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THERMAL DEGRADATION OF PHENOLIC RESINS—VI

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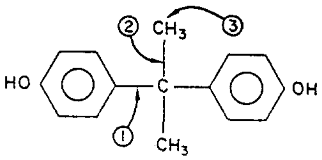
Abstract—Thermogravimetric studies have been made of the stabilities of resins made from diphenylolpropane and formaldehyde. It was confirmed that these resins are less thermally stable than phenol formaldehyde resins. When the aliphatic hydrogen atoms of diphenylolpropane are entirely substituted by fluorine atoms, stability of the resins formed with formaldehyde is sharply enhanced but the carbon residue is similar to unsubstituted bisphenol resins. When the central group of the diphenylol derivative was tetrafluorodichloropropylidene, the resulting resin was less stable. It was found that the addition of polytetrafluorethylene to phenolic resins inhibited degradation to a significant extent.

INTRODUCTION

WE HAVE previously reviewed the thermal degradation of phenolic resins and the use of thermal analysis techniques for elucidation of its mechanism.(1–4) We have considered whether the use of bisphenol A, 2,2 *bis*(4hydroxyphenyl)propane, instead of phenol would give enhanced thermal stability due to protection of some of the links between aromatic rings (see also Ref. 10). Under non-oxidizing conditions this did not occur, and we proposed the cause was lengthening of the bond 1 due to drift of local electrons into it (see formula a)

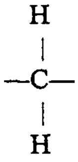


Workers from the Royal Aircraft Establishment(5) have reported on the thermal stability of polymers containing different linkages between aromatic nuclei; they indicated clearly that in an oxidizing atmosphere the resistance to heat of a carbonyl bridge is slightly less than that of a methylene link. Thus any attempt to improve high temperature resistance should be aimed at either improvement of resistance to heat of the carbonyl bridge or prevention of the formation of this bridge by some modification of its methylene precursor. It would also be possible to eliminate the linkage completely.

The possibility cannot be eliminated that the sterically stiff form of the bisphenol residue may result in a low incidence of successful crosslinking associated with predetermination of the position of a linkage between the *p*-positions of two rings.

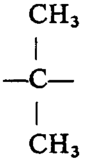
It is known that the presence of fluorine tends to increase the thermal stability of a polymer(7) and we reasoned that the strongly electronegative fluorine atom would cause electron drift towards the pendant carbon atom hence from bonds 2 and 1 (see formula a) reversing the effect we found with bisphenol A. Additionally it is to be expected that the fluorinated bridges would be more resistant to oxidation.(7, 8)

We set out therefore to prepare resins from bisphenols containing the following central groupings:



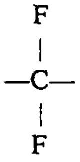
$$-\underset{\underset{H}{|}}{\overset{\overset{H}{|}}{C}}-$$

I



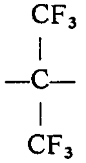
$$-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-$$

II



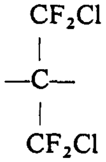
$$-\underset{\underset{F}{|}}{\overset{\overset{F}{|}}{C}}-$$

III



$$-\underset{\underset{CF_3}{|}}{\overset{\overset{CF_3}{|}}{C}}-$$

IV



$$-\underset{\underset{CF_2Cl}{|}}{\overset{\overset{CF_2Cl}{|}}{C}}-$$

V

We were able to do this except for III which did not give resins, and similarly 4,4-dihydroxydiphenyl did not react with formaldehyde under the conditions investigated.

It seemed possible that provision of a radical source or sink during the pyrolysis reactions might result in modification of the second stage of degradation. It is difficult to find either type of agent which is operative in the range 250°–550° so we proposed to use polytetrafluorethylene which degrades at temperatures above 400° to monomer by a radical process.

