Some Structure-Property Relationships in Polymer Flammability: Studies of Phenolic-Derived Polymers

Y. ZAKS, JEELEN LO,* D. RAUCHER, and E. M. PEARCE,† *Polytechnic Institute of New York, 333 Jay Street, Brooklyn, New York 11201*

Synopsis

The investigation of the thermal degradation of the char-forming phenol–formaldehyde resins is conducted to provide information for the systematic design of high temperature flame-resistant phenolics. Three different processes of curing are used: (1) Formaldehyde or s-trioxane is reacted with m-substituted phenol–formaldehyde oligomers under acidic conditions to give the methylene bridged-novolac resins. (2) Phenol and m-substituted phenols are reacted with CH_2O under basic conditions and then heated to give the methylene bridged resol resins. (3) p-Terephthaloyl chloride and m- and p-substituted novolac oligomers are reacted to give cured resins with ester linkages. The evaluation of the effect of various substituents indicates that the oxygen index (OI) increases from about 33 for unsubstituted phenolics to about 75 for meta-halogen substituted phenolics. The evaluation of the effect of various crosslinking agents shows that the OI for CH_2O-cured phenolics is 75 as compared to 50 for the trioxane cured phenolics and to 40 for the terephthaloyl chloride cured phenolics. A set of phenolic copolymers with different weight percentage content of halogen substituted phenols are synthesized as novolacs and resols. The results surprisingly indicate no increase of OI for the cured novolac copolymers, whereas the increase is observed for the cured resol copolymers. The activation energy for the thermooxidative degradation of the cured novolacs is about 12–15 kJ/mol lower as compared to that of the cured resols.

INTRODUCTION

Phenolic polymers are char-forming polymeric materials. The particular combination of thermochemical and thermophysical properties of these char-forming polymers have made them of special interest as high-temperature-resistant, flame-retardant polymeric materials.

The thermal degradation mechanistic studies of the char-forming phenol–formaldehyde-derived resins are conducted to provide information for the systematic design of high-temperature flame-resistant phenolic polymers and copolymers.

Many of the available flame retardants for polymers serve as a source of reactive chlorine and bromine.[1] This study has been conducted also for halogen-substituted and unsubstituted phenolic resins.

The oxygen index, a measure of one aspect of polymer flammability, has been shown by Van Krevelan[2] to have a linear correlation with TGA char formation for a large number of char-forming polymers. This reproducible and convenient laboratory method allows us to correlate polymers on a relative flammability basis as well as correlating the results with char formation for many cases.[3–5]

Our study attempts to provide information about the structure and the syntheses of the halogen containing phenol-formaldehyde derived oligomers and their relationships to the flammability of the crosslinked resins.

* In partial fulfillment of the requirements for degree of Doctor of Philosophy.
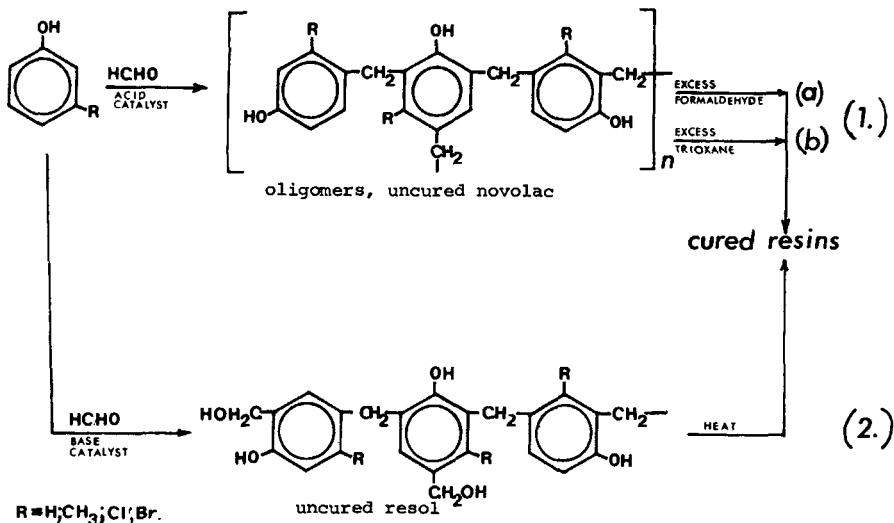† To whom inquiries should be addressed.

Fig. 1. Synthetic approach for the cured Phenolic resin. (1) Two-stage novolac cured resin; (2) one-stage resol cured resin.

EXPERIMENTAL

Synthetic Approaches

The objectives of the present work are

—the syntheses and the characterization of the oligomeric resins;

—the crosslinking of the resins and the characterization of the resulting polymers and copolymers;

—the flammability of these polymers and copolymers.

Phenol–formaldehyde resins based on phenol and monosubstituted phenols are synthesized and cured by three different approaches[6] (Figs. 1 and 2).

1. Formaldehyde (F) or s-trioxane (T) and phenol–formaldehyde (PF) or meta-derived phenol–formaldehyde, namely, m-cresol–formaldehyde (mCF), m-chlorophenol–formaldehyde (mCPF), m-bromophenol–formaldehyde (mBPF) oligomers are reacted to give novolac-cured resins with methylene bridges between aromatic rings (two-stage resins). These cured novolac resins will be named later as X(F)PF—N, X(F)mCF—N, X(F)mCPF—N, X(F)-
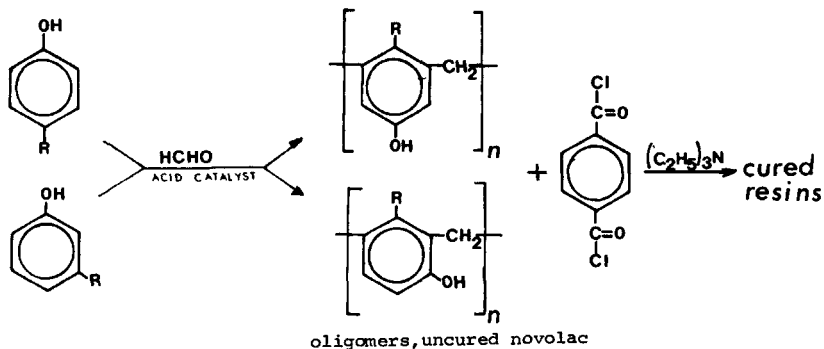

Fig. 2. Synthetic approach for the Phenolic resin cured with terephthaloyl chloride; two-stage cured resin.

mBPF—N, and X(T)PF—N, X(T)mCF—N, X(T)mCPF—N, X(T)mBPF—N in accordance with the crosslinking agents and the starting oligomers.

2. Phenol and m-substituted phenols and formaldehyde (F) are reacted and heated to give resol-cured resins crosslinked via methylene bridges (one-stage resins). These cured resol resins will be named as X(F)PF—R, X(F)mCF—R, X(F)mCPF—R, and X(F)mBPF—R in accordance with the starting phenols.

