SYNTHESIS, CHARACTERIZATION AND THERMAL BEHAVIOUR OF CHEMICALLY MODIFIED PHENOLIC AND SUBSTITUTED PHENOLIC POLYMERS

THESIS SUBMITTED TO THE
COCHIN UNIVERSITY OF SCIENCE AND TECHNOLOGY
IN PARTIAL FULFILMENT OF THE REQUIREMENTS
FOR THE DEGREE OF
Doctor of Philosophy
IN SCIENCE

BY

ROSY ANTONY

REGIONAL RESEARCH LABORATORY (CSIR)
THIRUVANANTHAPURAM-695 019
INDIA
MAY, 1993

वैज्ञानिक एवं औद्योगिक अनुसंधान परिषद्
COUNCIL OF SCIENTIFIC & INDUSTRIAL RESEARCH
क्षेत्रीय अनुसंधान प्रयोगशाला, तिरुवनन्तपुरम
REGIONAL RESEARCH LABORATORY, TRIVANDRUM.
तिरुवनन्तपुरम-695019
TRIVANDRUM-695 019.
भारत
INDIA

Dr. C.K.S. Pillai
Head, Polymer Section

April 24, 1993

CERTIFICATE

This is to certify that the thesis bound herewith is an authentic record of the research work carried out by Rosy Antony, M.Sc., under my supervision in partial fulfilment of the requirements for the Degree of Doctor of Philosophy in Science of Cochin University of Science and Technology and further that no part thereof has been presented before for any other Degree.

(C.K.S. Pillai)
Supervisor

Grams: 'CONSEARCH' Telex: 0435-232 Phones: PABX 76774/76769/76851/76852/70811.

DECLARATION

I hereby declare that this thesis is a bonafide record of the research work done by me and no part of the thesis has been presented earlier for any degree, diploma or similar title of any other University.

Rosy

Rosy Antony

May 1993

Thiruvananthapuram

ACKNOWLEDGEMENTS

I express my irredeemable depth of gratitude to my supervisor Dr. C.K.S. Pillai, Head, Polymer Section, Regional Research Laboratory (CSIR), Trivandrum, for his critical and enthusiastic guidance, inspiration and inexhaustible encouragement which made the present work possible.

I am extremely grateful to Dr. A.D. Damodaran, Director, RRL, Trivandrum, for his constant encouragement and support and for providing all the facilities during my research work.

I am sincerely thankful to Dr. K.J. Scariah, VSSC, Trivandrum, and Dr. C. Pavithran, RRL, Trivandrum for useful discussions and support in experimentation.

I would like to put on record my sincere thanks to my best friend Ms S. Sreelatha, whose advice, constant help, exhilarating company, cooperation and willingness are in no small part responsible for the eventual appearance of this thesis.

I owe my sincere thanks to Mr. M. Brahmakumar, Mr. V.S. Prasad, Mr. George John, Ms Rajalakshmi, Ms. J.D. Sudha, Mr. P. Anandan, Mr. A.R.R. Menon, Dr. S. Bera, Mr. M. Saminathan and Mr. A. Krishnankutty, my fellow collaborators in the laboratory for their friendly cooperation, help and warm companionship.

I bow down to my beloved family members and well-wishers for their moral encouragement, immense patience and loving care which could give me the strength to pursue my goal with success and dedication.

I wish to thank the council of Scientific and Industrial Research (CSIR), New Delhi, for the financial support during the course of this work.

Rosy

Rosy Antony

PREFACE

It is now well recognised that one of the problems that has assumed serious dimensions on the use of polymeric materials is their flammability. Although there are innumerable flame retardants (FRs) available now for flame retardation of polymers, there is no FR that can be widely used for a range of polymers without causing any undesirable change in property. Wide spectrum FRs with FR elements built into molecules that have both hydrophobic and hydrophilic moieties in the same molecule and that can be polymerised to a prepolymer are expected to bridge the gap in FR technology. Moreover, polymeric FR vis-a-vis its monomeric counterpart is expected to be much more effective in reducing flammability. The present work addresses to some of these problems.

This study is mainly concerned with the synthesis, characterisation, thermal and flammability evaluation of FR monomers, prepolymers and polymers of (1) cardanol, a monomer having the required structural features for transformation into wide spectrum flame retardants and (2) phenol, a structurally related monomer (for comparative evaluation) that can easily be chemically modified to introduce FR elements.

The present investigation forms part of a large programme being conducted at the Regional Research Laboratory, Trivandrum, to explore the potential of cardanol as a monomer source for the development of speciality polymers. So insights into the thermal and flammability behaviour of these polymers are expected to contribute to the generation of information for tailor making of polymers with specific properties such as ablation as observed in some earlier experiments in the laboratory.

The results of the present investigation have been published or are under publication as described below:

1. GPC studies on the cationic polymerisation of cardanol using BF_3 etherate as initiator, J. Appl. Polym. Sci., 41, 1765 (1992).

2. Synthesis, characterization and thermal studies of cardanol based polyphosphate esters, J. Polym. Sci. Polym. Chem. Edn. (accepted).

3. Synthesis and thermal characterization of chemically modified cardanol polymers, J. Appl. Polym. Sci. (accepted).

4. Synthesis, characterization, thermal and flammability studies on phosphorus and bromine containing phenolic resins (manuscript under preparation).

5. Synthesis and thermal characterization of boron containing cardanolic and phenolic polymers (manuscript under preparation).

6. A comparative evaluation of the effect of polymeric flame retardants and monomeric flame retardants on the thermal and flammability behaviour of polyethylene (manuscript under preparation).

7. A comparative evaluation of the thermal and flammability behaviour of cardanolic and phenolic FR monomers and polymers (manuscript under preparation).

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CHAPTER 1

INTRODUCTION

1.1 SIGNIFICANCE OF FLAME RETARDATION IN POLYMERS

Over the last few decades the world has witnessed spectacular growth and development in the use of polymeric materials in day-to-day life, industry and high performance applications. Production of polymers by volume has exceeded over that of steel and aluminium. They have successfully substituted advanced metals and ceramics in certain high performance applications and a host of polymers with unprecedent properties are emerging from advances in new methods of synthesis and processing. Although these developments have revolutionised the world of materials, polymers with the exception of a few are susceptible to deterioration on exposure to heat and flame. Fires have been reported to be one of the principal scourges of mankind and today with the increasing use of polymeric materials, this problem has aggravated to the extent of worldwide concern for improved protection for property and human life. The use of flame retardants for the control of the flammability of materials of organic origin dates back even to early Egyptian civilization, but only recently, search for newer and better flame retardants that fulfil the standards set for fire prevention and control and also for a better understanding of the mechanism and behaviour of flame retardants so that the existing ones could be improved upon, has begun on a systematic and scientific way.

1.2 HISTORICAL DEVELOPMENT OF FLAME RETARDANTS

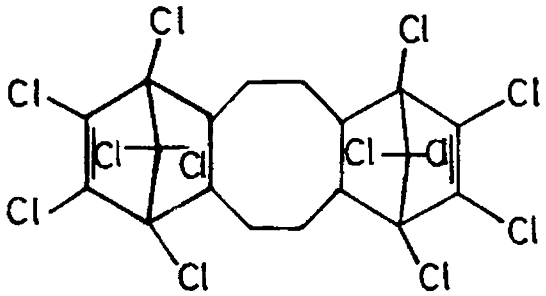
It was Gay-Lussac [1] who initiated for the first time in France in 1821 basic scientific investigation on flame retardants. He noted that the ammonium salts of sulfuric, hydrochloric and phosphoric acids were very effective fire retardants on hemp and linen and that the effect could be improved considerably by using mixtures of ammonium chloride, ammonium phosphate and borax. Thus the basic elements of modern fire retardant chemistry were defined early in recorded history and remained the state of the art until early in the twentieth century. The early historical developments [1-5] are listed in Table 1.1.

The demands of the armed forces in World War II for a fire-retardant waterproof treatment for canvas tenting led to the development of a combination treatment containing a chlorinated paraffin (CP), antimony oxide, and a binder [6,7]. This was the first use of the halogen-antimony synergistic combination treatment that has since proven so effective in many fire-retardant polymer products and marked the introduction of organic halogen compounds in place of inorgnic salts previously in vogue. Eventhough this new treatment was found to be useful in PVC both as a fire retardant and plasticizer additive, it tended to 'wash out' in many environments in which PVC was used. This deficiency of CP led to the conclusion that a reactive fire-retardant system would be preferred, some thing which would be chemically reacted into the polymer at some stage of the synthesis and/or fabrication of the final product and confer permanent fire-retardant properties on the final product.

Table 1.1: Early historical fire retardant developments

Development	Period
Alum used by Egyptians to reduce the flammability of wood	About 450 BC
Romans used a mixture of alum and Vinegar on wood	About 200 BC
Mixture of clay and gypsum used to reduce flammability of theater curtains	1638
Mixture of alum, ferrous sulphate and borax used on wood and textiles by Wyld in great Britain	1735
Alum used to reduce flammability of balloons	1783
Gay-Lussac reported a mixture of $(NH_4)_3PO_4$, NH_4Cl and borax to be effective on linen and hemp	1821
Perkin described a FR treatment for cotton using a mixture of sodium stannate and ammonium sulphate	1913

The first fire-retardant polyester containing a reactive fire retardant monomer was introduced by the Hooker Electrochemical Corporation in the early 1950s. It contained chlorendic acid (I) as the reactive monomer [8] as shown in Fig. 1.1.



(I)

Fig. 1.1

This pioneering development led rapidly to the introduction of various reactive halogen and phosphorus containing monomers, such as tetrabromophthalic anhydride, chlorostyrene and tetrabromobisphenol A, which found application in a wide variety of condensation polymer systems.

The next major development resulted from the need for an acceptable fire-retardant system for such new thermoplastics as polyethylene, polypropylene, and nylon. The use of a reactive monomer was not applicable to these polymers because the crystallinity upon which their desirable properties depended was reduced or destroyed by adding the fire-retardant. The introduction of inert fire retardant fillers in 1965 defined two novel approaches to fire-retardant polymers. One of these products was a thermally stable insoluble chlorocarbon prepared from cyclooctadiene and hexachlorocyclopentadiene. The extreme insolubility of this high-melting thermally stable hydrocarbon allowed it to be compounded into most thermoplastics without decomposition or discoloration. The other fire-retardant filler, hydrated aluminium oxide (or alumina) [9] exerts its fire-retardant effect in polymer compositions by dehydrating under flame conditions. Because of its relatively low decomposition temperature (245-320°C) hydrated alumina is most useful in polymer compositions requiring low processing temperatures such as unsaturated polyesters. The major advantages of this fire retardant system are low smoke production and the fact that no hydrogen halide off-gases are produced during pyrolysis on fire exposure. These developments can be summarised as follows (Table 1.2).

Table 1.2: Most important modern developments in polymer fire-retardance

Development
Chlorinated paraffin, antimony oxide and a binder as a treatment on canvas
Reactive fire retardants, chlorine containing unsaturated polyesters
Filler-like fire retardants
Oxygen Index method of evaluating relative polymer flammability
Intumescent fire-retardant systems
Inherently fire-retardant polymers
Wide-spectrum flame retardants

1.3 THE COMBUSTION OF POLYMERS

Since the action of FRs is to interfere in some step in the burning process of polymers [10], a brief discussion is here included on the combustion of polymers [11-23]. The combustion of polymers takes place in three stages involving a heating phase, a thermal pyrolysis stage and ignition [13,14]. The heating phase primarily depends on the relative flux and temperature of heat source. In the case of thermoplastics which melt during heating, the melt flowing away (dripping) from the heating source gives an apparently erroneous conclusion regarding resistance to flame. The flammability of a material is largely determined by the pyrolysis stage when a pyrolytic decomposition prior to ignition occurs with the elimination of gaseous products. The composition of the gaseous products determines primarily the flammability of the material. Ignition occurs when the gaseous products forming a mixture with oxygen in the air exceed the flammability limits. In fact a triad of fuel, air (oxygen) and heat has to be established to ensure burning to occur. The process of combustion can be represented in Fig.1.1.

The thermal feedback maintains the combustion process upon a continued supply of oxygen from the surrounding atmosphere.

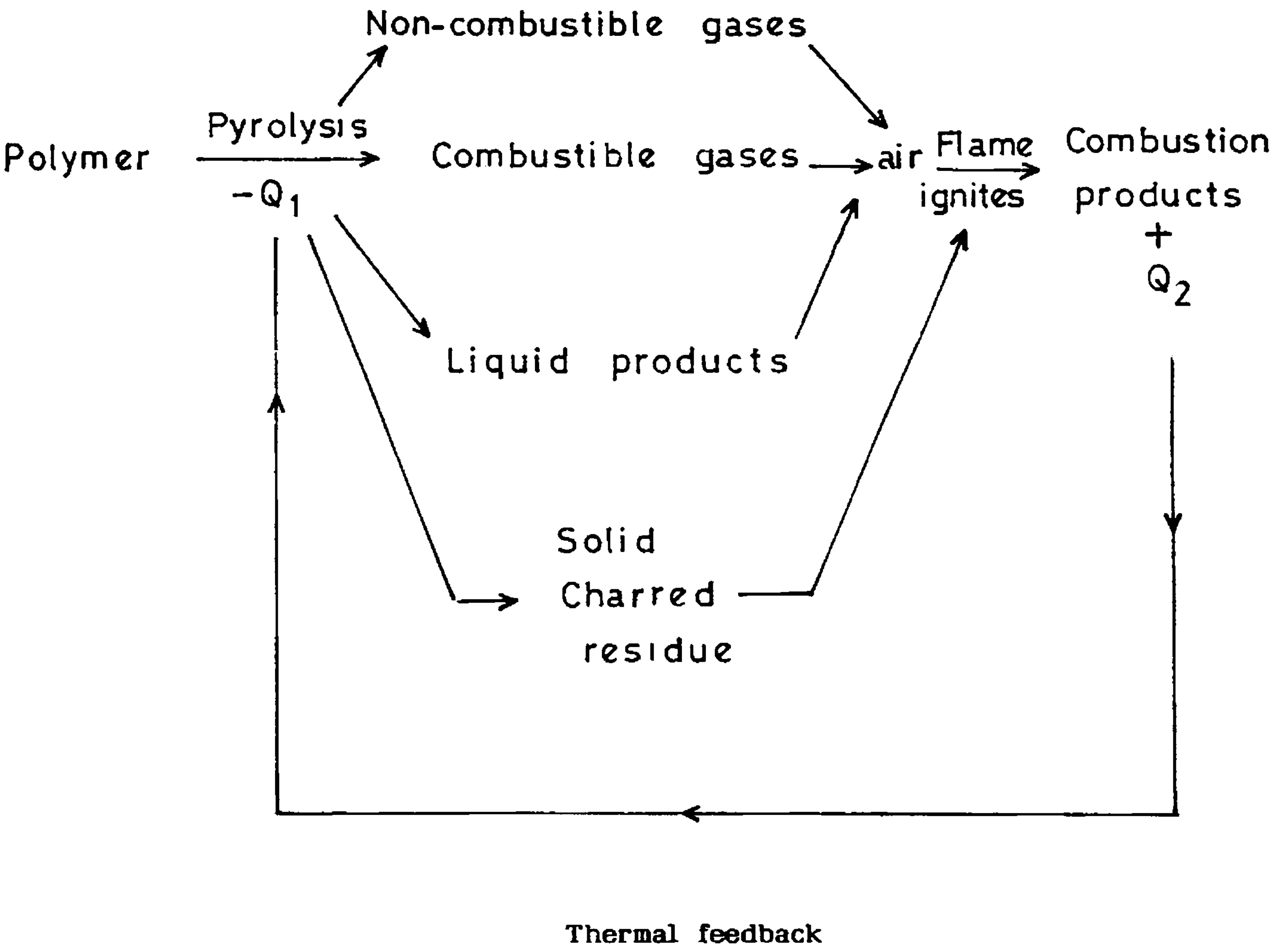


Fig. 1.2: Process of combustion of an organic polymer
Q_1, Q_2 = heat

1.4 THE MECHANISM OF FLAME RETARDANCY

The flame retardant may act in the condensed phase by altering the thermal breakdown of the polymer in such a way that either the nature or the rate of evolution of the gaseous decomposition products is changed. As a consequence when these products mix with the oxidant, the composition of the resulting mixture no longer lies within the flammable range [4,7,24-26]. It can also act in the gaseous phase, the flame retardant may dissociate into free-radical acceptors which react with the chain-propagating radicals of the combustion [4,7,24-26]. A combination of these two mechanisms is also possible.

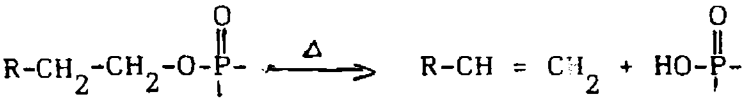
1.4.1 The mode of action of phosphorus flame retardants

Condensed phase mechanism

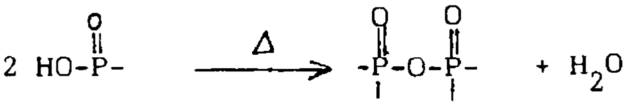
The behaviour of phosphorus based flame retardants has been studied extensively, but primarily in cellulose. The most generally accepted mechanism for phosphorus fire retardancy in cellulose is the condensed phase mechanism. The flame retardant is converted by thermal decomposition to phosphoric acid which alters the mechanism of decomposition of the cellulose in the condensed phase so that the principal products are carbonaceous char rather than levoglucosan and other flammable compounds [4,7, 24-28]. The formation of char involves catalytic dehydration of the hydroxyl groups, esterification by the polyphosphoric acid formed and finally cross-linking and skeletal rearrangement [29].

The generation of phosphoric acid is most easily explained as resulting from the well known decomposition of the alkyl phosphorus ester, to an olefin and the corresponding acid [29]. This reaction together with the postulated char forming dehydration of the cellulose is depicted in the following reactions:

Ester decomposition

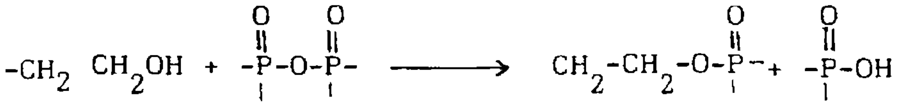


$$R\text{-}CH_2\text{-}CH_2\text{-}O\text{-}\overset{\overset{O}{\|}}{\underset{|}{P}}\text{-} \xrightarrow{\Delta} R\text{-}CH = CH_2 + HO\text{-}\overset{\overset{O}{\|}}{\underset{|}{P}}\text{-} \qquad (1)$$

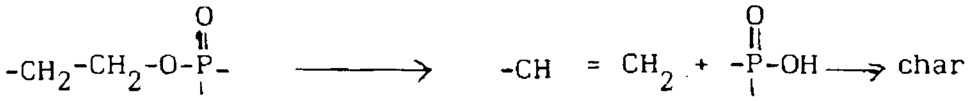


$$2\ HO\text{-}\overset{\overset{O}{\|}}{\underset{}{P}}\text{-} \xrightarrow{\Delta} \text{-}\overset{\overset{O}{\|}}{\underset{|}{P}}\text{-}O\text{-}\overset{\overset{O}{\|}}{\underset{|}{P}}\text{-} + H_2O \qquad (2)$$

Esterification and dehydration



$$\text{-}CH_2\ CH_2OH + \text{-}\overset{\overset{O}{\|}}{\underset{|}{P}}\text{-}O\text{-}\overset{\overset{O}{\|}}{\underset{|}{P}}\text{-} \longrightarrow CH_2\text{-}CH_2\text{-}O\text{-}\overset{\overset{O}{\|}}{\underset{|}{P}}\text{-} + \text{-}\overset{\overset{O}{\|}}{\underset{|}{P}}\text{-}OH \qquad (3)$$



$$\text{-}CH_2\text{-}CH_2\text{-}O\text{-}\overset{\overset{O}{\|}}{\underset{|}{P}}\text{-} \longrightarrow \text{-}CH = CH_2 + \text{-}\overset{\overset{O}{\|}}{\underset{|}{P}}\text{-}OH \longrightarrow \text{char} \qquad (4)$$

A second possibility of forming unsaturated compounds with subsequent charring is the acid-catalysed elimination of water from the cellulose:

$$R\text{-}CH_2\text{-}CH_2\text{-}OH \xrightarrow{H^+} R\text{-}CH_2\text{-}CH_2\text{-}OH_2^+ \longrightarrow R\text{-}CH = CH_2 + H_2O + H^+$$

(5)

The existence of a condensed phase mechanism is supported by the fact that all phosphorus compounds that are capable of decomposing to acid fragments are effective fire retardants for cellulose whereas fully neutralised salts of nonvolatile metals are not [29,30]. Addition of as little as 1.0% of phosphorus to cellulose causes a several fold increase in char yield under flame conditions [31]. Also the phosphorus from the fire retardant is found to be largely or completely retained in the residual char [32].

The high efficiency of phosphorus fire retardants in polyurethane (Pu) foams has also been suggested to be the result of acidic degradation products which then promote the formation of a structurally stable insulating char [33,34]. Similar condensed phase mechanism has also been proposed in the case of other hydroxylated or oxygenated polymers like epoxy resins [35-36] and polymethyl methacrylate (PMMA) [37].

In the case of non-oxygenated polymers such as polyethylene (PE), polypropylene (PP), polystyrene (PS) etc. the acid catalysed char forming mode of action of phosphorus plays a less evident role and in fact phosphorus is not so effective in such polymer systems as it is in oxygenated polymers (38-40]. The flame retardant effect observed in these cases has been attributed to the formation of polyphosphoric acid which acts as a physical barrier to passage of heat, oxygen or fuel [38-40]. Savides et al [41] also have presented evidence for a condensed phase mode of action involving char coating for phosphorus flame retardants in PP.

Gaseous phase mechanism

Considerable attention has been directed in recent years to a possible gaseous phase mechanism of action of phosphorus flame retardants [38-40]. Volatile phosphorus compounds have been shown to be some of the most efficient gas phase inhibitors in premixed flames [42-44]. Lask and Wagner have shown that trimethylphosphate is three times more effective as bromine in inhibiting a stoichiometric premixed n-hexane flame [43]. Hastie [45] and Granzow [44] have reported that compounds such as triphenylphosphine oxide break down in the flame as shown below to give small molecular species such as $P\dot{O}$. The rate controlling hydrogen atom concentration in the flame was shown spectroscopically to be greatly reduced,

$$(C_6H_8)_3\ PO \longrightarrow P\dot{O},\ \dot{P},\ \text{and}\ P_2$$

$$\dot{H} + P\dot{O} + M \longrightarrow HPO + M$$

$$\dot{O}H + P\dot{O} \longrightarrow HPO + \dot{O}$$

$$HPO + \dot{H} \longrightarrow H_2 + P\dot{O}$$

when the phosphorus species were present [45]. The mechanism proposed for flame retardancy in this situation is scavenging of

$\overset{\bullet}{H}$ by phosphorus radicals such as $\overset{\bullet}{PO}$ and thus reducing the energy of the flame [45].

The existence of gaseous phase mechanism for phosphorus compounds has been reported only in the case of a few polymer systems [46-48] compared to condensed-phase mechanism. In some cases, a combination of these two mechanisms is also possible [46-48], A vapour phase physical shielding has been postulated for tris(dibromopropyl) phosphate in polypropylene [46]. When certain polyester cotton blends having built-in phosphorus, in the form of phosphine oxide structure is burned, it has been found that part of the phosphorus is volatilized and part is retained in the char, thus suggesting the possibility of both the mechanisms [47,48].

Thermally stable but low boiling esters like triphenyl phosphate and tricresyl phosphate are found to induce no char in cellulose [49], PMMA [50] etc. The flame retardancy observed in these cases has been attributed to a gaseous phase mechanism [49,50]. These compounds may be acting in the same way as reported in the case of triphenyl phosphine oxide. However, it has been found that these compounds are less effective as flame retardants compared to compounds which give rise to phosphoric acid and act in the condensed phase [49,50]. Similarly, triphenyl phosphine oxide which acts in the gaseous phase is found to be less efficient compared to phosphoric acid which acts in the condensed phase in flame retarding polyethylene terephthalate [51].

Thus it can be seen that the mechanism by which phosphorus compounds act in flame retardation depends on the structure of the flame retardant as well as the nature of the substrate polymer.

1.4.2 Mechanism of action of halogen flame retardants

The halogenated flame retardants are generally considered to act through suppression of the gas phase radical reactions [29,52,53]. The very high energy $\dot{OH}$ and $\dot{H}$ formed by chain branching

$$\dot{H} + O_2 \longrightarrow \dot{OH} + \dot{O}$$

$$\dot{O} + H_2 \longrightarrow \dot{OH} + \dot{H}$$

are removed by the halogen containing flame retardant. At first the flame retardant breaks down into

$$R - x \longrightarrow \dot{R} + \dot{x}$$

The halogen radicals react to form a hydrogen halide.

$$\dot{X} + RH \longrightarrow \dot{R} + HX$$

which in turn interfere with the free radical mechanism

$$HX + \dot{H} \longrightarrow H_2 + \dot{X}$$

$$HX + \dot{OH} \longrightarrow H_2O + \dot{X}$$

Thus the high energy $\dot{H}$ and $\dot{OH}$ radicals are removed by the reaction with HX and replaced with the lower energy $\dot{X}$ radicals. The hydrogen halide consumed is regenerated by reaction with hydrocarbon so that the inhibition reaction can take place again.

Hindersinn and Witschard suggest that halogen containing flame retardants are also effective in the condensed phase [29]. Thus HBr acts as an oxidative catalyst, forming oxidized products with a tendency to cyclize and condense to yield carbonaceous products [29].

1.5 FLAMMABILITY TESTS AND TERMINOLOGY

Laboratory screening tests have been most generally used in fire retardant research. These screening tests or small scale tests compare burning rates of various plastics [54]. Such tests as D 635-74, flammability of rigid plastics, and D 1692-74, flammability of plastic foams and sheeting, fall into this category. ASTM E-84 tunnel test is the most common design for materials. Since it attempts to classify materials under actual use conditions, it requires large samples and extensive test equipment. Two most commonly used small scale tests are the Limiting Oxygen Index test and the Underwriter's Laboratory vertical flame test.

1.5.1 Limiting oxygen index

The LOI test was first developed by Fenimore and Martin in 1966 [55] from an idea originally proposed by Simmons and Wolfhard for gaseous and liquid fuels [56]. Oxygen index is not an ignition test but rather a test for measuring propagation and extinction related phenomena [57]. The LOI is the minimum percentage of oxygen in an oxygen-nitrogen atmosphere required to sustain combustion of a material after ignition and can be represented as follows:

$$\mathrm{LOI} = \frac{[O_2] \times 100}{[O_2] + [N_2]}$$

Two of the reasons for the wide acceptance of this method are its precision and reproducibility of the results obtained by different workers in different laboratories. Table 1.3 gives the LOI values for various polymers.

1.5.2 Underwriter's Laboratory vertical flame test

In the UL-94 vertical burn test specimens are 6 in. in length by 1/2 in. in width by either 1/4, 1/8 or 1/16 in. in thickness. Conditions during the test are more severe with a 1/16 in. thick specimen than with thicker test specimens. The specimen is clamped vertically and a blue Bunsen burner flame applied to the bottom end of the specimen for a period of 10 sec and then removed and the duration of combustion is noted. If combustion ceases within 36 sec. after removal of the burner flame, the burner flame is again placed under the specimen for 10 sec. immediately after the combustion stops. The burner flame is again withdrawn and the duration of combustion again noted.

Table 1.3: LOI values of polymers

Sl.No.	Polymer	LOI
1.	Polymethylene oxide	15
2.	Polyethylene oxide	15
3.	Polyethylene	18
4.	Polypropylene	18
5.	Polystyrene	18
6.	Polyisoprene (natural rubber)	18
7.	Polymethyl methacrylate	18
8.	Cellulose	18
9.	Polybutadiene	18
10.	Cellulose acetate	19
11.	ABS	19
12.	Epoxy	20
13.	Polyacrylonitrile	20
14.	Poly vinyl carbazole	22
15.	Poly vinyl alcohol	23
16.	Poly vinyl fluoride	23
17.	Chlorinated polyether	23
18.	Poly 3,3-bis(chloro methyl)-1,3 epoxy alkane	23
19.	Nylon 6	24
20.	Nylon 6,6	24
21.	Poly ethylene terephthalate	25

S.No.	Polymer	LOI
22.	Wool	25
23.	Polychloroprene	26
24.	Poly carbonate	27
25.	Polyphenylene oxide	29
26.	Poly-m-phenylene isophthalamide	29
27.	Silicone rubber	30
28.	Chlorinated modacrylics (vinyl chloride acrylonitrile copolymers)	30
29.	Poly arylene sulfones	30
30.	Poly(2,6-dimethyl) phenylene oxide	31
31.	Poly furfuryl alcohol	31
32.	Poly(2,6-diphenyl phenylene oxide)	34
33.	Polyarylate	34
34.	Phenolic resin	35
35.	Poly-bisphenol terephthalate	38
36.	Polyether sulfone	38
37.	Polyether ether ketone	40
38.	Polyvinyl chloride	42
39.	Polyamide-imide	43
40.	Polyphenylene sulphide	44
41.	Polyvinylidene fluoride	44
42.	Polyether-imide	47
43.	Polybenzimidazole	48
44	Polypyromellitimide	50

Sl.No.	Polymer	LOI
45.	Polyvinylidene chloride	60
46.	Polyethylne-CO-chlorotrifluoroethylene	60
47.	Carbon	60
48.	Polychlorotrifluoroethylene	95
49.	Polyether fluoroethylene	95

The rating of test specimens in the UL-94 test are as follows. V-O if combustion stops within 5 sec. and does not drip flaming particles V-1 if combustion stops within 25 sec. and does not drip flaming particles, and V-11 if combustion stops within 25 sec. but releases flaming particles or drips during that time. Specimens in which the combustion does not stop are categorised as nonrated (N.R.). Apart from these parameters, ignition delay [58-61] and burning rate [62-66] are also used to characterize combustion of polymers.

1.6 METHODS OF FLAME RETARDATION

The general methods that are applied to achieve flame retardancy in polymeric materials can be grouped in four major headings [26,67].

(a) Chemical methods involve use of appropriate chemical compounds or elements which function by modifying either the condensed phase or vapour phase processes. The chemical methods will involve any of the following modifications:

i. Use of flame retardant additive in the polymer. They are added prior to or during some step in fabrication. They must be stable under the conditions of fabrications and is the most widely used method particularly for polyester resins, epoxy resins, polyurethane foams etc.

ii. Copolymerisation with a fire retardant comonomer to get a block or graft copolymer. This is advantageous in the sense that the flame retardant becomes integral part of the polymer. Graft copolymerisation is emerging as a useful method.

iii. Use of reactive additive that can be chemically bonded to the polymer so that it is permanently fixed.

iv. Blending with other flame retardant polymers.

(b) The gas generation method uses FRs to produce non-combustible gases that dilute the fuel-oxygen mixture below the flammability limits.

(c) The coating methods provide a fire-retardant coating which insulates the substrate from contact with further heat and fuel-air mixtures. Intumescent coatings are noteworthy here because of their applicability and is practical in wood, cotton, wool etc. [68,69]. They are systems that puff up to produce foams that insulate the substrate and protect it from heat.

(d) The thermal techniques trigger components of the solid to consume by an endothermic process so that the heat generated during the pyrolysis cools the system below the ignition point [70]. Thus addition of FRs can raise the decomposition temperature of the polymer through for example crosslinking, reduce the fuel content of the chain scission and promote dripping, induce selective decomposition pathways such as reactions that lead to thermally stable structures (eg. char) or prevent heat/ oxygen by mechanical means from reaching the pyrolysis site (eg. coating).

1.7 ADDITIVITY, SYNERGISM AND ANTAGONISM IN FLAME RETARDANCY [27]

Combinations of flame retardants may be said to have additive, synergistic or antagonistic effects. An additive effect is the sum of the effects of the two components taken independently. A synergistic effect is an observed effect greater than the additive effect, and an antagonistic effect is one which is less than an additive effect.

Critical review of specific interactions:

1.7.1 Halogens with antimony

The interaction of antimony most commonly as antimony oxide with halogenated polymers or polymers containing halogenated additives is the classic case of flame-retardant synergism. The area of inorganic antimony compounds and certain other heavy-metal compounds as flame-retardant synergists with halogen donors has been thoroughly reviewed by J.J. Pitts [71].

In a number of systems reviewed by Pitts, the flame-retardant **effect** of antimony oxide has been shown to increase as halogen is added to the system upto an atomic ratio of three halogen atoms per antimony atom. Antimony halides have been shown to be potent flame repressants when directly volatilized into a gas flame. Therefore converging evidence points to the basis of the antimony-halogen synergism is being the formation of volatile flame-retardant $SbCl_3$ or $SbBr_3$.

1.7.2 Interaction of antimony and phosphorus

Scattered reports have appeared in the literature to the effect that less than additive or even antagonistic results may be obtained in some systems with combinations of phosphorus and antimony flame retardants. Fenimore [72] reported that the oxygen index of polyethylene containing both halogen and phosphorus was not increased by added $Sb_2 O_3$. Significantly, he reported that the antimony was not vaporized when the compositions burn. He hypothesized that phosphorus prevents the antimony-halogen synergism by preventing the vaporization of antimony.

1.7.3 Phosphorus-halogen interactions

Although the concept of a phosphorus-halogen synergism appears to have gained some currency as a result of its repetition in a number of reviews, it will be shown that evidence for the reality of this supposed phenomenon is dubious.

Piechota [34] conducted a thorough study of the effect of P-, Br-, and Cl-containing flame retardants, separately and in combination, in rigid urethane foams and found that there is no P-Br synergism but additive effect exists. Hindersinn [73] in his studies on phosphorus-halogen interactions in polyester resins indicated that a small but definite synergism exist between phosphorus and chlorine in the system.

The formulation of phosphorus halides and oxyhalides from phosphorus additives and halogen donors has been postulated probably by analogy with the antimony-halogen case and the phosphorus-halogen compounds have been considered to be either free-radical quenchers or flame retardants in some way [74].