EXPERIMENTAL

Resins were made from phenol(1) with 1·5 mol formaldehyde and bisphenol A (II) bisphenol 4KF (V) bisphenol 6KF (IV) all with 2·0 mol formaldehyde, because these are equivalent amounts required to give enough formaldehyde for complete crosslinking.* Reaction was carried out under reflux with 3·3 g $Ba(OH)_2$ catalyst per 100 g phenol until the formaldehyde content of the condensate returning to the reaction vessel was less than 1 per cent. Water was removed under reduced pressure until the resin temperature was 80°. A simple gel test was carried out by exposing 1 g of resin on a hotplate at 160°, as an additional control on the resin. Completed resins were neutralized with dil. sulphuric acid to pH 7·0, dissolved in acetone to approx. 30 per cent concentration and filtered. Part of the resin solution was evaporated *in vacuo* to isolate the solid polymer.

Samples of resin were cured in air as films 1–2 mm thick for a cycle of 72 hr at 78°, 2 hr at 107° and finally 24 hr at 130°. They were then crushed and the fraction between 44 and 85 mesh (BS) used for thermal analysis. Samples for thermal analysis were prepared by casting a 10 per cent acetone solution of each resin on a sodium chloride disc, removing acetone *in vacuo* and curing for 13 hr at 125° under dry nitrogen.

Thermal analyses were made using a thermobalance Mk L by Linseis (Selb Bavaria) at heating rates of 10° and 20°/min in air at 0·05 mmHg pressure. To reduce temperature gradients around the sample, it was contained in a small platinum boat surrounded by silica in the balance pan.

TABLE 1. INITIAL TEMPERATURE FOR RAPID DECOMPOSITION (°C)

		$C(CF_2Cl)_2$	$C(CH_3)_2$	CH_2	$C(CF_3)_2$
Heating Rate	10°C/min	260	320	360	390
	20°C/min	290	330	360	445

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* Sources of raw materials; Phenol, Analar, BDH Ltd. redistilled b.p. 176°; bisphenol A, BX Ltd. Plastics (materials group) Birmingham; bisphenol 4KF & bisphenol 6KF, Allied Chemicals, NJ, U.S.A.; formaldehyde, 37 per cent commercial, Synthite Ltd.

TABLE 2. PROCEDURAL ACTIVATION ENERGIES*

		$C(CF_2Cl)_2$	$C(CH_3)_2$	CH_2	$C(CF_3)_2$
Heating Rate	10°C/min	6·5	13·2	18·0	28·9
	20°C/min	6·75	15·0	20·0	29·5

* E_a in k.cal/mol calculated by method of Horowitz and Metzer.(12)

TABLE 3. INFRA-RED TRANSMITTANCE AGAINST TIME OF OXIDATION*

		$C(CF_2Cl)_2$	$C(CH_3)_2$	CH_2	$C(CF_3)_2$
Time hr	0	2·2	2·4	2·8	3·7
	0·5	1·6	1·9	2·6	2·5
	1	1·47	1·5	2·2	1·7
	2	1·2	1·05	1·5	1·11

* Expressed in terms of ratio of transmittance at 1655 cm^{-1} to that at 1615 cm^{-1} attributed to the ratio of carbonyl to aromatic ring.(9) As the diphenylol resin could not be prepared, figures are quoted for a plain phenol resin which contains analogous $—CH_2—$ groups.

TABLE 4. THEORETICAL LOSSES AS % OF ORIGINAL

	$C(CF_2Cl)_2$	$C(CH_3)_2$	CH_2	$C(CF_3)_2$
Loss of all X—C—X	45·7	6·7	15·8	40·3
all H & O	13·7	19·0	21·0	15·4
total	59·4	25·7	36·8	55·7
Actual losses	55·0	—	56·0	50/55

DISCUSSION

We have previously discussed the three stages of pyrolysis which have been mentioned repeatedly by previous workers(11) and these are clearly observed in Figs. 1–4. Qualitatively the results are clear and unequivocal and in accord with those previously recorded.

(1) There are certain variations in the thermograms up to about 300° but they are complex and may be instrumental in origin; we do not feel able to discuss them further.

(2) between 300° and 600°, major differences appear (Figs. 1–3)

(*a*) phenol formaldehyde resins start to degrade rapidly at 350° and their thermograms start to level out between 700° and 800° with the final yield of carbon at about 55 per cent (not shown in Fig. 1)

(*b*) bisphenol A resins begin to lose weight rapidly at about 350° leading to a terminal value of 35 per cent residue.

