

Synthesis and Thermal Characterization of Chemically Modified Phenolic Resins

ROSY ANTONY and C. K. S. PILLAI*

Polymer Section, Regional Research Laboratory (CSIR), Trivandrum 695 019, India

SYNOPSIS

Phenolic resins with improved/ altered thermal stability and flame retardancy were prepared by introducing flame retardant elements such as phosphorus and bromine at the monomer stage, followed by condensation with formaldehyde or hexamethylene tetramine (HMTA). Thus, monophenyl phosphoric acid (MPPA), monophenyl phosphoric acid-formaldehyde resin (MPPAF), brominated phenol-formaldehyde resin (BrPF) and 2,4,6-tribromophenyl-phosphoric acid-formaldehyde resin (BrMPPAF) were prepared and characterized. Thermal stability and flammability of these polymers were evaluated by TGA and LOI respectively and compared with those of phenol-formaldehyde resin (PF) and phosphorylated phenol-formaldehyde resin (PPF). The TGA (in air) of MPPAF showed enhanced thermal stability (char yield 66%) over that of PF (char yield 52%) and PPF (char yield 58%) indicating the role of phosphorus in imparting thermo-oxidative resistance to PF. The enhancement is better when phosphorus is introduced at the monomer stage. The incorporation of bromine, however, brought about an unexpected reduction in the thermal stability of PF (char yield: BrPF, 2%; and BrMPPAF, 26%). Both phosphorus and bromine are found to enhance the LOI values of PF (cured) from 35 to 50, 48, and 56, respectively, for MPPAF, BrPF, and BrMPPAF. A comparison of LOI values of these resins with their char yield suggests a condensed phase mechanism for phosphorus and a vapor phase mechanism for bromine operating during thermal decomposition. © 1994 John Wiley & Sons, Inc.

INTRODUCTION

Phenol-formaldehyde (PF) resins are a class of materials having wide applications in many areas, largely due to their high temperature resistance, high char yield, and moderate flame resistance.^{1,2} PF is one of the few polymers whose production and developmental work have been steadily increasing, with continued interest sustained by active research over the past eight decades. The interest in and consequent growth of PF resins began with the early work of Von Bayer³ and the historic heat and pressure patents of Bakeland.^{4,5} Even today, PF resins continue to be an active field in both academics and industry. Academic interest is centered around (a) improvement in its properties by way of chemical

modifications;⁶⁻⁸ (b) studies related to mechanistic understanding of the curing of phenolics,⁹⁻¹² and (c) the mechanism of decomposition of phenolics.¹³⁻¹⁵

Chemical modification of phenolic resins has been undertaken to improve their thermal behavior.^{6,16} The methods generally used to improve the thermo-oxidative resistance of phenolic resins include: (a) etherification and esterification of the phenolic hydroxyl group; (b) complex formation with polyvalent elements; and (c) replacement of the methylene linking group by heteroatoms. The esterification of phenol-novolac resins with inorganic polybasic acids such as phosphoric acid and boric acid, or with phosphorus oxyhalides, is of particular interest in increasing the heat- and flame-resistance of phenolic resins. The reaction of polyfunctional compounds with PF resins is often found to lead to gelation and consequently only low amounts of the active elements can be incorporated.^{6,16} Moreover, the reaction is also dependent on the nature of PF resins.

* To whom correspondence should be addressed.

These problems of gelation and structural differences could be overcome if chemical modification were effected at the monomer level and then polymerised to obtain the required product. This paper reports the synthesis and characterization of phenolics containing phosphorus and bromine introduced at the monomer stage by well-known reaction schemes. The thermal and flammability behavior of these polymers was studied by thermogravimetric analysis (TGA) and the limiting oxygen index (LOI) method.

EXPERIMENTAL

Materials

Phenol, purchased from BDH Laboratories, was used after distillation under reduced pressure. Phosphorus oxychloride (from S.D. Fine Chem., India) was distilled before use. Bromine (Merck, India), hexamethylenetetramine (Fluka, Switzerland), formaldehyde (BDH Laboratories) and oxalic acid (Merck, India) were used as such without further purification. Toluene and tetrahydrofuran were dried by refluxing with sodium, distilling, and then keeping over sodium wire.

Measurements

The infrared spectra were recorded on a Perkin-Elmer IR spectrophotometer model 882. $^1\text{H-NMR}$ spectra were recorded on a Hitachi R-24 B high-resolution NMR spectrometer in CDCl_3 using TMS as internal reference. $^{31}\text{P-NMR}$ spectra were recorded on a JEOL FX-90 Q FT spectrometer. The GPC data were obtained using Hewlett-Packard 1081 B HPLC equipped with an automatic sample injection system and a differential RI detector. The thermogravimetric studies were carried out on a Dupont Model 951 thermogravimetric analyser in nitrogen and air atmospheres at a heating rate of $20^\circ\text{C min}^{-1}$ with a sample weight of 5–10 mg. The LOI data were determined by using a Stanton Red Croft Model FTA-7101 LOI equipment. Phosphorus estimation was carried out using an ammonium molybdate reagent, and bromine content was determined by Volhard's method.¹⁷

Synthesis

1. Phenol-Formaldehyde Novolak Resin (PF)

PF resin was prepared as reported elsewhere.¹ Phenol (0.1 mol, 9.4 g) 37% aqueous formaldehyde

(0.084 mol, 6.8 g) and oxalic acid (0.001 mol, 0.13 g) were taken in a 250-ml 3-necked flask fitted with a mechanical stirrer and reflux condenser. The reaction mixture was heated under constant stirring at 100°C for 4 h. Water was distilled off and the product was dried in vacuum at 70°C .

