Synthesis and Thermal Characterization of Chemically Modified Cardanol Polymers

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SYNOPSIS

Cardanol was functionalised to incorporate elements such as phosphorus and bromine and polymerised with formaldehyde or hexamethylenetetramine (HMTA) to get flame retardant polymers. Thus, monocardanyl phosphoric acid (MCPA), its bromoderivative (BrMCPA), and their formaldehyde condensates (MCPAF and BrMCPAF) and cross-linked polymers were prepared and characterized by IR, NMR, and GPC. Flammability and thermal stability of these polymers were evaluated by LOI and TGA, respectively, and compared with those of conventional cardanol–formaldehyde (CF) resin and its bromoderivative. TGA of MCPAF showed that although it is initially less stable than that of CF, its stability increases above 500°C over that of CF. Char yields of MCPAF and BrMCPAF are 21 and 27, respectively, and corresponding LOI values are 27 and 49. The present data do not support any synergism nor any additive effect between phosphorus and bromine, but a positive interaction between them is indicated with phosphorus mainly contributing in the condensed phase and bromine in the vapour phase mechanism. The activation energies in the range 20–30 kcal/mol for MCPAF suggest an ionic mechanism for its decomposition, whereas mainly a free radical type of decomposition is inferred for BrMCPAF with an activation energy in the range of 35–50 kcal/mol. © 1993 John Wiley & Sons, Inc.

INTRODUCTION

Recent studies in this laboratory[1-10] and elsewhere[11,12] have shown that cardanol (an unsaturated hydrocarbon phenol obtained from the plant *Anacardium occidentale* L.) and its polymers have interesting structural features for chemical modification and polymerisation into speciality polymers. Cardanol has been in use for the manufacture of special phenolic resins for coatings, laminates, and friction materials.[13-15] When it was functionalised with orthophosphoric acid and oligomerised, the resulting prepolymer showed improved flame resistance and bonding characteristics and could be processed into a thermoset product.[2,4] When cardanol–formaldehyde (CF) resin was interpenetrated with polymethyl methacrylate (PMMA), the CF-PMMA semi-IPN registered a stabilization in PMMA from 50% to only 15% weight loss at 350°C.[5] Functionalisation of cardanol with acrylate moiety gave rise to cross-linked polymers with uniform bead size.[16,17] When it was oxidised with phase transfer catalysed permanganate and the oxidised product 8-(3-hydroxy phenyl) octanoic acid copolymerised with *p*-hydroxy benzoic acid, an interesting thermotropic liquid-crystalline copolyester was obtained.[18,19] One of the interesting observations has been the finding of ablative performance in cardanol polymers containing both phosphorus and bromine built into the same molecule.[6] This was unexpected because cardanol polymers with a pendant C$_{15}$ aliphatic side chain can give rise to only low char yields and so a study on the thermal behaviour of such cardanol polymers was performed. This paper reports the synthesis and thermal characterization of cardanol polymers containing both phosphorus and bromine.

EXPERIMENTAL

Materials

Cardanol was obtained by double vacuum distillation of CNSL at 3–4 mmHg and the fraction distilled at

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230–235°C was collected.[1] Phosphorus pentoxide (Merck, India), bromine (Merck, India), hexamethylene tetramine (Fluka, Switzerland), and oxalic acid (Merck, India) were used as received without further purification. The solvents were dried by standard methods[20] and distilled.