(*c*) bisphenol 4FK resins are almost identical with bisphenol A resin.

(*d*) bisphenol 6FK resin is stable to at least 450° then loses weight very rapidly indeed to give roughly the same yield of char as bisphenol A resin.

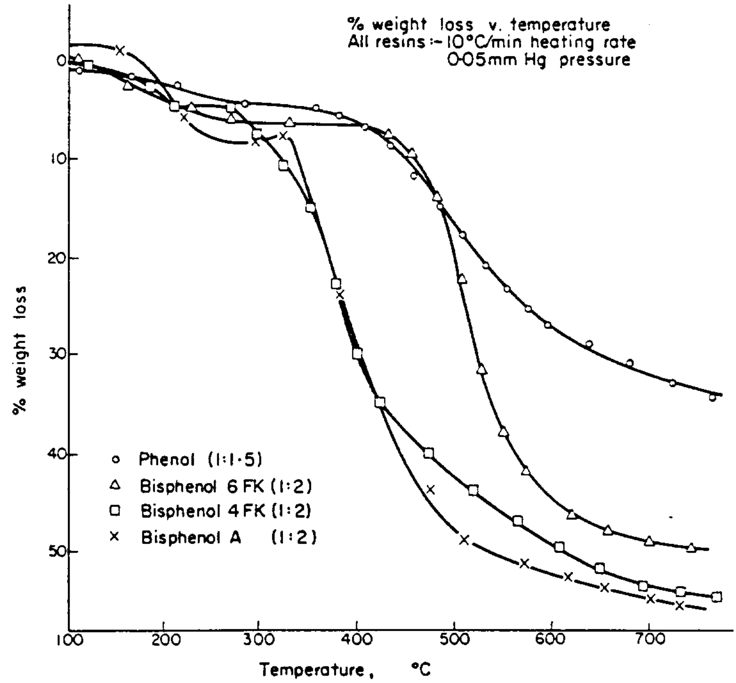
% weight loss v. temperature
All resins :- 10°C/min heating rate
0·05mm Hg pressure
% weight loss
0
10
20
30
40
50
○ Phenol (1:1·5)
△ Bisphenol 6 FK (1:2)
□ Bisphenol 4 FK (1:2)
× Bisphenol A (1:2)
100
200
300
400
500
600
700
Temperature, °C

FIG. 1

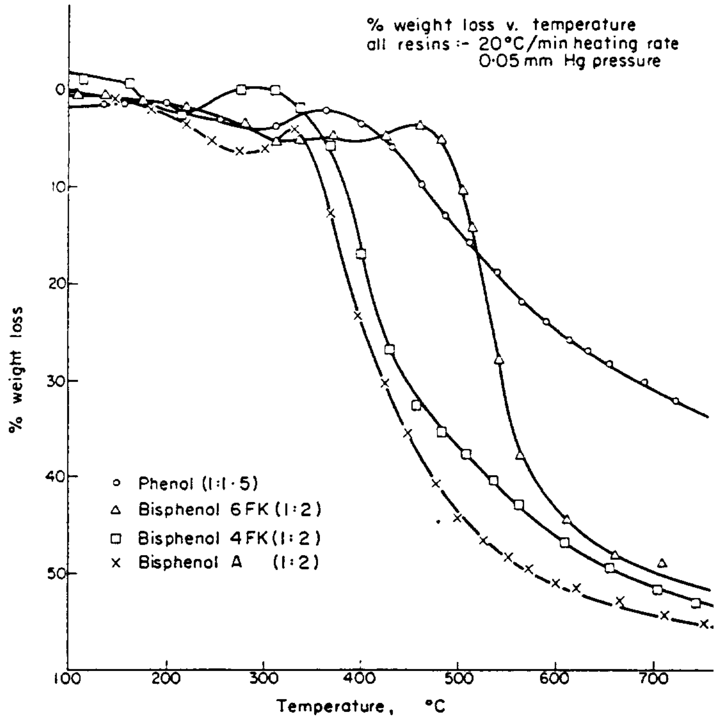
% weight loss v. temperature
all resins :- 20°C/min heating rate
0·05 mm Hg pressure
% weight loss
0
10
20
30
40
50
○ Phenol (1:1·5)
△ Bisphenol 6FK (1:2)
□ Bisphenol 4FK (1:2)
× Bisphenol A (1:2)
100
200
300
400
500
600
700
Temperature, °C