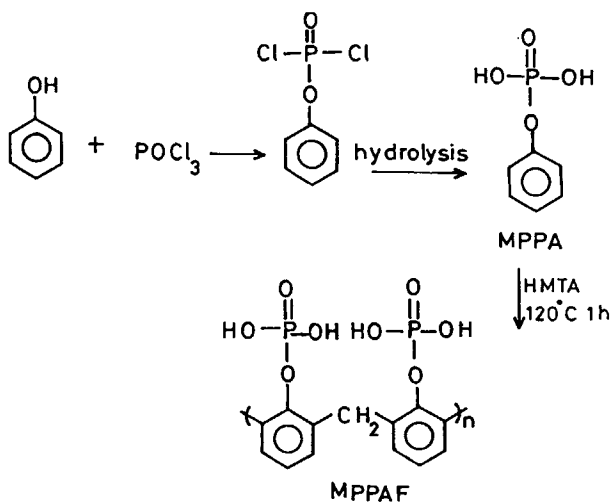
2. Monophenyl Phosphoric Acid-Formaldehyde Resin (MPPAF)

Monophenyl phosphoric acid (MPPA) was prepared as reported elsewhere.¹⁷ Phenol (0.2 mol, 18.8 g) in dry toluene (100 ml) was added dropwise to a refluxing solution of a mixture of POCl_3 (0.24 mol, 36.8 g) and anhydrous AlCl_3 (1 mol %, 0.27 g). The reaction was continued for 3 h. The AlCl_3 was filtered off and the excess POCl_3 and toluene were distilled out to get phenyl phosphorodichloridate. The dichloridate was hydrolyzed with excess cold water to get monophenyl phosphoric acid (MPPA).

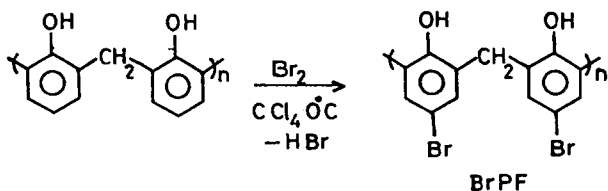
MPPAF was prepared by the reaction of MPPA with hexamethylene tetramine (HMTA) as shown in Scheme 1. MPPA (0.1 mol, 18.8 g) and HMTA (10 wt %, 1.88 g) were mixed well in a 100-ml R.B. flask and heated at 120°C for 1 h to get MPPAF.

3. Brominated Phenol-Formaldehyde Resin (BrPF)

Phenol-formaldehyde novolak resin was brominated to obtain BrPF, as shown in Scheme 2. PF (0.1 mol, 10.4 g) and CCl_4 (50 ml) were taken in a 500-ml



Scheme 1 Synthesis of MPPA and MPPAF. Yield: 90%; IR (neat): $960, 1190\text{ cm}^{-1}$ (P—O—C) stretching, 1250 cm^{-1} (P=O), 1600 cm^{-1} (C=C aromatic), 2950 cm^{-1} (P—OH), 2980 cm^{-1} (CH aliphatic), 3050 cm^{-1} (CH aromatic); $^1\text{H-NMR}$: 3.8 (m, Ar— CH_2 —Ar), 7.0 (m, Ar protons); $^{31}\text{P-NMR}$ —6.0; Phosphorus content: 16.5%.

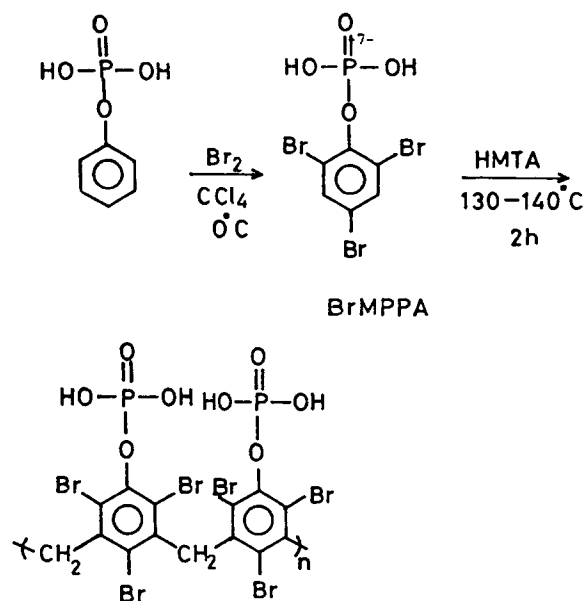


Scheme 2 Synthesis of BrPF. Yield: 95%; IR (neat): 740 cm^{-1} (C—Br) stretching, 1600 cm^{-1} (C=C aromatic) stretching, 2980 cm^{-1} (C—H aliphatic) stretching, 3050 cm^{-1} (C—H aromatic) stretching, 3500 cm^{-1} (C—OH) stretching; $^1\text{H-NMR}$: 3.8 (m, Ar—CH₂—Ar), 5.1 (s, OH), 7.2 (m, Ar protons); Bromine content: 43%.