Measurements

The transmission infrared spectra were recorded on a Perkin–Elmer IR Spectrophotometer Model 882. ^{1}HNMR spectra were measured on a Hitachi R-24 B high resolution NMR spectrometer in CCl_4 using TMS as internal reference. The GPC data were obtained using a Hewlett–Packard 1081 B HPLC, equipped with an automatic sample injection system and a differential RI detector. Thermogravimetric studies were carried out on a Dupont 951 thermal analyser in nitrogen at a heating rate of 20°C min^{-1} with a sample weight of 5–8 mg. The Limiting Oxygen Index data were obtained on Stanton Redcroft LOI equipment model FTA-7101. Phosphorus es-
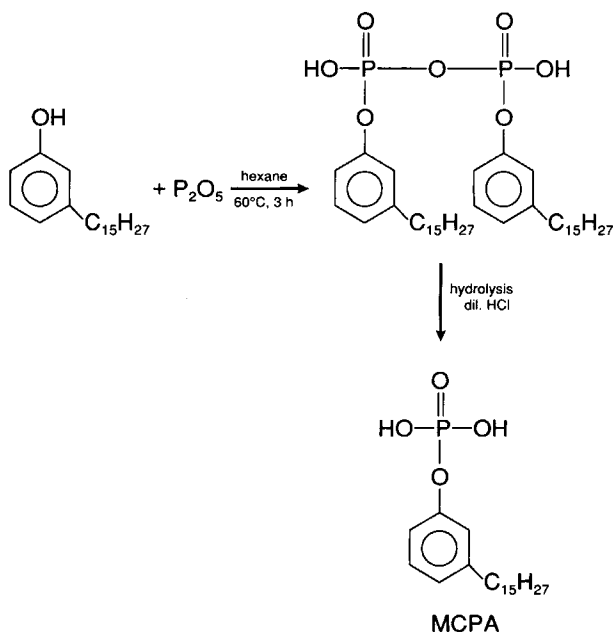
Yield 80%
IR(neat) 907 cm^{-1}, 630 (vinyl)
1250 (P=O), 2930 (P—OH), 960, 1150 (P—O—C), 3020 (C—H aromatic), 2980 (C—H aliphatic), 1620 (C=C aromatic).
^{1}H NMR δ0.9 (m, 3H, CH$_3$), 1.3 [m, 18H, (CH$_2$)$_n$], 1.9 (m, 2H, ar—CH$_2$)
5.2 (m, 4H, CH=CH), 6.7 (m, 4H, Ar)
Phosphorus 8.1%
content

Scheme 1 Synthesis of MCPA

Yield 90%
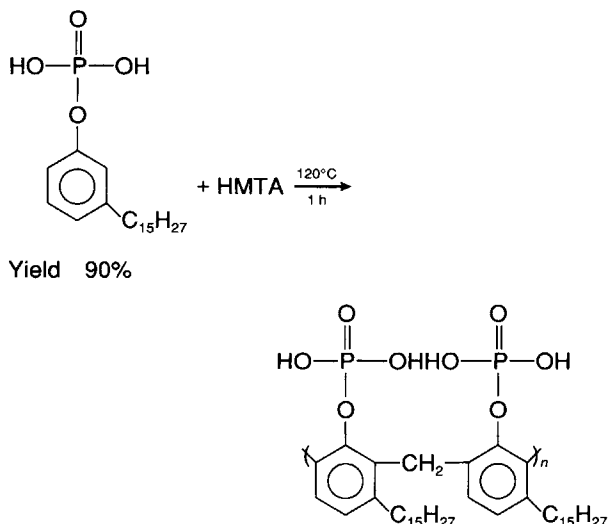
Scheme 2 Synthesis of MCPAF

timation was carried out by gravimetric method using ammonium molybdate reagent.[21] Bromine content was analysed by Volhard's method.[21]

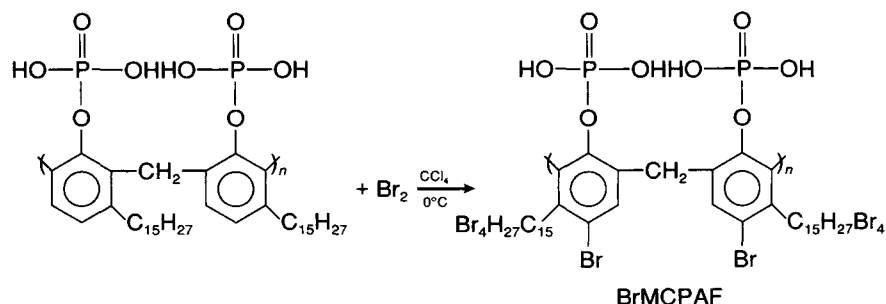## Synthesis

Monocardanyl Phosphoric Acid (MCPA)

MCPA was prepared by the reaction of cardanol with P_2O_5 in dry hexane as per Scheme 1. Cardanol (0.2 mol, 60 g) and dry hexane (500 mL) were taken in a 1 L 2-necked flask. To the stirring solution, P_2O_5 (0.13 mol, 18 g) was added portionwise. The reaction was continued for 6 h at 50–55°C. The pyrophosphate formed was hydrolysed with dil. HCl to produce MCPA.