FIG. 2

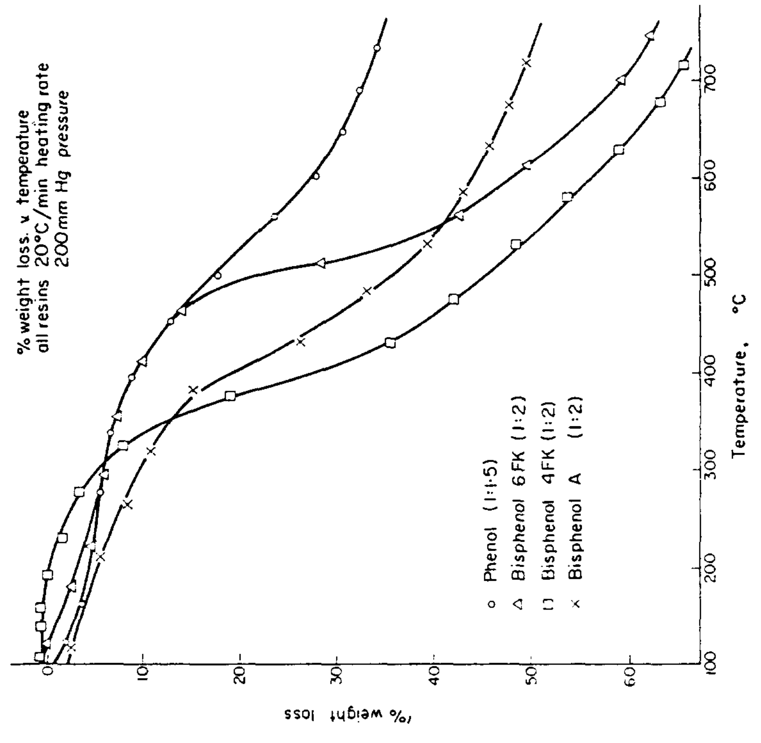
% weight loss. v temperature
all resins 20°C/min heating rate
200mm Hg pressure
o Phenol (1:1·5)
◁ Bisphenol 6FK (1:2)
□ Bisphenol 4FK (1:2)
× Bisphenol A (1:2)
% weight loss
0
10
20
30
40
50
60
Temperature, °C
100
200
300
400
500
600
700

FIG. 3

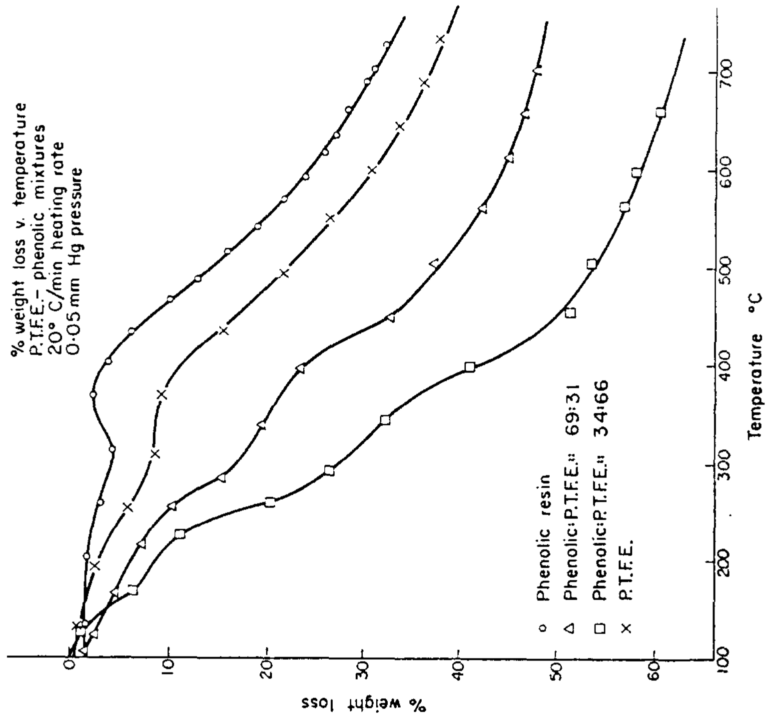
% weight loss v. temperature
P.T.F.E.- phenolic mixtures
20° C/min heating rate
0·05mm Hg pressure
o Phenolic resin
◁ Phenolic:P.T.F.E." 69:31
□ Phenolic:P.T.F.E." 34:66
× P.T.F.E.
% weight loss
0
10
20
30
40
50
60
Temperature °C
100
200
300
400
500
600
700

