide in t-butanol, and the expected t-butyl ether of pentafluorophenol, 1-t-butoxy-2,3,4,5,6-pentafluorobenzene, is formed in low conversion but good yield after 24 hr of reflux. Presumably higher conversions can be obtained by suitable modifications of the reaction conditions (e.g., longer reaction times and/or higher reaction temperatures).

The t-butyl ether of pentafluorophenol is distillable at atmospheric pressure in contrast to that of the heptafluoro-p-cresol, which undergoes liquid phase pyrolysis when subjected to atmospheric distillation. However, vapor phase pyrolysis of 1-t-butoxy-2,3,4,5,6-pentafluorobenzene does result in its decomposition into the phenol and isobutylene.

A similar result was obtained in the preparation of pentafluoroaniline via its N-t-butyl derivative. Hexafluorobenzene and excess t-butylamine were heated in a bomb at 200 °C for 1 hr. A low conversion but good yield of the expected N-t-butyl-2,3,4,5,6-pentafluoroaniline was obtained. The same reaction with octafluorotoluene succeeds to higher conversions under considerably milder conditions. Conversely, the product, N-t-butyl-2,3,4,5,6-pentafluoroaniline, can

be distilled under atmospheric pressure with only slight decomposition. As already noted the N-t-butyl derivative of heptafluoro-p-toluidine undergoes rapid decomposition when distillation under atmospheric pressure is attempted. Vapor phase pyrolysis of the N-t-butyl derivative of pentafluoroaniline, as expected, leads to the formation of pentafluoroaniline and isobutylene.

8.3. Reaction of Octafluorotoluene With Lithium t-Thiobutoxide

An attempt was made to prepare 2,3,5,6-tetrafluoro-4-trifluoromethylthiophenol by the method outlined above. The t-butyl derivative of heptafluoro-p-thiocresol, t-butyl-2,3,5,6-tetrafluoro-4-trifluoromethylphenyl sulfide, was prepared in 75 percent yield by the reaction of lithium t-thiobutoxide with octafluorotoluene in excess t-butanol. In contrast to the t-butyl derivative of heptafluoro-p-cresol and heptafluoro-p-toluidine, the t-butyl derivative of heptafluoro-p-thiocresol can be distilled at atmospheric pressure without decomposition. A preliminary study of its behavior when subjected to vapor phase pyrolysis also indicates a greater thermal stability compared to the other t-butyl derivatives. Only trace quantities of what appears to be the thiocresol were observed by gas liquid chromatographic analysis of various pyrolyzates obtained in the temperature range 400 to 500 °C. At these temperatures most of the t-butyl sulfide was recovered unchanged. However, at higher temperatures extensive decomposition occurred to give a foul-smelling liquid mixture of several components. Again, only trace quantities of the expected thiocresol were present. Apparently the t-butyl derivative of heptafluoro-p-thiocresol undergoes thermal decomposition by a different mechanism than that observed for the other t-butyl derivatives. From the lack of any appreciable quantities of thiocresol present in the pyrolyzates, it would appear that perhaps the initial step in the decomposition involves predominantly scission at the aryl carbon-sulfur bond to give the radicals shown below:

$$CF_3\text{—}\langle\text{ring}\rangle\text{—}S\text{—}C(CH_3)_3 \longrightarrow CF_3\text{—}\langle\text{ring}\rangle\cdot + \cdot SC(CH_3)_3$$
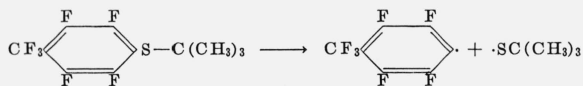
These radicals can then undergo the usual secondary radical reactions such as disproportionation, combination and transfer. However, further study of this decomposition reaction is required to establish the exact mechanistic process involved.