3. Terephthaloyl chloride is used to cure phenol–formaldehyde (PF), m-cresol–formaldehyde (mCF), p-cresol–formaldehyde (pCF), m-chlorophenol–formaldehyde (mCPF), p-chlorophenol–formaldehyde (pCPF), and m-bromophenol–formaldehyde (pBPF) oligomers to give ester bridges (two-stage resins). These cured resins will be named as X(C)PF, X(C)mCF, X(C)pCF, X(C)mCPF, X(C)pCPF, X(C)mBPF, and X(C)pBPF, respectively.

Preparation of the Oligomeric Resins

Phenols used in novolac preparation include: phenol, m-cresol, p-cresol, m-chlorophenol, p-chlorophenol, m-bromophenol, and p-bromophenol.

For a typical run, one mole of phenolic monomer, 8.3×10^{-1} mol of a 34.8% aqueous solution of inhibited (by 10–15% of methanol) formaldehyde, and 1.5 g of oxalic acid are reacted by refluxing at 95–97°C for 24 h with vigorous stirring. The precipitation of the resin is observed during the reaction. Excess water and a small amount of unreacted phenolic monomer are removed by vacuum distillation. The solid resin is then dissolved in methanol and precipitated into a large amount of acidified water (pH = 3.4). The precipitate is collected, washed with water, and dried under reduced pressure at room temperature. The resins are obtained in powder form. The yields are in the range of 80–85%, except for p-cresol–formaldehyde (25%) and p-bromophenol–formaldehyde (54%).

The oligomeric resins prepared are found to be completely soluble in methanol, ethanol, acetone, methylethyl ketone, ethyl, and butyl acetate, but insoluble in nonpolar solvents such as carbon tetrachloride and toluene.

The characterization data for the oligomers are given in Table I.

TABLE I
Number Average Molecular Weights $(\overline{M_n})$, Melting Temperature (T_m), Temperatures of Degradation (T_d), and % Char Yield at 800°C in N_2 (% CY).

Oligomers	$\overline{M_n}$	T_m (°C)	T_d, (°C)	% CY
Phenol–formaldehyde (PF)	1532	75	390	41
m-Cresol–formaldehyde (mCF)	678	85	270	30
	—	65[a]	220[a]	23[a]
p-Cresol–formaldehyde (pCF)	789	90	350	33
m-Chlorophenol–formaldehyde (mCPF)	3420	75	250	43
	—	60[a]	210[a]	39[a]
p-Chlorophenol–formaldehyde (pCPF)	1313	—	260	43
m-Bromophenol–formaldehyde (mBPF)	1398	75	290	35
p-Bromophenol–formaldehyde (pBPF)	1713	70	230	38

[a] These oligomers are obtained from phenols and s-trioxane.

Crosslinking of the Two-Stage Novolac Resins

Crosslinking with Formaldehyde (Fig. 1, Reaction 1a)

To a resin kettle is added 5.0 g of oligomeric resin, 200 g of 37.8% aqueous solution of inhibited (by 10–15% methanol) formaldehyde, and 3.0 g of p-toluenesulfonic acid. The mixture is heated to 92–94°C and refluxed with stirring for 5 h. The cured resin is then washed with distilled water and methanol.

Crosslinking with s-Trioxane (Fig. 1, Reaction 1b)

To a resin kettle is added a solution of 5.0 g of oligomeric resin; a large excess (36.0 g, 0.4 mol) of s-trioxane, and 3.0 g of p-toluenesulfonic acid in 200 mL of bis(2-ethoxyethyl) ether. The solution is heated at 95–100°C with stirring for 48 hours. The cured resin is washed with distilled water and methanol.

Crosslinking with Terephthaloyl Chloride (Fig. 2)

To a resin kettle equipped with two dropping funnels and a mechanical stirrer is added 5.0 g of oligomeric resin (containing 2.7–4.8×10^{-2} mol of phenolic hydroxyls) in 300 mL acetone. Excess (9.6 g, 4.7×10^{-2} mol) of terephthaloyl chloride in 100 mL of acetone is slowly charged into the solution. Simultaneously triethylamine (9.6 g, 9.5×10^{-2} mol) is added dropwise into the reaction mixture over a period of 15 min. The reaction is kept at room temperature for 12 h. At the end of the reaction the crosslinked resin precipitates from the solution. The product is washed successively with acetone, distilled water, dilute oxalic acid solution, distilled water, and acetone. The final resin is then dried under reduced pressure.

Crosslinking of the One-Stage Resol Resins

The reaction scheme is shown in Figure 1. To a 1-L flask is added 1.06 mol of phenolic monomers, 2.47 mol of 37.8% formaldehyde, and 12 g of a 25% aqueous sodium hydroxide solution. The mixture is heated to refluxing temperature for 20 min. The reaction mixture is neutralized and acidified to pH~4.5 by the addition of approximately 19.5 g of 51% aqueous lactic acid solution. The excess water is then removed by vacuum distillation at 40–50°C for 2 h. During the dehydration process the resin is withdrawn every 15–20 min to determine the extent of condensation. The end point is taken when samples of the resin placed on the hot plate at 160°C gelled in less than 70 s or when the cooled resin becomes brittle and nontacky at room temperature. This resin when heated at 80–110°C in an oven gives a clear, hard casting. The characterization data of the phenolic polymers are shown in Table II.

Preparation of the Crosslinked Copolymers

The crosslinked copolymers are prepared in the same manner as the pure polymers.

TABLE II
Characterization of Cured Phenolic Polymers: Oxygen Index (OI), % Char Yield at 800°C, N_2 (% CY)

Cured phenolic polymers	Methods of crosslinking (see Figures 1 and 2)											
	1(a)			1(b)			2			3		
	Notation	OI (%)	% CY	Notation	OI (%)	% CY	Notation	OI (%)	% CY	Notation	OI %	% CY
Phenol-formaldehyde	X(F)PF—N	34	56	X(T)PF—Nᵃ	35	57	X(F)cPF—R	36	54	X(C)PF	25	44
m-Cresol-formaldehyde				X(T)mCF—Nᵃ	33	51				X(C)mCF	23	34
m-Chlorophenol-formaldehyde	X(F)mCPF—N	75	50	X(T)mCPF—Nᵃ	26	33	X(F)mCPF—R	74	50	X(C)mCPF	39	39
				X(T)mCPF—Nᵇ	43	48						
m-Bromophenol-formaldehyde	X(F)mBPF—N	75	41	X(T)mBPFᵃ	50	38	X(F)mBPF—R	76	46	X(C)mBPF	43	40
p-Cresol-formaldehyde										X(C)pCF	25	39
p-Chlorphenol-formaldehyde										X(C)pCPF	42	46
p-Bromophenol-formaldehyde										X(C)pBPF	55	40

ᵃ The time of crosslinking = 22 h.
ᵇ The time of crosslinking = 47 h.

Novolac-Cured Copolymers

The mixture of the oligomers (PF and mCPF or mBPF) is reacted with excess formaldehyde under acidic conditions to yield the crosslinked copolymers which will be named below in accordance with crosslinking agent and the halogenated oligomers as X(F)PmCPF—N or X(F)PmBPF—N, respectively. The ratio of the unsubstituted phenol–formaldehyde oligomer (PF) to halogen substituted oligomers (mCPF or mBPF) is varied from 0–100 wt %.