1.7.4 Nitrogen-phosphorus interactions

Nitrogen-phosphorus synergism appears real in cellulose [75-77], but its occurrence and magnitude show a subtle dependence on the detailed structure of the nitrogen compound and even on the mode of application. The catalysis of cellulose phosphorylation by the nitrogen compound appears to be involved [75-77]. Many reports of synergism are of dubious significance because the effect is not well defined in reference to an additive model.

1.8 PROBLEMS IN FLAME-RETARDANT APPLICATION

There are many problems related to flame retardant applications in polymers. Though lot of research and developmental work have gone into solving these problems, some of them still remain potential areas of intense study.

One of the earlier problems when water soluble inorganic salts were used as flame retardants was the tendency of leachability which with the introduction of organic was partially solved. However, low molecular weight organic flame retardants bloom causing much discomfort. to the user. Also addition of large amounts of fire retardants are required in many cases and this tells upon the performance properties of the polymer and may cause deleterious effects of the flame retardants. The incorporation of effective amounts of flame retardants in polymers without impairing polymer properties is an extremely difficult problem [67].

The problem of retention of flame retardant activity throughout the life of a polymer has given rise to a lot of studies regarding the evaluation of the effect of environmental conditions which the product is likely to encounter in use (eg. light, temperature, abrasion, humidity, reactive gases and liquids etc.) [67] . The organic compounds of phosphorus and halogen are well known and can cause environmental hazards and pollution [78-80].

There are also problems concerned with compatibility and miscibility with various polymers. The evolution of smoke and toxic gases poses a major problem for flame retardant technologies. Another problem that is currently gaining interest is the combustion toxicity of polymers [81,82] which possibly needs appropriate definition and test methods for evaluation [83]. Another major concern is the added cost that comes with the addition of a new material.

1.9 WIDE SPECTRUM FLAME RETARDANTS

The literature on FRs is replete with innumerable examples for various applications, but there is no FR that satisfies all the requirements. For each application a separate flame retardant has to be selected, that too based on the nature of the polymer and its properties. This increases the complexity in FR development and evaluation. Attention towards the development of a wide spectrum FR that satisfies most of the FR requirements and at the same time compatible with a broad range of polymers has increased.

Recent developments indicate increased use of FRs containing more than one FR element in the same molecule [84]. There are indications that if the FR elements particularly Br is distributed between aromatic and aliphatic segments of the same molecule the FR effectiveness increases [85]. There is also a recent report [86] that the presence of aliphatic segments attached to the aromatic portion increases flame retardancy particularly Br attached to the aliphatic portion of such a molecule. Consider that such a molecule is an amphibilic system having both hydrophilic and hydrophobic moiety. Such a system is expected to be compatible and miscible with a wide range of polymers. This gives rise to possibilities for developing wide spectrum FRs. There are a variety of such amphibilic molecules existing in nature. One example is cardanol, obtained from the plant Anacardium occidentale L. as a byproduct of the cashew industry [87]. Such molecules have potentialities for chemical modifications to introduce FR groups and also have functional sites for polymerisation into polymeric FRs [88]. Since a higher loading of FR is needed in the case of polymeric FRs [27] the optimum way is to oligomerise them into prepolymers.Such prepolymers will have the advantage of being non-blooming because of higher viscosity than the conventional FRs. It is also not expected to affect deleteriously mechanical properties of the polymers compared to conventional FR chemicals. The availability of functional sites can be utilised to prepare reactive prepolymers that could be used to modify the polymer. Since the system is still in liquid nature processing is easier. In fact most of the drawbacks enlisted from conventional FRs could be overcome by the prepolymer techniques.

1.10 FLAME RETARDANT COMPOUNDS

Lewin et al [26] and Tesoro [67] identify an ideal FR as follows: (1) it should reduce flammability to a given standard, (2) reduce (or at least not to increase) smoke generation, (3) not to increase toxic products, (4) be retained in the product through normal life, (5) have accepted minimal deleterious effect on the performance properties of the polymer, (6) should be compatible with the polymer, and (7) should not cause economic penalty.

In general, compounds of the elements P, N, halogens, boron, antimony and salts of a few other metals are found to exhibit FR characteristics [7]. Based on their mechanism of action flame retardants can be classified as follows [7,26,27,67]: (1) chain transfer agents which slow down the free radical chain reactions in the gaseous phase e.g. organic compounds of halogens, (2) materials that act as char formers e.g. inorganic acids and salts that act as dehydrating agents and organic compounds of phosphorus that contribute to the solid phase mechanism, (3) endothermally decomposing inorganic salts which give rise to non-flammable gas such as H_2O, CO_2, NH_3 etc. e.g. $Al(OH)_3$, ammonium salts, $CaCO_3$ etc., (4) compounds that form glassy coatings, e.g. inorganic salts that melt and give coating preventing entry of O_2 and heat to the reacting phase, (5) molecules which reduce the volatility of flame resistant compound, (6) resin formers which act as coupling agents between the substrate and flame retardants, (7) compounds that act synergistically e.g. antimony compounds in the presence of halogens. the phosphorus-halogen and phosphorus-nitrogen compounds are also thought to act synergistically. The pertinent aspects of a few fire-retardant systems are discussed below.

1.10.1 Phosphorus compounds

Organic phosphorus compounds are successfully employed in fire retardation of a number of polymers [7,26,27,67.]. Cellulosics [89] and polyurethanes [7,26,27,90] are two examples worthy of mention.

In polyurethanes also, the action of phosphorus based fire retardants appear to involve char formation [91]. FRs are expected to condense with the depolymerised isocyanates or amines forming thermally stable resins and char.

The char formation on a smoldering combustion is further enhanced and smoldering prevented with the additions of FRs.

Phosphorus compounds can also act thermally to break down the polymer for enhanced drip [92]. It is also reported that certain phosphorus compounds such as trimethyl phosphate, triphenyl phosphine oxide etc. act to modify the vapour phase processes [93,94].

In poly(ethylene terephthalate) and poly(methyl methacrylate), phosphorus FRs produce aromatic residue and char and the char is thought to act as a thermal barrier [95]. In general, phosphorus flame retardants act as an acid precursor in the solid phase to induce selective decomposition path ways that result in the reduction in the rate of fuel formation and an increase in charring [96].

1.10.2 Halogens

Halogen fire retardants function generally in the vapour phase by radical transfer mechanisms [67,97]. This is predominantly the mechanism of bromine containing fire retardants (1.4.2) The predominant flame retardant action of chlorine compounds is centered in condensed phase process and is expected to increase char formation. Hilado and Casey reported that chlorinated rubber has a greater tendency to char than do styrene butadiene rubber, nitrile rubber etc. [98]. Bromine compounds are greatly twice as effective as chlorine compounds [67]. It is desirable for the fire retardant to decompose at lower temperature 60^{0} C less than the decomposition temperature of the polymer [99]. Bromine compounds with decomposition temperature in the range 200- 300^{0} C go well with the decomposition of most of the plastics [67]. Another mechanism of halogen action postulates that the halogen alter the physical properties density and heat capacity of the oxidant mixture so that the flame propagation is effectively prevented [100]. Both dripping and char formation interfere with the energy feed back cycle.

1.11 FLAMMABILITY Vs THERMAL STABILITY OF POLYMERS

Flammability of a polymer decreases as its thermal stability increases. Thus thermally stable polymer structures that are inherently flame resistant can be built up. Fig. 1.3 gives structures of a few polymers that are inherently flame resistant. Their high cost and processing difficulties, however restrict their use to high performance applications. It becomes therefore apparent that use of flame retardants as additives or reactive systems is the only way open to make polymers that are flammable flame resistant. However, knowledge on thermal stability of polymers is required for the selection and use of appropriate flame retardants.

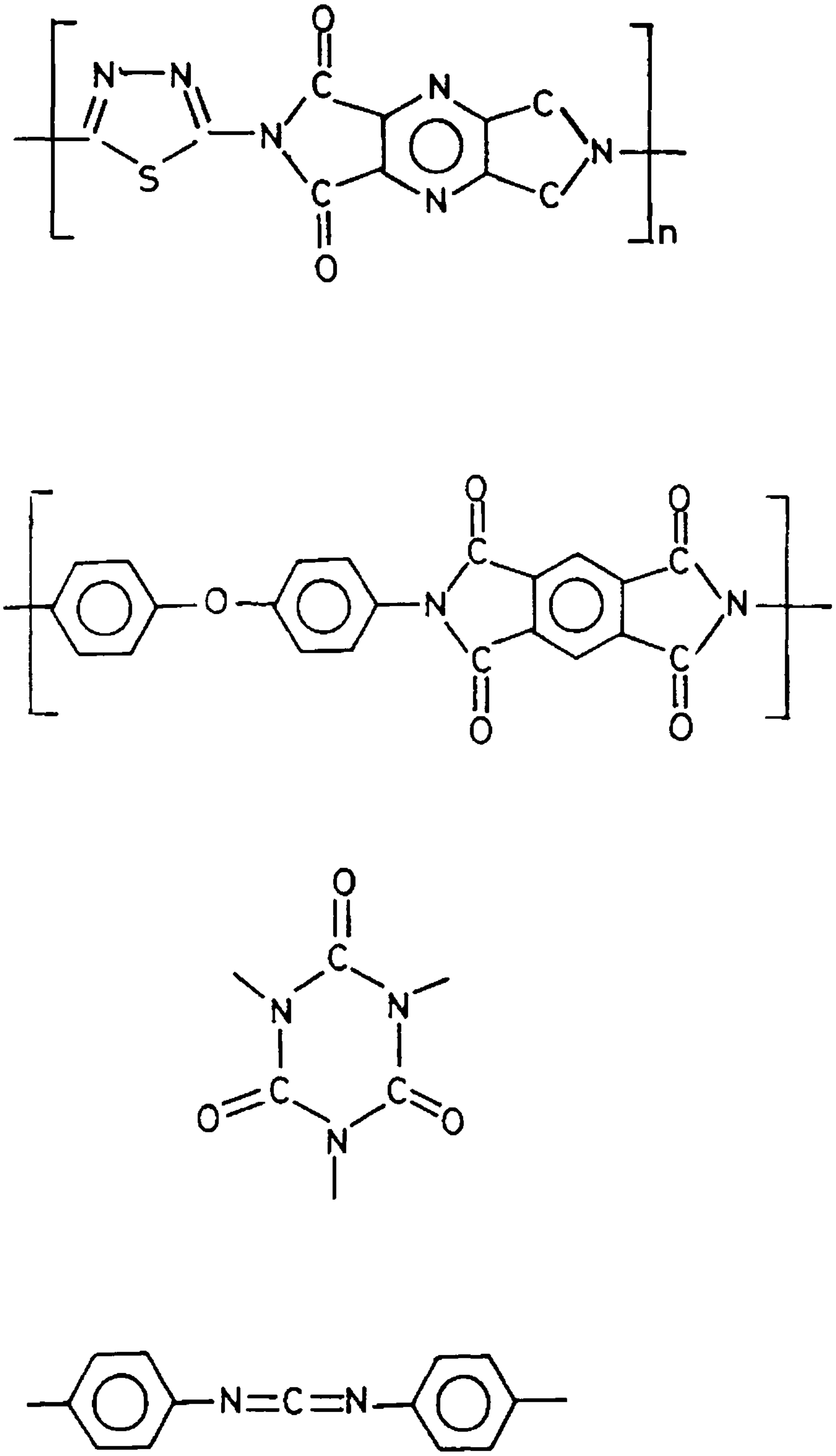


Fig.1.3: Inherently flame resistant structures

1.11.1 Thermally stable polymers

Extensive investigations have been carried out in the field of thermally stable or high temperature resistant polymers for the last three decades. Research in this field has received impetus mostly from defence and space requirements owing to the need for ablative systems, high temperature adhesives and coatings and heat and flame resistant fibres. Among the three broad group of polymers, organic, organo-inorganic and inorganic, organic polymers find more extensive commercial importance as heat resistant polymers. For a polymer to be considered as thermally stable, the thermal stress in terms of time and temperature that the material has to withstand is to be defined. An increase in either of these factors shortens the expected life time, and if both are increased the use time is shortened logarithmically. H.H. Levine[101]has specified the total thermal stress for a heat resistant polymer to withstand as 177°C (350°F) for 30,000 hours, 260°C (500°F) for 1000 hrs, 538°C (1000°F) for 1 hour or 816° C (1500°F) for 5 minutes.

The most widely used method for comparing the thermal stabilities of high temperature polymers is dynamic thermogravimetric analysis (TGA). TGA data provides information about the threshold temperature at which major fragmentation occurs and is therefore an indication of the inherent stability of the polymer structure [102]. In TGA, the sample weight loss is continuously monitored at a given heating rate and in a specified environment of vacuum, air or inert atmosphere. This method of analysis has the advantage of being rapid and reproducible when experimental conditions are carefully controlled. Since the heating rate employed in the analysis are relatively rapid (2-30^{o}C/min), TGA curves are generally considered as an index of short term stability. One disadvantage is that TGA curves are sensitive to experimental variables such as particle size and heating rate. Because of the sensitivity of TGA to experimental conditions a strict comparison of thermal stabilities can only be achieved by analysing samples of interest under identical conditions.

At times, isothermal thermogravimetric analysis (IGA) is also used, though it is not as popular as TGA. In isothermal thermogravimetric analysis weight loss as a function of time is recorded at a specified temperature. One limitation of this method is that at high temperatures, appreciable weight loss is incurred during the heat up period before thermal equilibrium is reached. Both TGA and IGA are based on weight loss and provide no information on such processes as glass transition temperature (Tg) or crystalline melting point (Tm) which do not involve weight loss. These properties can be measured by differential thermal analysis (DTA) and differential scanning calorimetry (DSC). Both DTA and DSC are used for detecting endothermic or exothermic changes suffered by the polymer[103]while heating the material at a constant rate. There are inherent limitations to these methods also due to variables such as heating rate, sample size and others. Other methods of thermal analysis such as torsional braid analysis (TBA), thermomechanical analysis (TMA) and mass thermal analysis (MTA) have been applied only to very few high temperature polymers.

1.11.2 Structural and theoretical requirements for thermal stability

The greatest source of thermal stability of a polymeric material is the primary bond energy that exists between the atoms in the chain. The strength of a chemical bond imposes an upper limit on the vibrational energy that a molecule may possess without bond rupture. Since heat increases the vibrational energy, the heat stability is related to the dissociation energy of the bond. Bond dissociation energy between two atoms can be determined by measuring the energy of dissociation into atoms or the heat of formation from the elements. The bond energies between atoms capable of forming the polymer chains are given in Table 1.4 [104].

Besides the primary bond energies, polymers may also derive additional stability from secondary valence forces. These forces have a pronounced effect on Tg and Tm. Secondary valence forces may arise as a result of several effects. The two important are dipole-dipole interaction (upto 8. 7 Kcal/mol) and hydrogen bonding (6-10 Kcal/mol).

The resonance stabilization of aromatic and heterocyclic

Table 1.4 : Bond energies between the atoms capable of forming polymer main chain

Bond	Bond energy, kcal/mole
$C_{al} - C_{ar}$	98.0
$C_{al} - C_{al}$	83.0
S-S	63.0
Si-Si	53.0
P-P	53.0
$B_{ar} - N_{ar}$	115.0
$C_{ar} - N$	110.0
$C_{ar} - O$	107.0
Si-O	106.0
B-N	105.0
$C_{al} - O$	93.0
$C_{al} - N$	82.0

structures contribute substantially to the bond strength and thermal stability. The resonance energies of these cyclic structures range from 40-60 Kcal/mol.

Another very important requirement for heat-resistant polymers is high melting or softening temperature. High softening systems could be achieved by (1) crystallisation, (2) crosslinking and (3) chain stiffening.

Most of the thermally stable polymers are (1) polymers containing aromatic or heterocyclic units in the main chain, (2) fluorine containing polymers, and (3) inorganic and hetero-organic polymers such as silicones and boron containing polymers.

1.12 SELECTION OF FLAME RETARDANT ELEMENTS AND FLAME RETARDANT POLYMER SYSTEMS FOR THE PRESENT STUDY

A number of elements are known to give rise to flame retardancy to polymers. These are phosphorus, halogens, nitrogen, boron, arsenic, antimony, certain heavy metals etc. Phosphorus is well known to impart flame retardancy to oxygenated polymers such as cellulose, phenolics, polyurethanes etc. In order to enhance the FR effect, halogens such as Cl or Br is also incorporated into the FR. Although addition of Br to phosphorus containing polymers enhances the LOI values, the mechanism of the combined effect of P and Br is still to be settled. There are contradictory reports on the combined effects of phosphorus and bromine on the flammability of these polymers. It was shown in a recent work at RRL, Trivandrum, that CNSL based thermoset polymers containing P and Br built into its structure exhibited good self-extinguishing property and ablation. The need for evaluating the thermal and flammability behaviour of model compounds containing phosphorus and bromine is thus apparent.

Phenolics and the analogous substituted phenolic polymers, for example, cardanolics (cardanol-formaldehyde resins and related resins are hereafter referred to as cardanolics) were selected for the present study because

1. Phenolics are highly oxygenated polymers where phosphorus is highly effective as FR
2. Phenol can easily chemically modified to introduce FR elements.
3. Cardanol has in its structure both hydrophobic and hydrophilic moieties that favours formation of wide spectrum flame retardants as discussed earlier.
4. Both phenol and cardanol are model compounds for incorporating P and Br so that their thermal and flammability behaviour could be correlated to have an understanding on the thermal and flammability behaviour of the ablative material mentioned earlier.
5. On going from phenol to cardanol the only structural difference is the aliphatic C_{15} side chain. A study on the effect of the side chain on the thermal and

flammability behaviour could be interesting and is expected to lead to a complete understanding on these systems.

1.13 THERMAL DEGRADATION AND FLAMMABILITY OF PHENOLIC RESIN

1.13.1 Phenol-formaldehyde reaction mechanism

The conditions mainly pH and temperature under which reactions of phenols with formaldehyde are carried out, have a profound influence on the character of the products obtained [105]. Two prepolymer types are obtained depending on pH.

Novolaks are obtained by the reaction of phenol and formaldehyde in the acidic pH region. In general, the reaction is carried out at a molar ratio of 1 mol phenol to 0.75-0.85 mol of formaldehyde. Novolaks are mostly linear condensation products linked with methylene bridges of a relatively low molecular weight upto 2,000. These resins are soluble and permanently fusible, i.e. thermoplastic and are cured only by addition of a hardener, almost exclusively formaldehyde applied as HMTA to insoluble and infusible products.

Resols are obtained by alkaline reaction of phenols and aldehydes, whereby the aldehyde is used in excess. P/F molar ratios between 1:1 to 1:3 are customary in technical resols. These are mono- or polynuclear hydroxy methylphenols (HMP) which are stable at room temperature and by application of heat, seldom of acids are transformed into three-dimensionally cross-linked, insoluble and infusible polymers (resits) over different intermediate stages (resitols).

1.13.2 The degradation of phenolic resins

The degradation, both thermal and thermo-oxidative of phenolic resins has been examined by Conley [106]. Infrared spectral analysis was used extensively in the investigations of phenolic-resin decompositions, as well as thermogravimetric analyses [107], elemental composition studies [107], gas chromatographic studies [108,109], model-compound and degraded polymer synthesis [110,111] and various curing procedures, to examine the effect of the degree of cure on the degradation of the phenolic-resin system [107-109,112]. The first step in the oxidation of phenolic resins can be visualized as shown in Fig. 1.4.

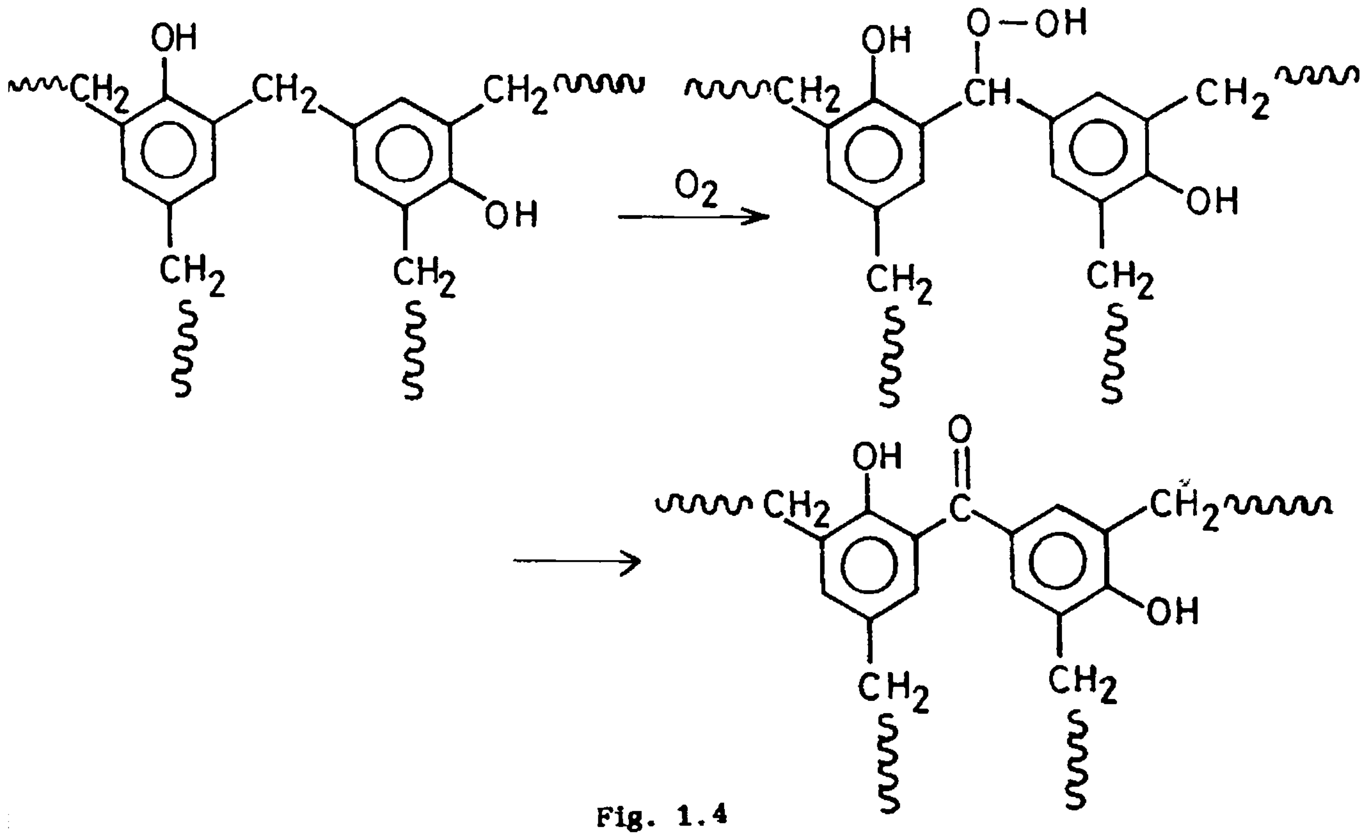


Fig. 1.4

Further oxidation resulted in evidence that was consistent with the following Fig.(1.5) which results in the formation of chain scission products.

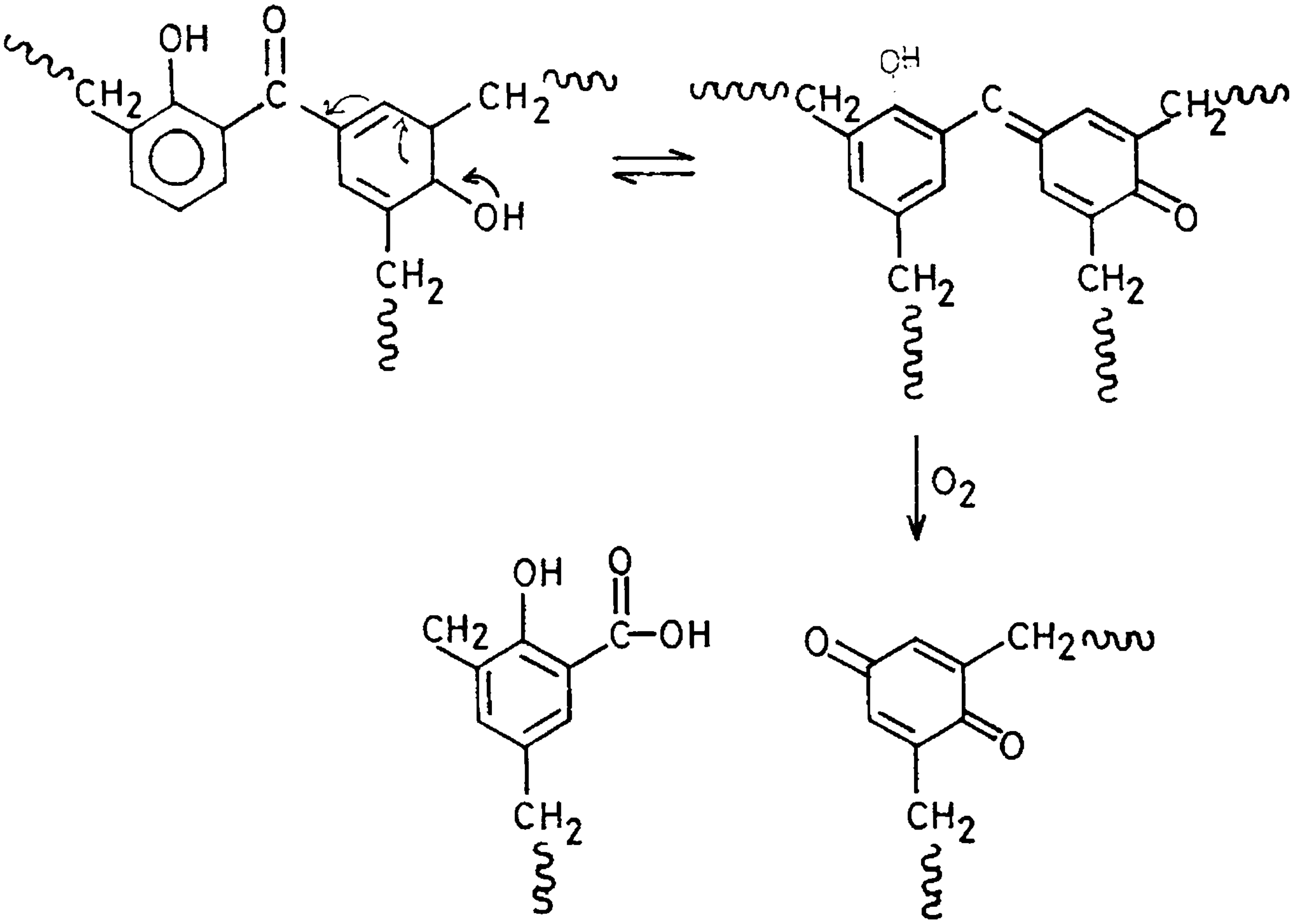


Fig. 1.5

Degradation above 250°C and as high as 1000°C has been examined [107-109,113,114]. Examination of the volatile products as a function of temperature and degree of pyrolysis showed that the chief products were CO, CO_2 and H_2O as expected for the extended oxidation of the resin. Paraformaldehyde, methane and aromatic products were also formed. From the available data, it seems clear that oxidation is the primary mode of phenolic resin decomposition through approximately 700^{o} C, regardless of whether the resin was decomposed in air, argon, or nitrogen atmospheres. The high-temperature pyrolysis (between 700 and 1000^{o}C) of phenolic resins in vacuuo was studied by mass spectral thermal analysis and the reactions which have been proposed to account for the observed product types are shown in Fig. 1.6 [109].

From the data reported concerning phenolic resin degradation it is possible to suggest that regardless of the particular resin species present before curing, the degradation processes occurring at elevated temperatures are dependent upon the thermal and oxidative stability of the dihydroxy diphenyl methane unit, and therefore these polymers all behave similarly from a chemical viewpoint once the curing processes are complete.

1.13.3 FLAME RETARDATION IN PHENOLIC RESINS

In general, phenolics are considered to have moderate nonflammability characteristics. They vary from slow burning to self-extinguishing The rapid loss of volatiles below the ignition temperature leaves a carbonaceous residue which is quite stable [106]. Within a short time the char undergo a highly exothermic reaction which raises the internal temperature of the material. Such reaction characteristics strongly suggest the formation of peroxide species in high concentration by a carbon-radical scavenging process during the cooling stage. Decomposition of

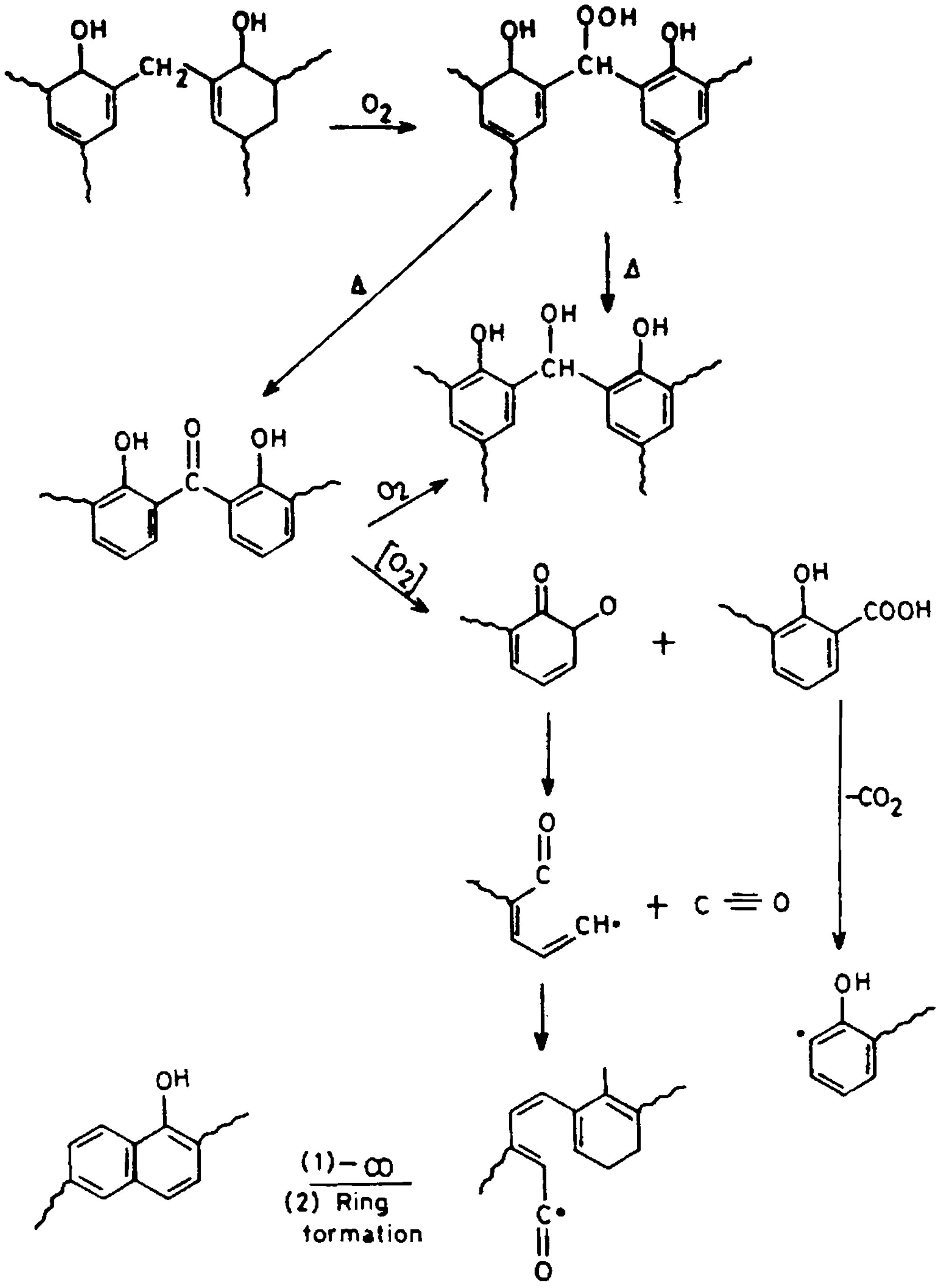


Fig.1.6: Proposed char forming reactions in phenolic resin system

the peroxidic species, is so highly exothermic that the char becomes incandescent.

However, most of the technology concerning flame retardation of phenolic resins involves either the incorporation of substances known to exhibit flame-retarding properties into the backbone structure of the organic polymers or the addition of various compounds or combinations of compounds into the resin system to impart flame-retardant characteristics [106].

1.13.4 Phosphorus and nitrogen compounds

Various types of phosphorus compounds have been added to phenolic resins to impart improved flame resistance [115]. Approximately 6% by weight of phosphorus in a phenolic resin will render it self-extinguishing. About 2% P and 2% N in a phenolic will also have the same effect [116]. These additives may facilitate the formation of ring structures which produce charring and aid flame retardancy.

1.13.5 Halogen compounds

Halogen compounds make phenolic resins more flame resistant but at the expense of increased smoke emission in some cases. Novolaks can be chlorinated by chlorine gas for improved flame retardancy [117]. Laminates, coatings, castings and molded articles were prepared from this composition and are self-extinguishing.

1.13.6 Miscellaneous

Boron compounds also improve the flame retardancy of phenolic compounds. It has been found that by adding aluminium chloride to an aqueous acid curing phenolic formaldehyde condensate its flame retardancy and self-extinguishing characteristics are greatly improved [118]. Nonfriable, self-extinguishing foamed constructions can be prepared by coating expanded phenolic panels with solutions of alkali-metals or alkaline-earth-metal silicates or fluoro silicates [119]. Table 1.5 lists some commercially available flame retardants for phenolics.