FIG. 4

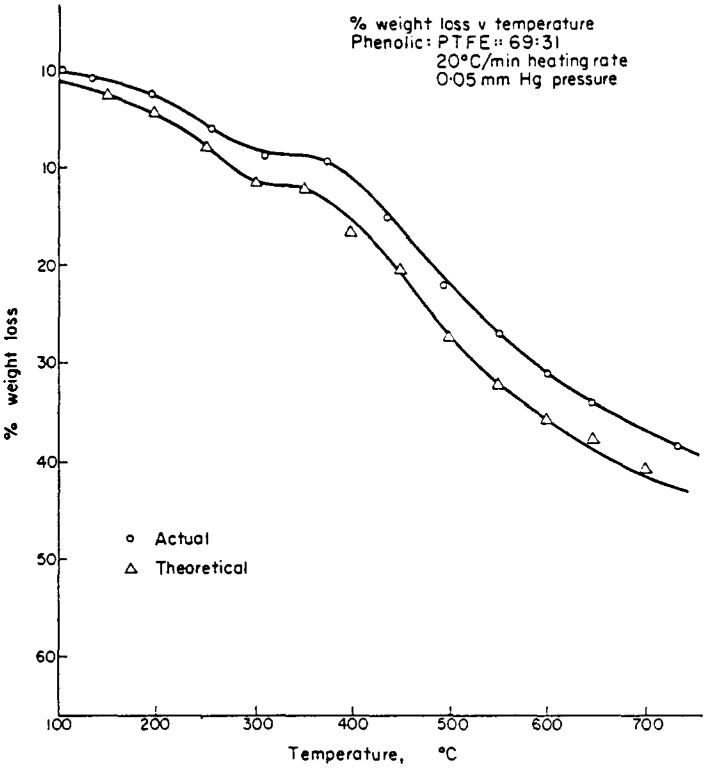

Fig. 5

(3) Thus, although bisphenol 6FK resins are considerably more stable than any other, the course of the pyrolyses of all bisphenol resins are very similar.

(4) Under oxidative conditions (e.g. Fig. 3), the bisphenol resin degrades rather more slowly and both fluorinated resins much more rapidly than the straight phenol resin.

While we have calculated activation energies according to the method of Horowitz and Metzer(12) and these seem to reflect the behaviour of the resin used (except for phenol resins where some anomaly appeared and previously recorded values have been used), these activation energies must be accepted with reservations. This is because they cover three successive separate types of reaction, namely postcuring, reforming and ring stripping, each of which is in itself complex. However it is not to be expected that either postcuring, which involves only the functional methylol groups, or ring stripping, which probably occurs after most of the alien fluorine atoms have been removed, will greatly affect the overall process. Hence we may assume that the activation energies have some empirical meaning and relate mostly to the reforming stage.