R.B. flask kept in an ice bath and added to bromine (0.1 mol, 16 g) in 50 ml CCl₄ dropwise with vigorous stirring. The CCl₄ was distilled out and the product dried in a vacuum at 80°C.

4. (2,4,6-tribromo)phenyl Phosphoric Acid-Formaldehyde Resin (BrMPPAF)

Monophenylphosphoric acid (MPPA) was brominated using bromine in CCl₄ to get 2,4,6-tribromophenyl phosphoric acid. MPPA (0.1 mol, 17.4 g) and CCl₄ (100 ml) were taken in a 500-ml R.B. flask kept in an ice bath and added to bromine (0.3 mol, 48 g) in 150 ml CCl₄ dropwise with vigorous stirring.



Scheme 3 Synthesis of BrMPPAF. Yield: 80%; IR (neat): 780 cm^{-1} (C—Br) stretching, $950, 1160\text{ cm}^{-1}$ (P—O—C) stretching, 1250 cm^{-1} (P=O) stretching, 1610 cm^{-1} (C=C aromatic) stretching, 2960 cm^{-1} (P—OH), 2980 cm^{-1} (CH aliphatic); $^1\text{H-NMR}$: 3.8 (s, Ar—CH₂—Ar); $^{31}\text{P-NMR}$: -15.3; Phosphorus content: 7.3%; Bromine content: 56.7%.

The product was stripped off from CCl₄ and dried in a vacuum at 80°C.

BrMPPA was polymerized with HMTA through the meta positions of the phenolic ring (possibly because of the activation of the meta positions by the electronegative bromine). BrMPPA (0.01 mol, 4.1 g) was mixed with HMTA (10 wt %, 0.41 g) in a 100-ml R.B. flask and heated at 130–140°C for 2 h to get BrMPPAF, as shown in Scheme 3.

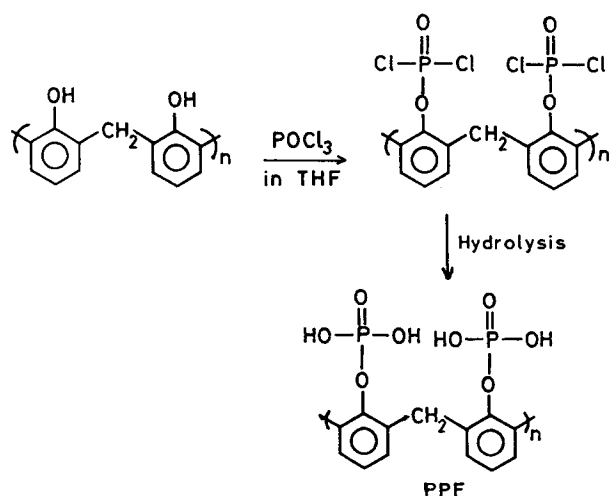
5. Phosphorylated Phenol-Formaldehyde Resin (PPF)

Phenol-formaldehyde resin was phosphorylated with POCl₃ in dry THF to get PPF, as shown in Scheme 4. PF (0.1 mol, 10.6 g) in dry THF (50 ml) was added dropwise to a refluxing solution of a mixture of POCl₃ (0.12 mol, 18.9 g) and anhydrous AlCl₃ (1 mol %, 0.27 g). The reaction was continued for 3 h. The AlCl₃ was filtered off and the excess POCl₃ and THF were distilled out to get the dichloridate. This was hydrolyzed with excess cold water to obtain the phosphoric acid of PF resin.

RESULTS AND DISCUSSION

Synthesis

Modified phenolic resins containing phosphorus and bromine in the main structure were synthesized. The



Scheme 4 Synthesis of PPF. Yield: 90%; IR (neat): $960, 1190\text{ cm}^{-1}$ (P—O—C) stretching, 1250 cm^{-1} (P=C), 1600 cm^{-1} (C=C aromatic), 2950 cm^{-1} (P—OH), 2980 cm^{-1} (CH aliphatic), 3050 cm^{-1} (CH aromatic), 3500 cm^{-1} (C—OH); $^1\text{H-NMR}$: 3.8 (m, Ar—CH₂—Ar), 5.1 (s, OH), 7.0 (m, Ar protons); $^{31}\text{P-NMR}$: -6.2, Phosphorus content: 15%.

Table I GPC Data of the Modified Phenolic Polymers

S. No.	Sample	\bar{M}_n	\bar{M}_w	$MWD = \frac{\bar{M}_w}{\bar{M}_n}$
1	PF	1520	5120	3.36
2	MPPAF	1700	3570	2.1
3	BrMPPAF	7000	9440	1.35
4	BrPF	1600	5280	3.30

monophenyl phosphoric acid-formaldehyde (MPPAF) prepared by the reaction of phenol with POCl_3 in dry toluene readily underwent polymerization with HMTA to give linear and crosslinked products. The soluble and fusible resins (linear resins) were used to characterize the polymers by IR and NMR spectroscopy and GPC (see Experimental section, above).