Table 1.5 : Commercial flame retardants for phenolics

Organic additive	Trade name	Manufacturer
1. Phosphate esters	Escoflex CDP	East Coast Chemical
	Antoxal	Eronel Industries
2. Cresyl diphenyl phosphate	Escoflex CDP	East Coast Chemical
	Santicizer 140	Monsanto
	Disflamoll DPK	Naftone
	Phosflex 112	Stauffer Chemical
3. Halogenated organic polyphosphate	Phosgard C-22-R	Monsanto
	PC-45	Upjohn
4. Chlorinated diphenyls and polyphenyls	Arroclor	Monsanto
	Clphen	Naftone

Organic additive	Trade name	Manufacturer
5. Tris(2-chloroethyl) phosphate	TCEP	British Celanese
	Fyrol CEF	Stauffer Chemical
6. Trichloropropyl phosphate	TCPP	British Celanese
7. Tris(2,3-dibromopropyl) phosphate	Firemaster T23P	Michigan Chemical
	LV-T23P	Great Lakes Chemical
	Fyrol 32 B and HB-32	Stauffer Chemical
8. Box dimer $C_{10}C_{12}$	Dechlorane	Hooker Chemical
9. Chlorinated paraffin	Chlorowax liquids and solids	Diamond Shamrock
	CP-40 and CU-50	Hooker Chemical
10. Chlorinated organic	Dechlorane plus 602	Hooker Chemical
11. Antimony trioxide dispersions	HSC-P series	Harwick Podell Industries
12. Barium metaborate dispersions	Busane 11-MI	Ware Chemical
13. Zinc borate	ZB-112, 325 & 237	Hamphrey Chemical
	Firebrake ZB	U.S. Borax
14. Di-(polyoxy ethylene)-hydroxy methyl phosphonate (reactive type of additive)	Fryol HMP	Stauffer Chemical

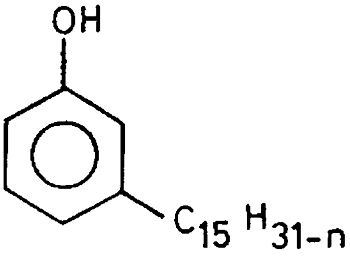
1.14 CARDANOL BASED POLYMERS AND THEIR FLAME RETARDANCY

Cardanol, obtained from the plant Anacardium occidentale L. has been shown to be a monohydric phenol with a C_{15} side chain in the meta position and is obtained from technical grade cashew nut shell liquid (CNSL) by vacuum distillation at 3-4 mm Hg and the fraction distilling at 228-235^{o} C was collected [120]. The physical properties of cardanol are given in Table 1.6.

Table1.6:Physical properties of cardanol

B.P. ^{o}C	228-235^{o}C (3-4 mm Hg)
Colour (Lovibond, Red	(1.0-3.0,1 cm cell)
Freshly distilled	Yellow (1.5-3.5)
Viscosity (30^{o}C) cP	45-52
Refractive index	1.50 μ

Cardanol is a mixture of four components differing in the degree of unsaturation of the side chain (Fig. 1.7) [121]. Molecular formula, molecular weight and percentage composition of each component of cardanol are given in Table 1.7 . The percent composition however may vary depending upon the source, method of extraction etc. There have been many attempts to separate the components of cardanol and foremost among them is the work of Tyman [122-124].



n = 0 $(CH_2)_{14}\ CH_3$

n = 2 $(CH_2)_7\ CH = CH\ (CH_2)_5\ CH_3$ 8'(Z)

n = 4 $(CH_2)_7\ CH = CH\ CH_2CH = CH(CH_2)_2CH_3$ 8'(Z), 11'(Z)

n = 6 $(CH_2)_7\ CH = CH\text{-}CH_2\text{-}CH = CH\ CH_2\text{-}CH = CH_2$ 8'(Z), 11'(Z) 14'(Z)

Fig. 1.7: Structure of cardanol

Table 1.7 : Chemical composition of cardanol

Component	M.wt.	%	Molecular formula
Cardanol with saturated side chain	304	5.4	$C_{21}H_{36}O$
Cardanol with one double bond in the side chain (monoene)	302	48.5	$C_{21}H_{34}O$
Cardanol with two double bonds in the side chain (diene)	300	16.8	$C_{21}H_{32}O$
Cardanol with three double bonds in the side chain (triene)	298	29.3	$C_{21}H_{30}O$

The structure of cardanol was established through the painstaking efforts of a series of workers such as Dawson and Wasserman [125], Paul and Yeddanappalli [126], Tyman and his group [127], Gedam et al etc. One of the significant aspects of its structure is its amenability to chemical modifications and polymerisations. An examination of Fig.1.7 shows that cardanol can undergo chemical modifications at the hydroxyl group, substitution reactions on the phenolic ring and oxidation/addition reactions at the side chain. The presence of active hydrogens of the phenolic ring and the unsaturation in the side chain make it polymerisable either by step reaction polymerisation or by chain reaction polymerisation or a combination of both as is practised in the preparation of resins for brakelining [128]. Cardanol thus possess interesting structural features for development of speciality polymers.

1.14.1 Chemical modification of polymerization of CNSL and cardanol

The Regional Research Laboratory, Trivandrum, has recently developed two prepolymers ANORIN-38 and ANORIN-44 [129-132] by reaction with orthophosphoric acid followed by halogenation. The presence of highly acidic environment oligomerises the phosphorylated molecules into a prepolymer simultaneously. ANORIN-38 contains only P (8%) and ANORIN-44 contains both P and Br (25%).

Both ANORIN-38 and ANORIN-44 are highly reactive with aldehydes, amines etc. [130,131]. They can be converted to thermoset products [130-132]. The limiting oxygen index of some of these products are given in Table 1.8.

Table 1.8 : Limiting oxygen index values of a few fully cured Anorin series fire-retardants

Resin	LOI value
Phos. CNSL	38.0
Phos. and bromine containing resin	43.5
NR + ANORIN-38	21
NR + ANORIN-44	28
NR + ANORIN-44 + Sb_2O_3	42.0

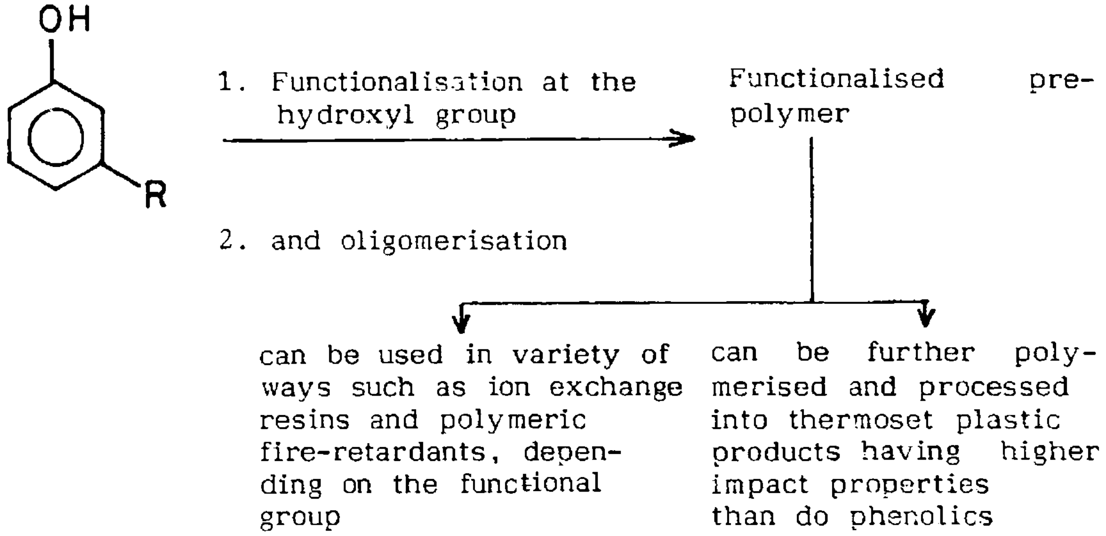
ANORIN-38 showed excellent miscibility and compatibility with a wide range of polymers. It showed comparatively good FR activity with polyethylene and polyurethane. Both ANORIN-38 and ANORIN-44 increased the mechanical properties of natural rubber [133] and enhanced processability. Another interesting observation was that ANORIN-44 in combination with Sb_2O_3 showed excellent synergism with natural rubber.

The use of halogen definitely gives rise to smoke, but blending with appropriate amounts of boric acid or aluminium trihydrate reduced the smoke level completely without deleteriously affecting the properties. The present data obtained with these two prepolymers indicate a wide range of applicability without deleterious effects and above all cost effectiveness, a factor that controls the market conditions. A composite panel prepared from fully cured ANORIN-44 does not burn even under oxy-acetylene flame around at 3000°C. This material was found to show excellent ablation characteristics.

1.14.2 High performance polymers from cardanol

The structural difference between phenol and cardanol is only the C_{15} unsaturated side chain and hence cardanol undergoes most of the reactions of phenol. Thus cardanol can be polymerised with formaldehyde to give resols and novolaks [134]. The presence of the side chain gives it an added advantage that it can be polymerised by chain reaction methods as well. This gives rise to opportunities for selection and control on polymerisation techniques for a particular product. For example, the preparation of resins for brakelining is reportedly made by making use of an acid catalysed side chain polymerisation followed by the conventional formaldehyde condensation. Apart from the variety in polymerisation reactions cardanol can also undergo chemical modifications at the hydroxyl, ring and the side chain. Moreover, the hydrocarbon side chain itself by its very presence imparts new properties such as internal plasticization, flexibility etc. [121]. A study by Pillai et al [135] have shown that high performance and speciality polymers could be produced from cardanol by a variety of methods such as:

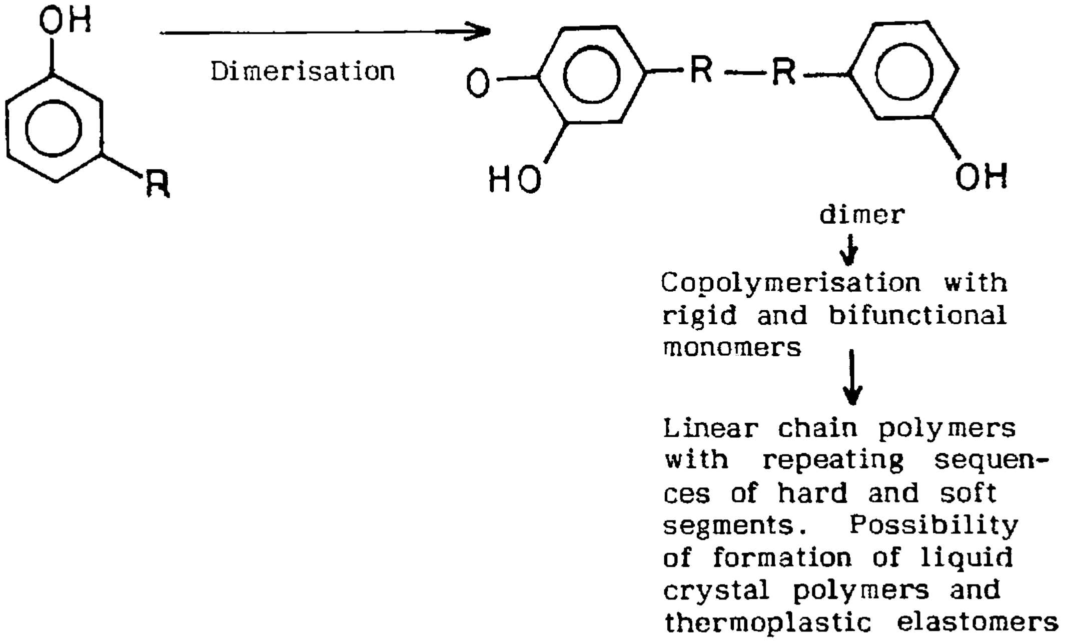
1. Prepolymer route:



can be used in variety of ways such as ion exchange resins and polymeric fire-retardants, depending on the functional group

can be further polymerised and processed into thermoset plastic products having higher impact properties than do phenolics

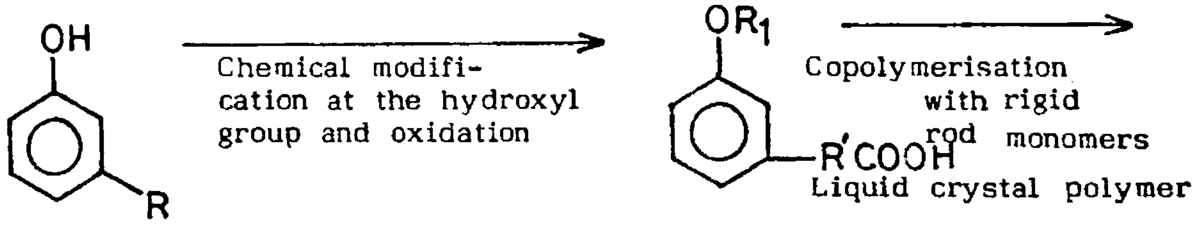
2. Dimer route:



Copolymerisation with rigid and bifunctional monomers

Linear chain polymers with repeating sequences of hard and soft segments. Possibility of formation of liquid crystal polymers and thermoplastic elastomers

3. Oxidation route:



When studies were initiated to develop speciality polymers from cardanol, it became apparent that there exists a wide gap between the technology and scientific understanding. There has been a total lack of data on kinetics and mechanism of polymerisation of cardanol except the work of Misra and Pandey who reported the kinetics of alkaline catalysed formaldehyde condensation [136]. It is well known that it is not possible to apply modern methods of polymer science and technology for the development of speciality polymers without basic data on polymerisation characteristics and structure-property correlations. So kinetics and mechanism of polymerisation of cardanol were studied using acid catalysts such as H_2SO_4, H_3PO_4 and Lewis acids such as BF_3 etherate [137]. These studies showed that cardanol undergoes oligomerisation under acidic conditions through the side chain unsaturation and the oligomerisation is initiated by protonation of the side chain followed by cationic chain growth. These studies led to the development of the prepolymer technology where cardanol was functionalised at the hydroxyl group using orthophosphoric acid [135]. The high acidic conditions simultaneously initiate oligomerisation giving rise to a prepolymer as the phosphorylated product. It was found that formation of the prepolymer (PCP) is advantageous in the sense that it can be used as a multipurpose resin because of the possibilities of its different end products as shown earlier. The introduction of the phosphate group raised the LOI value from 21.0 to 35.0 for the amine cured product and the lap shear strength for wood to wood bonding increased 500 fold (Table 1.9).

Table 1.9: LOI value of cured PCP/PCNSL resin

Resin	LOI
PCP (HMTA) cured	35.0
PCP (Paraformaldehyde) cured	33.0
Brominated PCP	42.0
Cardanol-formaldehyde (Novolak)	21.0
CNSL-formaldehyde	21.0
Polyethylene	16.9
PCP-Polyethylene	24.5

When it was used as matrix resin for asbestos fibre based brakelinings, a fade value as low as 19% was registered.

The presence of both hydrophilic and hydrophobic groups in the same molecule makes PCP an ideal candidate for wide spectrum [138] polymeric flame retardant. PCP resins were found to be compatible with a wide spectrum of polymers such as polyolefins, polyurethane and natural rubber.

One of the significant observations has been that introduction of bromine into the phosphorylated prepolymer imparts the property of ablation to the polymer [132]. When tested by oxy-acetylene panel experiments conducted as per ASTM method, the PCNSL based ablative reinforced thermoset product gave a total burn through time of 97 sec compared to 88 sec for conventional phenolic and 200 sec for a blend of PCNSL with phenolic resin suggesting synergism. Thermal analysis of brominated PCP did not show any significant contribution to ablation from thermal stability and char yield. So it was inferred that the ablation process might arise from the endothermic liberation of vapours of hydrobromic acid followed by transpiration cooling effected through the decomposition gases of the side chain [139].

In another study, it was shown that cardanol-formaldehyde (CF resins, both resol and novolak) form semi-interpenetrating networks with PMMA [140]. Although interpenetration of PMMA increases the mechanical properties only marginally, it showed a stabilization in PMMA at 350^{0}C from 50% decomposition to 15%. However, the Tg of CF registered an unusual increase from 128^{0}C to 144^{0}C suggesting restriction in the segmental motion of the CF phase brought about by mixing with another rigid polymer such as PMMA [141].

One of the remarkable achievements in converting cardanol into high temperature resistant polymer was the successful preparation of a homopolyester and a thermotropic liquid crystalline polymer [142]. When cardanol was subjected to phase transfer catalysed $KMnO_4$ oxidation the side chain was cleaved and oxidised to 3-HPOA (8-(3-hydroxy phenyl) octanoic acid.
3-HPOA is a bifunctional monomer possessing both 'kink' structure and flexible segment $(-(CH_2)_7)$ built into the same molecule.

These structural features are useful in bringing down the transition temperature of intractable liquid crystalline polymers such as P-HBA so that they could be made processable. While HPOA was copolymerised with P-HBA , the LC copolymers showed a transition at 256°C which is much lower than those of the commercial products Vectra and Xyder. The istropic melting of the polymer occurred at 409°C.

It appears that the opportunities for chemical transformation of cardanol into high value polymers are vast.

1.15 SOME PROSPECTIVE APPROACHES TO MORE EFFICIENT FLAME RETARDANT SYSTEMS [143]

1.15.1 Vapour phase flame retardants

The widely used flame retardant systems which contribute hydrogen chloride or hydrogen bromide to the vapour phase may be acting by not much more than a physical heat capacity effect [144]. The work on tris (dichloroisopropyl phosphate) in polyurethane foams by Weil et al also suggests a physical mode of action [145]. Flame studies in hydrogen oxygen flames show vaporized metals active as hydrogen atom recombination catalysts. Therefore it can be said that vapour phase flame retardants may be found for use in plastics.

Efficient physical barriers to heat, air and pyrolysis products

Carbonaceous char barriers may be formed by the normal mode of polymer burning and besides the reduction in the amount of material burned, the char may act as a fire barrier. For polymers with low char forming tendencies, such as poly olefins, one approach to get a char is to add a char-forming additive (generally bearing a resemblance to intumescent coating compositions) [146].

1.15.2 Permeability of carbonaceous foam

To work optimally the char or similar barrier should be coherent, adherent, oxidation-resistant and low in permeability to heat and gases. A closed cell foam prevents the penetration of combustion vapors and air through char layer. Gibov et al [147] showed that the incorporation of boric acid and ammonium phosphates helped cut down penetration of the char. The cracking or defoliation of the char can also cause exposure of the underlying material to burning. A general way to improve the coherence of char may be to use formulations of improved intumescent coatings [148],(by use of high aspect ratio inorganic filler).

1.15.3 Oxidative destruction of the char layer and its prevention

The char layer from a burning polymer while it exerts protective action, is itself vulnerable to oxidation. Studies on preventing combustion of carbon fibers, incorporation of borates, phosphates, or low melting glasses has been shown to be effective [149,150]. Other types of barriers include, (1) glassy coatings using low melting glasses, (2) glassy foams, (3) carbonaceous foams with substantial carbon content, (4) fluorocarbon films and coatings, and (5) metallic surface coatings. The char enhancing action of magnesium soaps, siloxane block polymers [151] and the char stabilizing action of lead salts [152] were studied in polyolefins by general electric investigators.

1.15.4 Free radical inhibitors in the condensed phase

Surface (condensed phase) oxidation plays a major part in the flaming degradation of polyolefins [153]. An antioxidant system in the condensed phase should have a flame retardant effect.

1.15.5 Catalytic modes of flame retardant systems

Certain catalytic modes have been well exploited in flame retardant systems, namely the dehydrating action of compounds which yield strong acids under flaming or smoldering conditions. If a hydrocarbon could be made to undergo oxidative dehydrogenation to form water and char, its heat of combustion could be cut to about one-third the heat of complete combustion to CO_2 and H_2O and this would afford a drastic reduction in flammability. There are some reports of the dehydrogenation/oxidative dehydrogenation mode of catalysis for flame retardation.

1.15.6 Polyblends of flame retardant with non-flame-retardant plastics

Since the chemical modification of polymers for improved flame retardancy increases cost and deleteriously affect some other properties, from a commercial stand point, the present trend is to utilize polyblending. For example, in the case of PPO-PS blends, the good char forming ability of the PPO greatly helps flame retardancy [154].

1.15.7 Synergism

The quantitatively-measured flammability of a polymer containing differing levels of a flame retardant is usually not linear, but is more likely to be synergistic or antagonistic. Careful attention to quantitative activity vs concentration relationships, to the effect of interaction terms in combinations and careful observation of the manner in which one mode of action supports and reinforces another seems to lead to highly efficient flame retardant systems.

1.16 FLAME RETARDATION BY INSITU GENERATION OF THERMALLY STABLE STRUCTURES

The existence of innumerable polymers whose mechanisms of combustion vary, calls for various approaches for flame retardation. As has already seen from the earlier discussions, it is clear that inhibition of flammability could be achieved by modifying reactions in the condensed phase or vapour phase processes of a burning polymer. It has already been shown that a a number of fire retardants function by increasing the char yield. Research should be directed to find a catalyst or a comonomer that catalyses the reaction of the polymer to yield ultimately carbon and water. Thus, it is possible to use a more stable aliphatic bromine compound that gives less smoke. In a recent study on brominated phenols containing allyl side chain, the allyl group is said to impart higher stability to the polymer . Similarly alicyclic structure that give more permanency and greater stability could be thought of. Coupled with such fire-retardants a greater understanding on the control of pyrolysis and control of dripping of polymers are needed.

It has been shown that though comparatively less flammable the weak portions of the phenolics are the methylene bridges. The methylene bridges could be replaced by more thermally stable curing agents such as 4-hydroxy benzoic acid, diphenols, furfural etc.

Fenimore and Martin in their study on oxygen index of polymers found that the LOI can be related to the char forming ability of the polymer. This possibility indicates that polymer flammability possibly depends more on the condensed phase reactions.

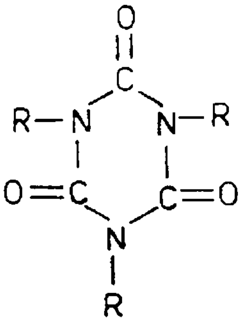
Piechota found definite correlations between raw materials formulation and fire-retardancy of polyurethane foams. Quin studied the effect of structural unsaturation and found that LOI increased with the unconjugated unsaturation and simultaneously the char forming tendency also increased.

The presence of certain structure or segments in a polymer is found to enhance thermal stability. Thus inducing the formation of polycarbodiimide structure and trimerization of isocyanates into thermally stable isocyanurates are two examples that could be applied in the polyurethane system.

$$2\ R\ N\ CO \longrightarrow NR = C = NR$$

Carbodiimide

$$3\ R\ N\ CO \longrightarrow$$



Isocyanurate

Since these structures contribute to stiffness, it would be difficult to build units of high thermal stability and still maintain flexibility.

Anderson has shown that weight loss in polyurethane foam decreases with an increase in cross-link density. Aromatisation, cyclisation and cross-linking of polymer during pyrolysis may favour enhanced char formation.

Certain organic acids such as pyromellitic acid, trimellitic acid and maleic acid are good char formers and oxalic acid and trimellitic acids are combustion modifiers. Ascorbic acid is a good char stabiliser. So polyurethane foam could be made fire retardant without smoke generation by using a combination of char former, combustion modifiers and char stabilizers.

It has been shown that the decomposition reactions of polyurethane can be altered by the addition of aromatic alcohols and aldehydes such as benzyl alcohol, benzaldehyde etc. These additives are believed to function by condensing with the depolymerised acids to form thermally stable resins and char.

When the overall function of a flame retardant including inhibition of smoke and toxic gas is considered, the data shown in this section are significant in the sense that they direct towards a higher level of safe flame retardation through appropriate understanding and control of structures and mechanisms. Possibly, this could turn out to be a better way of looking at the problems rather than going unscrupulously synthesising unlimited number of chemicals for flame retardation. However this attitude should go along with improved methods for measuring flame retardant effectiveness.

1.17 WIDE SPECTRUM FLAME RETARDANTS

This concept has been discussed earlier. This approach may be adopted to develop more effective flame retardants.

SCOPE AND OBJECTIVE

The significance and the need for flame retardation of polymeric materials have been brought out in the preceeding sections. It is clear from this treatment that although there are innumerable flame retardants (FR) with excellent LOI values there is no FR till today that meets all the requirements that specifies an intended use. A review of various approaches to the use of FR has shown that there are definite advantages in using FR, (a) built into the structure of the polymer, and (b) as a pre-polymer. The admirable qualities of wide spectrum flame retardants and their advantages have also been discussed. When all these aspects were considered, it was thought fit to select the system based on phenol (because of its amenability to chemical modifications so that the desired FR element could easily be introduced) and substituted phenols (for example, cardanol from which wide spectrum FR could be developed). So the objectives of the present work are the following:

1. In developing wide spectrum FR based on cardanol, it was evident that there are not enough data on the polymerisation characteristics of cardanol. So it was thought necessary to study kinetics and mechanism of polymerisation of cardanol using BF_3 etherate as initiator.

2. To synthesise and characterise wide spectrum FR pre-polymers and polymers from cardanol containing FR elements

such as P and Br and to evaluate their thermal and flammability behaviour (the elements P and Br were selected because an earlier work at the R.R.L., Trivandrum has shown that CNSL based thermosets containing P and Br exhibits ablation phenomenon).

3. To study separately and together the effect of P and Br on the mechanism of flame retardation with a view to assessing their suspected synergism-additive behaviour.

4. Phenolic resins are believed to degrade by a thermo-oxidative process. Introduction of phosphorus is expected to enhance resistance to thermo-oxidation. Direct phosphorylation of phenolics gives rise to early gelation and so in the present work P is introduced at the monomer level. So the fourth objective is to synthesise and characterise P and Br containing phenolics and evaluate their thermal and flammability behaviour.

5. Polyphosphate esters of phenol are well studied and are known to give good thermal and flammability behaviour. Replacing phenol with cardanol is expected to impart additional property such as improved processability, wide spectrum FR effects etc. So the fifth objective is to synthesise and characterize polyphosphate esters based on cardanol with hydroquinone, bisphenol, tetrabromobisphenol and phenolphthalein and to evaluate their thermal and flammability behaviour.

6. To study the effects of these FR on another polymer and to evaluate the relative performance of monomeric FR vis-a-vis polymeric/wide spectrum FRs, it is proposed to prepare blends of a few of these FRs with polyethylene and study their thermal and flammability behaviour.

7. As the element boron is known to give good thermal and flame-retardant characteristics, it is proposed to synthesise and characterise boron containing polymers of cardanol and phenol and evaluate their thermal and flammability behaviour.

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CHAPTER 2

POLYMERISATION CHARACTERISTICS OF CARDANOL

2.1 INTRODUCTION

A detailed discussion of cashewnut shell liquid and its distillation product cardanol has been presented in the introductory chapter. Cardanol is a monohydric phenol having an unsaturated aliphatic side chain at the meta position (see Table 1.6 for its properties). Being phenolic in nature, it has been used in the manufacture of special surface coatings, brakelining resins, epoxy resins etc. [1-5]. The literature on cardanol is replete with innumerable patents [6-8] and reports [3,4], but its industrial utilization has been lagging behind. Actual commercial ventures have been limited to a few industries and in most of the applications, the inherent properties of cardanol has not been properly utilized. Moreover, an analysis of the literature on cardanol indicates that most of the work is product oriented without much concern for basic studies such as fundamental aspects of polymerisation, structure-property correlations etc.It is well known that information on these aspects are essential for the design and development of advanced polymers to meet specific requirements. The reasons for this lacuna in the case of CNSL polymers may be many, but in the case of cardanol, the inherent problems associated with it is the fact that it is a mixture of four components (see Table 1.7) differing in their degree of unsaturation [9-11]. Although separation of these components has been worked out by many groups [12,13], it was difficult to get polymerisable quantities. Being an inexpensive raw material, large scale manufacturers still prefer cardanol and would not resort to separation [6] into its components on economic grounds. The scarcity of data on the polymerisation characteristics of cardanol and structure-property correlations of its polymers has been an impediment in the development of speciality polymers from cardanol.

One of the most interesting aspects of the structure of cardanol is its ability to undergo polymerisation by both step reaction and chain reaction mechanisms. Addedto this is its amenability to manipulations through chemical modifications (this aspect will be discussed in detail in the next chapter). Being phenolic in nature, cardanol undergoes the conventional aldehyde condensation reactions to give novolaks and resols depending on the conditions of polymerisation. The kinetics of formaldehyde condensation of cardanol has been reported only very recently [14]. In the case of chain reaction polymerisation, few systematic studies are reported except that of dimerization studies of cardanol by Tyman [1]. However, many of the patents [6-8,15] cite a cationic polymerisation involving acid catalysts such as sulphuric acid, phosphoric acid, diethyl sulphate etc. There are also examples of Lewis acids such as aluminium chloride in the polymerisation of cardanol. Even metals and metallic powders are reported to be used in the polymerisation of cardanol. In this perspective, Manjula et al undertook a systematic study of the polymerisation of cardanol using acid catalysts [16,17]. It was further shown that $BF_3.OEt_2$ is a good cationic initiator for the polymerisation of cardanol. The present work was undertaken to study in detail the polymerisation characteristics of cardanol using $BF_3.OEt_2$ as catalyst.

2.2 EXPERIMENTAL

2.2.1 Materials

Cardanol was obtained by double vacuum distillation of cashewnut shell liquid (CNSL-8007-24-7) at 3-4 mm Hg and the fraction distilled at 230-235 °C gave a refractive index of 1.509 and Brookfield viscosity of 450-520 cps at 30°C as reported for pure cardanol [18,19] (CNSL was purchased from Kerala State Cashew Development Corporation, Quilon, and was of standard specification IS:840 (1964). Borontrifluoridediethyletherate (48% BF_3, fluka Chemicals Corporation, Germany) was used as supplied without further purification.

2.2.2 Polymerisation

One typical polymerisation procedure is given below. Cardanol (20 g, 0.67 moles) was taken in a 100 ml 3-necked flask fitted with a mechanical stirrer, reflux condenser, and N_2 inlet, kept in a constant temperature oil bath at $140\pm1^{\circ}C$. The contents were allowed to attain the temperature of the bath and $BF_3.OEt_2$ (0.2 g, 1%) was added with vigorous stirring under nitrogen atmosphere. Samples (1 ml) were withdrawn at definite intervals of time, chilled and were analysed by GPC.

2.2.3 Measurements

The GPC data were obtained using Hewlet Packard 1081B HPLC, equipped with an automatic sample injection system and a differential RI detector. The GPC columns used in this work were styrene-divinyl benzene copolymers based microstyragel 100 A^0 and 500 A^0 (Waters Associates) connected in series. An additional column with a large porosity (10^3 A^0) was used along with the present set of columns to get better resolution. THF (HPLC grade) was used as the eluent. The GPC columns were calibrated [20-22] by the linear calibration method (Least Square Approximation) with monodisperse polystyrene standards, supplied by M/s. H. Knauer & Co., West Germany. Polystyrene standards used had molecular weight in the range of 800-19000 with a polydispersity of 1.08±0.02.

The transmission infrared spectra were recorded on Perkin Elmer IR Spectrophotometer Model 882 as neat films on NaCl windows by the smear techniques. ^1H NMR spectra were recorded on Hitachi R-24B high resolution NMR spectrometer in CCl_4 using TMS as internal reference. ^{13}C NMR spectra were recorded on a JEOL FX-90 Q FT spectrometer.

2.3 RESULTS AND DISCUSSION

The polymerisation of cardanol initiated by $BF_3.OEt_2$ was studied. Initial optimization studies showed that addition of $BF_3.OEt_2$ polymerises cardanol within a few minutes and that the optimum temperature of polymerisation is 140°C.

2.3.1 Effect of time and temperature

Fig.2.1 gives the GPC patterns of the polymerisation products of cardanol at 140°C for 4 min and for 5 hs in comparison to that of cardanol alone. Peaks marked I and II in the product mixture of cardanol correspond to monomer (cardanol) and dimer respectively, as evidenced by spiking the product mixture with authentic samples of monomer and dimer. Peak III corresponds to the polymer having a molecular weight of 3500-4000 (All molecular weights reported here are with respect to polystyrene standards). In no experiment, 100% conversion of the monomer to polymer was observed. Even after a period of 5 hs the product mixture was found to contain 8-12% monomer.

The concentrations of the different reaction products (monomer, dimer and polymer) as a function of time for the polymerisation of cardanol at various temperatures obtained from GPC measurements are presented in Fig.2.2a-e. It was observed that at all temperatures, the polymerisation reaction was rapid as revealed by the sudden disappearance of the monomer and the quick formation of the polymer.

The variation of the GPC patterns of the polymerisation products of cardanol with temperature is given in Fig.2.3a. It is evident that as temperature increases, peak I decreases in intensity, reaches a minimum at 140°C and then increases. Hence 140°C can be taken as the optimum temperature for the formation of the polymer. Further increase in temperature increases the monomer content indicating that possibly there is thermal decomposition or depolymerisation taking place above 140°C. Cardanol has been reported to be quite stable even at 180°C [18]. When the polymer obtained at 140°C was heated to 180°C and then analysed by GPC, the GPC pattern was found to be exactly similar to that obtained by direct polymerisation reaction at 180°C. The total percentages of the monomer, dimer and the polymer were identical and there was no other loss due to decomposition. This possibly indicates depolymerisation of the polymer above 140°C. Similar depolymerisation reactions have been reported in the cationic polymerisations of α-methyl styrene [23,24], aliphatic olefins [25,26] and styrene [27].

Similar trends were observed when the concentrations of monomer, dimer and polymer (obtained by integrating the area under the respective GPC peaks) were plotted against temperature as shown in Fig. 2.3b.

The rate of polymerisation at different temperatures was calculated from the slope of the corresponding percentage conversion-time curve, and is shown in Fig. 2.3c. It was observed that R_p increases with reaction temperature reaching the maximum value of 17.015×10^{-3} m L^{-1} sec^{-1} at 140°C and then decreases.

Fig.2. 4 shows that the polymerisation reaction follows first order kinetics with respect to monomer concentration. The rate constants were found to be 6.67 x 10^{-3} sec^{-1} at 130^{o}C and 8.75 x 10^{-3} sec^{-1} at 140^{o}C. Using the Arrhenius equation, activation energy was calculated to be 8.98 Kcal/mole.

2.3.2 Effect of initiator concentration on the polymerisation

It is observed that the percent conversion of the monomer to polymer is unaffected by the variation of the initiator concentration upto 2%. Beyond 2% initiator concentration, the reaction system was found to gel instantaneously and so the products could not be analysed by GPC. The molecular weights obtained ($\bar{M}n$ and $\bar{M}w$) with varying initiator concentrations are presented in Table 2.1 It is found that maximum molecular weight ($\bar{M}n$) is obtained at 1% initiator concentration.