9. Experimental Procedure

9.1. Synthesis of 2,3,5,6-Tetrafluoro-4-trifluoromethylphenol

a. Reaction of Octafluorotoluene With Potassium Hydroxide in t-Butanol

A mixture of 6 g (0.021 mole) of octafluorotoluene, 3.8 g (0.068 mole) of potassium hydroxide, and 50 ml of freshly distilled t-butanol was heated under reflux for 14 hr under an atmosphere of nitrogen. The t-butanol was removed by flash vacuum distillation (1 mm pressure). The residue in the flask consisted of a solid mass. Water was added to this residue and after vigorous agitation, the insoluble portion was separated by filtration. The light tan solid was washed repeatedly with hot water to remove any residual soluble material, such as potassium fluoride and the potassium salts of any phenolic products. The aqueous filtrate was acidified with concentrated hydrochloric acid and then extracted with ether several times (continuous extraction may have been preferable at this point). The ether extracts were combined, dried, and then subjected to atmospheric distillation using a 6-in glass-helix-packed column. After the ether had been removed, the residue was distilled without the column to give 3.4 g (57% yield) of a clear, phenolic-smelling liquid with a wide boiling range (140–155 °C). Vapor phase chromatographic analysis of this liquid, using two 10 ft by 1/4 in columns packed with 20 percent SE 30 on 60–80 mesh acid-washed Chromosorb W and 20 percent neopentyl gylcol succinate on 60–80 mesh acid-washed Chromosorb P, respectively, revealed that the product consisted of three components with close retention times. The principal component comprised about 90 percent of the mixture and appears to be the *meta* isomer of heptafluorocresol (2,3,4,6-tetrafluoro-5-trifluoromethylphenol). One of the minor components had the same retention time as an authentic sample of heptafluoro-p-cresol. The filtered solid, after drying, weighed 2.5 g and had a melting range of 65 to 70 °C. It was soluble in ether, acetone, and tetrahydrofuran, and probably is a mixed copolymer of the *para* and *ortho* heptafluorocresols. Molecular weight determinations using vapor phase osmometry indicated a molecular weight range of 3000 to 4000. The solvent used was anhydrous tetrahydrofuran.

b. Reaction of Octafluorotoluene With Lithium t-Butoxide in t-Butanol

A mixture of 11 g (0.047 mole) of octafluorotoluene and 3.8 g (0.047 mole) of lithium t-butoxide in 30 ml of t-butanol was heated under reflux for 15 hr. After removal of the insoluble solids (lithium fluoride), the solvent (t-butanol) was removed by distillation at atmospheric pressure through a 6-in glass-helix-packed column. After the bulk of the t-butanol was removed, the pot temperature was raised to permit distillation of the higher boiling t-butyl ether. Shortly thereafter a vigorous reaction ensued and a gas with an olefinic odor (iosbutylene) was emitted through the distillation head. The reaction was allowed to continue while a water-white liquid with a phenolic odor was collected, bp 142 to 144 °C. The yield of liquid product was 8 g (72% yield). The liquid product was shown by vapor phase chromatography (using the two columns mentioned previously) to consist of but one substance. Near-infrared analysis of the type reported for similar halophenols [10] appears to suggest either a *para* or *meta* orientation of the hydroxyl

group with reference to the trifluoromethyl group. Nuclear magnetic resonance analysis confirms the *para* orientation. A solid residue of about 2 g remained in the distillation flask.

9.2. Polymerization of 2,3,5,6-Tetrafluoro-4-trifluoromethylphenol

a. Polymerization With Dilute Aqueous Sodium Bicarbonate

About 1 g of the heptafluoro-*p*-cresol and 15 ml of 5 percent aqueous sodium bicarbonate were heated under reflux for 17 hr. The white polymeric solid was separated by filtration, washed about ten times with large quantities of hot water, and then allowed to suck-dry overnight. The solid was then dissolved in diethyl ether; the solution was filtered and the ether removed under vacuum distillation (15 mm) using moderate heating. The dried crystalline solid, about 1 g, had a softening point of 70 to 75 °C.

b. Polymerization With Dilute Aqueous Potassium Fluoride

About 0.5 g of the heptafluoro-*p*-cresol was added to 10 ml of a 1 percent aqueous solution of potassium fluoride. The mixture was refluxed with stirring (magnetic bar) for 3 hr. A hard, white solid was formed along with a white, tacky substance. The hard, white solid was separated from the tacky material, washed with copious amounts of water, filtered and dried under vacuum.