As tribromophenol did not undergo formaldehyde condensation, brominated PF novolak resin was prepared by the bromination of PF through the ortho/para position available after polymerization. The bromine content (43%) was found to be in accordance with the structure given in Scheme 2.

The 2,4,6-tribromophenylphosphoric acid prepared by the bromination of MPPA did not possess any ortho/para position available for formaldehyde condensation. Surprisingly, however, on heating with HMTA, it gave a linear resin soluble in all common solvents. The occurrence of the vibrations at 2980 cm^{-1} , which is due to CH aliphatic stretching and the presence of two singlet protons ($\text{Ar}-\text{CH}_2-\text{Ar}$) at 3.8 in the $^1\text{H-NMR}$, shows that the formaldehyde condensation has taken place to give the phenolic resin. This could be interesting since generally meta positions are known to be inactive for formaldehyde condensation and, in particular, since halogens are well known to deactivate all nuclear positions in the phenol molecule.^{1,2} The brown-colored, viscous, tacky resin was dissolved in chloroform, precipitated from hexane, and dried in a vacuum at 80°C . Pale-brown colored fluffy powder was obtained. The polymer showed an \bar{M}_n value of 7000, which is quite high for a novolak-type resin (see Table I). The polymer was found to be soluble in chloroform, acetone, tetrahydrofuran, etc. BrMPPAF could not be crosslinked to a thermoset product as there is no site available for reacting with formaldehyde. The phosphorus content (7.3%) and bromine content (56.7%) agree with the theoretical values as calculated from the structure given in Scheme 3.

For a comparative study, the phosphorylated phenol formaldehyde (PPF) resin was synthesized by reaction of PF novolak resin with POCl_3 in dry THF, using AlCl_3 as catalyst. Even though the reaction was carried out with molar excess of POCl_3 , only 90% of the hydroxyl groups were phosphorylated. Hence the IR spectrum of PPF exhibited the characteristic phosphoric acid ester groups at 960 and 1190 cm^{-1} ($\text{P}-\text{O}-\text{C}$), 1250 cm^{-1} ($\text{P}=\text{O}$), and 2950 cm^{-1} ($\text{P}-\text{OH}$), as well as the $\text{C}-\text{OH}$ group at 3500 cm^{-1} (for the unreacted hydroxyl groups of PF resin). The $^1\text{H-NMR}$ spectrum also indicated the $-\text{CH}_2-$ protons at 3.8, $\text{C}-\text{OH}$ protons at 5.1, and aromatic protons at 7.0.

PF, MPPAF, and PPF were crosslinked to thermoset products with HMTA. The curing reaction was carried out at high temperatures (140 – 150°C) using 5–10% HMTA. The cured products were extracted with acetone to remove any unreacted HMTA as well as any linear resin present. The products were again dried in vacuum at 70 – 80°C for a long time. These materials were used with the linear resins for TGA and LOI studies.

Table I gives the molecular weights of the linear resins. \bar{M}_n values are in the 1500–1700 range for the linear resins except for BrMPPAF. Polydispersities are in the range of 2–3.4. In the case of BrMPPAF, the \bar{M}_n value is quite high (7000) and D is only 1.35.

Thermal and Flammability Studies

The thermal degradation of phenolic resins has been studied by a number of workers,^{13,18–26} the most extensive of which are a series of reports by Conley and coworkers.^{13,21–25} Conley¹³ applied IR spectroscopy to char formed at various temperatures from phenolic resins and concluded that whether the pyrolysis reaction occurs in an oxidative or inert atmosphere, the thermal degradation of phenolics takes place through a thermo-oxidative process. Further evidence as to this mechanism was provided by Fife et al.¹⁴ in a CP/MAS solid state NMR spectroscopic work. It was realized quite early that chemical modification of the hydroxyl group with elements such as phosphorus, boron, or heavy metal would enhance thermo-oxidative resistance of phenolics.¹ The present study shows that the thermo-oxidative resistance of phenolics is greatly improved on modification with phosphorus. In order to avoid problems such as gelation, and to ensure a higher loading of phosphorus, modification was effected at the monomer stage. The effects of various flame-retardant elements on the flammability of phenolic