Resol-Cured Copolymers

The mixture of phenolic monomers (phenol and m-chlorophenol or m-bromophenol) is reacted with formaldehyde under basic conditions to give the corresponding crosslinked copolymers, which will be named as X(F)PmCPF—R and X(F)PmBPF—R. The amount of the halogenated and the nonhalogenated phenolic monomers are varied to give copolymers with different amounts of halogen content (from 0–100 wt %).

Phenolic Copolymers Cured via Ester Linkages

The mixture of PF and m- or p-substituted oligomers (mCPF, mBPF, or pBPF) is reacted with p-terephthaloyl chloride in the presence of triethylamine to give the corresponding copolymers [X(C)PmCPF, X(C)PmBPF or X(C)-PpCPF, and X(C)PpBPF]. The ratio of the unsubstituted phenol–formaldehyde oligomer to the halogen substituted oligomers is 50:50 wt %.

The characterization data of the copolymers are given in Table III.

Measurements

Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) of the oligomers, the polymers and the copolymers are performed using DuPont 910 and 900 thermal analyzer with a heating rate of 10°C/min under nitrogen.

The char yield of a polymer has been defined as the char residue in wt % at 800°C in a TGA measurement under nitrogen atmosphere.[2,3] Thermooxidative degradation studies of the polymers are conducted by using TGA under 100 mL/min of flowing air.

The melting temperature (T_m) and the decomposition temperature (T_d) are measured as the on-set temperatures from DSC and TGA curves, respectively.

The number-average molecular weights ($\overline{M}_n$) are determined by NMR measurements using Varian HR/HTC TT-220 proton NMR spectrometer. The number of repeating units is calculated from the ratio of total aromatic protons and hydroxyl protons to the total number of methylene protons.[7]

Measurements of the oxygen index are taken with the use of an oxygen index flammability gauge (General Electric Co., model #280 FM11B).[8]

The IR spectra of oligomers and resins have been obtained from KBr pellets and analyzed by Fourier transformer infrared spectroscopy (FT–IR). The cured resin content (% crosslinking) of synthesized polymers and copolymers are determined by extraction with acetone in a Soxlet apparatus for 24 h.[9]

TABLE III

Characterization of Cured Phenolic Copolymers: Oxygen Index (OI), % Char Yield at 800°C, N$_2$, % Crosslinking (% Cross.)

Copolymer	(mole ratio) of phenol hal–phenol	Methods of crosslinking (see Figure 1)								
		Novolacs			Resols			Terephthaloyl chloride curing		
		OI(%)	% CY	% cross	OI(%)	% CY	% cross	OI(%)	% CY	% cross
Phenol–meta-chlorophenol formaldehyde		X(F)PmCPF—N			X(F)PmCPF—R			X(C)PmCPF		
	20/80	40	49	95.1	44	63	100			—
	30/70	36	39	90.1						
	40/60	38	48	93.1						
	50/50	35	52	70.8	50	63	100	28	43	
	70/30	46	56	96.8	60	60	100			
Phenol–para-chlorophenol formaldehyde								X(C)PpCPF		
	50/50							28	43	—
Phenol–meta-bromophenol-formaldehyde		X(F)PmBPF—N			X(F)PmBPF—R			X(C)PmBPF		
	25/75	36	49		49	59	100			—
	50/50	38	52	96.7	62	63	100	30	45	
	75/25	42	52		67	62	100			
Phenol–para-bromophenol-formaldehyde								X(C)PpBPF		
	50/50							30	44	—

RESULTS AND DISCUSSION

Relationships of Phenolic Polymers with Flame-Retardant Properties and Methods of Preparation

Phenolic novolac resins (two-stage resins) are selected for this study to understand the relationship between the structure of the oligomers (first-stage) and the flammability of the cured resins based on these oligomers (second-stage).

The reaction of formaldehyde with unsubstituted phenol leads to either soluble oligomers or crosslinked resins since condensation occurs at either ortho or para positions.[6]

The methylene bridges formed during the condensation of unsubstituted phenol and formaldehyde can result in three different forms assigned as para–para' (I), ortho–para' (II), and ortho–ortho' (III) depending upon the position of the hydroxyl groups on the adjacent aromatic rings relative to the methylene bridge.
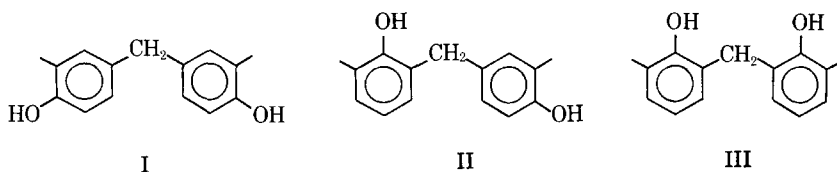
Monosubstituted phenol (ortho or para) can react with formaldehyde to give only low molecular weight products (novolac oligomers). These o-substituted (IV) and p-substituted (V) novolac oligomers cannot further react with formaldehyde to give resins. The crosslinking can be achieved only through the hydroxyl groups.
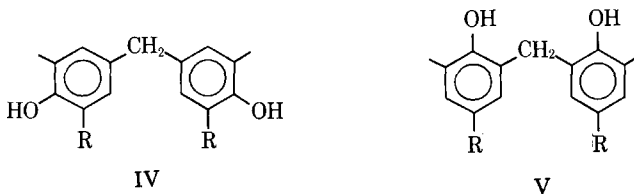
Meta-substituted phenols having available ortho and para positions can react with formaldehyde to give oligomers (VI) and the cured resins.
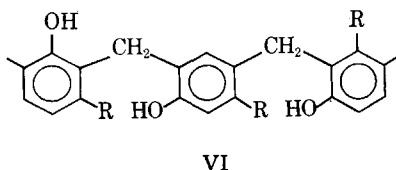
This study is initiated with a goal to modifying the flame-retardant behavior of phenolic resins by the use of substituents. The structure of a typical unsubstituted resin indicating possible substitution types and major groups presented in the cured resin[10] is shown in Figure 3.
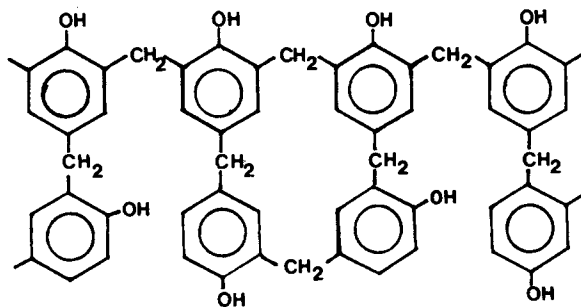
Fig. 3. Structure of typical Phenolic resin cured via methylene bridges.

The structure of a typical unsubstituted phenolic resin cured with tereph-thaloyl chloride has been proposed by Lei and Khamis[11] as occurring by inter- and intramolecular reactions with phenolic hydroxyls to form ester bridges (Fig. 4).