2.3.3 Molecular weight and molecular weight distribution

The plot of the number average molecular weight vs temperature (Fig. 2.3d) indicates that the average molecular weight increases from 730 at 30^{o}C to 3575 at 140^{o}C and then decreases to 1720 at 180^{o}C. Poly-dispersity was found to increase from 1.2 at 30^{o}C to 3.4 at 140^{o}C.

Many patents cite the polymerisation temperature of cardanol as 180^{o}C, when cationic initiators such as H_2SO_4, H_3PO_4, $AlCl_3$ etc. have been used. Further studies have to be done to see whether depolymerisation occurs or not, with these catalysts at this temperature.

2.3.4 Spectral studies

The infrared spectra of pure cardanol and polymerised cardanol are given in Fig.2.5a and 2.5b respectively. The peaks at 1620 cm^{-1} (c = c Str), 3040 cm^{-1} (C-H Str of alkene) and 790 cm^{-1} (C-H out of plane deformation) [28] were found to diminish in intensity in the spectrum of polymer, indicating that polymerisation has taken place through the double bonds in the side chain. The ^1H NMR spectra of cardanol and polycardanol are shown in Fig.2.6a and 2.6b. The multiplet at δ 5.2 - 5.4 ppm ($C\underline{H} = C\underline{H}$) [14] was found to decrease in intensity in the spectrum of the polymer. From Table 2.2 it is clear that the intensity of ^{13}C NMR spectral absorption bands of olefinic carbons at (δ 111-115 ppm) [29] of polycardanol is less than that of cardanol. These observations indicate that polymerisation has taken place through the side chain double bonds.

As revealed by the time-conversion curves (Fig.2.2a-c) polymerisation reaction was rapid suggesting a chain mechanism [30]. The IR and NMR spectra also indicate involvement of unsaturation in polymerisation. $BF_3.OEt_2$ is often used in the polymerisation of olefins, vinyl ethers etc. Worsfold and Bywater [31] investigated the polymerisation of α -methyl styrene and Giusti [32] studied that of styrene using $BF_3.OEt_2$ in the presence and absence of H_2O. These studies showed that BF_3 etherate is less reactive but more convenient than $BF_3:H_2O$. In both cases the formation of a protonated species appears to be the initial step.

GPC data show that the percentage weight of the monomer which remained unpolymerised under optimum conditions is only 8-12%, which is equivalent to the percentage of the saturated component present in cardanol. So this indicates conversion of all the unsaturated components into dimer/polymer. Taking monoene (which is the major component) [7] as example, the polymerisation could be depicted as follows (Fig. 2.7):

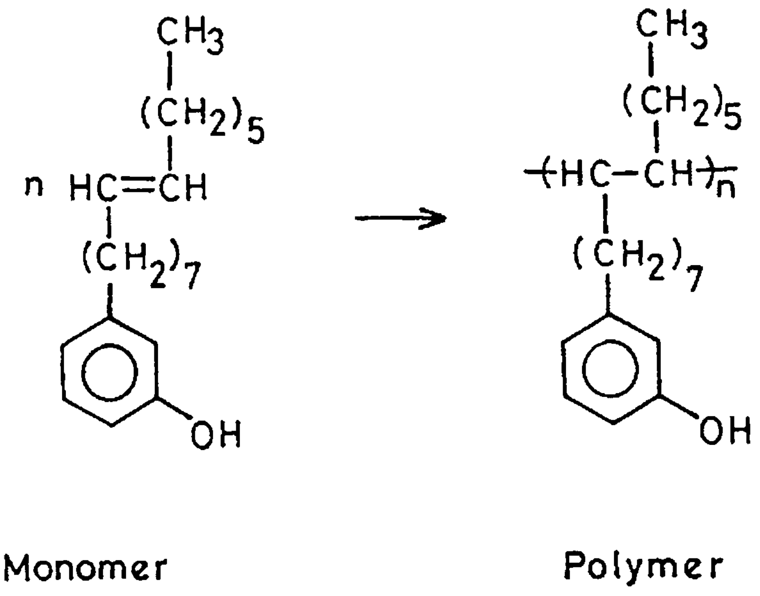


Fig. 2.7

Tyman [1] has proposed that the polymerisation of cardanol under acidic conditions might involve the formation of an allylic carbonium ion from the more reactive triene component. However, Tyman does not provide any experimental evidence regarding the involvement of the triene component alone. As the present data indicate conversion of all the monoene, diene and triene components into the polymer, further understanding of the system requires data on the rates of reaction of the individual components. Manjula [17] also proposed a carbocationic mechanism with the addition of a hydrogen ion to one of the double bonds of the side chain. Thus the complex nature of the system cautions not to make conjectures on the nature of the mechanism of polymerisation. However, it appears that the polymerisation of cardanol under $BF_3.OEt_2$ could be said to be carbocationic [30] in nature and might involve protonation of cardanol as the initiation step. With a first order kinetics it is probable that the termination would involve a transfer to the monomer.

Table 2.1: Effect of initiator concentration on polymerisation of cardanol[a]

$BF_3.OEt_2$ %	Monomer %	Dimer %	Polymer %	Polymer $\bar{M}n$	Polymer $\bar{M}w$	Polymer D[b]
0.25	18	14	68	3000	8633	2.88
0.5	15	13	72	3376	9542	2.83
1.0	12.6	12.6	74.6	3763	11507	3.06
2.0	14	14	72	3184	10045	3.15
3.0[c]						

a: Polymerisation was carried out at 140°C for 10 minutes

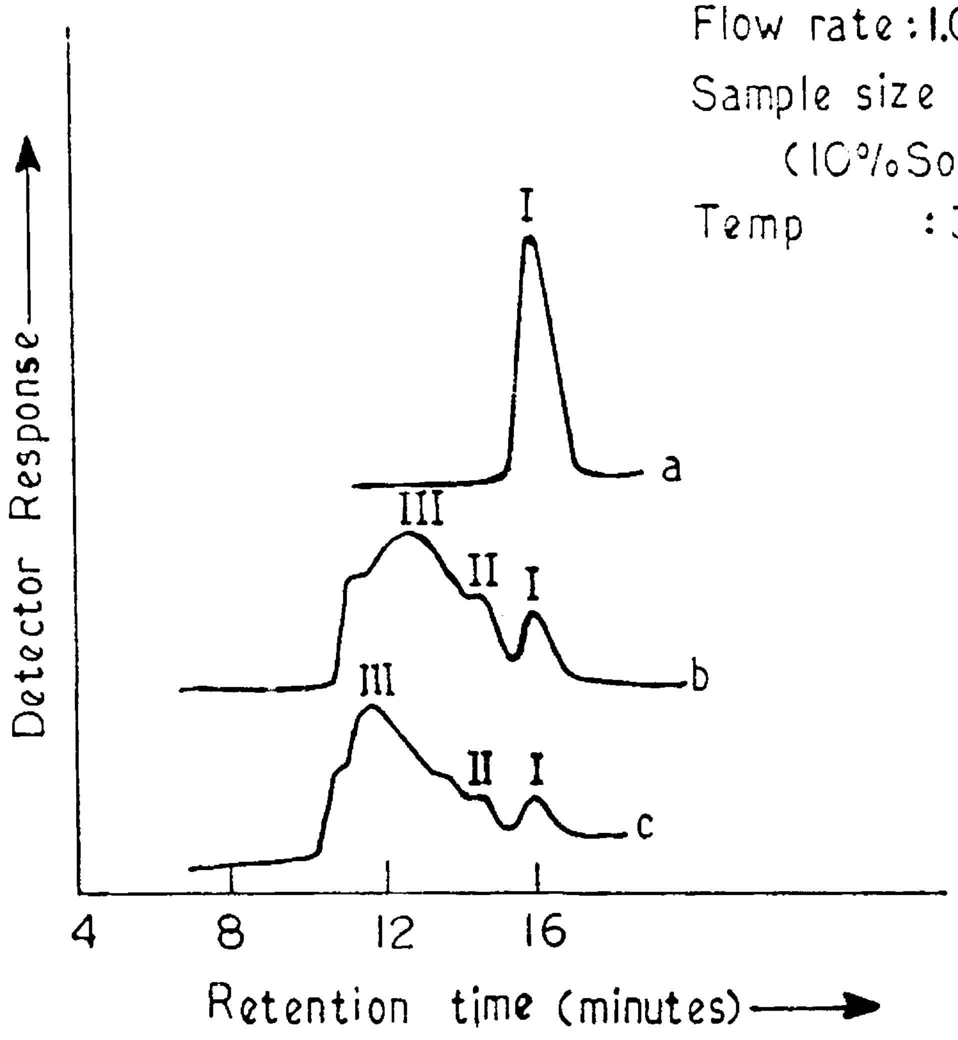
b: $D = \frac{\bar{M}w}{\bar{M}n}$ = Polydispersity

c: Gelled instantaneously

Table 2.2: ^{13}C NMR absorption bands with relative intensities

Cardanol		Polymer	
ppm	Intensity	ppm	Intensity
108.24	164	112.628	1467
112.737	2968	113.874	125
114.741	399	114.308	111
115.500	4237	115.445	1911
121.080	2830	116.962	97
126.822	209	120.759	1824
127.635	354	122.00	151
128.068	1063	123.788	174
128.231	999	128.176	234
129.422	3869	129.26	2428
129.964	2446	129.856	659

Eluent : THF
Flow rate : 1.0ml/min.
Sample size 20 μl.
(10% Solution in THF)
Temp : 30°C



2.1: GEL PERMEATION CHROMATOGRAMS OF (a) Cardanol (I)

(b) Polymerization product of I(140°C, 4min)

(c) Polymerization product of I(140°C, 5hrs)

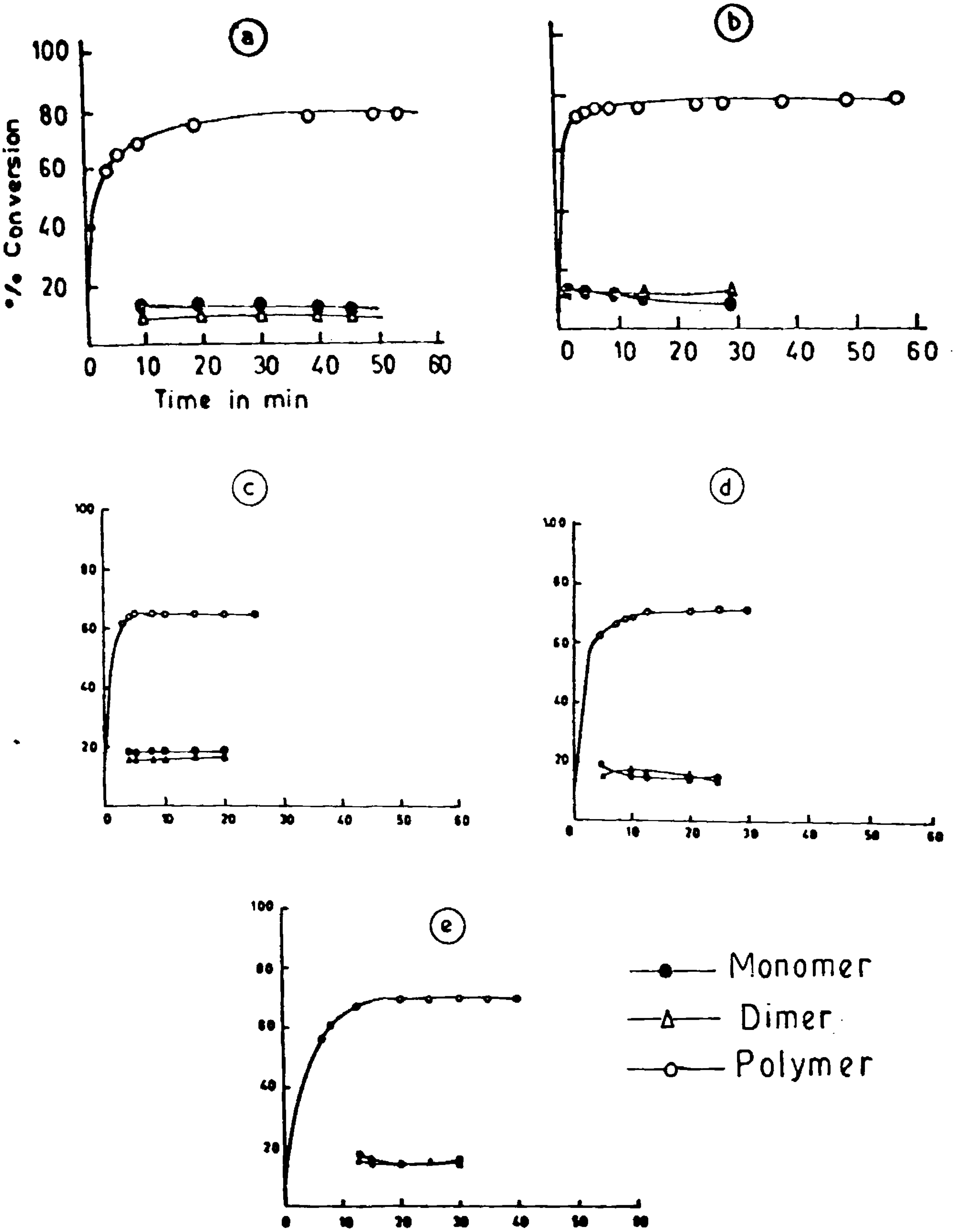


Fig 2.2: - Concentration of the components appearing in the polymerization of cardanol determined by GPC. a.130°C b.140°C c.150°C d.160°C e.180°C

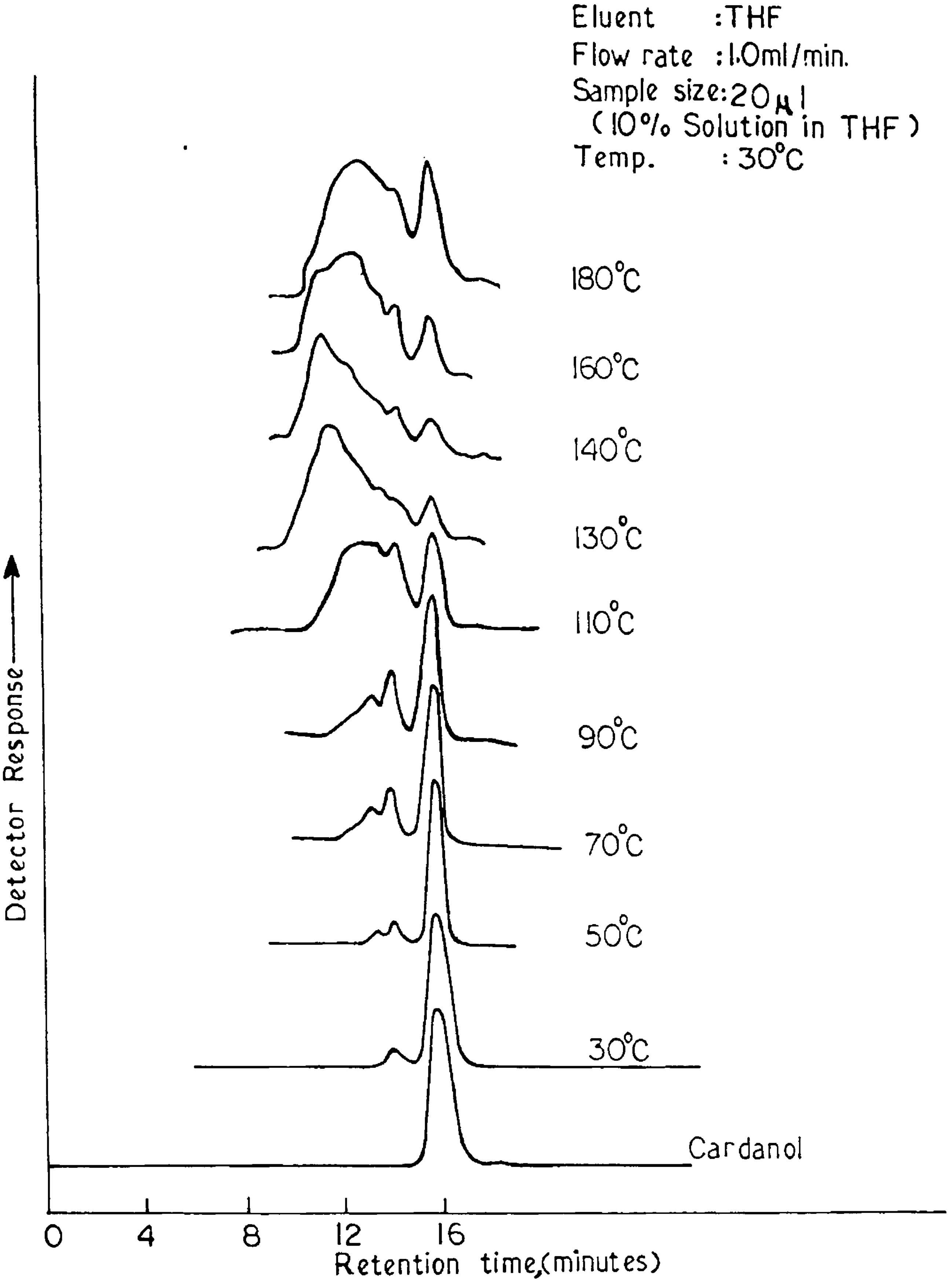


Fig. 2.3(a) GEL PERMEATION CHROMATOGRAMS OF POLYMERIZATION PRODUCTS OF CARDANOL AT DIFFERENT TEMPERATURES.

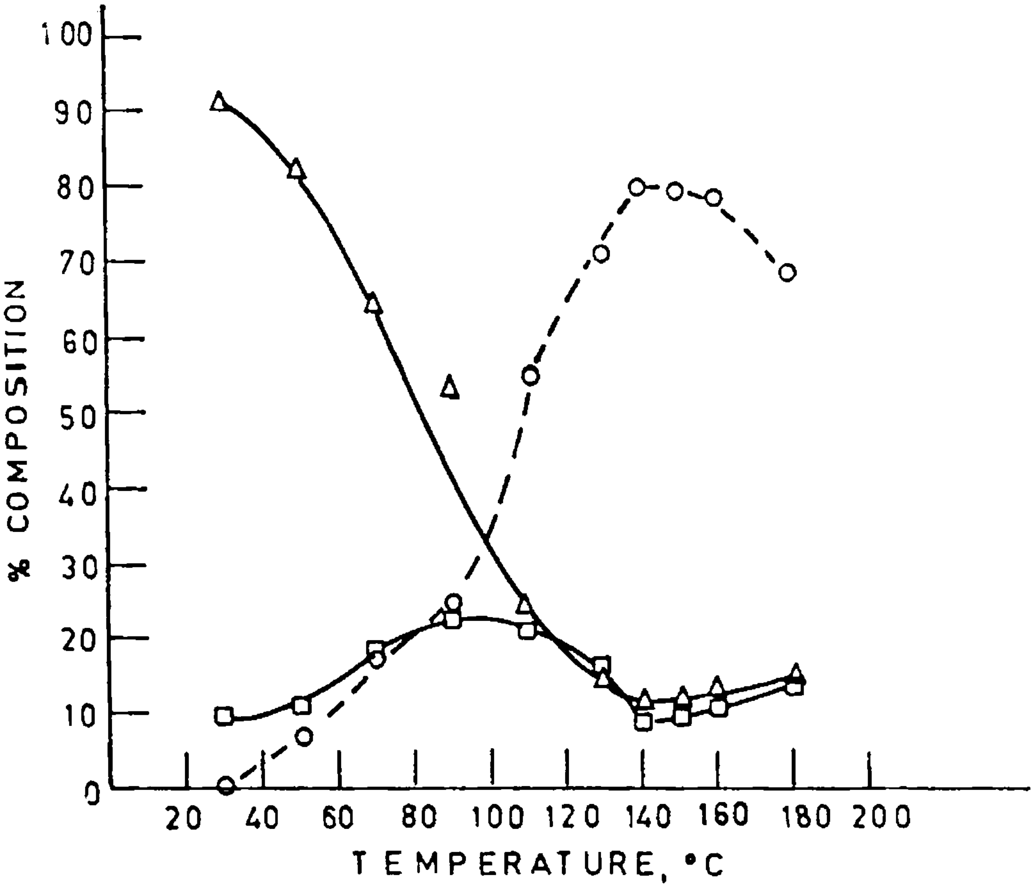


Fig. 2.3(b). Percentage composition of monomer (-△-△-△-), dimer (-□-□-□-) and polymer (-o-o-o-) Vs temperature

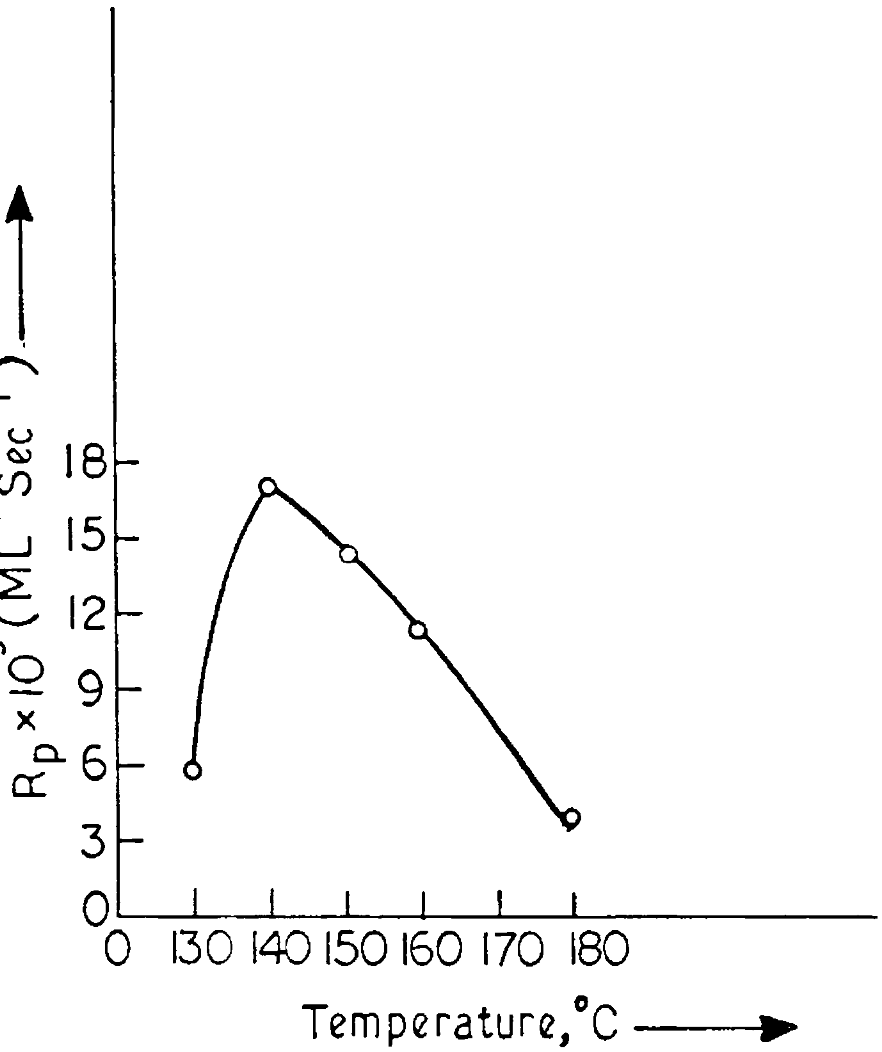


Fig. 2.3(c) RATE OF POLYMERIZATION Vs. TEMPERATURE

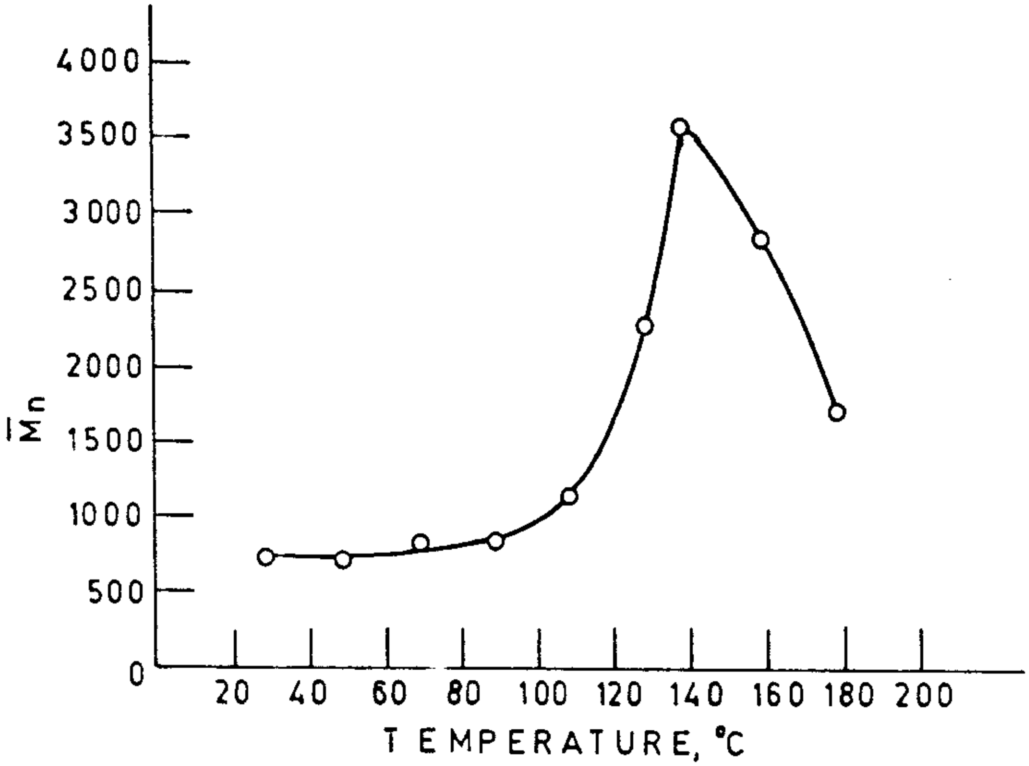


Fig. 2.3(d) Number average molecular weight Vs temperature

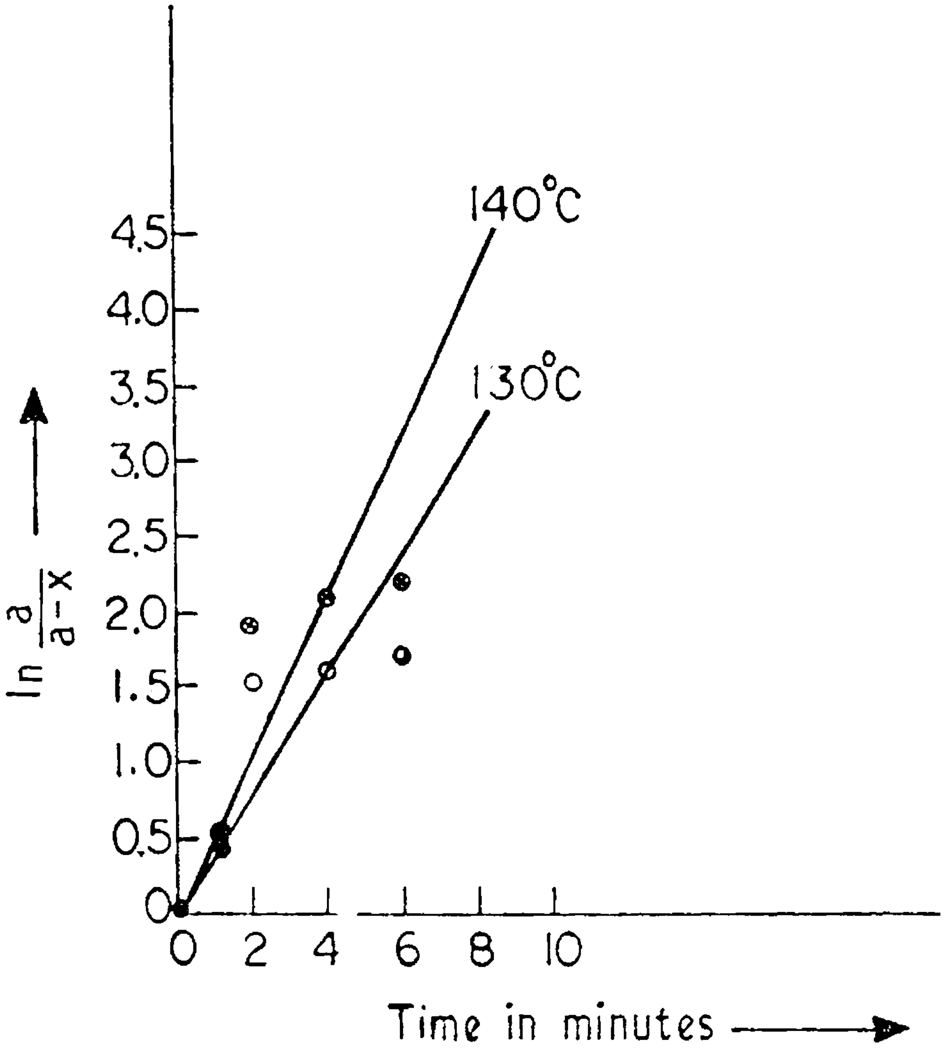


Fig. 2.4 $\ln \frac{a}{a-x}$ Vs. TIME FOR THE POLYMERIZATION OF CARDANOL. a. is the concentration of the monomer and x. is the amount reacted during polymerization.

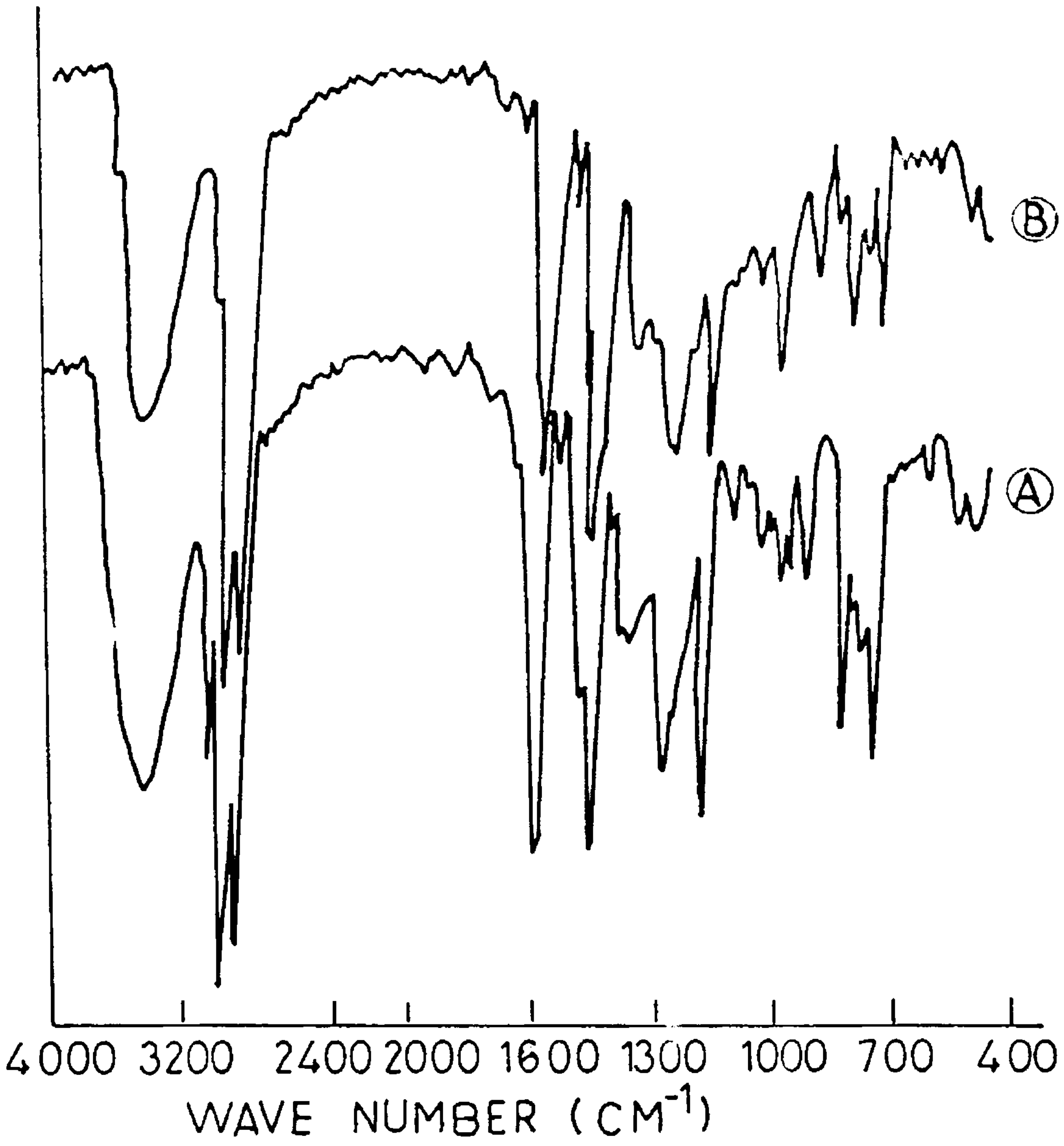


Fig. 2.5 Infrared absorption spectra of cardanol (A) and cardanol after polymerization (B)

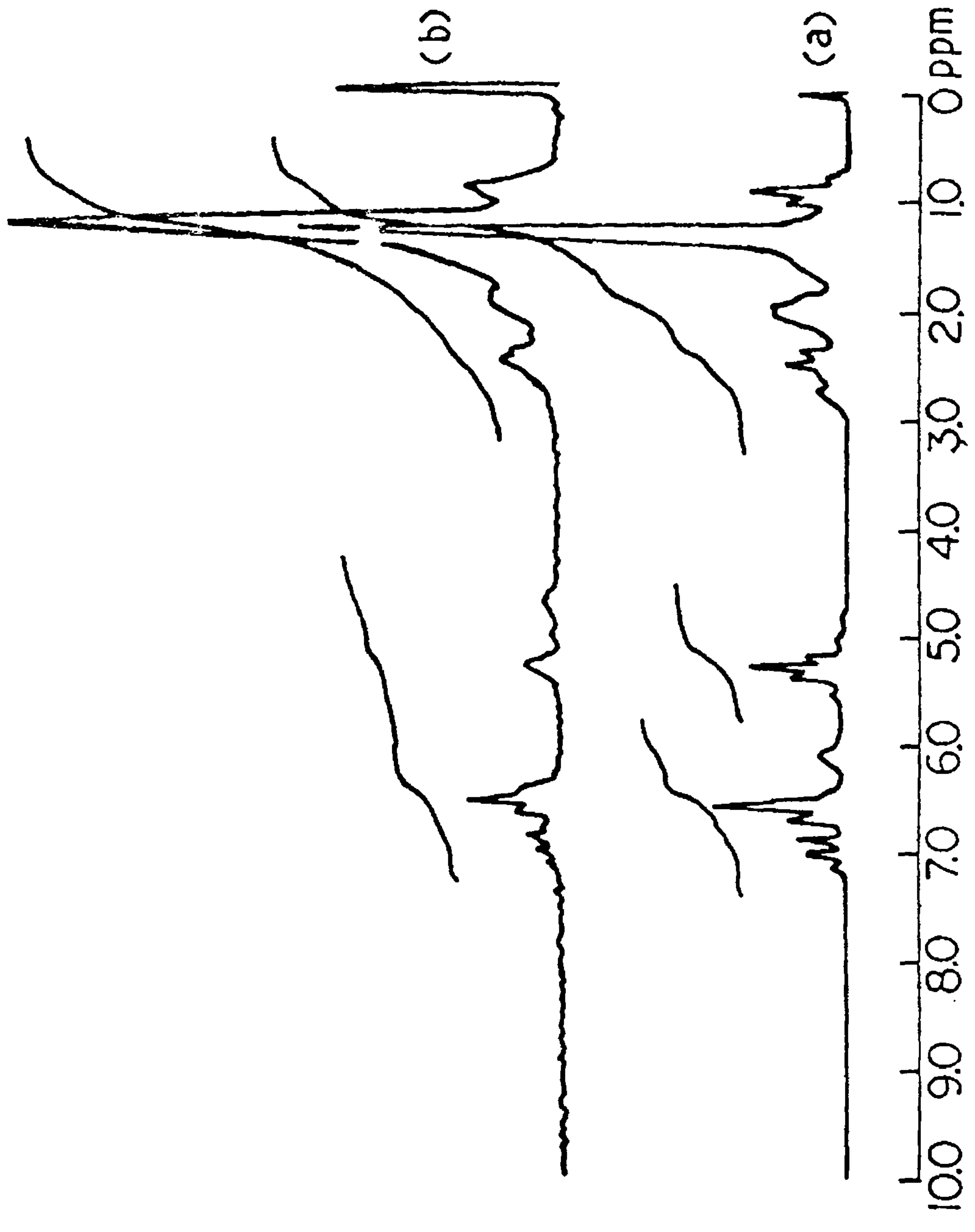


Fig. 2.6 ^{1}H NMR SPECTRA OF (a) Cardanol (b) Cardanol polymer.