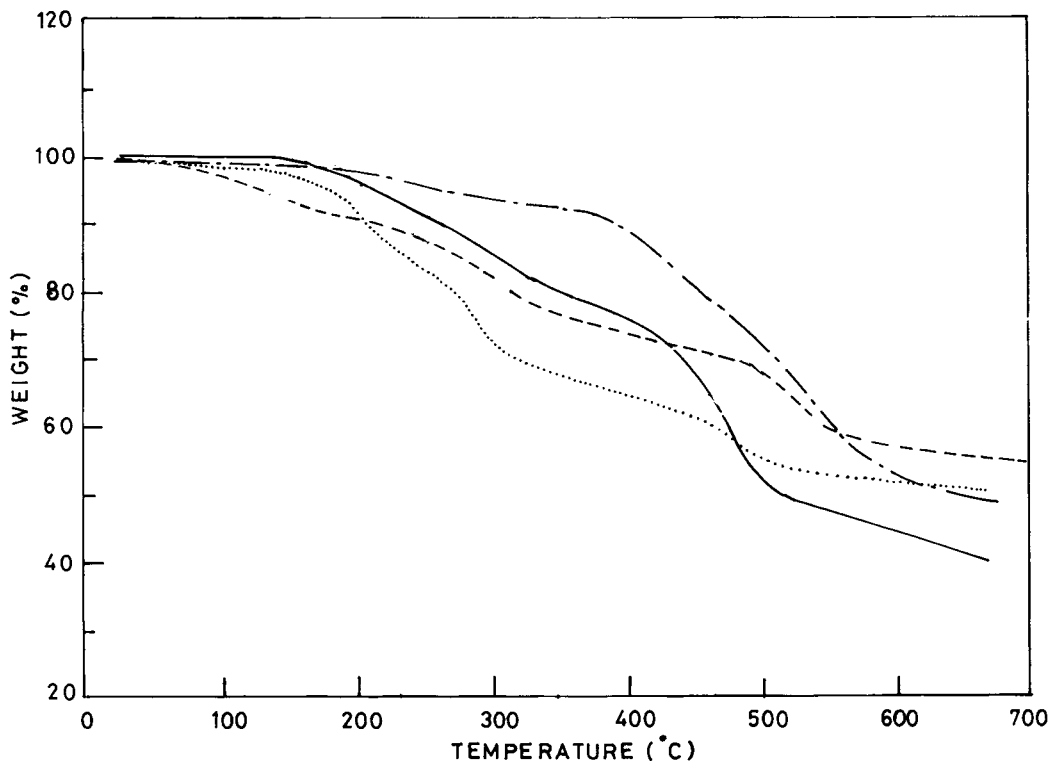


Figure 1 Thermogravimetric traces of: — PF (linear); - - - PF (cured); ····· PPAF (linear); and - - - - MPPAF (cured); in nitrogen.

resins have been reviewed by Conley and Quinn²⁷ and Sunshine.²⁸

The present study compares the thermal and flammability behaviour of PF with MPPAF, BrPF, BrMPPAF, and PPF. The parameters studied are the temperature corresponding to 10% weight loss (T_{10}), the temperature corresponding to 50% weight loss (T_{50}), and the char yield at 600° (C_y).

Figure 1 shows that the TG curve of PF is in agreement with that reported by earlier workers.^{1,13} At 300°C, the decomposition is only marginal; at 400°C, it is rapid; and at 550°C, the char value becomes stabilized. In the case of MPPAF, rapid degradation occurs at 300°C. This might possibly be due to the initial splitting off of phosphoric acid,²⁹ as is observed in the case of phosphated flame retardant polymers. At 400°C there is a sharp change in the slope, showing the faster decomposition typical of phenolic resins. The char yield for cured MPPAF at 600°C is only 58%, compared to 62% for PF. Thus, in a nitrogen atmosphere, the effect of incorporating phosphorus into PF is not very visible in the TG curves. In contrast, the TG curves measured in air (Fig. 2) show that up to 300°C MPPAF is much more resistant to degradation than PF, but

it loses material at a faster rate than PF between 300°C and 500°C. Above 500°C, while the TG curve of PF falls sharply, that of MPPAF stabilizes with only marginal loss of material up to 700°C. Formation of a stable, possibly "highly crosslinked" char²⁷ is indicated. The char yield for MPPAF in air, as expected, showed an enhanced value of 66%, whereas that of PF showed a fall from 62% to 52%. This clearly shows the role of phosphorus in imparting thermo-oxidative resistance to PF. Similar results have been reported by Zibazaki et al.³⁰ for PF resins containing phosphorus introduced at the polymer stage. As phosphorylation of phenolic resin is restricted by the onset of gelation,³⁶ the amount of phosphorus introduced could be lowest; this will be reflected in the thermal stability. Thus PPF prepared by phosphorylation of PF exhibited lower T_{10} (210°C) and C_y (58%) values in comparison to those of MPPAF (T_{10} , 320°C; and C_y , 66%). (See Fig. 2.) Tugetape and Ozgumus³¹ also report a similar case of thermo-oxidative resistance buildup when elements such as titanium and silicone are introduced into phenolic resins. Conley and Quinn²⁷ and Sunshine²⁸ cite a number of similar cases of improvements in flame retardancy of phenolic resins