The structures of the oligomeric novolacs are studied by NMR spectroscopy. The absorptions due to the phenolic hydroxyl protons are observed in the region from 8.00 to 9.25 ppm. The aromatic protons are observed in the region from 6.25 to 7.50 ppm. The methylene protons (except for these of para-substituted phenolic oligomers) can be resolved into peaks due to p,p'-, o,p', and o,o'-methylene bridges (I, II, and III, respectively).
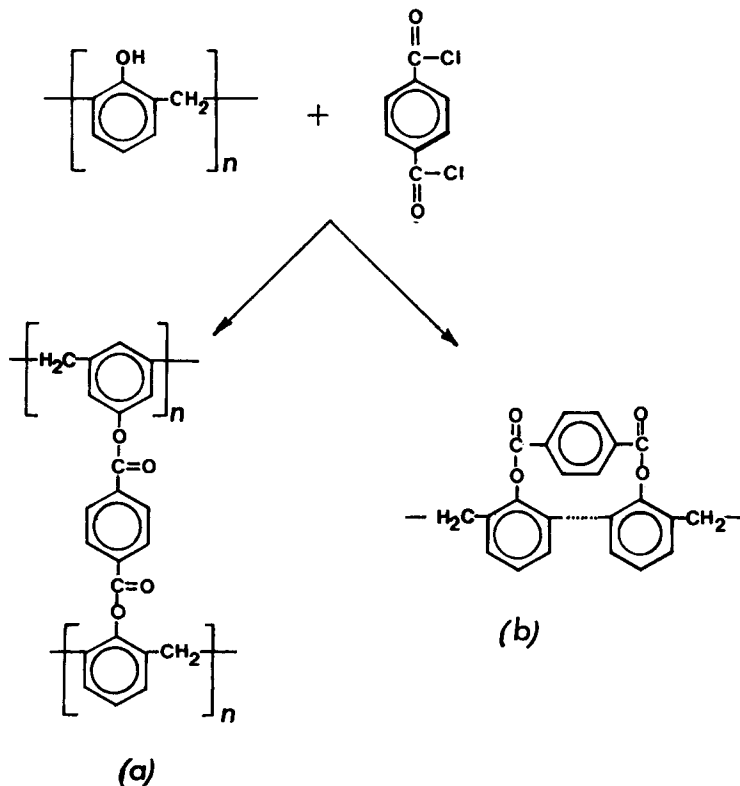
Fig. 4. Structure of Phenolic resin cured via ester bridges: (a) intermolecular crosslinking, (b) intramolecular crosslinking.

The o,o'-resonance is observed as a shoulder on the o,p'-peak. Similar observations have been found by Hirst et al.[12]

The substituent groups have altered the chemical shift of the methylene protons slightly. The differences in shift are related to the field effect arising from the substituents. The methyl groups (+I) move the chemical shift of methylene protons to a higher field (3.87 ppm for pCF). On the other hand, halogens (−I) move the chemical shift to a lower field (3.93 ppm for pBPF and 4.00 ppm for pCPF). The effects of halogens are in agreement with the order of electronegativity, that is, Cl > Br. For unsubstituted and meta-substituted phenolic oligomers the chemical shift of methylene protons of a particular linkage, for example, ortho-' methylene bridge, also increase in the order of electronegativity of the substituents: −Cl (4.25 ppm) > −Br (4.12 ppm) > −H (3.87 ppm) > −CH$_3$ (3.75 ppm).

The field effect arising from the electronic dipole moment of the substituents is dependent on the orientation of the dipoles and charges with respect to the C—H bond. The meta substituents are at the para position with respect to the methylene protons. Therefore, they have a greater influence on the chemical shift of the methylene protons than the para substituents.

The possible side products such as, hemiformals, polyformals, and the dibenzyl ether type of bridges will give rise to the absorptions in the 4.70–5.20 ppm region.[12] The absorptions are not found in the NMR spectra of all the samples being studied.

A number of studies have been concerned with developing correlations between the structure of the polymers and their char formation. Char yield thus becomes an important measurement in the flammability studies. Van Krevelan has developed a linear relationship between char yields and oxygen indices of polymers. The linear relationship is valid for halogen-free polymers only.[2] In this work the OI's are determined for the sets of crosslinked phenolic polymers, and the results are correlated to char yields (Fig. 5). An approximate correlation between OI and CY is found among the halogen-free phenolics according to the following relationship:

$$\% \text{ OI} = 2.4 + 0.57 \ (\% \text{ CY})$$

The meta- and para-cresol formaldehyde resins give slightly lower OI than the unsubstituted phenolics. As a general observation, the halogenated phenolics are found to have higher OI with lower CY than the nonhalogenated phenolics. The increase of OI without the change of CY has been observed in the case of the chlorine-containing aramides as compared to nonhalogenated aramides.[13]

It is found that the major factor influencing the flammability of the halogenated phenolics is the crosslinking agent. The halogen-containing resins cured via methylene bridges (novolac and resol types) give the highest OI. The resins cured via ester bridges give lower OI than novolacs and resols. The results also show that the s-trioxane-cured resins (except for PF) have lower CY and OI than the corresponding formaldehyde-cured resins. The relative amount of change in char formation due to the use of different crosslinking agent can be seen in the thermograms, as shown in Figure 6. The polymer X(T)mCPF—N has considerably lower thermostability with a weight loss of 35% at 180°C (Curve 1). The formaldehyde cured resin (Curve 3) has a relatively low weight loss.
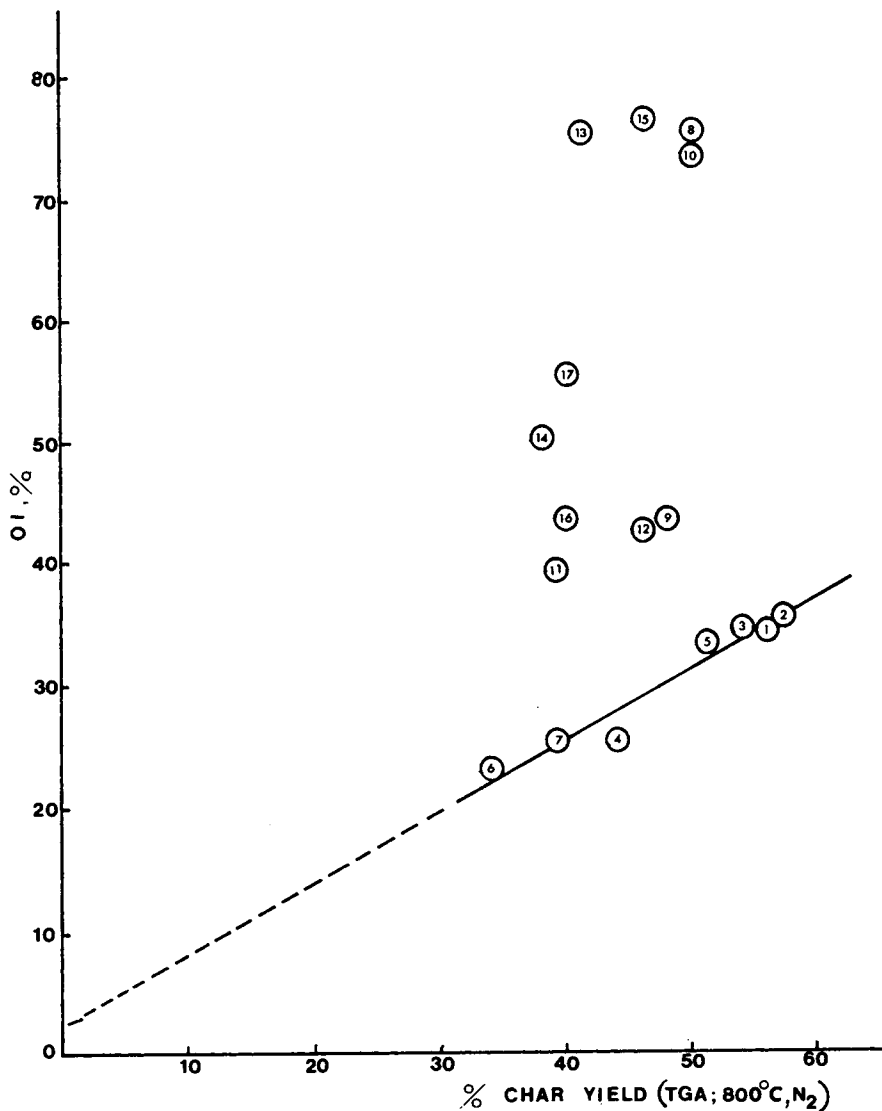
Fig. 5. Correlation between oxygen index (OI) and percent char yield (CY). (1) X(F)PF—N; (2) X(T)PF—N; (3) X(F)PF—R; (4) X(C)PF; (5) X(T)mCF—N; (6) X(C)mCF; (7) X(C)pCF; (8) X(F)mCPF—N; (9) X(T)mCPF—N; (10) X(F)mCPF—R; (11) X(C)mCPF; (12) X(C)pCPF; (13) X(F)mBPF—N; (14) X(T)mBPF—N; (15) X(F)mBPF—R; (16) X(C)mBPF; (17) X(C)pBPF.