After this treatment it exhibited a tough crystalline appearance and had a softening range of 70 to 80 °C. The tacky solid had a phenolic odor and probably represented a lower molecular weight fraction.

c. Thermal Polymerization

It was found that the method developed by Szwarc [22, 23] to polymerize *p*-xylene to poly-*p*-xylylene by vacuum pyrolysis could be extended to both *p*-trifluoromethylphenol and heptafluoro-*p*-cresol. By use of the apparatus and technique described below, it was possible to polymerize *p*-trifluoromethylphenol at 820 °C and 1 to 5 mm pressure to a tough, yellowish transparent film. The film was insoluble in common organic solvents (ether, acetone, benzene, etc.) and the infrared analysis showed little, if any, unreacted hydroxyl groups. The same method was employed with heptafluoro-*p*-cresol. About 1 g of heptafluoro-*p*-cresol was allowed to vaporize under a slow stream of nitrogen over a 30 min period through a quartz tube (48 cm by 1.5 cm) heated to 980 °C and evacuated to a pressure of 1 to 5 mm. The quartz reactor was placed vertically in a heated zone of about 25 cm and was connected at the lower end to three traps in a series. The first trap was a 50 ml sidearm, round-bottom flask maintained at room temperature. The other two traps were cooled in a slurry of solid carbon dioxide and acetone. The quartz tube was connected at the upper end through a capillary bore stopcock to a 5 ml sidearm, round-bottom flask with a nitrogen inlet tube attached to its sidearm.

A yellow film was deposited on the sides of the first trap. The second trap contained an acid smelling liquid which appeared to be primarily unconverted cresol. The third trap contained only a trace of volatile material. The yellow film crumbled to a waxy solid when it was removed from the sides of the flask with a spatula. The solid softened over the range 110 to 120 °C and appeared to lose little weight up to 300 °C. The conversion to polymer was of the order of 20 to 30 percent.

The pyrolysis of heptafluoro-*p*-cresol at lower temperatures (below 800 °C) gave little polymer formation. Somewhat higher temperatures (800 to 850 °C) resulted in the formation of a greasy solid in low conversion. Higher temperatures above 950 °C tended to give some carbonization in the tube as well as polymer formation. The optimum conditions for this type of polymerization are still under investigation.

9.3. Synthesis of Other Monomers

a. Attempted Synthesis of 2,3,5,6-Tetrafluoro-4-trifluoromethylaniline

A mixture of 20 g (0.085 mole) of octafluorotoluene and 20 g (0.27 mole) of *t*-butylamine was heated under reflux for 2 hr. After the mixture had cooled, approximately 40 ml of water was added to the mixture to remove the amine salt. The organic layer was separated and dried over anhydrous sodium sulfate. Any unreacted *t*-butylamine was removed by distillation. Further distillation at atmospheric pressure caused the yellow liquid to undergo a vigorous reaction which was accompanied by the evolution of isobutylene and hydrogen fluoride. A brownish-red glassy solid formed in the bath. The heating was continued until the temperature reached about 190 °C. A small amount of pungent liquid was collected and tentatively identified as 2,3,5,6-tetrafluoro-4-trifluoromethylaniline. The material in the etched flask was scraped out to give a hard crystalline brownish red solid. The solid dissolved in ether, acetone and hexafluorobenzene. It melted over a wide range 80 to 135 °C to a viscous yellow liquid. Preliminary studies indicate the polymer has a thermal stability comparable to that observed for the poly-*p*-oxyperfluorobenzylene polymer.