From Tables 1 and 2 it is seen that the order of stability of the materials tested, as indicated both by activation energy and by decomposition temp., suggests stability of the central groups in the order $CF_2Cl < C(CH_3)_2 < CH_2 < C(CF_3)_2$. This sequence corresponds to the order of the inductive effects present in the central aliphatic grouping except that CF_2Cl is anomalous. Since only one third of the methylene groups in any resin are substituted (assuming consistent crosslinking), we have considered whether the inductive effect of the central group can be transmitted to the aromatic nucleus and thence to the plain methylene bridges. It does not seem likely that the inductive effect is transmitted so far and it is clear spectroscopically that the nature of the group does not affect the oxidation of the plain methylene groups. We think that it is more likely that the effect is localized to the interatomic central linkage and produces changes in the length of bond 1 (see formula a) as the result of variation in the electron availability (eventual scission at bond 1 will result in complete loss of the isopropylidene group whether plain or substituted).

The anomalous position of the 4FK resin may be due to loss of chlorine atoms by homolytic fission at about 250°. This may be the explanation of the marked stages in the weight loss at 18 per cent corresponding to the loss of chlorine followed by a loss of 18–35 per cent corresponding to the complete loss of fluorine. Indeed the shape of the latter part of the thermogram is the same as with phenol resin displaced by the 35 per cent loss of total halogen (Table 4).

It must be remembered that we still have not established the effect of steric stiffness of the growing network on the number of crosslinks actually achieved; this number may be lower when the resin precursors include methylol bisphenols.

The addition of polytetrafluorethylene (ptfe) to a phenol resin was found to give a yield of char in excess of the calculated value assuming complete loss of ptfe. This may be due to transient presence of free radicals due to fission of the ptfe, but the effect has not been fully investigated.

Comparison of the curves *in vacuo* and in air suggests that either the methylene and oxidized methylene groups have about the same stability or even *in vacuo* the mechanism is still oxidative. This would explain the similarity of both sets of thermograms up to about 600° when the char oxidizes away rapidly when oxygen is present.

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Résumé—On a effectué des études thermogravimétriques sur la stabilité des résines obtenues à partir de diphénylolpropane et de formaldéhyde. On a confirmé que ces résines sont thermiquement moins stables que celles obtenues à partir de phénol et de formaldéhyde. Quand les atomes d'hydrogène aliphatiques du diphénylolpropane sont tous substitués par des atomes de fluor, la stabilité des résines formées à partir de formaldéhyde est nettement accentuée mais le résidu carboné est semblable aux résines non substituées du bisphénol. Quand le groupement central du dérivé du diphénylol est formé de tetrafluorodichloropropylidène, la résine résultante est moins stable. On a trouvé que l'addition de polytetrafluoroéthylène aux résines phénoliques inhibait leur dégradation de façon significative.

Sommario—Sono stati condotti studi termogravimetrici delle stabilità di resine ottenute da difenilpropano e formaldeide. E' stato confermato che queste resine sono termicamente meno stabili delle resine di fenolo formaldeide. Quando gli atomi di idrogeno alifatici di difenilpropano sono interamente sostituiti da atomi di fluoro, la stabilità delle resine formate con la formaldeide cresce notevolmente, ma il residuo carboniso è simile a quello di resine di bisfenolo insostituite. Quando il gruppo centrale del derivato di difenolo è tetrafluorodicloropropilidene, la resina risultante è meno stabile. Si è torvato che l'aggiunta di politetrafluoroetilene a resine fenoliche ha inhibito la degradazione notevolmente.

Zusammenfassung—Zur Bestimmung der Stabilität von Harzen aus Diphenylolpropan und Formaldehyd wurden thermogravimetrische Untersuchungen durchgeführt. Es wurde festgestellt, daß diese Harze thermisch weniger stabil sind als Phenol-Formaldehydharze. Durch vollständige Substitution der aliphatischen Wasserstoffatome des Diphenylolpropans durch Fluoratome wird die Stabilität der mit Formaldehyd erhaltenen Harze stark erhöht, aber der Kohlenstoffrückstand ist dem von unsubstituierten Bisphenolharzen ähnlich. Wenn die zentrale Gruppe des Diphenylolderivatives Tetrafluordichlorpropyliden war, wurde ein weniger stabiles Harz erhalten. Es wurde gefunden, daß die Zugabe von Polytetrafluoräthylen zu phenolischen Harzen den Abbau weitgehend hemmt.