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CHAPTER 3

SYNTHESIS AND THERMAL CHARACTERISATION OF CHEMICALLY MODIFIED CARDANOL POLYMERS

3.1 INTRODUCTION

In the last few decades considerable attention has been paid in controlling the flammability of commercial polymers [1-10]. A host of flame retardants that control the flammability of polymers have been developed based on the following elements. Phosphorus, bromine, chlorine, antimony, nitrogen, boron, aluminium, magnesium, zinc and tin [2-4]. Of these, phosphorus and halogens are the most widely used. These elements may be added in the form of additives to the substrate polymer or incorporated into the structure of the polymer itself. The latter approach is sometimes preferred because the polymeric flame retardants have better resistance to extraction, migration, volatile loss etc. and the flame retardancy is thus permanently fixed [11,12]. In this connection the wide spectrum flame retardants[13] discussed in chapter 1 are interesting because they are prepolymers and apart from having the desirable properties of polymeric flame retardants, they are expected to be compatible with a wide spectrum of polymers [14]. Thus cardanol, having both hydrophilic and hydrophobic moieties [15] is a suitable candidate for chemical modification (whereby the FR elements could be introduced) and polymerisation into a prepolymer [16] so that the product is expected to behave as a wide spectrum flame retardant .

Earlier work carried out at the Regional Research Laboratory, Trivandrum , has shown that phosphorylation of cardanol results in simultaneous polymerisation so as to give a phosphorylated prepolymer (PCP) that showed enhancement in thermal stability and flame resistance [17]. As the polymerisation takes place simultaneously it was not possible to control the polymerisation in the desired way. So in the present work, the phosphorylated monomer was prepared by a different method and polymerised so that data on both monomer and polymer could be made available. It was also shown in this laboratory that when both phosphorus and bromine are present, the thermoset CNSL product exhibited the property of ablation [18] much superior to that of conventional phenolics. In order to understand the origin of the ablation process, the thermal behaviour of model compounds containing both phosphorus and bromine based on cardanol were required and so the monocardanyl phosphoric acid and its bromo-compound were selected for the present study. The present chapter deals with the synthesis, characterisation, thermal and flammability behaviour of cardanol polymers containing both phosphorus and bromine.

3.2 EXPERIMENTAL

3.2.1 Materials

Cardanol was obtained by double vacuum distillation of cashewnut shell liquid as given in chapter 2 (2.2.1). Phosphorus pentoxide (Merck, India), bromine (Merck, India), hexamethylene tetramine (Fluka, Switzerland), oxalic acid (Merck, India) and formaldehyde solution (BDH Laboratories) were used as such without further purification. Hexane was dried with calcium chloride and then distilled. Carbontetrachloride was distilled before use.

3.2.2 Measurements

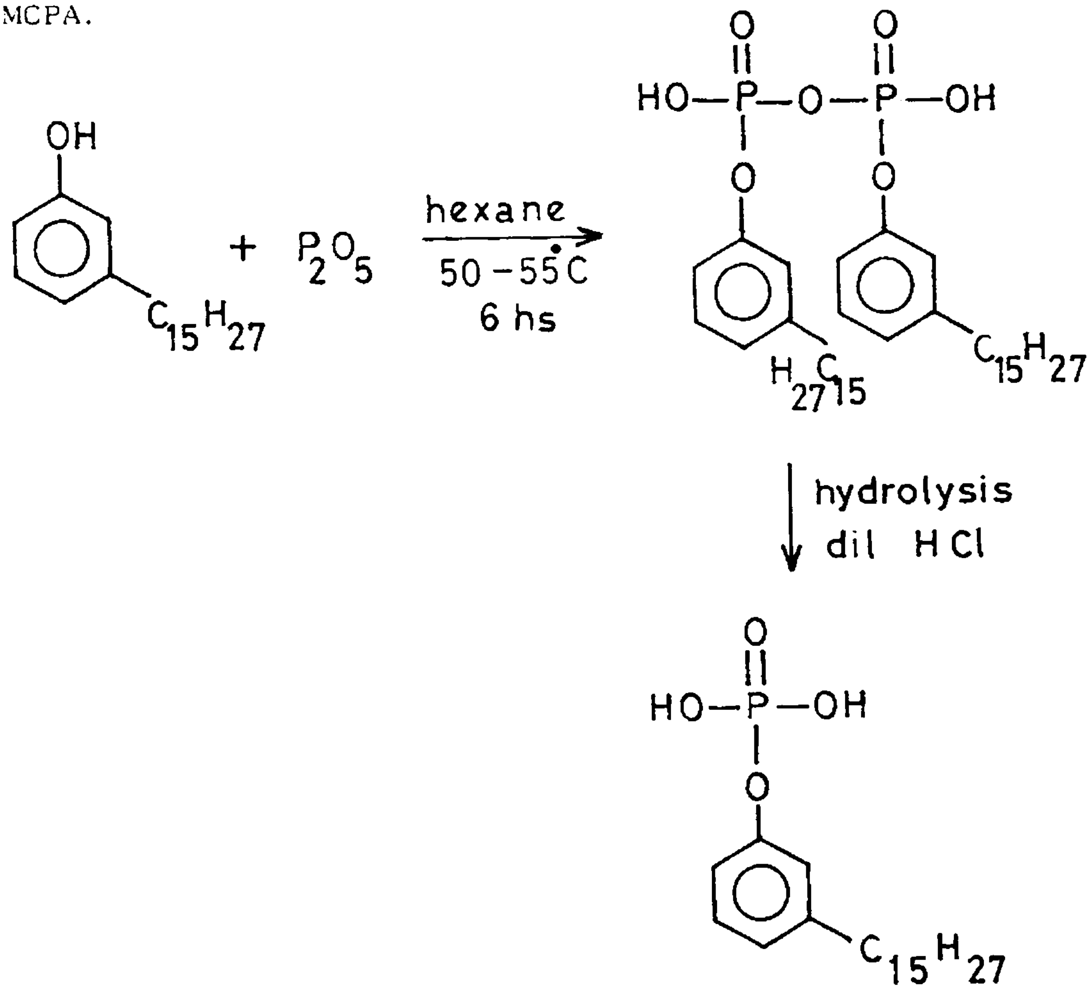
The transmission infrared spectra were recorded on Perkin-Elmer IR spectrophotometer model 882 as neat films on NaCl windows by the smear technique. ^{1}H NMR spectra were recorded on Hitachi R-24 B high resolution NMR spectrometer in CCl_4 using TMS as internal reference. The GPC data were obtained 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 Du Pont thermogravimetric analyser model 951 in nitrogen atmosphere at a heating rate of 20^oC min^{-1} with a sample weight of 5-8 mg. The LOI data were determined by using a Stanton Redcroft LOI equipment of model FTA 7101. Phosphorus estimation was carried out by gravimetric method using ammonium molybdate reagent [19]. Bromine content was analysed by Volhard's method [19].

3.2.3 Synthesis

1. Monocardanyl phosphoric acid (MCPA)

MCPA was prepared by the reaction of cardanol with phosphorus pentoxide in dry hexane as per Scheme 3.1. Cardanol

(0.2 mol, 60 g) and dry hexane (500 ml) were taken in a IL 2-necked flask. To the stirring solution, P_2O_5 (0.13 mol, 18 g) was added portionwise. The reaction was continued for 6 hs at 50-55 °C. The pyrophosphate formed was hydrolysed with dil. HCl to get MCPA.



Scheme 3.1

Yield 80%

IR (neat) 907 cm^{-1}, 630 (vinyl)

1250 (P=O), 2930 (P-OH),

960, 1150 (P-O-C),

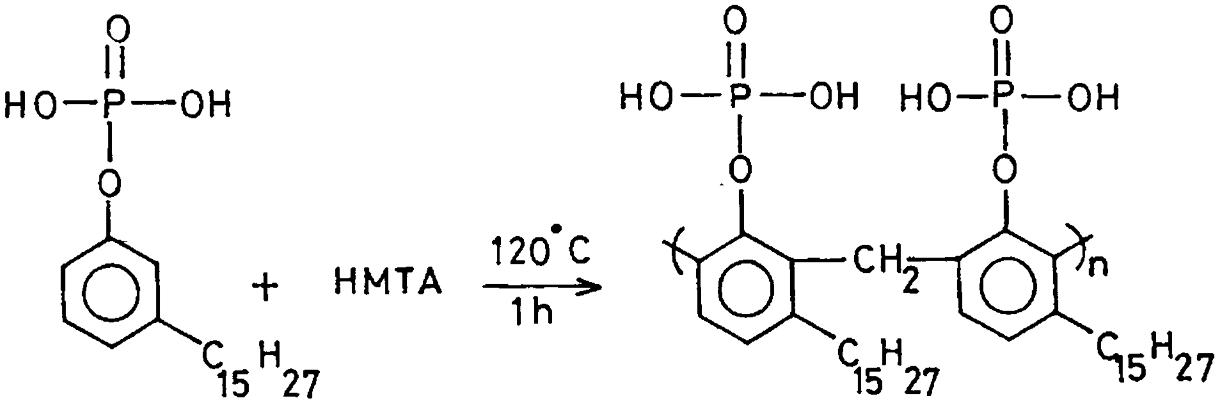
3020 (C-H aromatic),

2980 (C-H aliphatic)

^{1}H NMR	0.9 (T, 3 H, CH_3) 1.2-1.4 (m, 12 H, $(CH_2)_6$), 1.8-2.0 (m, 4 H, allyl) 1.9 (m, 2 H, benzyl), 2.1 (m, 2 H, benzyl), 2,5-2.7 (m, 2 H, diallyl), 5.1-5.3 (m, 4 H, vinyl) 5.2 (m, 4 H, CH=CH), 6.7 (m, 4 H, Ar), 6.6-6.8 (m, 4 H, aryl)
Phosphorus content	8.1%

2. Monocardanyl phosphoric acid-formaldehyde resin (MCPAF)

The polymerisation of MCPA was carried out by reaction with hexamethylenetetramine (HMTA) as shown in Scheme 5....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 get MCPAF.

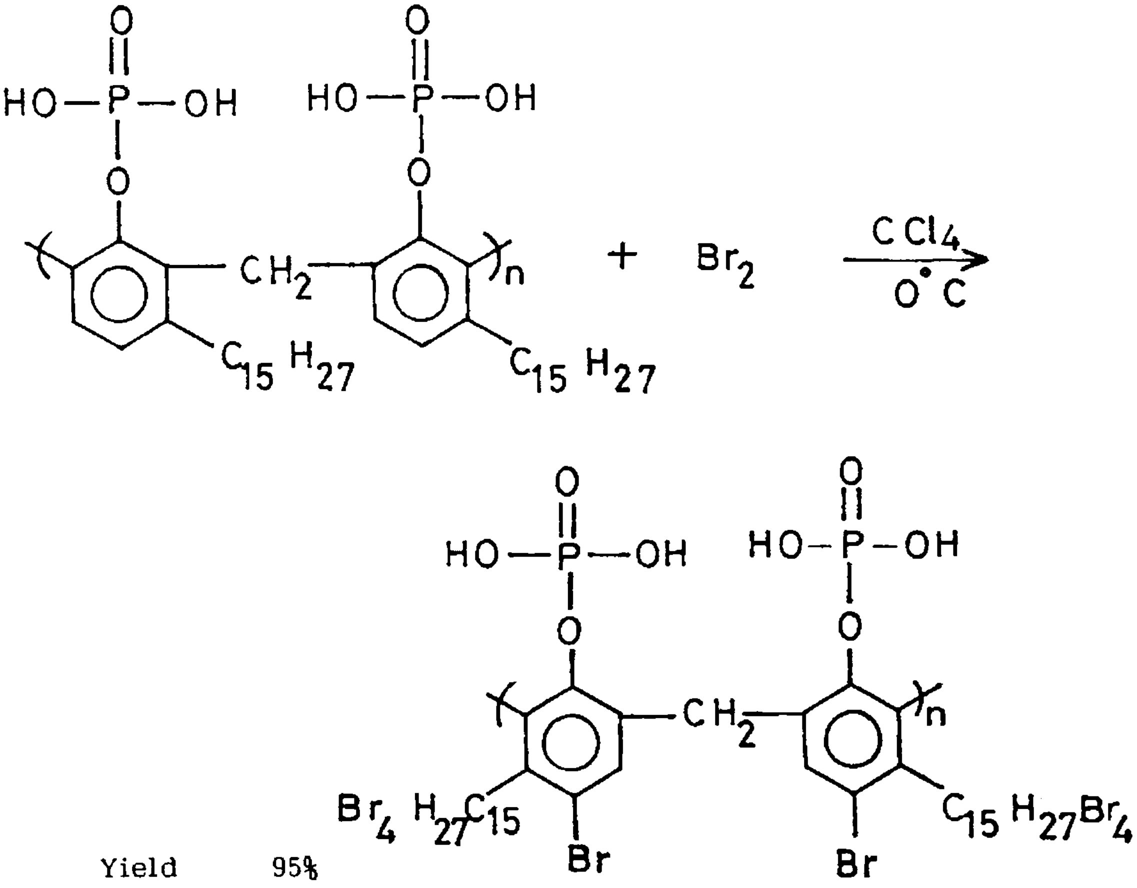


Scheme 3.2

Yield: 90%

3. Brominated derivative of MCPAF resin (BrMCPAF)

BrMCPAF was synthesised as per Scheme 3.3. 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, over a period of 2 hs and stirring continued for 2 hs more. The solvent was distilled off and product was dried in vacuum at 80°C.



Scheme 3.3

Yield 95%

IR (neat) 780 cm^{-1} (C-Br)

^1H NMR δ 2.7 (m, Ar-$\underline{CH_2}$-Ar)

4.2 (m, 4 H, CHBr)

7.0 (S, 1 H, Ar)

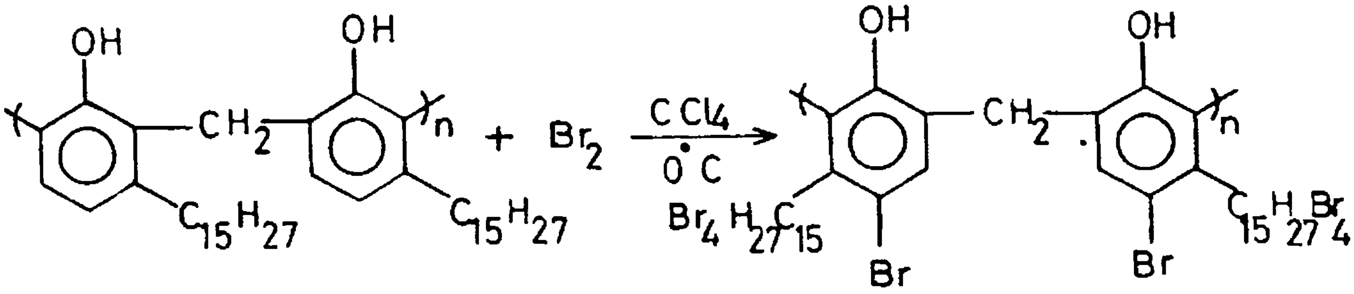
Bromine content: 50%

4. Cardanol-formaldehyde Novolac resin (CF)

CF resin was prepared as reported earlier [20]. 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 3-necked flask fitted with a mechanical stirrer and reflux condenser. The reaction mixture was heated under constant stirring at 100°C for for 4 hs Water was removed at 70°C under reduced pressure and the product was dried in vacuum oven at 70°C.

5. Brominated cardanol-formaldehyde resin (BrCF)

BrCF was synthesised as per Scheme 3.4 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 200 ml CCl_4 dropwise over a period of 2 hs with vigorous stirring. The stirring was continued for another 2 hs more and the solvent was stripped off. The product was dried in vacuum oven at 80°C.



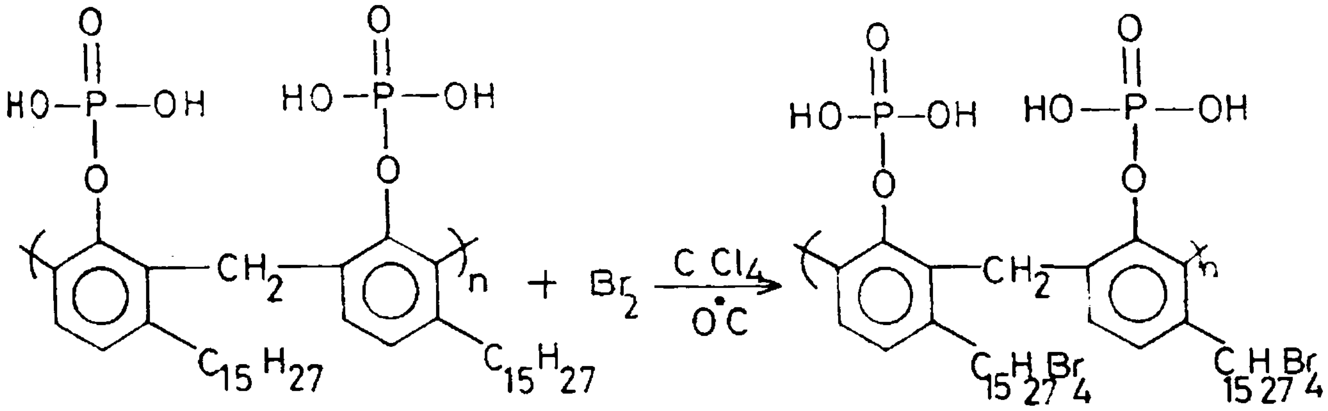
Scheme 3.4

Yield	95%
IR neat	780 cm^{-1} (C-Br)
^1H NMR	δ 2.7 (m, Ar-$\underline{CH_2}$-Ar) 4.2 (m, 4 H, CHBr) 7.0 (S, 1 H, Ar)

Bromine content: 56%

6. Synthesis of partially brominated MCPAF resin (PBrMCPAF)

MCPAF resin was brominated in the side chain only. 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 (0.2 mol, 32 g) in 150 ml of CCl_4 dropwise over a period of 1 h with vigorous stirring. The stirring was continued for 1 h more and CCl_4 was distilled out. The polymer was dried in vacuum oven at 80°C. The reaction is shown in Scheme 3.5.

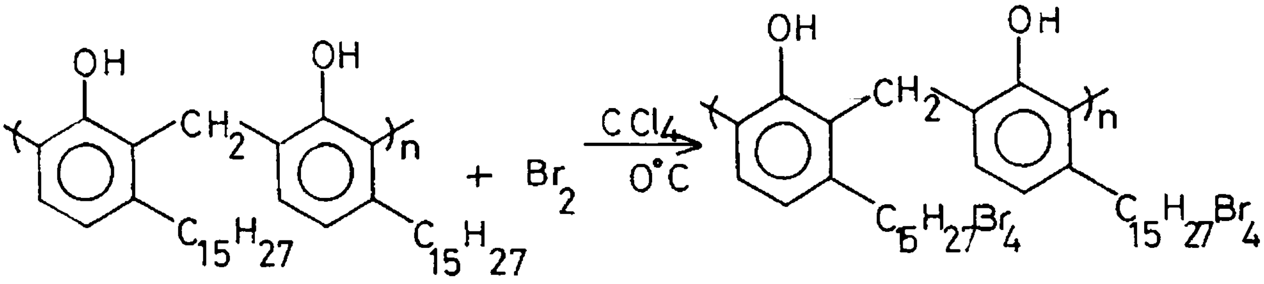


Scheme 3.5

Yield	95%
Bromine content	45%

7. Synthesis of partially brominated cardanol-formaldehyde resin (PBrCF)

CF resin was brominated at the double bonds present in the side chain only to get PBrCF. 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 (0.2 mol, 32 g) in 100 ml CCl_4 drop-wise with vigorous stirring over a period of 1 h. The stirring was continued for another 1 h more and CCl_4 was distilled off. The polymer was dried in vacuum oven at 80°C. The reaction is shown in Scheme 3.6.



Scheme 3.6

Yield: 95%

Bromine content: 50%

3.2.4 Preparation of crosslinked polymers

1. CF and PBrCF

Curing was effected by heating with 10% HMTA. CF resin

(0.01 mol, 3.1 g) and HMTA (10 weight %, 0.3 g) were mixed well in petridish and heated at 130°C for 2 hs. PBrCF also was crosslinked to thermoset product by similar procedure.

2. MCPAF and PBrMCPAF

MCPAF and PBrMCPAF could not be cured when heated with HMTA or paraformaldehyde. However, crosslinked products could be obtained when heated with HMTA in presence of amines such as paraphenylenediamine or melamine. MCPAF (0.01 mol, 3.9 g), HMTA (10 weight %, 0.39 g) and paraphenylenediamine (1 weight %, 0.039 g) were mixed thoroughly in a petridish and heated at 130°C for 2 hs. PBrMCPAF also was crosslinked to a thermoset product by similar procedure.

3.3 RESULTS AND DISCUSSION

3.3.1 Synthesis

Earlier attempts to prepare phosphorylated cardanol by direct reaction with orthophosphoric acid always resulted in the formation of oligomeric species due to simultaneous polymerisation through the unsaturation in the side chain [17]. 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 which was quite in agreement with the theoretical value 380. The IR absorption frequencies are given along with Scheme 3.1. The IR spectrum of MCPA exhibited P=O and P-OH peaks at 1250 and 2930 cm^{-1} respectively. 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. The ^{1}H NMR chemical shift values are given along with Scheme 3.1.The ^{1}H NMR spectrum of MCPA registered the unsaturated protons at δ 5.2.

Polymerisation of MCPA was carried out by condensation with HMTA. Condensation was carried out to the extent to get only soluble oligomers. The $\overline{Mn}$ value of the oligomer is 1750 and polydispersity is 2.7 (Table 3.1). Unlike the phenol-formaldehyde [21] and cardanol-formaldehyde [20] novolac systems, MCPAF could not be cured to insoluble and infusible crosslinked polymers, when reacted with HMTA or paraformaldehyde or any other similar aldehydes. However, curing could be initiated and crosslinked products obtained in the presence of amines (1%) such as paraphenylenediamine, melamine etc.

Bromination of CF and MCPAF was carried out till five bromine atoms were introduced. Thus BrCF and BrMCPAF have bromine contents 56% and 51% respectively. As the unsaturation of the aliphatic side chain of cardanol is about two [15], four bromine atoms could have been introduced into the side chain [22,23] and one bromine to ortho or para position of the aromatic ring. The ^{1}H NMR spectra of the brominated regions did not show any unsaturated protons at δ 5.2 and showed a new peak at δ 4.2 (CHBr protons) and as expected the aromatic protons were short by one. BrCF and BrMCPAF also did not undergo further polymerisation and crosslinking to a thermoset product and therefore used as such for thermal and LOI studies. LOI measurements for these linear resins were done using a modified method reported by Annakutty et al for powders and viscous resins [24]. However, crosslinked products were obtained by partial bromination of CF and MCPAF through the side chain, which were then cured with HMTA (in presence of paraphenylenediamine for PBrMCPAF).

3.3.2 Thermal and flammability studies

The TGA of CF resin in air was first reported by O'Conner and Blum [25] who showed that the stability of substituted phenols decreases as the length of the side chain increases. Later Manjula et al [26] studied the thermal decomposition of CF in comparison to PF and showed that CF resin decompose at a faster rate. The present study compares the thermal behaviour of CF with MCPAF, BrMCPAF and BrCF. The effect of phosphorus and bromine on the thermal behaviour of both linear and cured polymers was investigated. Figures 3.1 and 3.2 give the TGA of linear and cured polymers respectively. The parameters studied are the temperatures corresponding to initial decomposiition (T_i), 50% weight loss ($T_{1/2}$) and char yield at $600^{\circ}C$ (C_Y) and are given in Table 3.2. As could be expected of fully cured phenolics, all cured polymers gave higher T_i and $T_{1/2}$ values and correspondingly higher C_Y and LOI values in comparison to those of the linear polymers. It can be seen that both linear and cured systems follow the same trend. The MCPAF resins have lower T_i values than CF resins. The $T_{1/2}$ values are more or less the same or slightly higher than that of CF resins. Thus T_i value has decreased from 220°C of CF to 160°C for MCPAF for linear polymers. For cured systems T_i decreased from 270°C of CF to 250°C of MCPAF. The $T_{1/2}$ values are 450°C and 480°C for linear and cured MCPAF resins, respectively, and those for CF are 415°C and 480°C for linear, and cured polymers. The char yields are higher for the MCPAF polymers. Thus C_Y values have increased from 1 (linear) and 11 (cured) of CF resins to 20 (linear) and 21 (cured) of MCPAF resin. This indicates that the stability of MCPAF improves over that of CF above 500°C as could be seen from figures 3.1 and 3.2. Vertical burning studies carried out as per UL-94 did not give any propagation of flame and no afterglow. The LOI values have increased from 18 and 19 of CF resins to 24 and 27 of MCPAF resins for the linear and cured polymers respectively. 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, retard carbonisation of polymers and increase pyrolysis residue. Annakutty and Kishore [24] 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 [24] 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 cured CF (11%) and MCPAF (21%) in comparison to that (60%) of phenolics is thus a direct effect of structure on thermal stability.

As 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 for metallated phosphates [29]) supporting the assumption that the non-metallated flame retardant might be functioning through the early release of acidic fragments. The initial generation thermally of an acid component such as phosphoric acid from the flame retardant alters the pyrolytic decomposition 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 non-flammable gaseous products [30].

Figures 3.1 and 3.2 and Table 3.2 show that bromination of CF and MCPAF brings down considerably both T_i and $T_{1/2}$ values. In the case of CF resins, T_i decreased from 220 to 210 for linear polymer and from 270 to 220 for cured system. For

MCPAF resins, T_i decreased from 160 to 130 for linear and from 250 to 200 for cured system. $T_{1/2}$ values have decreased from 415 to 320 for linear CF and from 480 to 425 for cured polymer whereas for linear MCPAF $T_{1/2}$ reduced from 450 to 280 and for cured polymer from 480 to 430. But it should be noted that the C_Y values of both BrCF and BrMCPAF have increased considerably, that is from 1 to 6.6 for linear BrCF and 11 to 18 for cured BrCF whereas from 20 to 21 for linear BrMCPAF and 21 to 27 for cured 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 MCPAF could be attributed to the presence of phosphate in BrMCPAF which being acidic might initiate earlier decomposition and liberation of HBr which is known to be a free radical generator and promoter of low temperature decomposition [30,31]. Experiments have shown that copious amounts of HBr are liberated just above the T_i value. The high LOI value of BrCF (52 for linear and 45 for cured) and BrMCPAF (62 for linear and 49 for cured) can be understood on this basis. Brominated flame retardants are known to release volatile species which 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 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 as could be inferred from the higher values of 62 and 49 for BrMCPAF polymers in comparison to 52 and 45 of BrCF polymers. 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 due to the facile β -cleavage at the double bonds [26] in comparison to that of PF resins [21] ($T_{1/2}$ above 800^{o} C). The incorporation of bromine to the side chain might still reduce the T_i and $T_{1/2}$ values, as 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 HBr at lower temperature (200^{o} 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 which 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] and the results are given in Table 3.3. The activation energies of CF linear is 27.5 kCal/mol and CF cured is 29.0 kCal/mol whereas those of MCPAF linear is 20 kCal/mol and MCPAF cured is 27.5 kCal/mol. For the brominated polymers the values are higher. For BrCF it is 41 kCal/mol for linear and 37.0 kCal/mol for cured polymer. 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 kCal/mol indicate an ionic decomposition mechanism [26]. Manjula et al [26] have also earlier proposed an ionic decomposition mechanism for CF based on application of 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 35-45 kCal/mol for the brominated products possibly suggest a free radical process. The copious liberation of HBr and the high LOI values (62 and 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 cured MCPAF to 27% of cured BrMCPAF might suggest as indicated earlier possible involvement of bromine in condensed phase mechanisms as well. It might as well be said that the increase in char yield from 21 of cured MCPAF to 27% of cured BrMCPAF could be due to the positive effect of combined action of phosphorus and bromine in the condensed phase.