Both resins are compared with the oligomer (Curve 2). It is assumed that the lower thermostability of s-trioxane-cured resins is due to the ether linkages in the crosslinked structure. The infrared spectrum of X(T)mCPF (Fig. 7) shows a strong ether absorption at 1100 cm^{-1}, which is observed as a weak peak in the spectrum of X(F)mCPF. The methylol absorption at 1000 cm^{-1} is relatively stronger. The bands at 1250–1200 cm^{-1} and 940–900 cm^{-1} (strong) are characteristic of aromatic ether such as methylene-1,2-dioxybenzenes.[14] The relatively low intensity of the OH stretching absorption indicates that the hydroxyl groups are involved in the s-trioxane crosslinking reactions. From the above
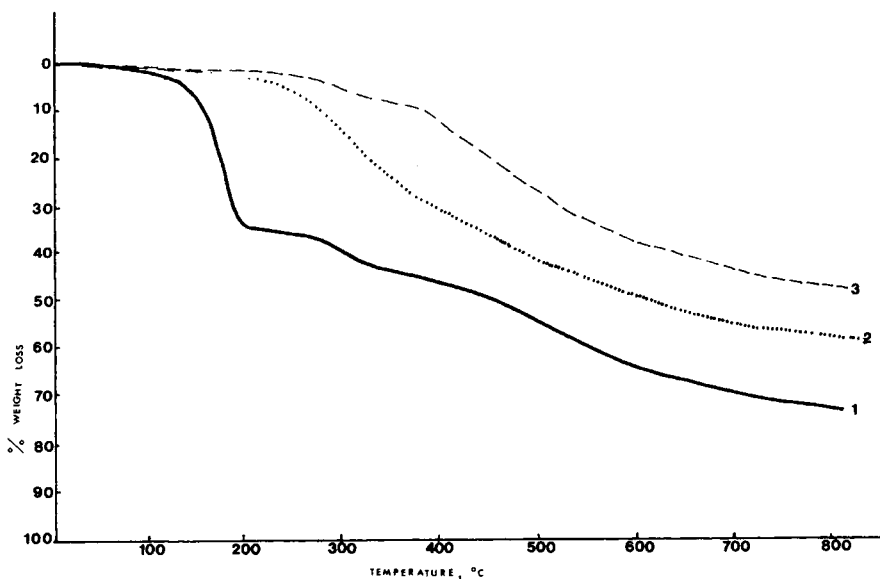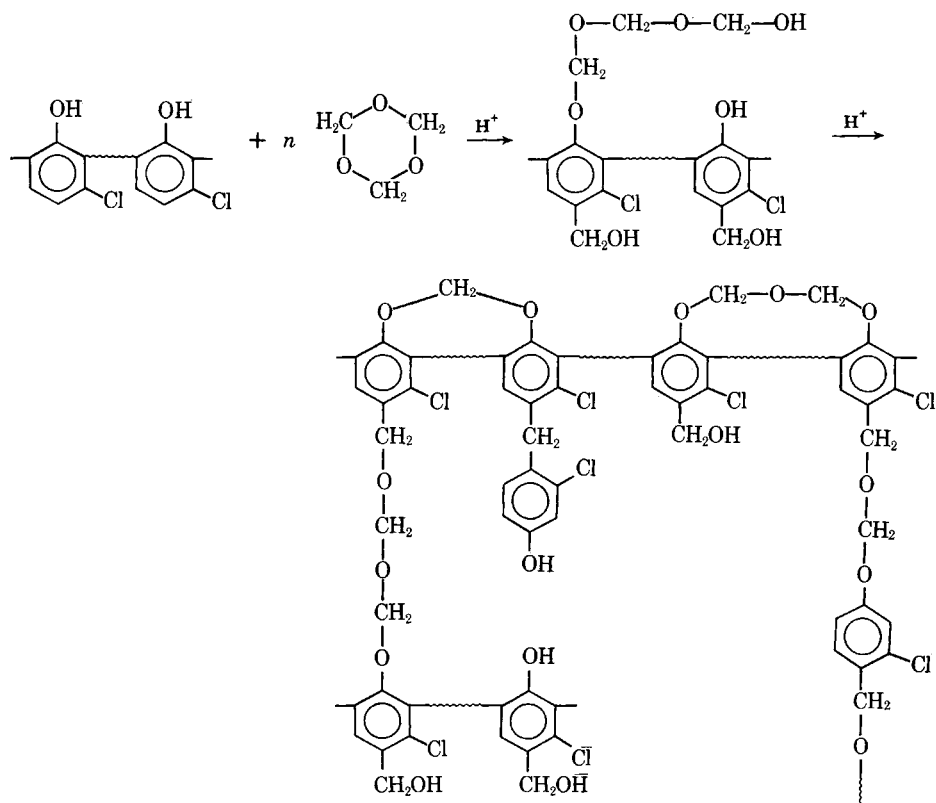
Fig. 6. Weight losses by thermal decomposition (TGA,N₂) of different chlorinated Phenolic resins: (1) X(T)mCPF—N; (2) mCPF; (3) X(F)mCPF—N.