A sample of the polymer was heated under reflux for 45 min with a 5 percent aqueous solution of potassium carbonate. The solid was filtered, washed with copious quantities of hot water and finally dried in vacuo overnight. At this point the solid had a tan crystalline appearance and a softening point of 120 to 140 °C.

b. Reaction of Hexafluorobenzene With Lithium *t*-Butoxide in *t*-Butanol

A mixture of 18.6 g (0.1 mole) of hexafluorobenzene and 8.0 g of lithium *t*-butoxide in 50 ml *t*-butanol was heated under reflux for 24 hr. The mixture was allowed to cool and then diluted with 50 ml of *n*-

pentane. The insoluble lithium fluoride was removed by filtration. The filtrate was washed several times with water and dried over anhydrous sodium sulfate. The pentane was removed by careful distillation through a 10-in glass-helix-packed column. Approximately 10 g of hexafluorobenzene was recovered unchanged along with a few ml of t-butanol. The high boiling liquid in the pot was then carefully distilled at atmospheric pressure through a 6-in. glass-helix-packed column to give 6 g of a clear colorless liquid, bp 175 to 177 °C. The t-butoxy-2,3,4,5,6-pentafluorobenzene was shown by vapor phase chromatographic analysis (10-ft by 1/4-in 20% SE column) to be better than 99 percent pure. The small amount of lower boiling impurity present had the same retention time as pentafluorophenol. The conversion to product was only 25 percent but the yield of t-butyl ether was 55 percent. Vapor phase pyrolysis of the t-butyl ether (400 to 550 °C) resulted in the formation of pentafluorophenol and isobutylene, as determined by vapor phase chromatographic and infrared analyses.

c. Reaction of Hexafluorobenzene With t-Butylamine

A mixture of 5.8 g (0.08 mole) of t-butylamine and 7.4 g (0.04 mole) of hexafluorobenzene was placed in a platinum lined bomb of 80 ml capacity. The bomb was sealed and heated to 200 °C for 1 hr. After the bomb had cooled, the contents were poured into about 50 ml of water. The organic layer was separated, washed several times with water and finally dried over anhydrous sodium sulfate. After the removal by distillation of any excess t-butylamine and any unreacted hexafluorobenzene (6 g), 1.6 g of clear, colorless liquid, bp 190 to 193 °C, was obtained. During the final stages of the distillation, the pot residue began to decompose and the odor of isobutylene was prevalent. Vapor phase chromatographic analysis revealed that the liquid product was composed of one component (only a trace pentafluoroaniline was present). The conversion was about 20 percent but the yield based on unrecovered hexafluorobenzene was 70 percent. Vapor phase pyrolysis (400 to 550 °C) resulted in the formation of pentafluoroaniline and isobutylene, as determined by vapor phase chromatographic and infrared analyses.

d. Reaction of Octafluorotoluene With Lithium t-Thiobutoxide

A mixture of 60 ml of t-butanol and 0.8 g (0.1 mole) of lithium hydride was stirred for 1 hr. To this mixture was added 9.0 g (0.1 mole) of t-butylmercaptan. The mixture was heated under reflux for 1 hr. Approximately 23.6 g (0.1 mole) of octafluorotoluene was added to the refluxing mixture. The mixture was then heated under reflux for an additional 7 hr. After the

mixture cooled to room temperature, the solids were removed by filtration. The filtrate was fractionated through 10-in glass-helix-packed column to give, after removal of the t-butanol and a small amount of octafluorotoluene (0.5 g), 23.0 g of a pale yellow liquid, bp 212 to 214 °C. Vapor phase chromatographic analysis (10-ft by 1/4-in 20% SE 30 column) revealed that the t-butyl-2,3,5,6-tetrafluoro-4-trifluoromethylphenylsulfide was of high purity ($> 99\%$).

Vapor phase pyrolysis at relatively low temperatures (400 to 500 °C) resulted in the recovery of the t-butyl-sulfide virtually unchanged. Pyrolysis at higher temperatures (above 500 °C) resulted in a complex mixture of products and some carbonization. Very little, if any, of the heptafluoro-p-thiocresol was formed (vapor phase chromatographic analysis indicated that perhaps a small amount — less than 1% — of the thiocresol was formed).

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