Monocardanyl Phosphoric Acid–Formaldehyde Resin (MCPAF)

The polymerization of MCPA was carried out by reaction with hexamethylenetetramine (HMTA) as shown in Scheme 2. MCPA (0.01 mol, 3.8 g) was taken in a 50-mL R.B. flask and HMTA (0.0027 mol, 0.38 g) was added and heated at 120°C for 1 h to yield MCPAF.

Brominated Derivative of MCPAF Resin (BrMCPAF)

BrMCPAF was synthesised as per Scheme 3. MCPAF resin (0.1 mol, 39.4 g) and CCl_4 (250 mL) were taken in a 1-L R.B. flask, kept in an ice bath and added bromine (0.3 mol, 48 g) in 250 mL of CCl_4 dropwise with vigorous stirring. The product was dried in vacuum.

Scheme 3   Synthesis of BrMCPAF

Cardanol-Formaldehyde Novolac Resin (CF)

CF resin was prepared as reported earlier,[8] Cardanol (0.1 mol, 30 g), 37% aqueous formaldehyde (0.084 mol, 6.8 g), and oxalic acid (0.001 mol, 0.13 g) were taken in a three-necked flask fitted with a mechanical stirrer and reflux condenser. The reaction mixture was heated under constant stirring at 100°C for 4 h. The product was dried in vacuum at 70°C.

Brominated Cardanol-Formaldehyde Resin (BrCF)

BrCF was synthesised as in Scheme 4. CF resin (0.1 mol, 31 g) and CCl_4 (250 mL) were taken in a 1-L R.B. flask kept in an ice bath and added bromine (0.3 mol, 48 g) in CCl_4 dropwise with vigorous stirring. The solvent was stripped off and the product was dried in vacuum.
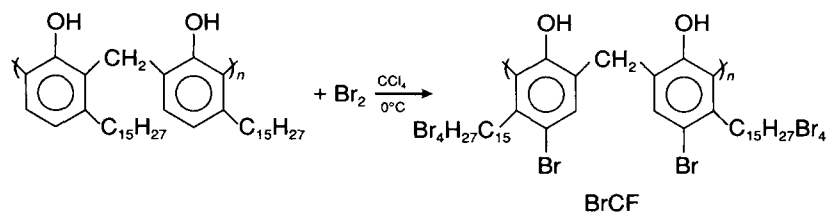
RESULTS AND DISCUSSION

Synthesis

Earlier attempts to prepare phosphorylated cardanol by direct reaction with orthophosphoric acid always

resulted in the formation of oligomeric species caused by simultaneous polymerization through the unsaturation in the side chain.[2] The preparation of the monomer in the pure form was achieved in the present case by using P_2O_5 in anhydrous conditions when protonation of the side chain was not favoured. The MCPA obtained had a molecular weight of 381 (determined using VPO) that was in agreement with the theoretical value of 380. The IR spectrum of MCPA shows the presence of $C=C$ peaks at 1620 cm^{-1} as was observed in the case of cardanol.[1] The terminal vinyl group at 907 cm^{-1} and also the vinyl peak at 630 cm^{-1} remained unaffected whereas they had completely vanished in the case of phosphorylated oligomer.[2] The ^{1}HNMR spectrum of MCPA also registered the unsaturated protons at $\delta 5.2$. The presence of the phosphate group in MCPA was indicated by the IR vibrations at 1250 cm^{-1} and 2930 cm^{-1} that might arise because of stretching vibrations of $P=O$ and $P—OH$, respectively.