observations the mechanisms for such reactions can be assumed to proceed in the following way:
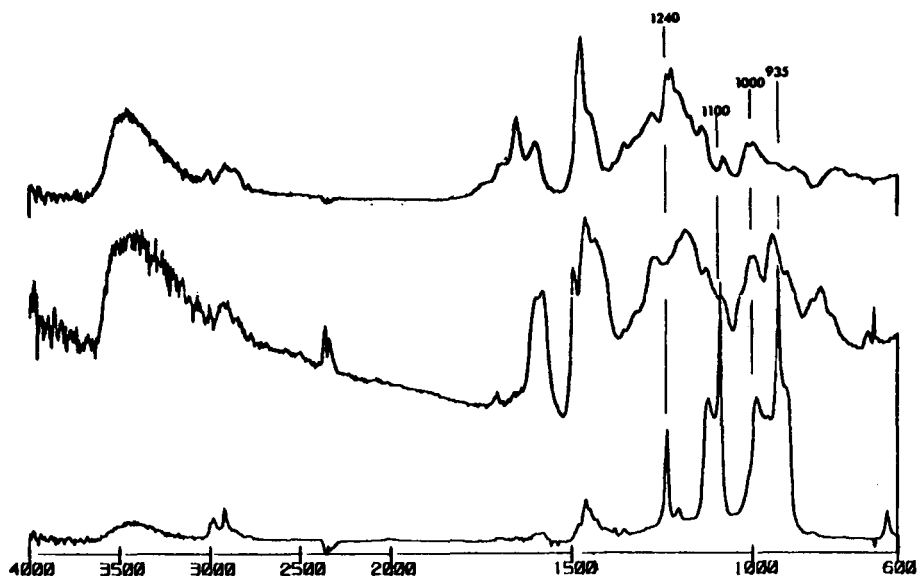
Fig. 7. IR spectra of (a) X(T)mCPF; (b) mCPF, and (c) X(F)PF; KBr pellet.

The curing of the oligomers with terephthaloyl chloride allows us to determine the influence of the position of the substituent on OI. In Table IV are given the thermal properties of all the polymers cured with terephthaloyl chloride. The p-substituted phenolics give higher OI and higher temperature for 50% weight loss than the corresponding m-substituted phenolics.

Relationship of Phenolic Copolymers with Flame-Retardant Properties and Methods of Preparation

The halogenated novolac and resol polymers give a higher OI. It is interesting to know the flame-resistant properties obtained from copolymer systems containing these halogenated resins. For this purpose a set of phenolic copolymers containing 0–100% halogenated and unhalogenated phenols have been synthesized and characterized (Table III).

TABLE IV
Thermogravimetric Analysis of Phenolic Polymers Cured with Terephthaloyl Chloride

Polymer	Temperature 50% wt loss (°C)	Char yield at 800°C, N$_2$ (%)	T_g (°C)	OI (%)
X(C)mCF	520	34	410	23
X(C)pCF	550	39	480	25
X(C)mCPF	570	39	300	39
X(C)pCPF	740	49	440	42
X(C)mBPF	540	40	440	43
X(C)pBPF	570	37	440	55

An anomalous effect is found in the OI of these systems at higher concentrations of halogenated phenols. As shown in Figure 8, the OI value of samples prepared by a resol copolymerization shows a proportional increase with halogen content (Curves 2 and 3). In contrast, the OI's of novolac copolymers and mixture of halogenated and nonhalogenated polymers show a plateau effect for the OI values for composition containing 0–80% halogen phenol (Curves 1 and 1a, respectively). The reason for this effect is presently not clear.

Thermal properties obtained from the TGA data for novolac and resol copolymers are essentially not different.

Selected samples of cured novolac and resol resins are analyzed by FT–IR. Many articles have appeared in the literature on the identification of phenolic resins by means of infrared spectroscopy. Secrest[15] has summed up the available results in the field and supplemented these with his own findings. These results provide useful information for the assignment of the absorption bands in this study.

In Figures 9 and 10 are presented the FT–IR spectra of halogen-free phenolic polymers and the halogen-containing phenolic copolymers which are synthesized by all three curing processes. Also are shown the spectra of corresponding oligomers. Both the phenolic and the aliphatic hydroxyl groups absorb strongly in the region of 3600–3100 cm^{-1}. The aliphatic hydrogens can be observed as
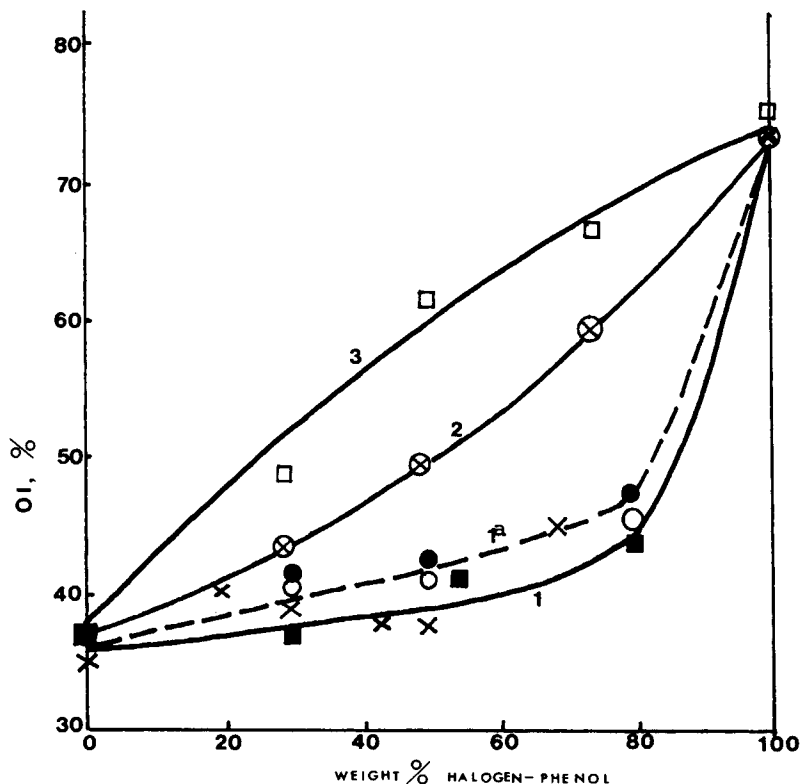