Table 3.1: GPC results of modified cardanol polymers

S.No.	Sample	$\overline{M}n$	$\overline{M}w$	MwD = $\frac{\overline{M}w}{\overline{M}n}$
1	MCPAF	1750	4700	2.7
2	CF	1550	3050	1.98
3	BrCF	1900	3990	2.1
4	BrMCPAF	2200	5720	2.6

Table 3.2: TGA and LOI results of modified cardanol polymers

S.No.	Sample	T_i	$T_{1/2}$	C_y at 600°C	LOI
1	MCPAF linear	160	450	20	24
2	MCPAF cured	250	480	21	27
3	CF linear	220	415	1	18
4	CF cured	270	480	11	19
5	BrMCPAF linear	130	280	21	62
6	BrMCPAF cured	200	430	27	49
7	BrCF linear	210	320	6.6	52
8	BrCF cured	220	425	18	45

Table 3.3: Kinetics of thermal decomposition of modified cardanol polymers

S.No.	Sample	E	n
1	MCPAF linear	20.13	0.90
2	MCPAF cured	27.5	0.80
3	CF linear	27.5	0.90
4	CF cured	29.0	0.85
5	BrMCPAF linear	44.4	0.90
6	BrMCPAF cured	37.0	0.95
7	BrCF linear	41.4	0.80
8	BrCF cured	42.0	0.95

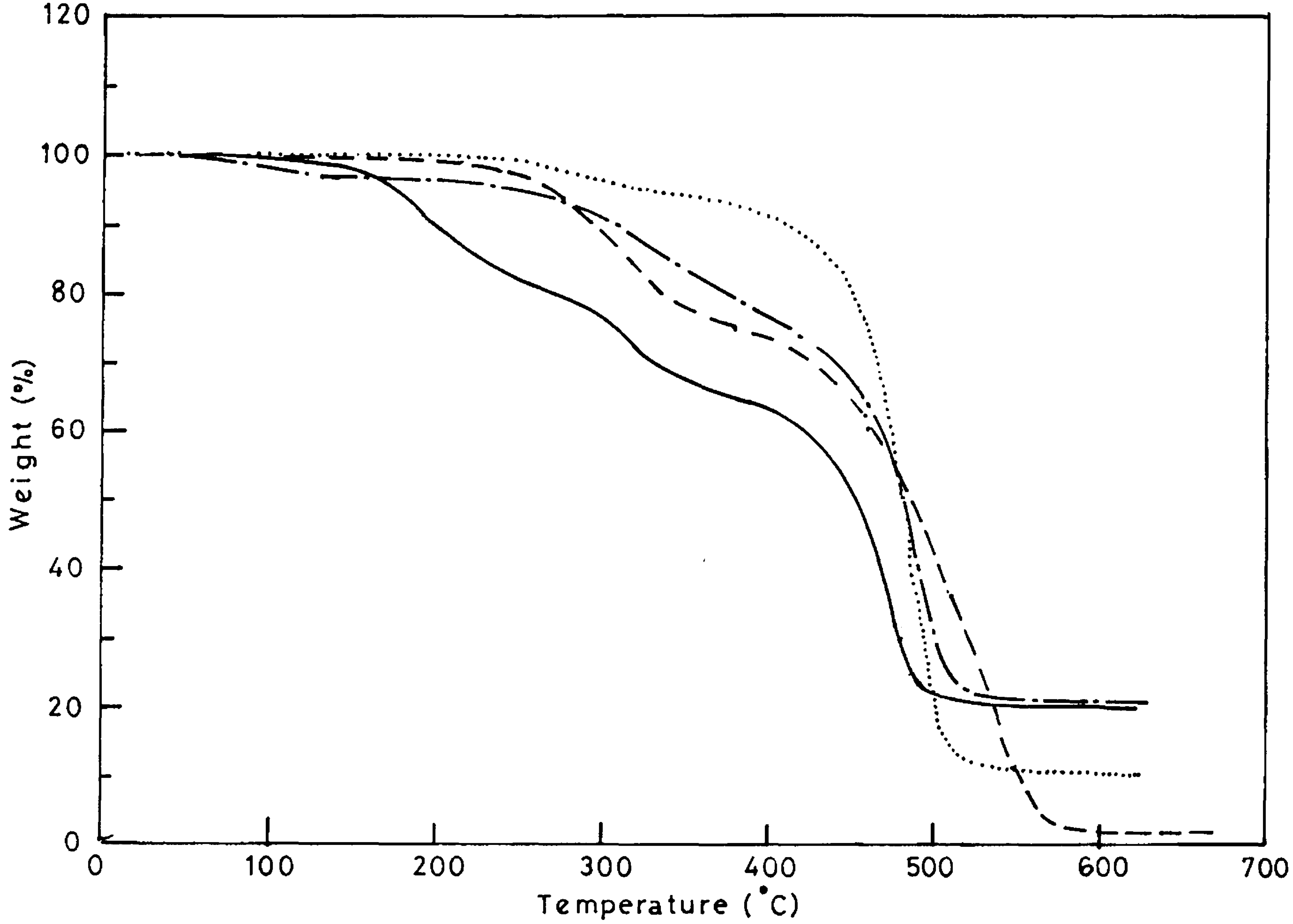


Fig .3.1. Thermogravimetric traces of · ——— MCPAF linear

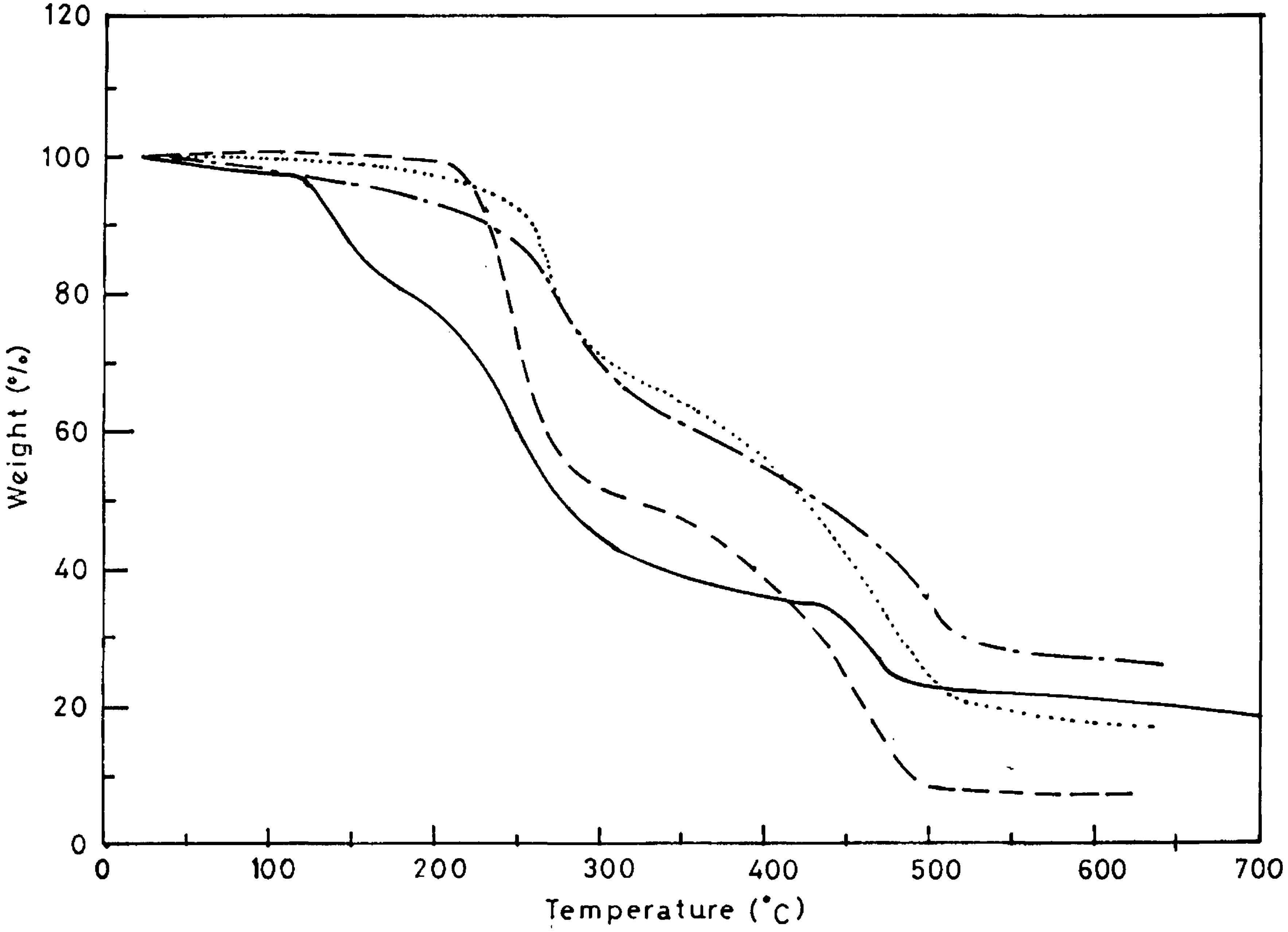


Fig 3.2 Thermogravimetric traces of —— Br MCPAF Linear, -—- BrMCPAF Cured , — — — BRCF Linear, ······· BRCF Cured .

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CHAPTER 4

SYNTHESIS, CHARACTERIZATION AND THERMAL STUDIES OF CHEMICALLY MODIFIED PHENOLIC POLYMERS

4.1 INTRODUCTION

Phenol-formaldehyde (PF) resins are usually classified among high performance polymers because of their high temperature resistance, high char yield and moderate flame resistance [1-5]. They are characterized by excellent ablative properties and structural integrity at high temperature and therefore have found wide application in many areas [4,5]. It is a unique class of materials [1,6] 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 Bayer [7] and the historic heat and pressure patents of Bakeland [8,9] followed by a series of inventions [10-12]. PF resins even today continue to be an active field both academically and industrially. Academic interest is centered around (1) improvement in its properties by way of chemical and structural modifications [13-17], (2) studies related to mechanistic understanding of the curing of phenolics [18-20], and (3) the mechanism involved in the decomposition of phenolics [21-26].

Chemical modification of phenolic resins have been undertaken to improve their thermal behaviour. The methods generally used to improve the thermooxidative resistance of phenolic resins include (a) etherification or esterification of phenolic hydroxyl group, (b) complex formation with polyvalent elements, and (c) replacement of methylene linking group by heteroatoms [1]. The esterification of phenol-novolak resins with inorganic polybasic acids such as phosphoric acid and boric acid or the reaction of phosphorus oxyhalides are of particular interest in increasing the heat and flame resistance of phenolic resins [1]. Dannels et al [15] reported the preparation of phosphate ester derivatives of orthonovolaks by treating novolak resin with phosphorus pentoxide whereas Shibazaki et al [27] used $POCl_3$ for preparing the phosphoric ester. Crosslinkable thermoplastic esters of phenolic resins containing phosphorus, aresenic or antimony were prepared by Shepard et al [28-30]. Incorporation of PF with p-bromophenol and tricresyl phosphate was done to make paper flame resistant. PF resins containing halides of phosphorus, sulphur, boron, titanium and silicon were made to prepare fire resistant fibres. The reaction of polyfunctional compounds with PF resins is often found to lead to gelation [31] and consequently only low amounts of the active element could be incorporated. The reaction was found to be dependent on the nature of the PF resin [14,15,31]. Thus with random novolak units molecular crosslinking takes place as shown in Fig. 4.1.

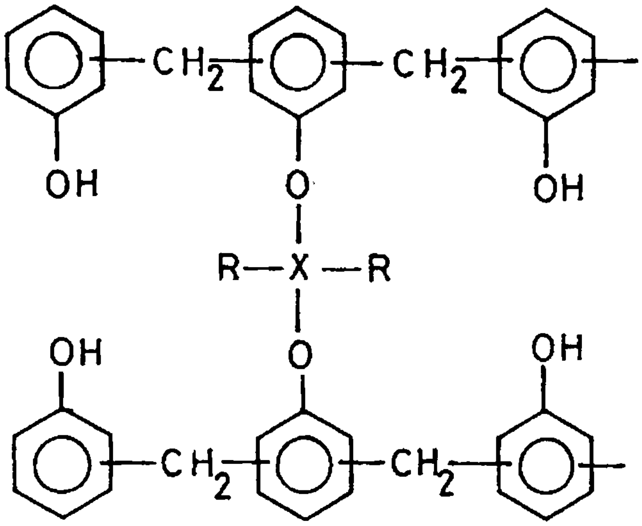


Fig. 4.1

whereas with orthonovolaks, an intramolecular etherification esterification is preferred leading to 8-membered rings as shown in Fig. 4.2..

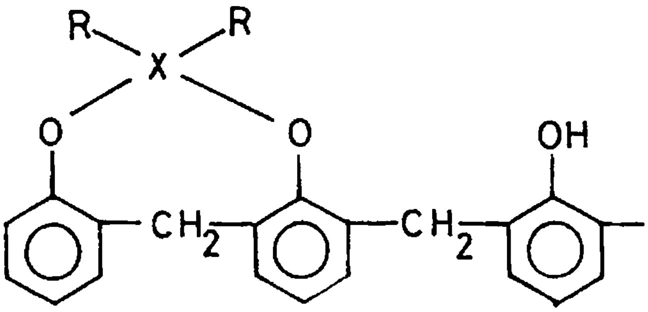


Fig. 4.2

These problems of gelation and structural differences could be overcome if chemical modification is effected at the monomer level and then polymerised to get the required product. This chapter deals with the synthesis and characterization of phenolics containing phosphorus and bromine introduced at the monomer stage by well known reaction scheme.

4.2 EXPERIMENTAL

4.2.1 Materials

Phenol was purchased from NICE, India and was distilled under reduced pressure. Phosphorus oxychloride (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 kept over sodium wire.

4.2.2 Measurements

The infrared spectra were recorded on a Perkin-Elmer IR spectrophotometer model 882. ^1H NMR spectra were recorded on Hitachi R-24 B high resolution NMR spectrometer in $CDCl_3$ using TMS as internal reference. ^{31}P NMR spectra was recorded on a JEOL FX-90 Q FT spectrometer. The GPC data were obtained using Hewlet-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 thermogravimetric analyser model 951 in nitrogen and air atmospheres at a heating rate of 20^{o} min^{-1} with a sample weight of 5-10 mg. The LOI data were determined by using a Stanton Red Croft LOI equipment of model FTA-7101. Phosphorus estimation was carried out using ammonium molybdate reagent [32] and bromine content was determined by Volhard's method [32].

4.2.3 Synthesis

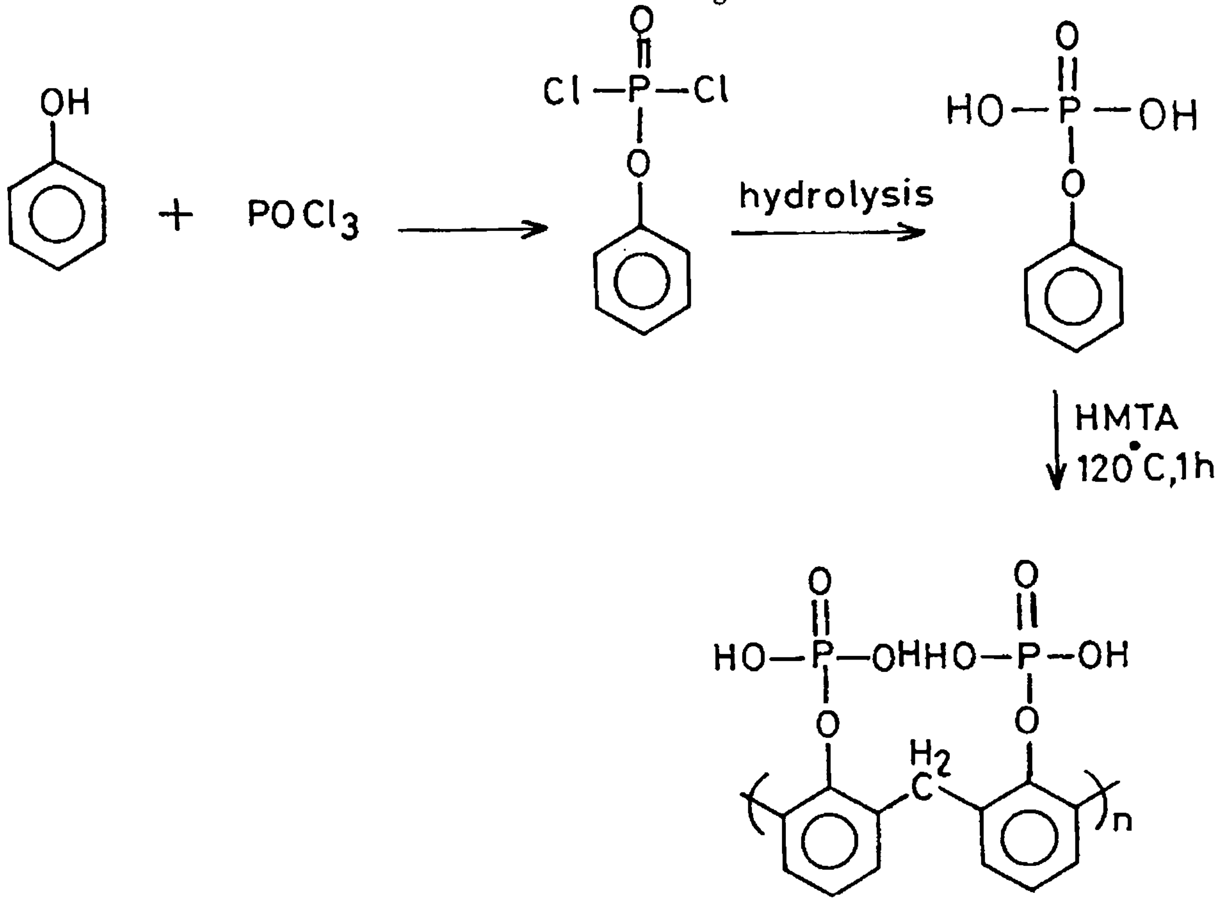
1. Phenol-formaldehyde Novolak resin (PF)

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^{o} C for 4 hs. Water was distilled off and the product was dried in vacuum at 70^{o}C.

2. Monophenyl phosphoric acid-formaldehyde resin (MPPAF)

Monophenyl phosphoric acid (MPPA) was prepared as reported elsewhere [33,34]. 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 hs. The $AlCl_3$ was filtered off and the excess $POCl_3$ and toluene were distilled out to get phenyl phosphorodichloridate. The dichloridate was hydrolysed 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 4.1. 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.



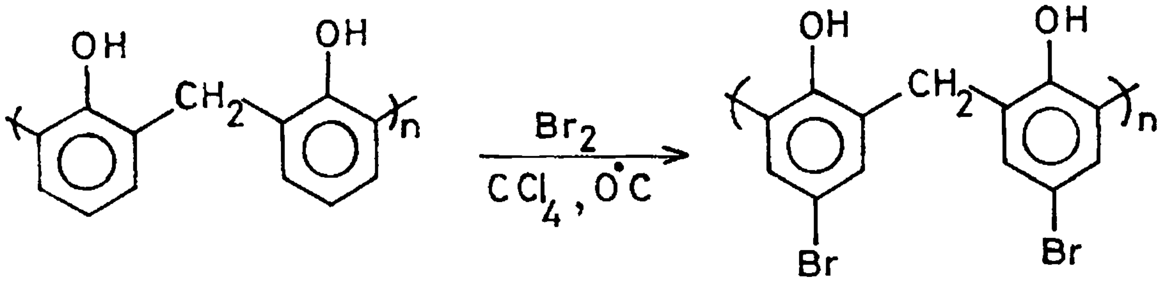
Scheme 4.1

Yield	90%
IR (neat)	960, 1190 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)
^1H NMR	δ 3.8 (m, Ar-<u>CH_2</u>-Ar)
	7.0 (m, Ar protons)
^{31}P NMR	δ -6.0
Phosphorus content	16.5%

3. Brominated phenol formaldehyde resin (BrPF)

Phenol-formaldehyde novolak resin was brominated to get BrPF as shown in Scheme 4.2. PF (0.1 mol, 10.4 g) and CCl_4 (50 ml) were taken in a 500 ml R.B. flask kept in an ice bath and added bromine (0.1 mol, 16 g) in 50 ml CCl_4 dropwise with vigorous stirring. The CCl_4 was distilled out and the product dried in vacuum at 80^oC.



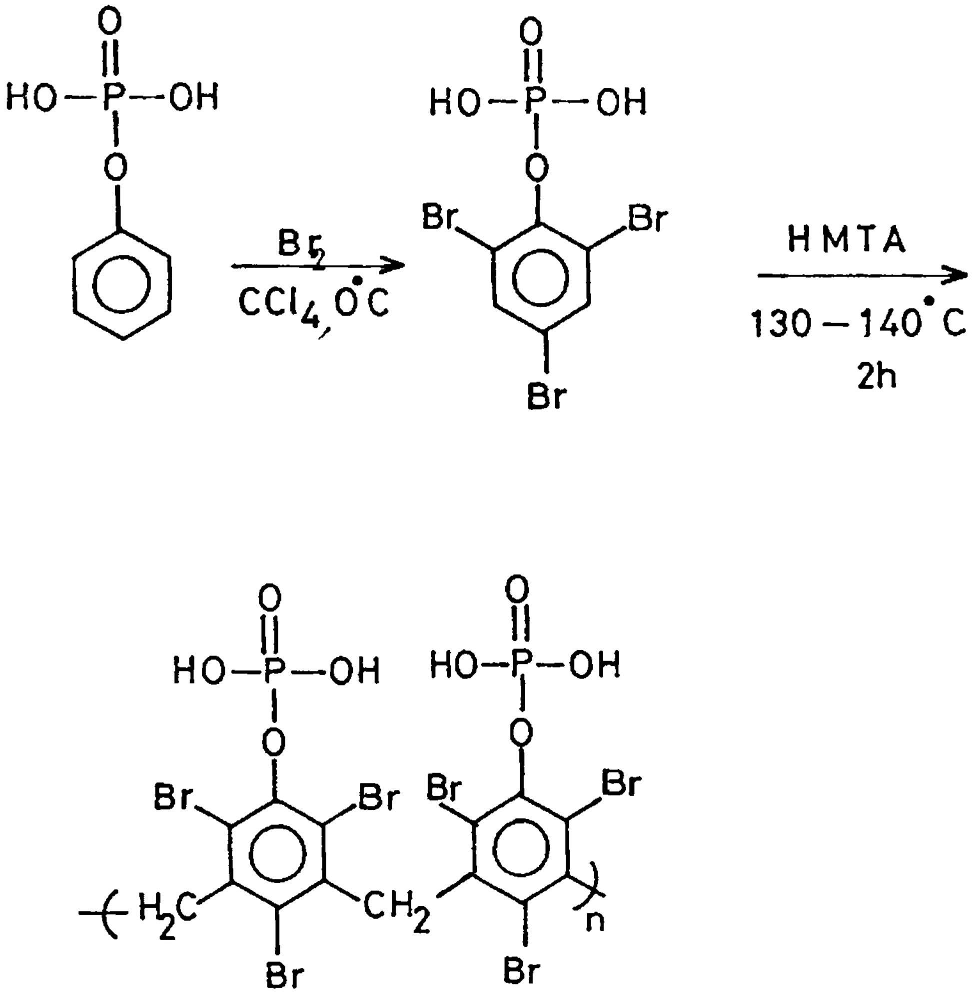
Scheme 4.2

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}H NMR	δ 3.8 (m, Ar-$\underline{CH_2}$-Ar)
	5.1 (S, $\underline{OH}$)
	7.2 (m, Ar protons)
Bromine content	43%

4. (2,4,6-tribromo)phenyl phosphoric acid-formaldehyde resin (BrMPPAF)

Monophenylphosphoric acid (MPPA) was brominated using bromine in CCl_4 to get 2,4,6-tribromophenyl phosphoric acid. MPPA (0.1 mol, 17.4 g) and CCl_4 (100 ml) were taken in a 500 ml R.B. flask kept in an ice bath and added bromine (0.3 mol, 48 g) in 150 ml CCl_4 dropwise with vigorous stirring. The product was stripped off from CCl_4 and dried in vacuum at 80°C.

BrMPPA was polymerised with HMTA through the meta positions (possibly because of the activation of the meta positions by the electronegative bromine) of the phenolic ring. BrMPPA (0.01 mol, 4.1 g) was mixed with HMTA (10 weight %, 0.41 g) in a 100 ml R.B. flask and heated at 130-140°C for 2 hs to get BrMPPAF and is shown in Scheme 4.3.



Scheme 4.3

Yield	80%
IR (neat)	780 cm^{-1} (C-Br) stretching
	950, 1160 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)

^1H NMR δ 3.8 (S, Ar-$\underline{CH_2}$-Ar)

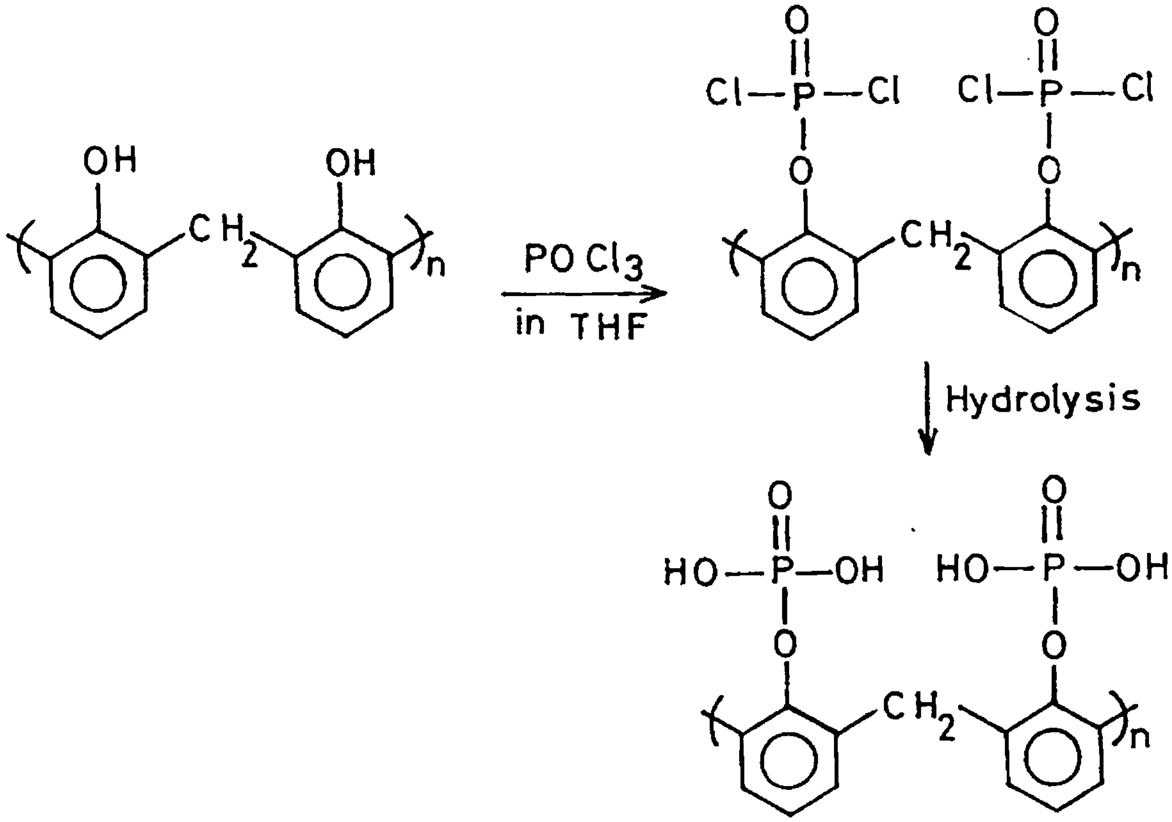
^{31}P NMR δ -15.3

Phosphorus content 7.3%

Bromine content 56.7%

5. Phosphorylated phenol-formaldehyde resin (PPF)

Phenol-formaldehyde resin was phosphorylated with $POCl_3$ in dry THF to get PPF as shown in Scheme 4.4. PF (0.1 mol, 10.6 g) in dry THF (50 ml) was added dropwise to a refluxing solution of a mixture of $POCl_3$ (0.12 mol, 18.9 g) and anhydrous $AlCl_3$(1 mol%, 0.27 g). The reaction was continued for 3 hs. The $AlCl_3$ was filtered off and the excess $POCl_3$ and THF were distilled out to get the dichloridate. It was hydrolysed with excess cold water to get the phosphoric acid of PF resin.



Scheme 4.4

Yield	90%
IR (neat)	960, 1190 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}(C-H aliphatic)
	3050 cm^{-1} (C-OH)
^1H NMR	δ 3.8 (m, Ar-$\underline{CH_2}$-Ar)
	5.1 (S, $\underline{OH}$)
	7.0 (m, Ar protons)
^{31}P NMR	δ -6.2
Phosphorus content	15%

4.3 RESULTS AND DISCUSSION

4.3.1 Synthesis

Modified phenolic resins containing phosphorus and bromine in the main structure were synthesised. The monophenyl phosphoric acid-formaldehyde (MPPAF) was prepared by the reaction of phenol with $POCl_3$ in dry toluene and then polymerisation with HMTA. Both linear and crosslinked products were prepared. The soluble and fusible resins (linear resins) were used to characterize the polymers by IR and NMR spectroscopy and GPC. The IR spectrum exhibited the characteristic phosphoric acid ester groups at 2950 cm^{-1} (P-OH), 1250 cm^{-1} (P=O), 960 cm^{-1} and 1190 cm^{-1} (P-O-C) stretching vibrations. The ^1H NMR spectrum showed peaks at δ 3.8 corresponding to the Ar-$\underline{CH_2}$-Ar protons and at δ 7.0, for the aromatic protons. ^{31}P NMR exhibited a sharp peak at δ -6.0 for the phosphorus present in the polymer.

Brominated PF novolak resin was prepared by the bromination of PF through the ortho/para position available after polymerisation. The IR spectrum of BrPF exhibited the characteristic C-Br peak at 740 cm^{-1} . The ^1H NMR spectrum showed peaks at δ 3.8 for the $-CH_2-$ protons and at δ 7.2 for the aromatic protons. The bromine content (43%) was found to be in accordance with the structure given in Scheme 4.2.

2,4,6-tribromophenylphosphoric acid was prepared by the bromination of MPPA. The tribromophenylphosphoric acid has no ortho/para position available for formaldehyde condensation. But surprisingly, BrMPPA on heating with HMTA resulted in 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 (Ar-CH_2-Ar) at δ 3.8 in the ^1H NMR show that the formaldehyde condensation has taken place to give the phenolic resin. The high electronegativity of the three bromine atoms might have activated the meta hydrogens to undergo the reaction. This could be interesting as generally meta positions are known to be inactive for formaldehyde condensation [1]. The brown coloured viscous tacky resin was dissolved in chloroform, precipitated from hexane and dried in vacuum at 80^{o} C. Pale brown coloured fluffy powder was obtained. The polymer showed an $\bar{M}n$ value of 7000, which is quite high for a novolak type resin. The polymer was found to be soluble in chloroform, acetone, tetrahydrofuran etc. The IR spectrum of the polymer exhibited peaks at 950 and 1160 cm^{-1}, 1250 cm^{-1} and 2960 cm^{-1} for P-O-C, P = O and P-OH stretching vibrations respectively and at 780 cm^{-1} for C-Br vibration. The ^{1}H NMR spectrum showed only one peak i.e. at δ 3.8 corresponding to the $-CH_2-$ protons of the methylene bridge between the repeating units. The ^{31}P NMR spectrum of the polymer indicated a sharp peak at δ -15.3 for the phosphorus present in the molecule. BrMPPAF could not be crosslinked to a thermoset product as it has got no site available for reacting with formaldehyde. This also gives another proof for its linear structure. The phosphorus content (7.3%) and bromine content (56.7%) agree with the theoretical values as calculated based on the structure given in Scheme 4.3.

To have a comparative study, the phosphorylated phenol formaldehyde (PPF) resin was synthesised by reaction of PF novolak resin with $POCl_3$ in dry THF using $AlCl_3$ as catalyst. Eventhough 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} (P-O-C), 1250 cm^{-1}(P=O) and 2950 cm^{-1} (P-OH) as well as the C-OH group at 3500 cm^{-1} (for the unreacted hydroxyl groups of PF resin). The ^{1}H NMR spectrum also indicated the $-CH_2-$ protons at δ 3.8, C-OH protons at δ 5.1 and aromatic protons at δ 7.0. The ^{31}P NMR exhibited a singlet at δ -6.2 for the phosphorus present in the polymer.

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 long time. These materials were used along with the linear resins for TGA and LOI studies.

Table 4.1 gives the molecular weights of the linear resins. $\bar{M}n$ values are in the range 1500-1700 for the linear resins except for BrMPPAF. Polydispersities are in the range 2-3.4. In the case of BrMPPAF, the $\bar{M}n$ value is quite high (7000) and D is only 1.35.

4.3.2 Thermal and flammability studies

In the present study phenolic resins were modified with P and Br, the modification made at the monomer stage so that a high loading of the flame retardant element is incorporated and the problem of gelation is overcome. Thus the present study compares the thermal and flammability behaviour of PF, MPPAF, PPF resins and their cured products and BrPF and BrMPPAF. The effect of phosphorus and bromine separately and together on the thermal and flammability behaviour of these polymers was also investigated. Thermal stabilities in N_2 as well as in air atmospheres were determined so as to study their thermooxidative resistance. The thermogravimetric traces of the polymers are given in Figs.4.3-4.6. The thermal stabilities of the polymers are given in Table 4.2. The parameters studied are the temperature corresponding to 10% weight loss (T_{10})., temperature corresponding to 50% weight loss (T_{50}) and the char yield at 600°C (C_y). Comparison of these values shows that among the linear resins, MPPAF exhibits an overall higher thermal stability than that of PF in nitrogen atmosphere. Eventhough the T_{10} value is slightly lower for MPPAF (205° C) than for PF (220° C), the T_{50} (480) and C_y (43) values are higher for MPPAF. The T_{50} and C_y values have increased from 440°C and 39% for PF to 480° C and 43% respectively for MPPAF. When the experiment was conducted in air, the thermal stability of MPPAF was found to register a steep rise. Thus, T_{10} and C_y values have increased from 140° C 32% for PF to 275° C and 51% for MPPAF. In the case of cured systems, although the T_{10} values are lower both in N_2 and air for MPPAF (220°C and 320°C respectively) than that for PF (410°C and 440° C respectively), the char yield (66%) is higher in air for MPPAF than that for PF (52).

The higher values of char yield and T_{10} and T_{50} of the phosphorus modified resin in air than those in N_2 agree well with those reported by Shibazaki et al [27] and are indicative of enhancement of thermooxidative resistance introduced into phenolic resins when modified with phosphorus. Similar results have been reported by Tugetepe et al [35] also for heavy metal modified phenolic resins.

From Table 4.2 it can be seen that thermal stability of BrPF is lower than the unbrominated linear resin. Thus BrPF has a T_{10} value of 185 ^oC, T_{50} value of 370^{o}C and char yield of 30%, in nitrogen atmosphere. The T_{50} and C_y values are still lower in air i.e. T_{50} 400^{o}C and char yield 2%. Thus, bromination of PF lowers its thermal stability and thermooxidative resistance. BrMPPAF has higher T_{10} and T_{50} values in air than in nitrogen. The BrMPPAF gives T_{10} values of 210 and 230 and T_{50} values of 330 and 345^{o}C in N_2 and air respectively. The lowering of the thermal stabilities of BrPF and BrMPPAF could be attributed to further oxidation by HBr which is known to be promoter of low temperature combustion [36,37].

From Table 4.2 it can be seen that the P-PF resins prepared by the phosphorylation of the linear PF resins are thermally less stable than the MPPAF resins. This could be understood on the basis of the lower phosphorus content of P-PF resins than that of MPPAF resins. As expected the cured PPF is thermally stabler than the linear one. Thus linear

PPF shows T_{10} value of 200 and T_{50} value of 475°C in N_2 whereas the cured polymer has a T_{10} of 300°C. The T_{10} values are lower in air for both linear and cured systems. P-PF linear has got a T_{10} value of 170 only whereas P-PF cured has got a T_{10} value of 210. The linear resin has got higher T_{50} (530) and C_y values (42) in air than those (T_{50} 475 and C_y 41) in N_2. The char yield of the cured system also showed an increase in air (58) than in N_2 (57). These results indicate that PPF resins exhibit higher thermooxidative resistance at high temperature.

The limiting oxygen index value of all the polymers are given in Table 4.3. It can be seen that the LOI values increase with phosphorus content in general. The PF linear resin has LOI value of 25 which on phosphorylation increases to 33. Similar is the case with the cured resin also. Thus cured PF shows an LOI value of 35 and cured MPPAF has got an LOI value of 50. The introduction of phosphorus into PF has thus raised its thermal stability, char content and LOI values. Phosphorus as flame retardant is well known to act in the condensed phase in the case of oxygenated polymers and the present data also support this mechanism operating in MPPAF [36,38]. On the other hand the high values of LOI for BrPF (48) and BrMPPAF (56) with low char contents (2% and 26% respectively) suggest a vapour phase mechanism. Brominated flame retardants are known to release volatile species which interfere with the free radical chain branching reactions to remove high energy $OH^{\bullet}$ and $H^{\bullet}$ radicals and inhibit the combustion process [39]. The PPF resins have LOI values of 30 and 46 which are lower than the MPPAF resins and can be due to their low phosphorus contents.