Polymerization of MCPA was carried out by condensation with HCHO or HMTA. Condensation was carried out to the extent of producing only soluble oligomers. The molecular weights of the oligomers

Scheme 4   Synthesis of BrCF

Table I   GPC Data of Polymers

| No.	Sample	$\bar{M}_n$	$\bar{M}_w$	$M_{WD} = \bar{M}_w/\bar{M}_n$
1	MCPAF	1750	4700	2.7
2	CF	1550	3050	1.98
3	BrCF	1900	3990	2.1
4	BrMCPAF	2200	5720	2.6

are given in Table I. Unlike the CF and PF novolac system,[22] MCPAF could not be cured to insoluble and infusible cross-linked polymers, when reacted with HMTA or paraformaldehyde or any other similar aldehydes. However, curing could be initiated and cross-linked products obtained in the presence of amines (1%) such as paraphenylenediamine, melamine etc. MCPA was also polymerized cationically by opening the double bonds of the side chain to get a prepolymer (DP $\sim$ 3–4) that was further polymerized and cross-linked through the active hydrogens of the phenolic ring using HCHO or HMTA.

Bromination of CF and MCPAF was carried out until five bromine atoms were introduced. Thus, BrCF and BrMCPAF have bromine contents of 56 and 51%, respectively. As the unsaturation of the aliphatic side chain of cardanol is about two,[13] four bromine atoms could have been introduced into the side chain[23,24] and one bromine to *ortho* or *para* position of the aromatic ring. The ^{1}HNMR spectra of the brominated regions did not show any unsaturated protons at $\delta5.2$ and showed a new peak at $\delta4.2$ (CHBr protons) and as expected the aromatic pro-

tons were short by one. BrMCPAF also did not undergo further polymerization and cross-linking to a thermoset product and were therefore used as such for thermal and LOI studies (LOI measurements were done using a modified method[25]). However, cross-linked products were obtained by partial bromination of MCPAF through the side chain that was then cured with HMTA in the presence of paraphenylenediamine. (The bromine content of the product was only 45%). The brominated product (poly BrPCP), which exhibited ablation phenomenon reported earlier,[6] was prepared by phosphorylation with orthophosphoric acid (when simultaneous oligomerization through the side chain also takes place) followed by partial bromination and cross-linking with HMTA. Both the products gave identical IR spectra.

Thermal and Flammability Studies

The TGA of CF resin in air was first reported by O'Conner and Blum[26] who showed that the stability of substituted phenols decreases as the length of the side chain increases. Later Manjula et al.[5] studied the thermal decomposition of CF in comparison to PF and showed that CF resins decompose at a faster rate. The present study compares the thermal behaviour of CF with MCPAF, BrMCPAF, and the effect of phosphorus and bromine on the thermal behaviour of these polymers. Figure 1 gives the TGA of the cured polymers. The parameters studied are the temperature corresponding to initial decompo-
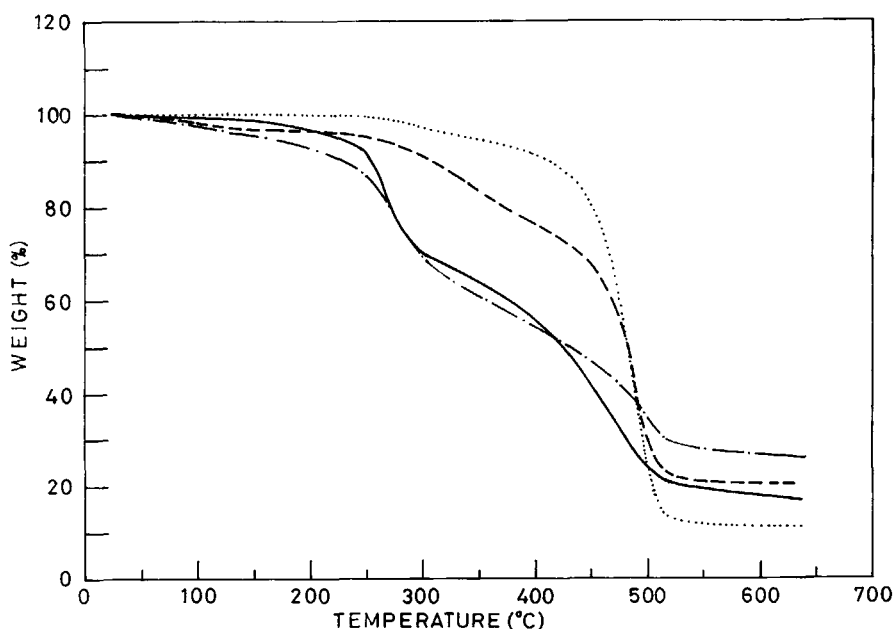
Figure 1   Thermogravimetric traces of MCPAF, BrMCPAF, CF, and BrCF.