Fig. 8. Correlation between oxygen index (OI) and weight percentage of halogenated phenol: (1) (X AND ■) X(F)PmCPF—N and X(F)PmBPF—N, respectively; (1a) (O and ●) mixtures of X(F)PF—N + X(F)mCPF—N, and X(F)PF—R + X(F)mCPF—R, respectively; (2) (⊗) X(F)-PmCPF—R; (3) (□) X(F)PmBPF—R.
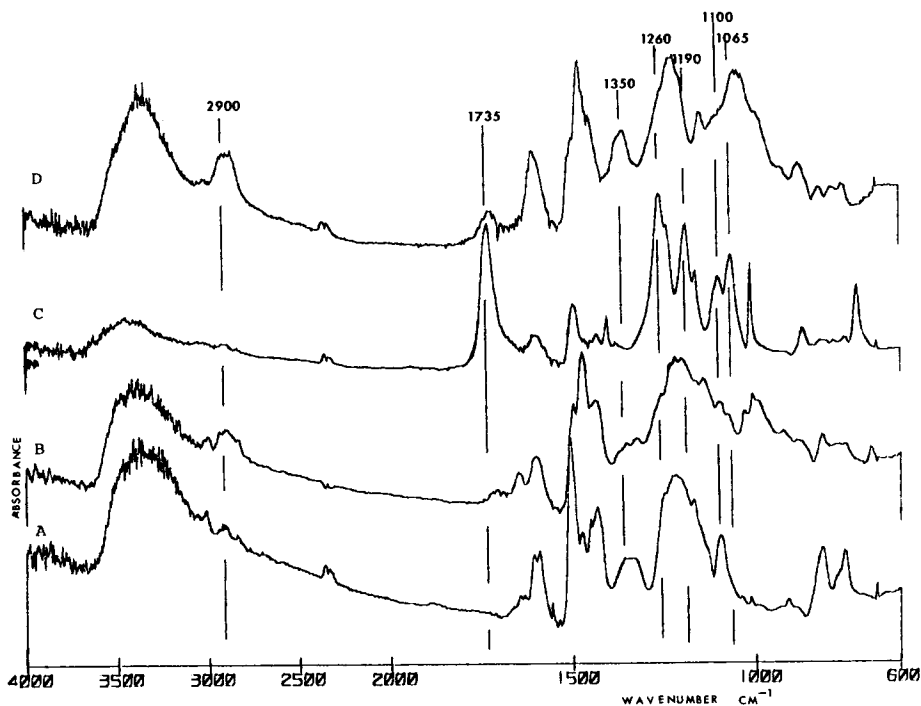
Fig. 9. IR spectra of PF (A), X(F)PF—N (B) X(C)PF (C), and X(F)PF—R (D).

a weak peak at 2900 cm^{-1}. The 1600 cm^{-1} band involves "quadrant stretching" of the benzene ring C$\doteq$C bands. The intensity of the absorption is dependent on the nature and the position of the substituents. The absorption is stronger for meta-substituted phenols because of the dipole moment change provided by the unsymmetrical substituents. Two bands in the region of 1550–1400 cm^{-1} are due to semicircle stretching of the benzene ring. The band at 1450 cm^{-1} is stronger in the meta-substituted phenolic resins. The band between 1400–1300 cm^{-1} is assigned to the OH deformation of phenol. This band is absent in the spectrum of X(C)PF in which the hydroxyl groups are reacted with the curing agent, while it remains in the spectrum of the resin cured through methylene linkages. Substituted phenolic give rise to an absorption band in the region of 1300–1180 cm^{-1} due to C—O stretching vibration of phenol. Depending on the positions of substituents, the intensity and the position of the absorption of phenols vary. The m-substituted phenol absorbs strongly at 1300–1250 cm^{-1}. The band at 1100 cm^{-1} arises from the ether groups.[15]

In the formaldehyde-cured resin the changes are observed as in increased absorption at 2900 cm^{-1} from the methylene CH stretching, 1700 cm^{-1} (weak) from the aldehyde carbonyl group which is developed by splitting of the ether linkages, and 1000 cm^{-1} from the methlol groups. These results are in agreement with the crosslinked structure (Fig. 3).

The cured resol resins have an additional absorption at 1065 cm^{-1}, which is attributed to the ether linkage.[9] In cured novolac resins the intensity of this peak is relatively small.

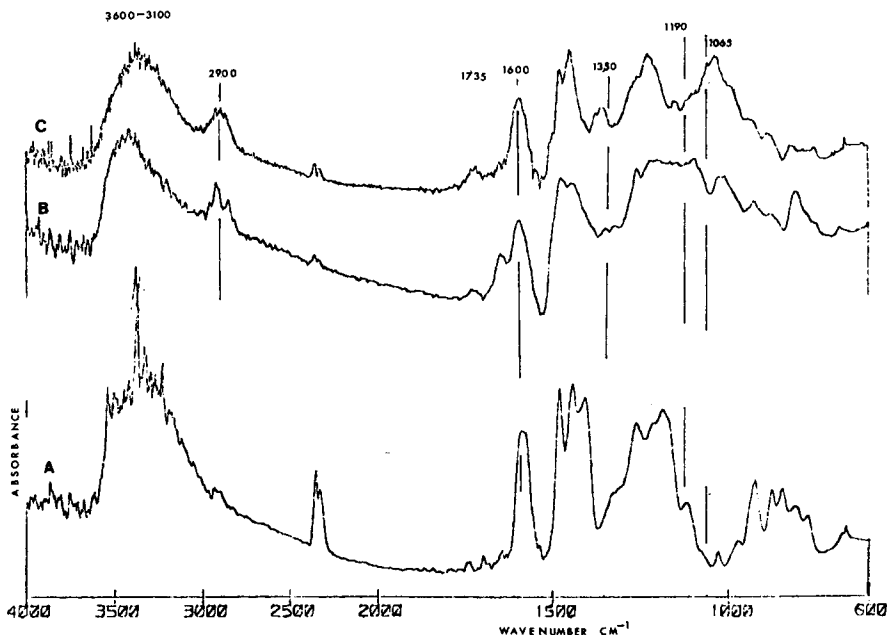The curing of phenolic resins with terephthaloyl chloride may have occurred

Fig. 10. IR spectra of mBPF (A), X(F)PmBPF—N (B) and X(F)PmBPF—R (C).

inter- and intramolecularly with hydroxyls to form esters.[11]   The resulting resin
is expected to give absorptions at 1735, 1260, 1190, and 1065 cm^{-1} due to the
carbonyl groups, the ester C—O groups, ϕ—C—O, and C—O—C, respectively
(Fig. 9).

   Conley[10] has shown that the course of the oxidative degradation of phenolic
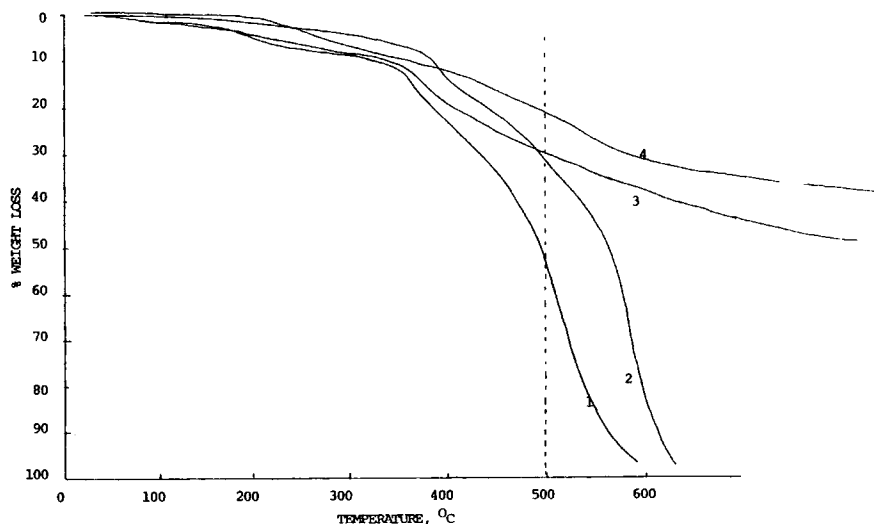novolac resins is essentially the same as that of a phenolic resol resin, as shown