Further information on the thermal behaviour of these polymers were obtained from activation energies calculated by the method of Freeman and Anderson [40] as modified by Freeman and Carroll [41] and the results are given in Table 4.3. The cured systems are having higher E values than the linear resins and can be due to their increased thermal stability. BrPF and BrMPPAF have higher E values. This might be understood from the free radical type of decomposition of the brominated compounds. Fractional orders in the range of 0.7 to 0.90 were obtained for the decomposition reactions.

Table 4.1: 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

Table 4.2: Thermal stabilities of the modified phenolic polymers

S.No.	Sample	Thermal stabilities in N$_2$			Thermal stabilities in 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 4.3: Thermal decomposition kinetics (in N_2) and 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

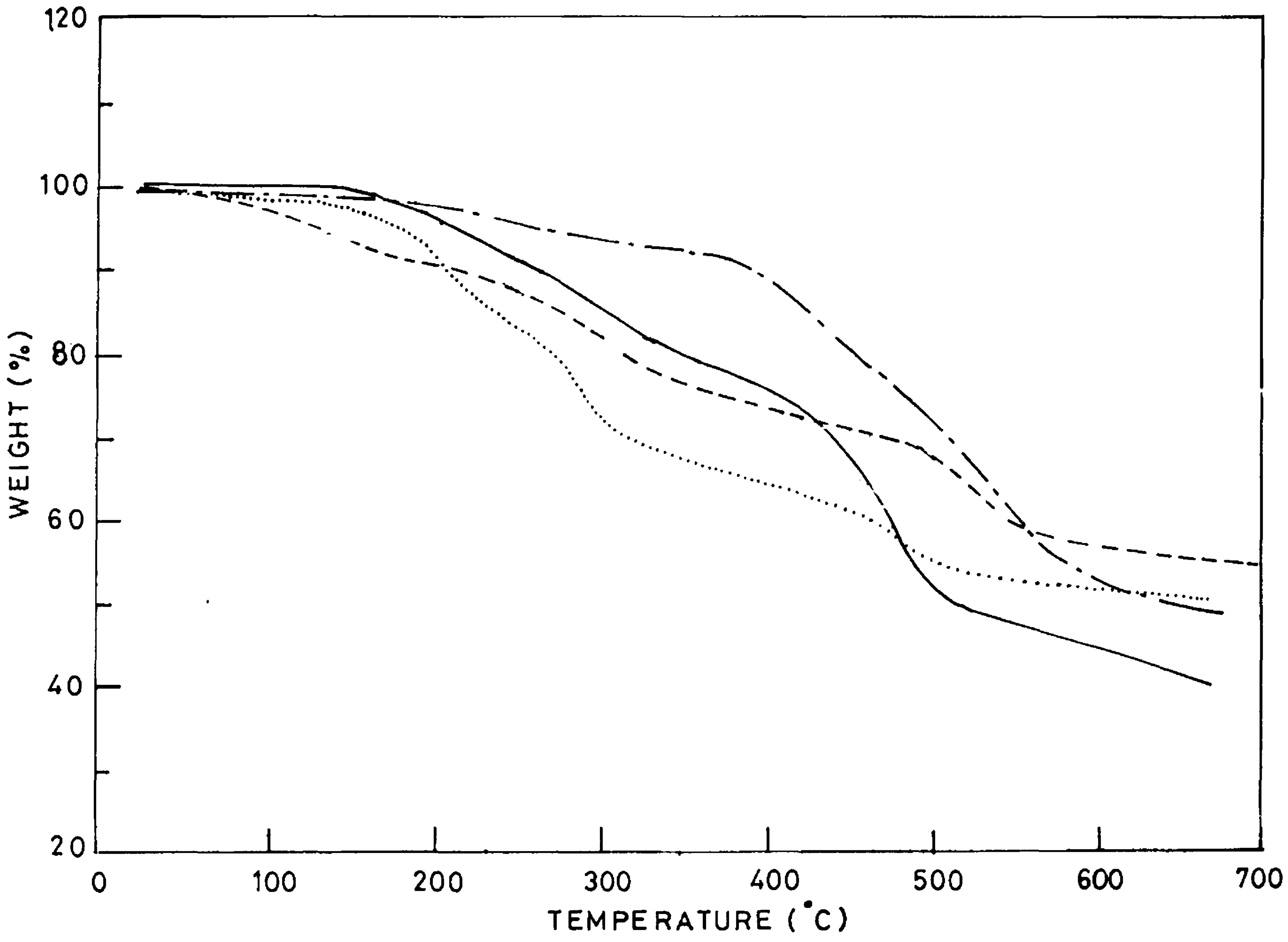


Fig 4.3 Thermogravimetric traces of ——— PF Linear, —.— PF cured .... MPPAF Linear & - - - -MPPAF cured in Nitrogen

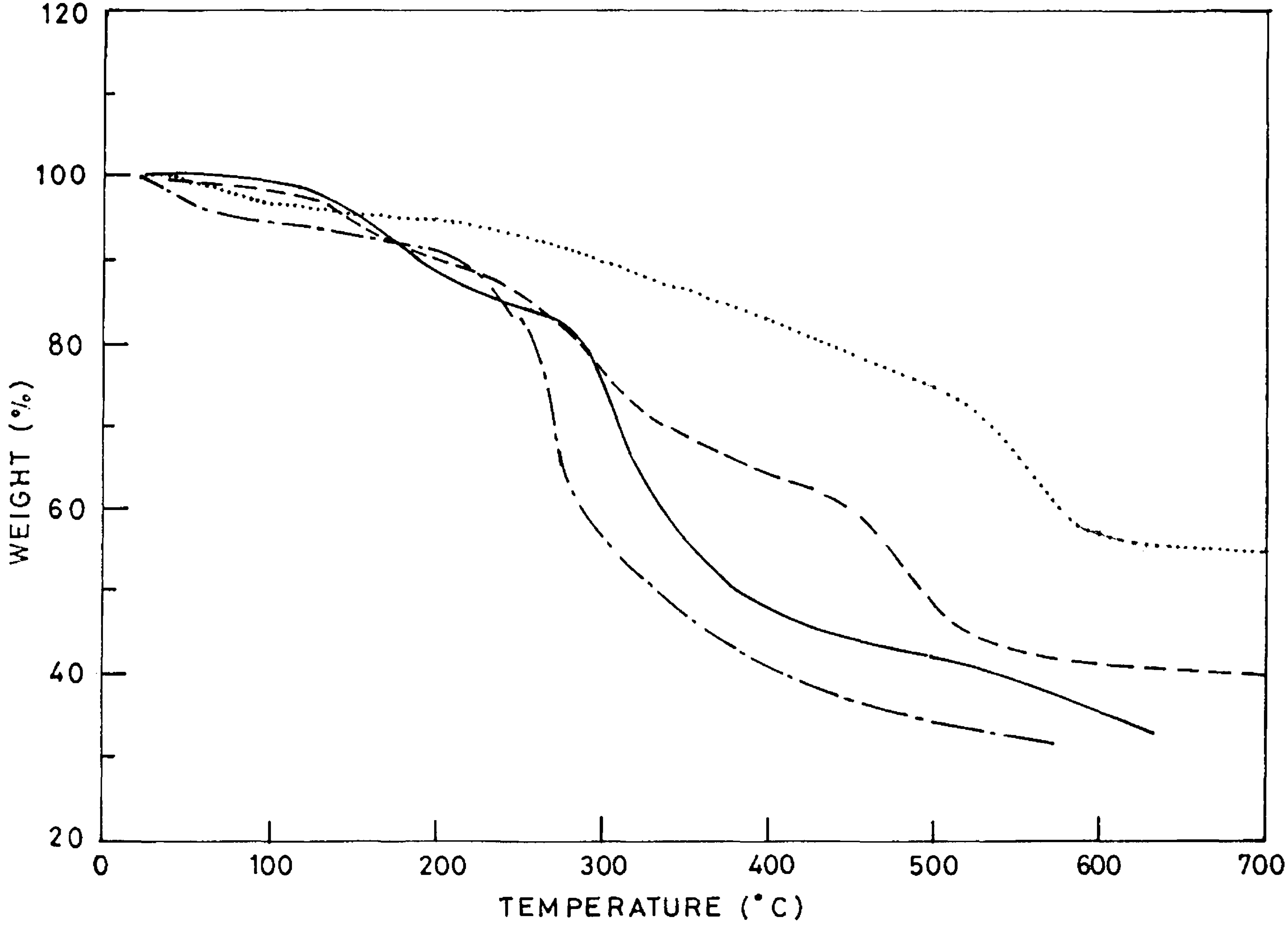


Fig.4.4. Thermogravimetric traces of —— BRPF —·— BRPPAF
– – – – P-PF Linear & ······· P-PF cured in Nitrogen

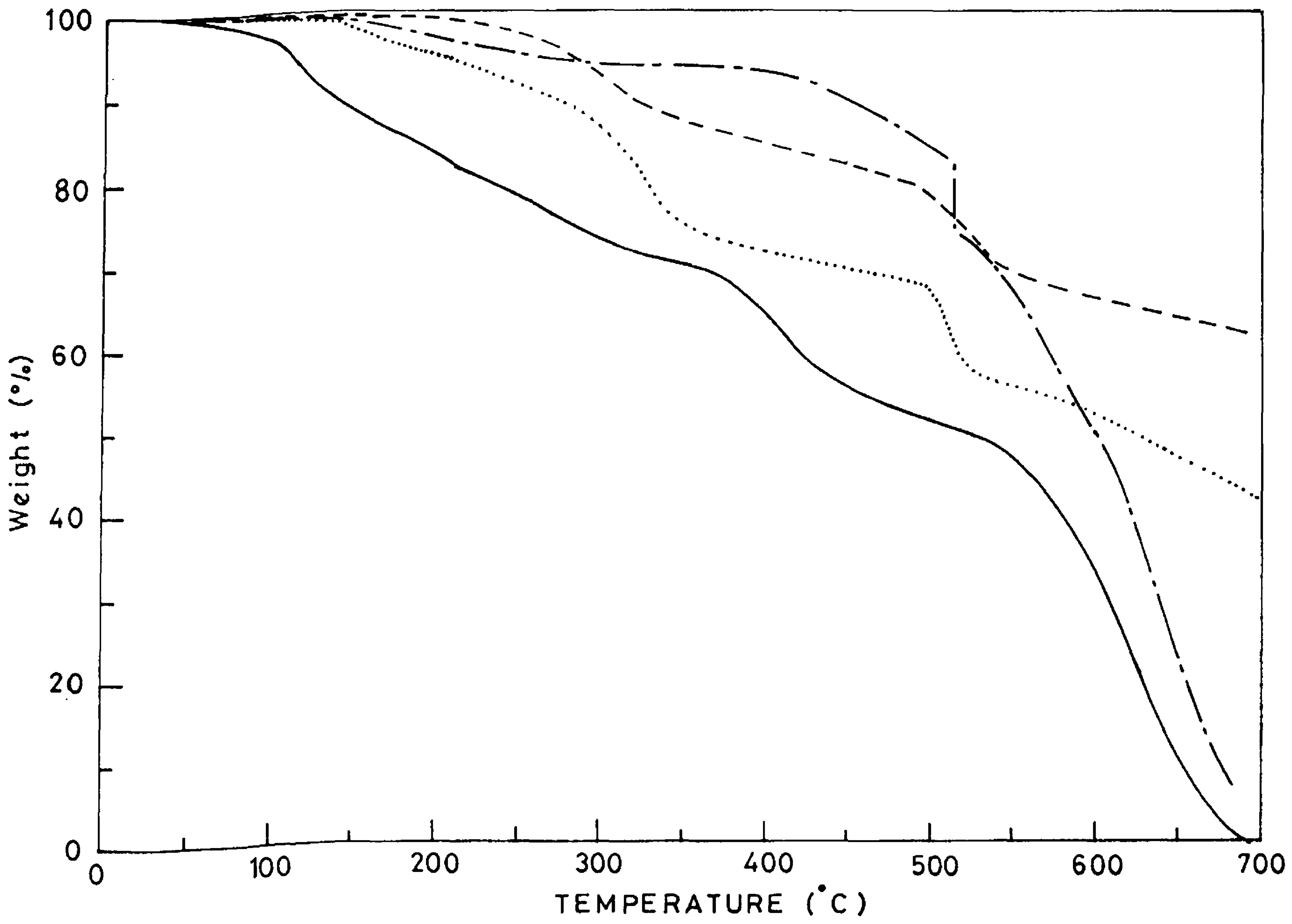


Fig 4.5 Thermogravimetric traces of ——— PF Linear, —·— PF Cured, ……. MPPAF Linear & – – – – MPPAF cured in air

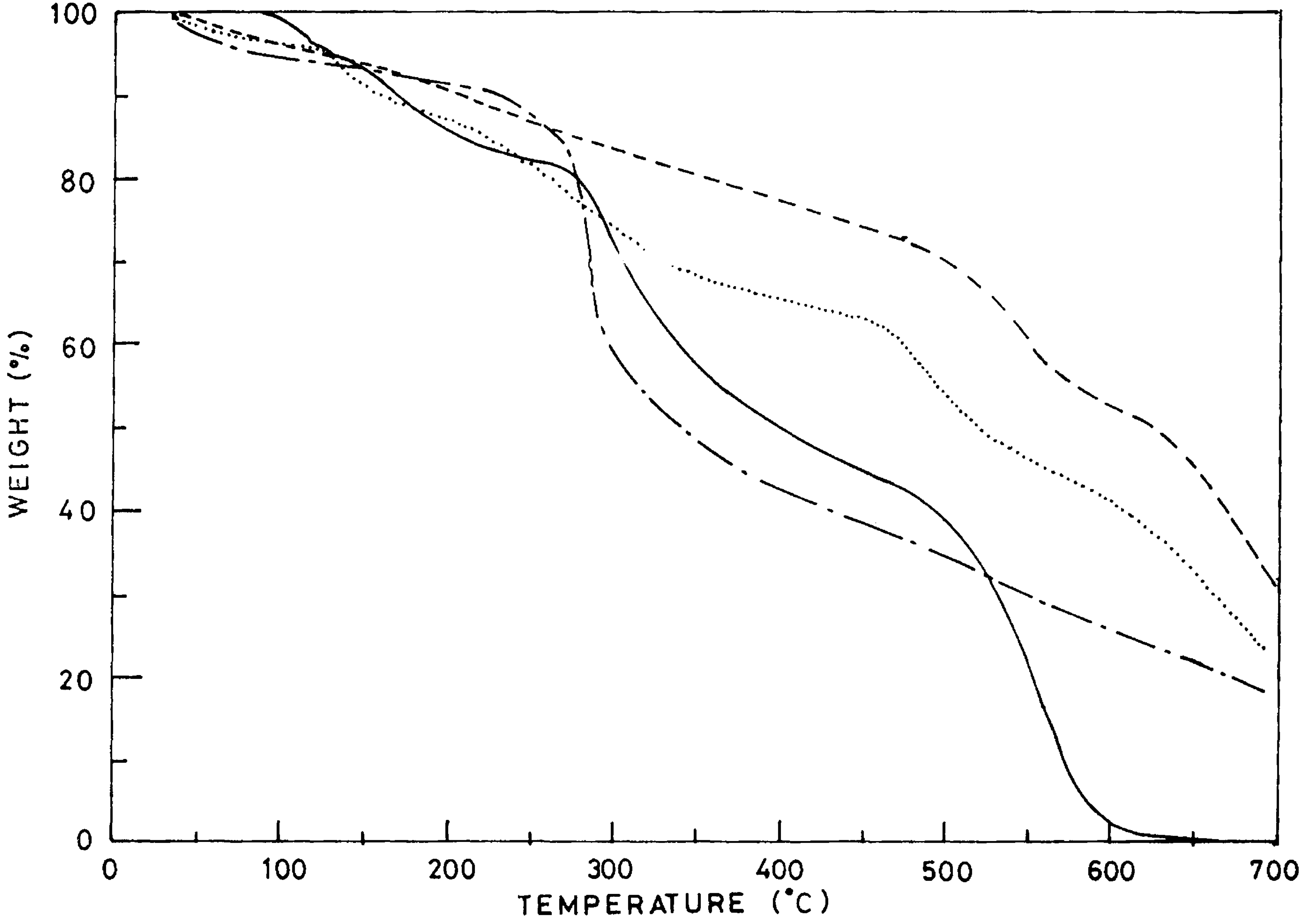


Fig '4.6' Thermogravimetric traces of —— BRPF , —·— BRMPPAF ,
.... P-PF Linear & ---- P-PF Cured in air

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CHAPTER 5

SYNTHESIS, CHARACTERIZATION AND THERMAL STUDIES OF CARDANOL BASED POLYPHOSPHATE ESTERS

5.1 INTRODUCTION

Phosphorus-containing polymers have received considerable attention in the recent past owing to their effectiveness as flame retardants [1-15]. These polymers have several advantages over the halogen-containing ones such as higher thermal and photo stabilities and mechanical properties [2]. Moreover, relatively small amounts of phosphorus make a polymer sufficiently flame retardant compared to the high add-on levels of halogenated compounds [12] . The polyphosphate esters are an important class of phosphorus-containing polymers. In addition to their flame retardant characteristics as in the case of other organophosphorus polymers, they also possess plasticizing properties [16]. Some attention has recently been drawn on polyphosphates, mainly as polymeric flame retardant additives to other polymers. The polymeric additives are preferred to conventional non-polymeric ones owing to their better resistance to extraction, migration, volatile loss etc. and thus making the flame retardancy available permanently [17,18].

The most important method for the synthesis of polyphosphates is the esterification of alkyl or aryl phosphorodichloridates with diols or dihydric phenols. The polymerisation is usually carried out by melt, solution or interfacial polycondensation. Melt polycondensation is carried out by heating the reactants in the absence of any solvent [19-21]. Solution polycondensation has mostly been carried out in the presence of bases like pyridine, triethylamine etc. and in solvents like ether, benzene, toluene [22,23] etc. Zenftman et al [24,25] have reported the synthesis of aromatic polyphosphates which were found to be useful as adhesive or coating with good flexibility and Coover et al [26,27] synthesised polyphosphates which can be drawn into flame retardant fibres. However, reports on the synthesis of polyphosphates by interfacial polymerisation are limited. Rabek and Prot [28] have used this method for the preparation of polyphosphates whereas Frank and Carraher [29] have extensively studied the synthesis of polyphosphonates by interfacial polymerisation. Kishore et al [30-33] have reported the synthesis of polyphosphates by both solution and interfacial polycondensation. The present chapter describes the synthesis of a series of polyphosphate esters based on phosphorodichloridates of 3-pentadecylphenol and brominated cardanol with dihydric phenols such as hydroquinone, bisphenol, tetrabromobisphenol and phenolphthalein by an interfacial polycondensation using a phase transfer catalyst. The spectroscopic as well as the thermal characterization of these polymers were studied.

5.2 EXPERIMENTAL

5.2.1 Materials

Cardanol (37330-39-5) was obtained by double vacuum distillation of cashew nut shell liquid (CNSL-8007-24-7) at 3-4 mm Hg, as given in chapter 2 (2.2.1) at 230-235^{o}C. Cardanol was hydrogenated in a Parr medium hydrogenator in methanol using platinum oxide as catalyst to give 3-pentadecylphenol [34]. $POCl_3$ was purchased from S.D. Fine Chem., India, and distilled before use. The dihydric phenols such as hydroquinone, bisphenol and phenolphthalein were purchased from Merck India and recrystallised from petroleum ether. Aliquat 336 was obtained from Fluka, Switzerland and was used as such. Anhydrous $AlCl_3$ and sodium hydroxide were purchased from E. Merck, India, and were used as such without further purification. Hexane and chloroform were dried with calcium chloride and then distilled.

5.2.2 Measurements

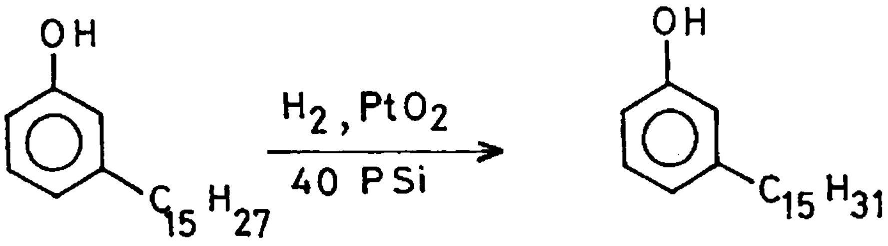
The transmission infrared spectra were recorded on Perkin Elmer IR spectrophotometer Model 882 as neat films on NaCl windows by the smear techniques. ^{1}H NMR spectra were recorded on Hitachi R-24 B high-resolution NMR spectrometer in $CDCl_3$ using TMS as internal reference. ^{13}C and ^{31}P NMR spectra were taken on a JEOL FX-90 Q FT spectrometer. The GPC data were obtained using Hewlet -Packard 1081 B HPLC, equipped with an automatic sample injection system and a differential RI detector. THF

(HPLC grade) was used as the eluent. The thermogravimetric studies were carried out on a Dupont thermogravimetric analyser model 951 in nitrogen and air atmospheres at a heating rate of 20°C min with a sample weight of 5-8 mg. The LOI data were determined by using a Stanton Red Croft LOI equipment of model FTA-7101.

5.2.3 Synthesis

1. Hydrogenation of cardanol to 3-pentadecylphenol

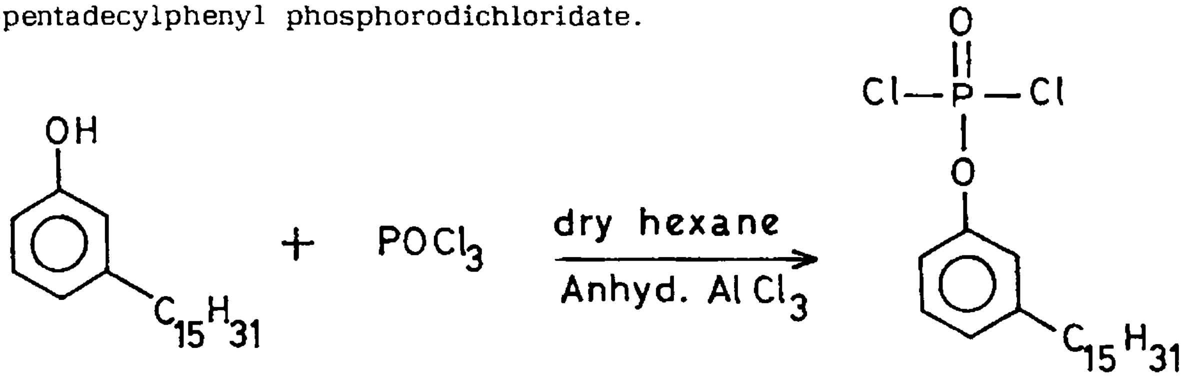
Cardanol (0.33 mol, 100 g) in methanol (100 ml) was hydrogenated in a Parr medium hydrogenator at 40 psi using platinum oxide (50 mg) at ambient temperature. The hydrogenation was completed in 2 hs. The crude 3-pentadecylphenol was distilled under reduced pressure (4 mm Hg). The fraction obtained at 200 °C to 210 °C was recrystallised from hexane to get pure 3-pentadecylphenol. M.P. 51°C. The reaction is given in Scheme 5.1.



Scheme 5.1

2. Synthesis of 3-pentadecylphenyl phosphorodichloridate

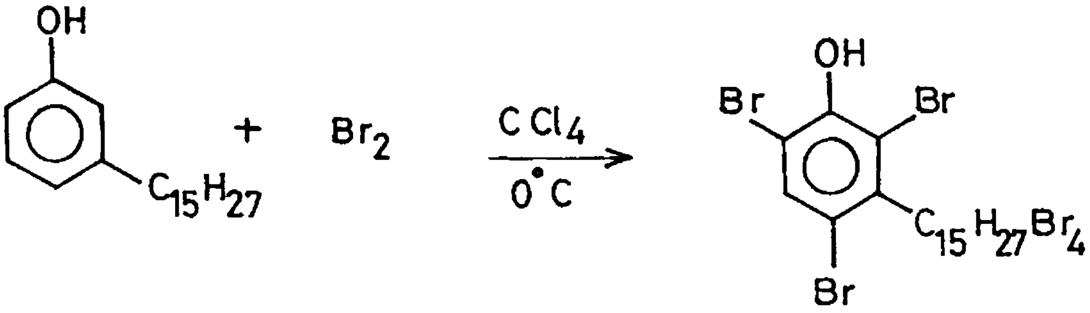
3-pentadecylphenyl phosphorodichloridate was prepared by phosphorylation using $POCl_3$[35,36] as given in Scheme 5.2. A typical phosphorylation was carried out as follows. A mixture of $AlCl_3$ (0.01 mol %, 0.44 g) and phosphoryl chloride (0.39 mol, 60.0 g) in dry hexane (100 ml) was heated to reflux and 3-pentadecylphenol (0.33 mol, 100 g) dissolved in dry hexane (200 ml) was added dropwise with stirring over a period of 30 minutes. The $AlCl_3$ was filtered off and solvent was stripped off to get 3-pentadecylphenyl phosphorodichloridate.



Scheme 5.2

3. Synthesis of brominated cardanol

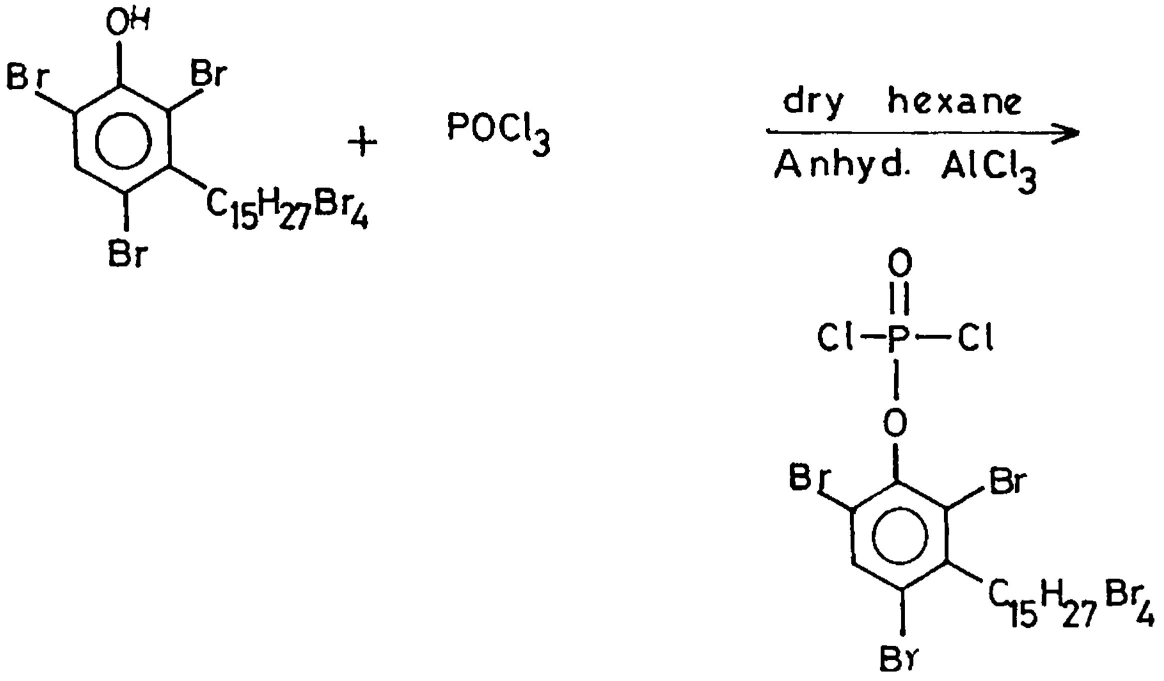
Cardanol was brominated using bromine in CCl_4 as given in chapter 3 (3.2.3). Cardanol (0.1 mol, 30 g) and CCl_4 (100 ml) were taken in a 500 ml 2-necked flask kept on an ice bath and added bromine (0.5 mol, 80 g) (in 100 ml CCl_4) dropwise with vigorous stirring. CCl_4 was stripped off and the product was dried in vacuum at 70°C. The reaction is shown in Scheme 5.3.



Scheme 5.3

4. Synthesis of tetrabromo-3-pentadecyl-2,4,6-tribromophenyl phosphorodichloridate

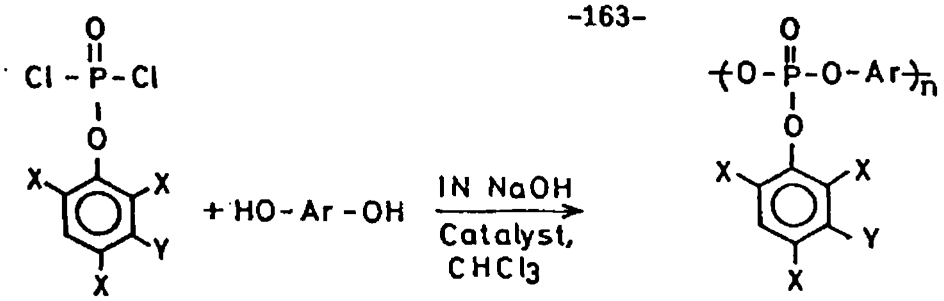
Brominated cardanol was phosphorylated using $POCl_3$ in dry hexane and $AlCl_3$ catalyst [35,36]. A mixture of $AlCl_3$ (0.01 mol %, 0.13 g) and phosphorylchloride (0.12 mol, 18 g) in dry hexane (25 ml) was heated to reflux and brominated cardanol (0.1 mol, 86 g) dissolved in dry hexane (200 ml) was added dropwise with stirring over a period of 30 minutes. The $AlCl_3$ was filtered off. Hexane and the excess $POCl_3$ were distilled out to get tetrabromo-3-pentadecyl-2,4,6-tribromophenyl phosphorodichloridate. The reaction is shown in Scheme 5.4.

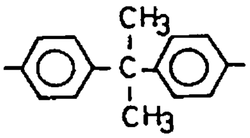
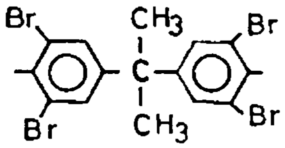
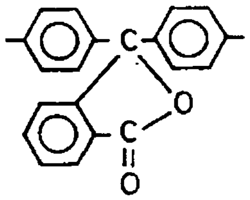
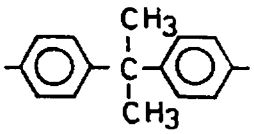
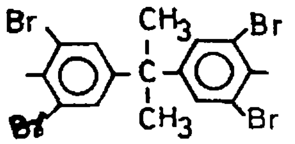
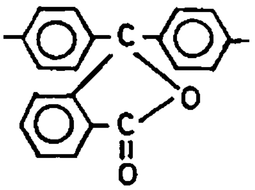


Scheme 5.4

5. Synthesis of polyphosphates

Typical procedure for the synthesis of polyphosphate ester from aryl phosphorodichloridate and dihydric phenol is given below. Hydroquinone (0.01 mol) and 50 ml aqueous NaOH (0.05 mol) were taken in a 500 ml flask fitted with a magnetic stirrer. To this 2 weight % of Aliquat 336 (Tricapryl methyl ammonium chloride) was added and stirred well. A solution of aryl phosphorodichloridate (0.015 mol) in 50 ml dry chloroform was added to the stirring mixture and the reaction continued for another 10 minutes. The chloroform layer was separated and poured into a large quantity of methanol to precipitate the polymer. The precipitation was repeated for 2-3 times to remove the low molecular weight fractions. The polymer was collected and dried in vacuum oven at 80 °C for long time. The polymers (I-IV) are white powders and (V-VIII) are brown coloured powders. Yields of these polymers were 80-90%. They were soluble in acetone, chloroform, tetrahydrofuran, dimethyl formamide etc. All the eight polymers were prepared by similar procedures. The reaction is shown in Scheme 5.5.



Polymer No.	X	Y	Ar
I	H	$C_{15}H_{31}$	
II	H	$C_{15}H_{31}$	
III	H	$C_{15}H_{31}$	
IV	H	$C_{15}H_{31}$	
V	Br	$C_{15}H_{27}Br_4$	
VI	Br	$C_{15}H_{27}Br_4$	
VII	Br	$C_{15}H_{27}Br_4$	
VIII	Br	$C_{15}H_{27}Br_4$	

Scheme 5.5

5.3 RESULTS AND DISCUSSION

A series of polyphosphate esters (Polymers I-VIII) have been prepared from the phosphorodichloridates of 3-pentadecylphenol and brominated cardanol with dihydric phenols such as hydroquinone, bisphenol, tetrabromobisphenol and phenolphthalein by an interfacial polycondensation reaction using Aliquat 336 as catalyst as illustrated in Scheme 5.5. The polymerisation proceeded rapidly with yields in the range of 80-90%. The $\bar{M}n$ values of the polyphosphates are in the range from 1100 to 2500 with polydispersities in the range 1.7 to 3.9. The yields and molecular weights are given in Table 5.1.

The characteristic IR absorption frequencies of all the polymers were similar and are given in Table 5.2. The polymers exhibited intense absorption peaks at 1250 cm^{-1} corresponding to the P=O stretching vibration. The absorptions at 1150 and 980 cm^{-1} indicate P-O-C aromatic stretching vibrations. Polymers IV and VIII exhibited absorptions at 1780 cm^{-1} corresponding to the carbonyl group of phenolphthalein [37] and polymers III, V, VI, VII and VIII showed the characteristic C-Br stretching vibrations at 790 cm^{-1}. The ^1H NMR chemical shift values of the polymers are given in Table 5.3. The multiplet in the region δ 7.0 to δ 7.6 corresponds to the aromatic protons of the arylphosphorodichloridate and the corresponding dihydric phenols. Polymers II, III, VI and VII exhibited the isopropylidene peak at around δ 1.6 [30]. The bromomethyl protons of the polymers

(V to VIII) were observed at δ 4.2. The ^{13}C NMR spectrum of a typical polymer III is shown in figure 5.1; the characteristic carbon resonances are indicated in the spectrum itself [38]. The ^{31}P NMR spectra (Table 5.4) of the polymers showed signals at around δ -18.0 corresponding to the phosphorus in the repeat unit and at around δ -5.0 for the phosphorus at the chain end [30].