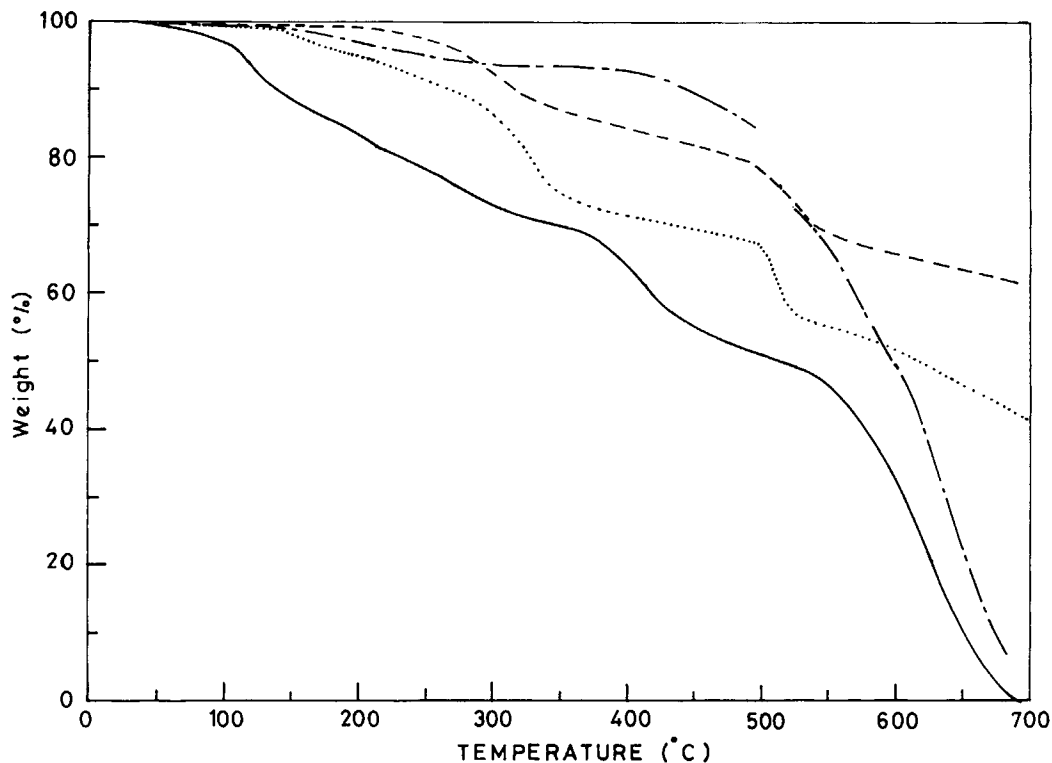


Figure 2 Thermogravimetric traces of: — PF (linear); - · - · PF (cured); · · · · MPPAF (linear); and - - - - MPPAF (cured); in air.

with the incorporation of elements such as phosphorus, boron, aluminium, zinc, etc. An improvement in the thermal stability of a substituted phenol on phosphorylation has recently been reported by Pillai et al.³²

Further understanding of the stabilization of phosphorus-modified phenolic resins vis-à-vis the

introduction of phosphorus at the monomer stage or polymer stage was obtained from a comparison of their char yields with LOI values. The data given in Table II for char yields at 600°C in air show that introduction of phosphorus enhances the char yield (52%) of PF (cured) to 66% and 58%, respectively, for MPPAF (cured) (prepared by introducing phos-

Table II Thermal Stabilities of the Modified Phenolic Polymers

S. No.	Sample	Thermal Stabilities in					
		N ₂			Air		
		T ₁₀	T ₅₀	C _y at 600°C	T ₁₀	T ₅₀	C _y at 600°C
1	PF (linear)	220	440	39	140	515	32
2	PF (cured)	410	—	62	440	—	52
3	MPPAF (linear)	205	480	43	275	—	51
4	MPPAF (cured)	220	—	58	320	—	66
5	BrPF (linear)	185	370	30	170	400	2
6	BrMPPAF (linear)	210	330	31	230	345	26
7	P-PF (linear)	200	475	41	170	530	42
8	P-PF (cured)	300	—	57	210	—	58

Table III Thermal Decomposition Kinetics (in N₂) in LOI Data of the Modified Phenolic Polymers

S. No.	Sample	E	n	LOI
1	PF (linear)	22	0.80	25
2	PF (cured)	36	0.80	35
3	MPPAF (linear)	25	0.80	33
4	MPPAF (cured)	33	0.80	50
5	BrPF	33	0.90	48
6	BrMPPAF	38	0.70	56
7	P-PF (linear)	24	0.85	30
8	P-PF (cured)	32	0.90	46

phorus at the monomer stage) and PPF (cured) (prepared by introducing phosphorus at the polymer stage). The corresponding LOI values (see Table 3) for PF (cured), MPPAF (cured), and PPF (cured) are 35, 50, and 46, respectively. These data clearly show that phosphorus modification of PF carried out at the monomer stage gives a resin (MPPAF) with better thermal stability and flame retardancy than that obtained by modification at the polymer stage (PPF).