Fig. 11. Weight loss by thermal decomposition (TGA,N$_2$) and by thermooxidative degradation
(TGA, air) of cured novolac copolymers, ratio PF/hal—PF=50/50. Air: (1) X(F)PmBPF—N;
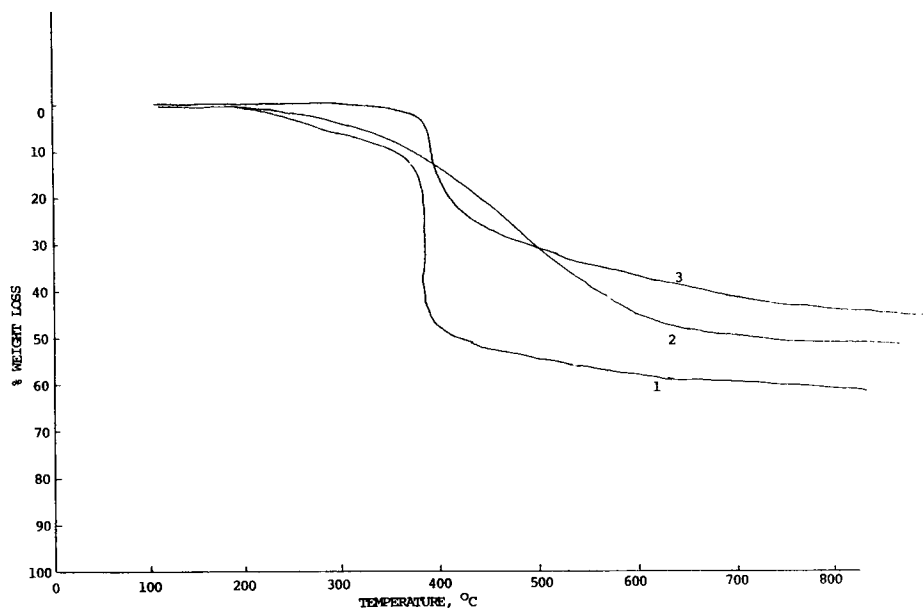(2) X(F)PmBPF—R; N$_2$: (3) X(F)PmBPF—N; (4) X(F)PmBPF—R.

Fig. 12. Weight losses by thermal decomposition (TGA,N_2) of X(F)PmBPF—N, ratio PF/hal—PF=70/30.   (1) Before extraction; (2) after extraction with DMF; (3) after extraction with acetone.

by the changes in the IR spectra.   The same carbonyl groups appear at the same frequencies in the identical order of appearance.   Therefore, it is convenient to speak of both types of phenolic resins in general when discussing the course of degradation, since no differentiation can be made by infrared analysis.

Thus, the absence of differences in oxygen indices of novolac and resol polymers are connected with the similar chemical structure of these polymers and copolymers as shown by IR spectra.   As far as the phenolics cured via ester bridges are concerned, lower OI's are connected with the lower thermostability of the ester linkages.   It can be assumed that the chemical structure and the thermal properties which are found to be approximately equivalent cannot be the reason for the difference in flame-retardant behavior of the polymers, both of the novolac and resol types.

Taking into account the fact that the novolac copolymers are synthesized from the oligomers but that the resol copolymers are synthesized from the monomers, it is assumed that the reason for this difference is related to the incompatibility of the novolac oligomers.   Therefore, the polymerization of the novolac oligomers occurs under heterogeneous conditions while the polymerization of resol phenolics occurs under homogeneous conditions.   From this point of view it is easy to understand the difference in the percent of crosslinking for both corresponding cases.   For resol copolymers the degree of crosslinking is always equal to 100% while for novolac copolymers this level is never obtained (Table III).

The course of the thermal degradation for the novolac and the resol copolymers are essentially similar.   However, the difference in the thermooxidative behavior of the copolymers obtained by TGA measurements in an air atmosphere is well noticeable in the temperature range of 400–500°C (Fig. 10).

The activation energy for the copolymers obtained from thermooxidative isotherms at different temperatures are

$$X(F)PmBPF\text{—}N\ (50/50) \quad 92 \pm 5 \text{ kJ/mol}^{-1}$$

$$X(F)PmBPF\text{—}R\ (50/50) \quad 105 \pm 7 \text{ kJ/mol}^{-1}$$

$$X(F)PmCPF\text{—}R\ (50/50) \quad 98 \pm 5 \text{ kJ/mol}^{-1}$$

Another reason which can account for the decreased OI for the novolac co-polymers is the simultaneous formaldehyde polymerization to para-formaldehyde which is known to be thermally unstable. The presence of para-formaldehyde is shown by $DSC(T_m)$ and TGA data. The thermograms of the extracted and the non-extracted X(F)PmBPF (ratio 70/30) show the differences in char formation (Fig. 12). The higher char yields for the samples after the extraction with DMF and acetone are presumably due to the elimination of para-formaldehyde. The results allow us to suggest that the source of the differences in thermal stability of the novolac and the resol copolymers is the formation of para-formaldehyde rather than the chemical structures of the resins. It appears that the resol process of copolymerization gives products with better flame resistance.

References

1. S. Salman and D. Klempner, *Plastics Eng.*, **XX**, 39 (1979).

2. D. W. Van Krevelan, *Chimia*, 28 504 (1974); *Polymer*, **16**, 615 (1975).

3. E. M. Pearce, S. C. Lin, M. S. Lin, and S. M. Lee, "Relationship between Polymer Structure and Char Formation", *Eastern Analytical Symposium in Thermal Methods in Polymer Analysis*, S. W. Shalaby, Ed., Franklin Inst. Press, 1978.

4. W. W. Wright, *The Development of Heat Resistant Organic Polymers*, Halsted Press-Wiley, New York, 1975, pp. 43–47.

5. J. H. Parker, G. M. Fohlen, and P. M. Sawko, "Development of Transparent Composites and Their Thermal Responses", paper presented at Conference of Transparent Aircraft Enclosures, Las Vegas, Nevada, Feb. 3–8, 1973.

6. S. R. Sandler, and W. Karo, *Polymer Synthesis*, Vol. 2, Academic, New York, 1977, pp. 46–61.

7. Jeelen Lo, Ph.D. dissertation, "Flammability and Photo-Stability of Selected Polymer Systems", Polytechnic Institute of New York, Brooklyn, New York, 1981.

8. A. B. Deshpande, E. M. Pearce, H. S. Yoon, and R. Liepins, *J. Appl. Polym. Sci., Appl. Polym. Symp.*, **31**, 257 (1977).

9. J. Urbanski et al., *Handbook of Analysis and Synthetic Polymers and Plastics*, Wiley, New York, 19XX.

10. R. T. Conley, *J. Appl. Polym. Sci.*, **7**, 103 (1963).

11. G. Lei and A. Khamis, *Polym. Prepr.*, **19**, N2 (1978).

12. R. S. Hirst, D. M. Grant, R. E. Hoff, and W. J. Burke, *J. Polym. Sci. A*, **3**, 2091 (1965).

13. A. K. Chaurdhuri, B. Y. Min and E. M. Pearce, *J. Polym. Sci., Polym. Chem.*, **18**, 2949 (1980).

14. N. B. Colthup, L. H. Daly, and S. E. Wikerly, *Introduction to Infrared and Raman Spectroscopy*, 2nd ed., Academic, New York, 1976, p. 312.

15. P. J. Secrest, *Offic. Digest*, **37**, 187 (1965).