sition (T_i), 50% weight loss $(T_{1/2})$, and char yield (C_y) at a specified temperature[25] (600°C in the present case). Comparison of these values in Table II shows that although an overall thermal stability was expected for MCPAF, it has a lower T_i value (250°C) than that of CF (270°C) and the $T_{1/2}$ for both the polymers is 480°C. The TGA of MCPAF given in Figure 1 shows that its stability improves over that of CF above 500°C. The C_y value has hence registered a rise from 11 of CF to 21 of MCPAF. Vertical burning studies carried out as per UL-94 did not give any propagation of flame and no afterglow. The LOI value has risen from 19 of CF to 27 for MCPAF. This can be understood from the contribution of phosphorus in the system. It is generally believed[27,28] that phosphorus decreases the temperature of pyrolysis, retards carbonisation of polymers, and increases pyrolysis residue. Annakutty and Kishore[25] studied the thermal behaviour of a series of polyphosphates and arrived at the conclusion that there exists a relationship between thermal stability, LOI, and phosphorus content in the case of polyphosphate esters. Unfortunately, the present data on MCPAF did not fit in well with their equation[25] correlating these parameters. The significance of the effect of structure on thermal stability and flammability is thus apparent here as cardanol polymer differs in structure from phenolics in having a labile aliphatic side chain. The low char yield of CF (11%) and MCPAF (21%) in comparison to that of phenolics (60%) is thus a direct effect of structure on thermal stability.

Because phosphorus flame retardants are well known to act in the condensed phase mechanism,[28] the increase in char for MCPAF indicates possible formation of acidic decomposition products in the earlier stages. When MCPAF was complexed with a metal ion such as Ba^{+2}, the resultant product exhibited considerably reduced flame retardancy (as is expected of metallated phosphates[29]) supporting the assumption that the nonmetallated flame retardant might be functioning through the early release of acidic fragments. The initial thermal generation of an acid component such as phosphoric acid from the flame retardant alters the pyrolytic decompo-

sition of the polymer in the condensed phase so that the decomposition products are changed from combustible intermediates and flammable gases to thermally stable char and nonflammable gaseous products.[30]

Figure 1 and Table II show that bromination of CF and MCPAF bring both T_i and $T_{1/2}$ values down considerably (T_i from 270 to 220 for BrCF and 250 to 200 for BrMCPAF whereas $T_{1/2}$ from 480 to 425 for BrCF and 480 to 430 for BrMCPAF). But it should be noted that the C_y values of both BrCF and BrMCPAF have increased considerably, that is from 11 to 18 for BrCF and from 21 to 27 for BrMCPAF. This gives rise to the suspicion that although halogen flame retardants are well known to act in the gas phase mechanism,[30] bromine in BrMCPAF and BrCF might contribute to condensed phase mechanism as well. The lower values of T_i and $T_{1/2}$ for BrMCPAF in comparison to BrCF could be attributed to the presence of phosphate in BrMCPAF that being acidic might initiate earlier decomposition and liberation of HBr known to be a free radical generator.[30,31] Experiments have shown that copious amounts of HBr are liberated just above the T_i value. The high LOI value of BrCF (45) and BrMCPAF (49) can be understood on this basis. Brominated flame retardants are known to release volatile species that interfere with the free radical chain branching reactions to remove high energy $OH^\cdot$ and $H^\cdot$ radicals and inhibit the combustion process.[32] The comparison of the LOI value of CF and MCPAF with those of BrCF and BrMCPAF does not indicate any synergism between phosphorus and bromine nor any additive effect. However, there is a positive effect that could be inferred from the higher value of 49 for BrMCPAF in comparison to 45 for BrCF. This probably indicates that phosphorus and bromine act mostly independently—phosphorus in condensed phase and bromine in the gaseous phase.