The increase in char yield and LOI values of MPPAF over PF is expected of a phosphorus-containing flame retardant that acts in the condensed phase³³ as an acid precursor inducing charring and reduction in the rate of fuel formation.^{29,34} Recently, Annakutty and Kishore³⁵ studied thermal behavior of a series of polyphosphates and concluded that a relationship exists between thermal stability, LOI, and phosphorus content. Earlier, Fennimore and Martin³⁶ had studied the LOI of a series of polymers and concluded that the LOI is related to the char-forming ability of a polymer. Later, Van Krevelen³⁷ made a detailed study and correlated LOI with the concentration of the flame retardant. In a previous study,³⁸ we have shown that LOI is related to the structure and char-forming ability in the case of monocardanyl phosphoric acid-formaldehyde resin. Apparently, the data on thermal stability, char yield, and LOI of PF and MPPAF suggest an interrelationship. However, definite conclusions could be reached only after due consideration of factors pointed out by Cullis and Hirschler³⁹ and, more recently, by Wiel et al.,⁴⁰ who express doubts about such correlations on the grounds that the present day measurement of LOI needs improvement.

In contrast to observations of phosphorus-modified phenolic resins, the introduction of bromine, surprisingly, brings down the thermal stability of PF. This is evident from the TG curves of Figures

3 and 4 and the data given in Table II. Initially there is a stabilisation with T₁₀ increasing from 140°C of PF (linear) to 170°C of BrPF (in air). But the T₅₀ value shows a sharp reduction of 115°C, from 515°C of PF (linear resin) to 400°C of BrPF. The char yield (in air) of BrPF has shown a steep reduction from 32% of PF (linear resin) to 2%. Even if allowance is made for the large molecular weight of bromine that leaves the condensed phase as a decomposition product, this reduction is too large. BrMPPAF also has its char yield (in air) reduced from 51% of MPPAF (linear resin) to 26%. The involvement of bromine or its derivative in altering the mechanism of PF degradation is then indicated. It is also possible that the char is preferentially oxidized by some decomposition product of BrPF/BrMPPAF, possibly hydrogen bromide⁴¹⁻⁴³ (in presence of steam), which is known to be a low-temperature promoter⁴³ of combustion. If this is true, a similar reduction in the char of the structurally related polymer of brominated cardanol-formaldehyde resin (BrCF) recently investigated by us³⁸ could also have been observed. On the contrary, BrCF shows an enhancement of char from 6% of CF (cardanol-formaldehyde resin) to 18% of BrCF on thermal degradation. This difference in behavior between BrPF and BrCF could be understood on the basis of the high oxygen content of BrPF in comparison to that of BrCF where the C₁₅ aliphatic side chain considerably reduces the oxygen content of the system. Similar arguments, however, cannot hold good in the case of polyesters containing both phosphorus and bromine which, on thermal degradation, registered an increase in char content.⁴⁴ The difference in the behavior of bromine-containing polyesters and PF could possibly be attributed to the difference in their mechanism of decomposition.

Although introduction of bromine in PF and MPPAF effected a lowering of thermal stability and char yield, it has, nevertheless, brought about a reduction in their flammability behavior. Table III thus shows that the LOI values of BrPF and BrMPPAF has risen to 48 and 56, respectively. This is in conformity with the general behavior of bromine-containing flame retardants.⁴² As both BrPF and BrMPPAF exhibited only low char yields, the flame retardant effect could result from vapor phase reactions of bromine-containing decomposition products, which might interfere with or poison the flame-propagating reactions and prevent movement of heat flux from flame to fuel.^{41,42,45} The possibility of such free radical reactions taking place in the combustion zone could account for the higher values of activation energy (see Table III) for BrPF (39 K