The presence of the side chain as a pendant group in the polymer is expected to influence the thermal stability and flammability of BrMCPAF also. This could be inferred from the decomposition pattern of CF itself. In CF, the degradation of the side chain is expected to occur at a relatively low temperature because of the facile β-cleavage at the double bonds[5] in comparison to that ($T_{1/2}$ above 400°C) of PF resins.[22] The incorporation of bromine to the side chain might still reduce the T_i and $T_{1/2}$ values, because aliphatic bromine is known to be thermally unstable in comparison to aromatic bromine.[33] Moreover, as discussed earlier the acidic phosphate might initiate decomposition for early liberation of

Table II TGA and LOI Data of Cured Products

No.	Sample	T_i	$T_{1/2}$	C_y at 600°C	LOI
1	MCPAF	250	480	21	27
2	CF	270	480	11	19
3	BrMCPAF	200	430	27	49
4	BrCF	220	425	18	45

HBr at lower temperature ($200°C$). Peciorek et al.[34] and later Day et al.[35] have in their studies on thermal behaviour of tris(2,3-dibromoalkyl)phosphates postulated dehydrobromination as the first step followed by liberation of phosphoric acid as subsequent steps in its decomposition (pyrolysis studies are now underway on the present system to specifically identify the decomposition products and to chart out the mechanistic pathways) that also agrees with the present observations.

Further information on the thermal behaviour of these polymers were obtained from activation energies calculated by the method of Freeman and Carroll[36] as modified by Anderson and Freeman[37] (Table III). The activation energies of CF and MCPAF are 29.0 and 27.5, respectively, whereas those of BrCF and BrMCPAF are 42.0 and 37.0, respectively. One can note a definite trend in the decomposition pattern of these compounds as the low values of CF and MCPAF in the range of 20–30 indicate an ionic decomposition mechanism.[5] Manjula et al.[5] also proposed earlier an ionic decomposition mechanism for CF based on application of the Coats–Redfern equation to the system assuming the order parameter to be $n = 1$. However, the higher value of activation energies in the range of 40–50 for the brominated products possibly suggest a free radical process. The copious liberation of HBr and the high LOI value (49) of BrMCPAF thus support a vapour-phase mechanism similar to the well-known free radical trap theory[30] of halogen flame retardation. However the increase in char yield from 21% of MCPAF to 27% of BrMCPAF might suggest possible involvement of bromine in condensed-phase mechanisms as well. Although contributions to condensed-phase mechanism have been reported in the case of chlorine,[38] involvement of bromine in condensed phase is rarely reported. It might as well be said that the increase in char yield from 21 (MCPAF) to 27% (BrMCPAF) could be caused by the positive effect of the combined action of phosphorus and bromine in the condensed phase.

This laboratory has reported[6] earlier that asbestos fibre-reinforced phosphorus and bromine con-

taining cardanol polymers (cross-linked BrMCPAF) exhibit the property of ablation. Oxyacetylene panel tests conducted as per ASTME 285-70 gave an ablation rate value of 3.2×10^{-3} in./s in comparison to 3.6 mL/s for asbestos–phenolic.[38] Ablative polymers are known to function either by build up of char that acts as a heat shield and blocks heat from entering the system or by transpiration cooling whereby the decomposition gases carry off the heat, or by a combination of both.[39] As the char content of cross-linked BrMCPAF is only 27%, in comparison to 60% for conventional phenolics,[22] mechanisms involving transpiration processes might be playing a vital role in this case. This could be aided by endothermic processes such as the liberation of HBr. The gases generated from the decomposition of the aliphatic side chain (the side chain in cardanol amounts to 69% of the total weight of cardanol) segments would also play a significant role in the ablation process. The present study therefore concludes that although BrMCPAF does not have the thermal stability to function as an ablative by way of a char former, other mechanisms involving endothermic liberation of HBr and transpiration cooling by the decomposition gases might contribute to its exhibiting the property of ablation.

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Table III **Activation Energy (E) and Order (n) of Thermal Decomposition for Cured Products**

No.	Sample	E	n
1	MCPAF	27.5	0.80
2	CF	29.0	0.85
3	BrMCPAF	37.0	0.95
4	BrCF	42.0	0.95

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