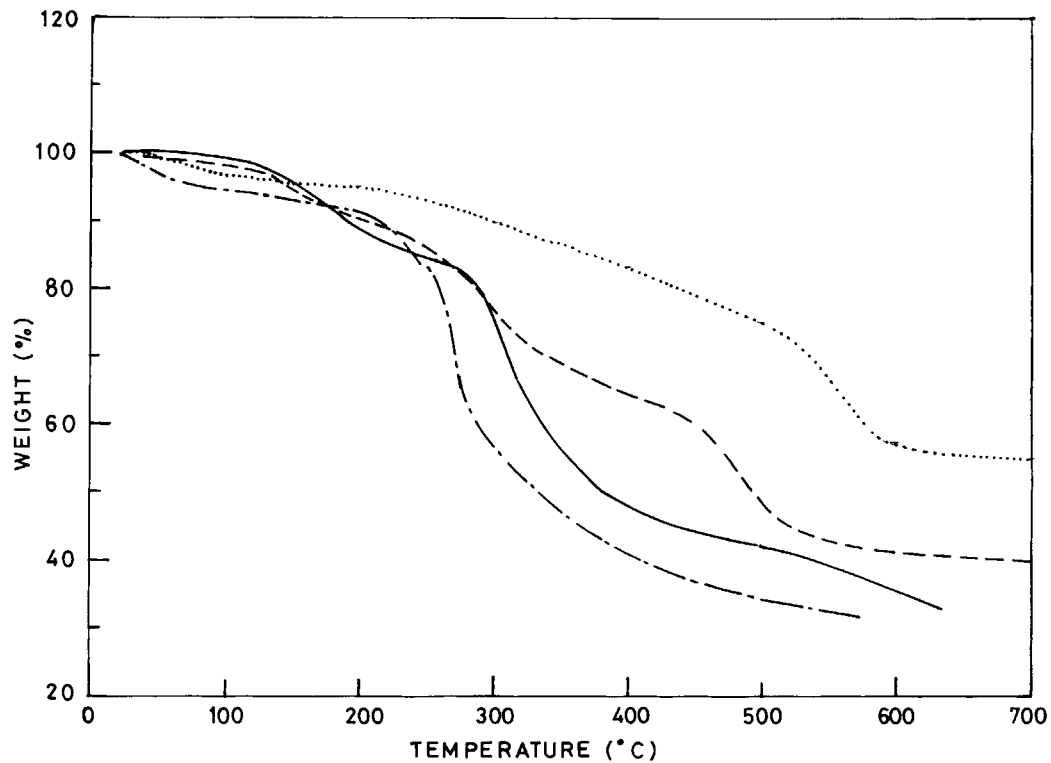


Figure 3 Thermogravimetric traces of: — BrPF; - · - BrMPPAF; ----- PPF (linear); and · · · · PPF (cured); in nitrogen.

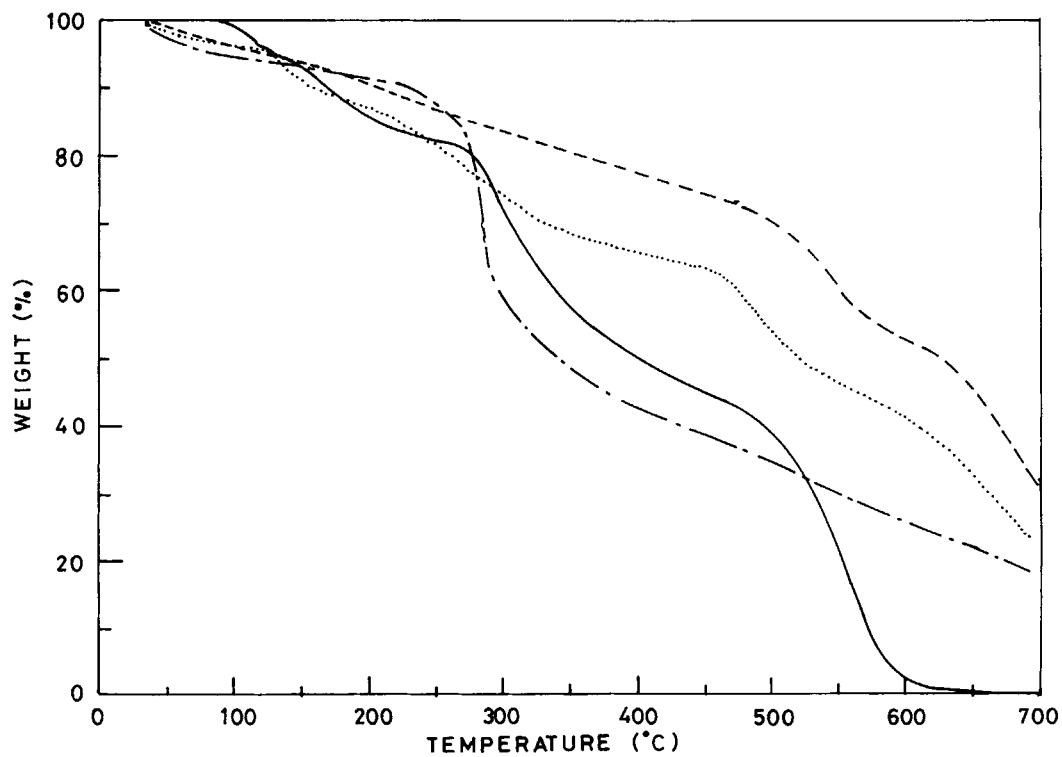


Figure 4 Thermogravimetric traces of: — BrPF; - · - BrMPPAF; · · · · PPF (linear); and ----- PPF (cured); in air.

Cal/mole) and BrMPPAF (38 K Cal/mole) than those of PF (linear resin) (22 K Cal/mole) and MPPAF (linear resin) (25 K Cal/mole). (The activation energies were calculated by the method of Freeman and Anderson as modified by Freeman and Carroll.⁴⁴ In comparison to the linear polymers, the cured systems have higher E values, indicating their higher thermal stability.) Costa and Camino⁴⁷ report a similar case of a reduction in flammability (an increase in LOI) with a decrease in thermal stability in the case of polypropylene on addition of chloroparaffin. While this behavior could be attributed to the aliphatic nature of the polymer, an improvement in thermal stability is generally expected of an aromatic system. Naturally, the T₁₀ value (in air) of BrPF is 30°C higher than that of PF (linear) (140°C). The destabilization of BrPF takes place mainly at higher temperatures.

The present study thus shows that the addition of phosphorus to PF resins at the monomer stage enhances their thermal stability and LOI significantly over that obtained by the addition of phosphorus at the polymer stage. Addition of bromine, on the other hand, while raising the LOI value, brings down the thermal stability and char yield. A comparison of the LOI values (Table III) of these resins with their char yields (Table II) suggests a condensed phase mechanism for phosphorus flame retardation and a vapor phase activity for bromine operating during thermal decomposition of the respective polymers.

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