The dynamic TGA curves of the polyphosphates in nitrogen atmosphere are given in Fig. 5.2 and 5.3. The thermal stabilities and thermal degradation kinetics are presented in Tables 5.5 and 5.6. The parameters studied are T_i- Initial decomposition temperature, $T_{1/2}$ - temperature at which 50% decomposition occurs. T_{max} - temperature at which maximum rate of weight loss occurs and C_y - char yield at 600^{o} C and are given in Table 5.5. The thermal stabilities of all the polymers are quite comparable and all are stable in the temperature range 210 to 275^{o} C in nitrogen atmosphere. As $T_{1/2}$ was found to be more reliable than T_i in interpreting thermal stability in relation to char yield, $T_{1/2}$ was taken as the criteria of thermal stability for the present study. It can be seen from Table 5.5 that the polymers I-IV (derived from 3-pentadecylphenol) exhibit higher thermal stability than polymers V-VIII (derived from brominated cardanol). The initial decomposition temperature T_i also supports such a trend. All the polymers exhibited two T_{max} values; the first in the temperature range 240-320^{o} C and the second in the temperature range 450-575^{o}C and this indicates a two stage decomposition.

The first stage may be the loss of the labile aliphatic side chain of the cardanol moiety which is reported to occur in the temperature range of 250-300^{o}C in other cardanol based polymers [39]. The second stage could probably be due to the breakdown of the partially crosslinked and/or cyclized structures formed prior to or during the initial stages of decomposition. The char yields of 20-29% (Table 5.5) exhibited by these polymers also indicate crosslinking and or cyclization reactions.

Comparison of the values given in Table 5.5 shows that among the first four polymers (derived from hydrogenated cardanol) IV is the most stable ($T_{1/2}$ - 455 and C_y - 26). Polymer IV is derived from phenolphthalein, whose structural rigidity might be contributing to its stability [37,40]. Moreover, the rearrangement of the lactide group may also give rise to improved stability [41]. Polymers II and III are derived from bisphenol and tetrabromobisphenol. Although tetrabromobisphenol is known to be thermally more stable than bisphenol A [30], the present data show that $T_{1/2}$ and char yield for polymer III is lower than that of polymer II. This is true for polymers VI and VII as well. Although these data seem perplexing, it should be noted that the molecular weights of polymers III and VII are extremely low ($\bar{M}n$ 1150 and 1550) (The molecular weights of the repeating units for polymers III and VII are 888 and 1445). So polymers III and VII are not considered here for a comparative evaluation of thermal stability and thermal degradation kinetics. The low values of $T_{1/2}$ (435) and C_y (20.3) for polymer II in comparison to polymer I can be understood from the presence of the labile isopropylidene group in polymer II. The high phosphorus content in polymer I (6.8%) might also contribute to its higher $T_{1/2}$ value (450) and char yield (26). The polymers derived from brominated cardanol (V to VIII) exhibit a lower thermal stability than that of the polymers I-IV. The presence of bromine in the aliphatic side chain of cardanol might be the factor that reduces the thermal stability of those polymers. It appears from these studies that the thermal stability of these polymers is directly related to char yield. For example, the least stable polymer (among those derived from 3-pentadecylphenol) polymer II has got the lowest char yield of 20.3. Further, the most stable polymer (IV) has got the highest C_y value of 26%. Among the polymers derived from brominated cardanol also, the least stable polymer (VI) has the lowest C_y (21) and the most stable polymer (VIII) has the highest C_y (29).

These data have been further supported by deriving the kinetic parameters of the polymers. The thermal decomposition kinetic parameters (Table 5.6) (energy of activation E and order of thermal decomposition n) were calculated by the method of Freeman and Carroll [42] as modified by Anderson and Freeman [43]. Since the TGA of the polymers exhibited two stage decomposition, the kinetic parameters were determined separately for the two steps. The activation energies for the first stage of decomposition are in the range 23-33 kCal/mol (the E values for the second stage are slightly higher i.e. in the range

28-35 kCal/mol). In the first stage, the most stable polymer IV (among those derived from 3-pentadecylphenol) is having the highest E value of 33 and the least stable polymer (II) has got the lowest activation energy of 23 kCal/mol. In the second stage, the most stable polymer IV has the highest E (35 kCal/mol) and the least stable polymer II has the lowest E value of 28 kCal/mol. In the case of polymers derived from brominated cardanol also, the least stable polymer VI has the lowest E value of 24.7 kCal/mol and the most stable polymer VIII has the highest value of 28.3 kCal/mol. Again, for the second stage of decomposition E for VI is 31 kCal/mol and that for VIII is 34 kCal/mol. Fractional orders in the range 0.5 to 0.9 were observed for the degradation reactions. Because the kinetic parameters for these polyphosphates are comparable, it is indicated that all polymers degrade primarily by similar mechanisms. The thermal stabilities of these polymers in air were also determined and are given in Table 5.7. It can be seen from Table 5.7 that both $T_{1/2}$ and C_y values are lower in air than in nitrogen indicating lower thermo-oxidative resistance of these polymers. However, for the polymers derived from brominated cardanol, the $T_{1/2}$ values are slightly higher in air than in nitrogen atmosphere.

The Limiting Oxygen Index (LOI) values of the polyphosphates are found to vary with bromine content in general (Table 5.6). The polymers derived from brominated cardanol are found to exhibit significantly higher LOI values. Brominated flame retardants are known to release volatile species which interfere with the free radical chain branching reactions to remove high energy $OH^{\bullet}$ and $H^{\bullet}$ radicals and inhibit the combustion process [44]. In the case of the polymers I-IV (derived from 3-pentadecylphenol) III has got the highest LOI value of 27 as it has contribution from bromine built into the ring (bromine content 35.9). Out of the other three polymers, eventhough phosphorus content is the highest for I (6.8%) LOI values are the same for I and IV. This can be understood from the increased thermal stability of IV as explained earlier. Again, polymer II with a phosphorus content of 5.4 which is higher than that of IV (4.7%) has the lowest LOI value of 22.. This is in agreement with the lower thermal stability of polymer II ($T_{1/2}$ 435 ^{o}C) in comparison to that of polymer IV ($T_{1/2}$ 455 ^{o}C). On comparing the LOI values of the polymers derived from brominated cardanol (V to VIII) it can be seen that polymer VII with the highest bromine content (60.7%) has got the highest LOI value (62). Although the phosphorus and bromine contents of polymer VIII are the lowest among polymers V-VIII, it exhibits a higher LOI value of 50 and can be explained on the basis of its higher thermal stability. Polymer V has higher phosphorus content (3%), bromine content (55.%) and thermal stability ($T_{1/2}$ 310) than those of VI (phosphorus content 2.7%, bromine content 49.6% and $T_{1/2}$ - 300) and hence exhibits a higher LOI value (49) than that of VI (48). These results clearly indicate that in the case of these polymers flammability is a function not only of phosphorus and bromine contents in it but also has direct relation to its thermal stability and structure.

It is well known that the thermal stability and char yield have a direct relationship with LOI of polymers. Fenimore and Martin [45,46] in their study on oxygen index of polymers showed that LOI is related to the char forming ability of polymers. Further studies correlating thermal stability with LOI were undertaken by Vankrevelen [47] who showed that LOI in hydrocarbon polymers is directly related to char yield. Later Annakutty and Kishore [20] showed that LOI is a function of both phosphorus content and thermal stability in polyphosphates. Correlation of thermal stability with LOI has not been reported for polymer systems containing phosphorus and bromine together. It appears from the present study that the LOI of polymers containing both phosphorus and bromine also has a direct relationship with char yield and thermal stability.

Table 5.1: Yields and molecular weights of the polyphosphates

Polymer	Yield	Molecular weights		
		$\overline{M}n$	$\overline{M}w$	D
I	80	1100	3520	3.2
II	85	2500	6750	2.7
III	90	1150	3350	3.0
IV	85	2470	4090	1.7
V	80	1450	5700	3.9
VI	84	2000	5350	2.7
VII	88	1550	4650	3.0
VIII	84	1900	5470	2.9

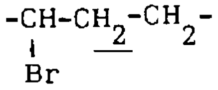
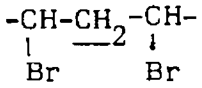
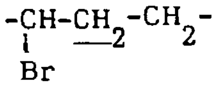
Table 5.2: Infrared absorption frequencies of the polyphosphates
(Wavenumber cm^{-1})

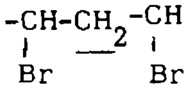
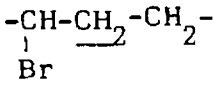
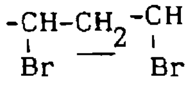
Polymer	I	II	III	IV	V	VI	VII	VIII	
	690(W)	690(M)	690(W)	680(W)	695(W)	690(M)	695(W)	690(W)	Out of plane deformation of C-H bonds of aromatic rings
	840(M)	830(S)	850(S)	840(S)	850(S)	840(S)	860(S)	840(S)	
	-	-	790(S)	-	795(S)	790(S)	790(S)	790(S)	C-Br stretching
	980(M)	980(S)	980(S)	980(S)	980(S)	980(S)	980(S)	980(S)	P-O-C stretching
	1150(S)	1150(S)	1150(S)	1140(S)	1150(S)	1160(S)	1150(S)	1160(S)	
	1020(M)	1010(M)	1010(W)	1020(S)	1020(W)	1020(W)	1015(W)	1020(W)	Inplane deformation of C-H bonds of aromatic rings
	1050(M)	1050(M)	1050(W)	1060(M)	1050(W)	1050(W)	1050(W)	1050(W)	
	1110(W)	1100(W)	1100(W)	1110(W)	1100(W)	1105(W)	1110(W)	1100(W)	
	1250(S)	1250(S)	1250(S)	1260(S)	1260(S)	1250(S)	1250(S)	1260(S)	P=O stretching
	1420(W)	1415(W)	1415(W)	1420(W)	1415(W)	1420(W)	1420(W)	1415(W)	
	1440(W)	1450(S)	1450(S)	1450(M)	1460(W)	1460(S)	1460(S)	1460(M)	C=C ring stretching
	1500(S)	1500(S)	1500(M)	1500(M)	1500(S)	1500(S)	1500(M)	1500(S)	
	1600(S)	1590(S)	1590(S)	1595(S)	1600(S)	1590(S)	1590(S)	1590(S)	
	-	-	-	1780(S)	-	-	-	1780(S)	C=O stretching
	2860(M)	2870(M)	2850(S)	2860(M)	2860(M)	2860(M)	2860(M)	2860(M)	Aliphatic C-H stretching
	2930(S)	2930(S)	2930(S)	2930(S)	2930(S)	2930(S)	2930(S)	2930(S)	P-OH stretching
	3020(W)	3030(W)	3020(W)	3020(W)	3020(W)	3030(W)	3030(W)	3030(W)	Aromatic C-H stretching

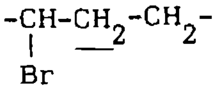
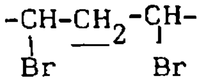
S = Strong; M = Medium; W = Weak

Table 5.3: ^{1}H NMR spectral data[a] for the polyphosphates

Polymer	Description of peaks, multiplicity[b], number of protons[c] and peak assignment	
I	0.9 (t, 3 H)	CH_3
	1.2 (m, 26 H)	$(CH_2)_{13}$
	2.1 (m, 2 H)	Benzyl protons
	7.0 (m, 4 H)	Aromatic protons of 3-pentadecyl phenol
	7.3 (m, 4 H)	Aromatic protons of hydroquinone
II	0.9 (t, 3 H)	CH_3
	1.3 (m, 26 H)	$(CH_2)_{13}$
	1.6 (s, 6 H)	Two (CH_3) of bisphenol
	2.0 (m, 2 H)	Benzyl protons
	7.0 (m, 4 H)	Aromatic protons of 3-pentadecyl phenol
	7.2 (m, 8 H)	Aromatic protons of bisphenol
III	0.9 (t, 3 H)	CH_3
	1.2 (m, 26 H)	$(CH_2)_{13}$
	1.6 (s, 6 H)	Two (CH_3) of bisphenol
	2.1(m, 2 H)	Benzyl protons
	7.0 (m, 4 H)	Aromatic protons
	7.6 (m, 4 H)	Aromatic protons of bisphenol

Polymer	Description of peaks, multiplicity[b], number of protons[c] and peak assignment	
IV	0.9 (t, 3 H)	CH_3
	1.2 (m, 26 H)	$(CH_2)_{13}$
	2.1 (m, 2 H)	Benzyl protons
	7.0 (m, 4 H)	Aromatic protons of 3-pentadecyl phenol
	7.4 (m, 12 H)	Aromatic protons of phenol phthalein
V	0.9 (t, 3 H)	CH_3
	1.3 (m, 12 H)	$(CH_2)_6$
	1.9 - 2.0 (m,4 H)	 $-\underset{\displaystyle Br}{\underset{\vert}{CH}}-\underline{CH_2}-CH_2-$
	2.1 (m, 2 H)	Benzyl protons
	2.7 - 2.9 (m,2 H)	 $-\underset{\displaystyle Br}{\underset{\vert}{CH}}-\underline{CH_2}-\underset{\displaystyle Br}{\underset{\vert}{CH}}-$
	4.2 (m, 4 H)	Four CH protons of the bromomethyl group of side chain
	7.10 (s, 1 H)	Aromatic proton of brominated cardanol
	7.3 (m, 4 H)	Aromatic protons of hydroquinone
VI	0.9 (t, 3 H)	CH_3
	1.3 (m, 12 H)	$(CH_2)_6$ of side chain
	1.7 (s, 6 H)	Two CH_3 of bisphenol
	1.9-2.0 (m, 4 H)	 $-\underset{\displaystyle Br}{\underset{\vert}{CH}}-\underline{CH_2}-CH_2-$

Polymer	Description of peaks, multiplicity[b], number of protons[c] and peak assignment	
	2.1 (m, 2 H)	Benzyl protons
	2.7-2.9 (m, 2 H)	 $-\underset{Br}{CH}-\underline{CH_2}-\underset{Br}{CH}$
	4.2 (m, 4 H)	Four CH protons of bromomethyl group of side chain
	7.1 (s, 1 H)	Aromatic protons of brominated cardanol
	7.2 (m, 8 H)	Aromatic protons of bisphenol
VII	0.9 (t, 3 H)	CH_3
	1.2 (m, 12 H)	$(CH_2)_6$ of side chain
	1.6 (s, 6 H)	Two CH_3 of bisphenol
	1.9-2.0 (m, 4 H)	 $-\underset{Br}{CH}-\underline{CH_2}-CH_2-$
	2.1 (m, 2 H)	Benzyl protons
	2.7-2.9 (m, 2 H)	 $-\underset{Br}{CH}-\underline{CH_2}-\underset{Br}{CH}$
	4.2 (m, 4 H)	Four C-H protons of bromomethyl group of side chain
	7.1 (s, 1 H)	Aromatic protons of brominated cardanol
	7.6 (m, 4 H)	Aromatic protons of bisphenol

Polymer	Description of peaks, multiplicity[b], number of protons[c] and peak assignment	
VIII	0.9 (t, 3 H)	$-CH_3$
	1.3 (m, 12 H)	$(CH_2)_6$ of side chain
	1.9-2.0 (m, 4 H)	 $-\underset{\mathrm{Br}}{\underset{\vert}{\mathrm{CH}}}-\underline{\mathrm{CH_2}}-\mathrm{CH_2}-$
	2.1 (m, 2 H)	Benzyl protons
	2.7-2.9 (m, 2 H)	 $-\underset{\mathrm{Br}}{\underset{\vert}{\mathrm{CH}}}-\underline{\mathrm{CH_2}}-\underset{\mathrm{Br}}{\underset{\vert}{\mathrm{CH}}}-$
	4.2 (m, 4 H)	Four CH protons of bromomethyl group of side chain
	7.10 (s, 1 H)	Aromatic proton of brominated cardanol
	7.4 (m, 12 H)	Aromatic protons of phenol phthalein

a. Chemical shift (δ ppm, relative to TMS)

b. s = singlet.
t = triplet
m = multiplet

c. Determined by relative areas under the peak

Table 5.4: ^{31}P NMR spectral data[a] for the polyphosphates

Polymer	Peak due to repeating unit	Peak due to the chain end
I	-18.6	-5.83
II	-18.4	-5.41
III	-19.80	-5.70
IV	-18.99	-5.61
V	-17.94	-5.19
VI	-18.98	-5.46
VII	-23.24	-5.88
VIII	-19.59	-5.55

[a] chemical shift (δ ppm, relative to H_3PO_4)

Table 5.5: Thermal stabilities of the polyphosphates in nitrogen

Polymer	Thermal stabilities in N_2			
	T_i	$T_{1/2}$	T_{max}	% char yield
I	265	450	300 450	26
II	270	435	315 470	20.3
III	275	430	320 450	20
IV	260	455	320 470	26
V	220	310	270 480	27
VI	230	300	250 575	21
VII	210	320	270 470	20
VIII	210	350	240 480	29

Table 5.6: Thermal degradation kinetics and LOI values of the polyphosphates

Polymer	% P content	% Br content	LOI	Thermal degradation kinetics			
				Ist stage		2nd stage	
				E	n	E	n
I	6.8	0	24	24.1	0.7	30	0.80
II	5.4	0	22	23.2	0.6	28	0.75
III	3.5	35.9	27	25.1	0.6	29	0.75
IV	4.7	0	24	32.9	0.7	35	0.90
V	3	55.4	49	24.9	0.8	32	0.80
VI	2.7	49.6	48	24.7	0.6	31	0.85
VII	2.1	60.7	62	22.5	0.5	32	0.75
VIII	2.5	45.9	50	28.3	0.9	34	0.90

Table 5.7: Thermal stabilities of the polyphosphates in air

Polymer	Thermal stabilities in air		
	T_i	$T_{1/2}$	C_y
I	210	350	23
II	220	340	21
III	250	330	19
IV	250	395	27.5
V	210	350	18
VI	210	340	17.5
VII	230	325	17
VIII	240	395	23

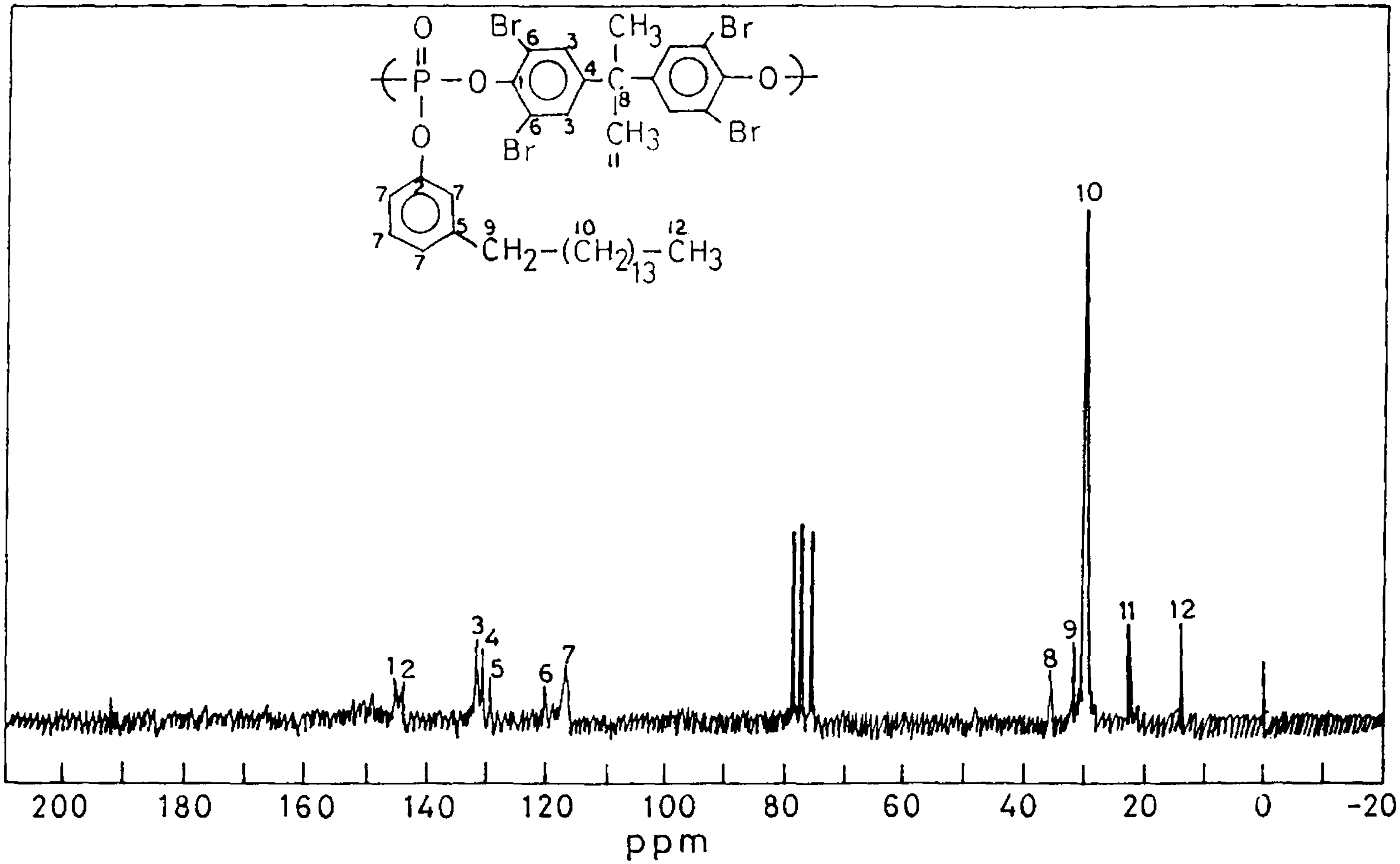


Fig 5.1 ^{13}C-NMR spectrum of polymer III

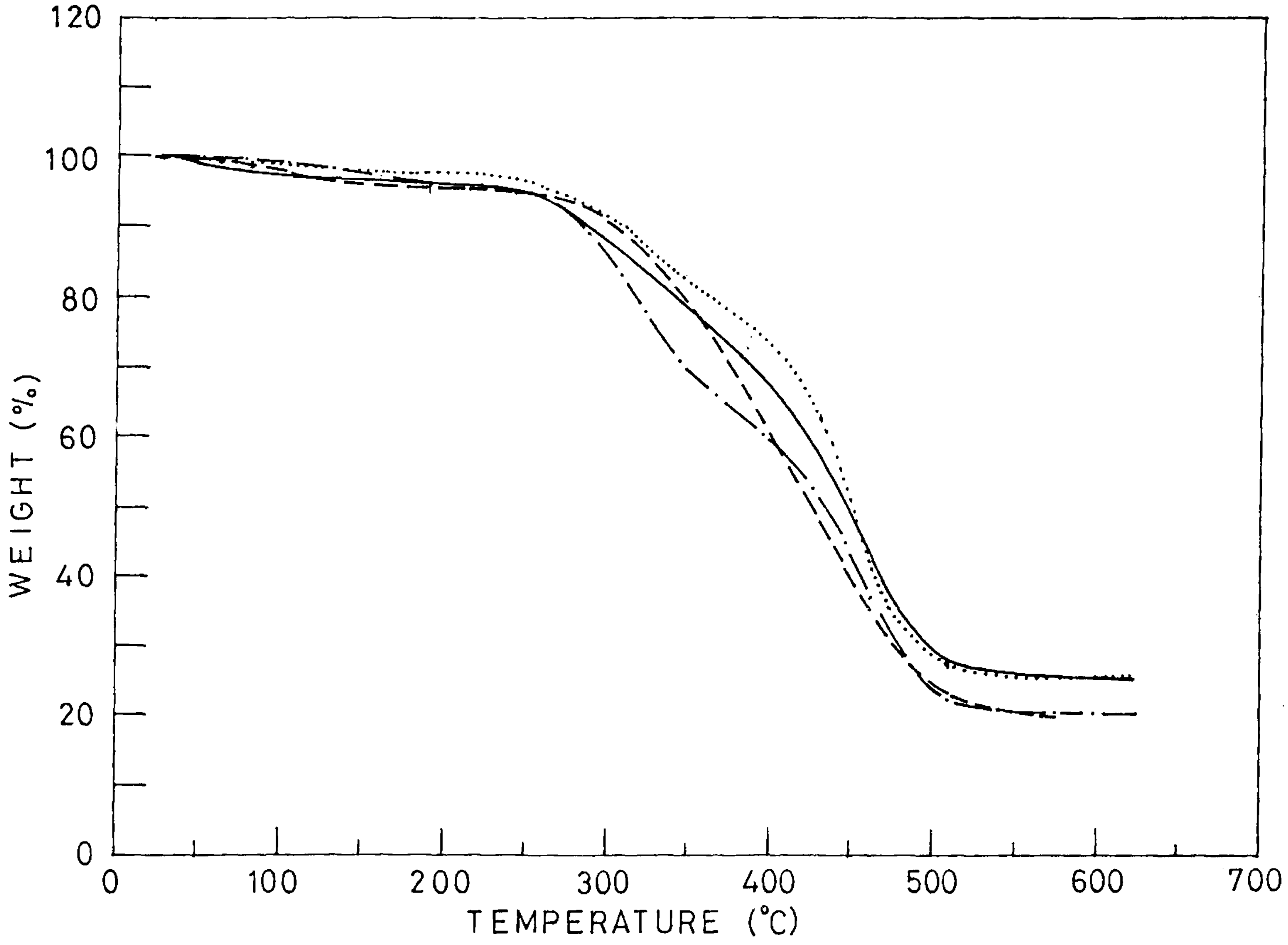


Fig. 5.2. Thermogravimetric traces of polymers I-IV
—— I. —·— II. ---- III. ······ IV

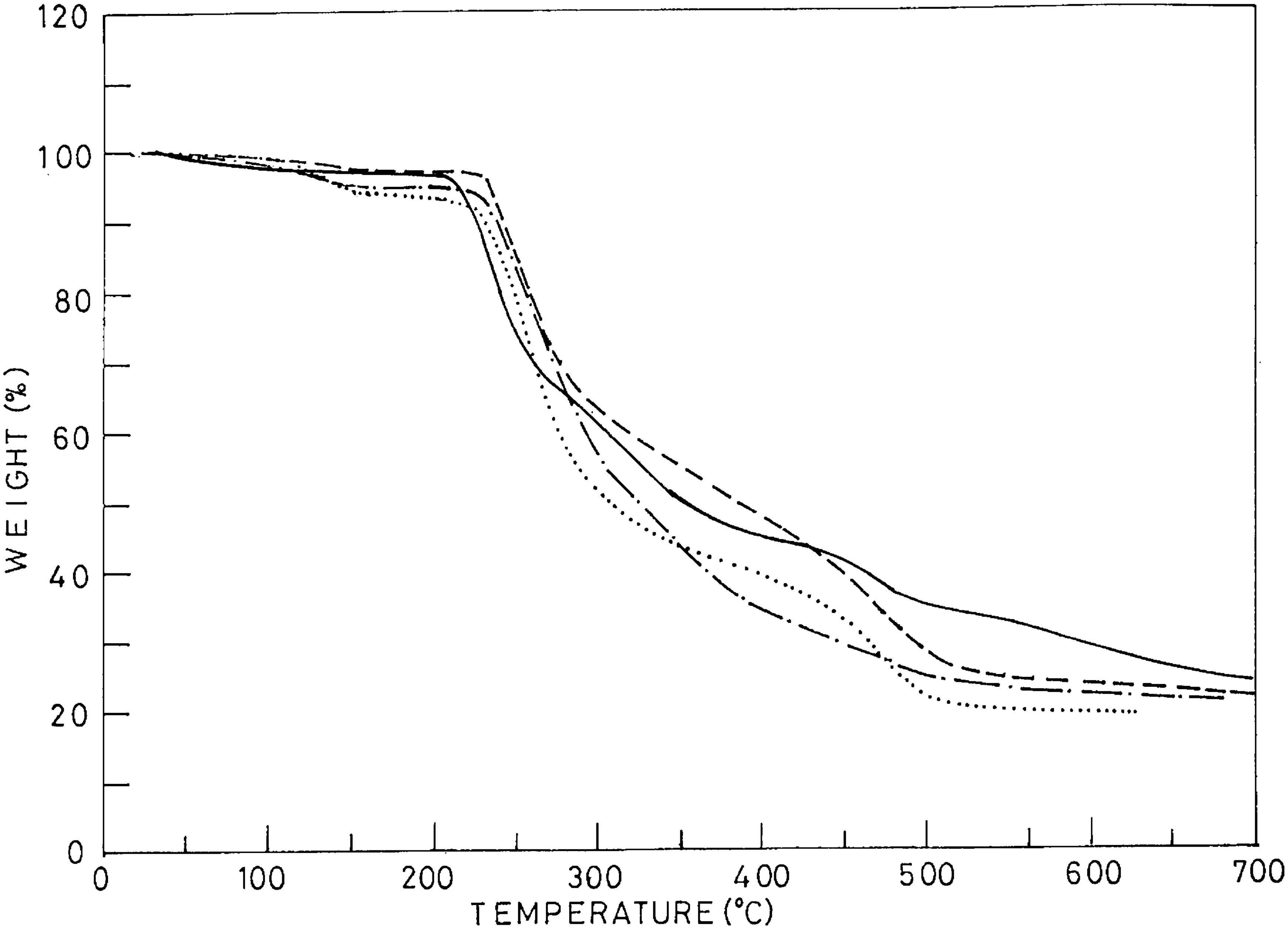


Fig. 5.3 Thermogravimetric traces of polymers V - VIII

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CHAPTER 6

SYNTHESIS, CHARACTERIZATION AND THERMAL STUDIES OF BORON CONTAINING PHENOLIC AND CARDANOLIC POLYMERS

6.1 INTRODUCTION

Although filler (inorganic) loaded phenolics are already considered temperature resistant, their thermooxidative resistance can be further improved by chemical modification [1-4]. The following methods as discussed in chapter 4 (4.1) are suitable to improve the thermooxidative resistance of phenolic resins.

a. Etherification or esterification of the phenolic hydroxyl group

b. Complex formation with polyvalent elements (Ca, Mg, Zn, Cd etc.)

c. Replacement of the methylene linking group by heteroatoms (O, S, N, Si etc.)

The esterification of phenol novolak resins with inorganic polybasic acids such as phosphoric and boric acid are of particular importance in increasing the heat and flame resistance of phenolic resins [1].

Polymers with good thermal stability and fire resistance have been produced by treating phenolic novolaks with boric acid [2]. It is claimed that the boron atom is chemically bound in a cyclic structure with two of its bonds joined to a phenoxy radical. The increased thermal resistance of phenolic resins modified with boron is attributed to structures [5] (Fig. 6.1).

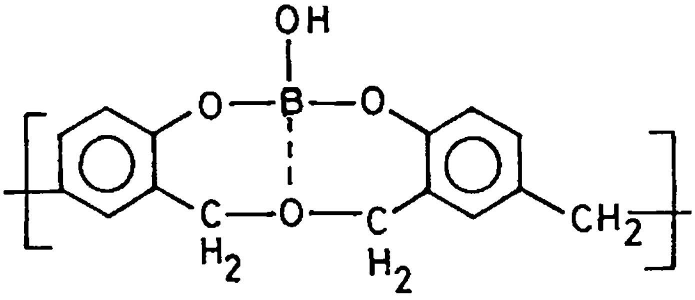


Fig. 6.1

Boron compounds when added as additives also improve the flame retardancy of phenolic compounds. Nonflammable phenolic molding compounds have been prepared by adding boric acid and sodium borate. A number of patents have been issued which describe the formation of noncombustible phenolic resins when modified with boric acid, boric oxide or borate salts [6-9]. Resins modified in this manner have been reported to fail to ignite in a flame and to produce exccellent flame resistance when used as an impregnating material for paper. Resols have been copolymerised in the presence of boric acid in a ratio $\leq$ 1 mole per 3 moles of phenolic for flame retardancy improvement [10]. A mixture of boric acid, phosphoric acid, and a polyphenol was reacted to give a thermoplastic resin that was thermoset afterward with formaldehyde to give a nonflammable composition [11].

Most of the technology concerning the flame retardation of phenolic resins involves either the incorporation of substances known to exhibit flame retarding properties into the backbone structure of the organic polymers or the addition of various compounds or combinations of compounds into the resin system to impart flame resistant characteristics [3]. The reaction of polyfunctional compounds with PF resins is often found to lead to gelation [12] and consequently only low amounts of the active element could be incorporated. The reaction was found to be dependent on the nature of the PF resin [12-14]. These problems of gelation and structural differences could be overcome if chemical modification is effected at the monomer level and then polymerised to get the required product. Incorporation of hydrocarbon side chain to the phenolic ring is expected to improve, (1) the processability, and (2) compatibility with other polymers, although a reduction in flame resistance is expected [15]. Cardanol with its C_{15} hydrocarbon side chain [16] is thus a suitable monomer for boration for the preparation of wide spectrum flame retardants [15]. This chapter deals with the synthesis and characterization of triaryl borates of phenol and cardanol and their polymers. This study also includes investigations of their flammability and thermal behaviour.

6.2 EXPERIMENTAL

6.2.1 Materials

Cardanol was obtained by double vacuum distillation of CNSL at 3-4 mm Hg and the fraction distilled at 230-235 ^{o}C was collected. Phenol (NICE, India) was distilled under reduced pressure before use. Trimethyl borate and hexamethylenetetramine were purchased from Fluka, Switzerland and used as such without further purification. Benzene was dried over sodium wire and then distilled.

6.2.2 Measurements

The IR spectra were recorded on a Perkin-Elmer IR spectrophotometer model 882 as neat films on NaCl windows by the smear techniques. ^{1}H NMR spectra were recorded on Hitachi R-24B high-resolution NMR spectrometer in CCl_4 using TMS as internal reference. ^{11}B NMR spectra were recorded on a JEOL FX-90Q FT spectrometer. The GPC data were obtained using Hewlet Packard 1081 B HPLC, equipped with an automatic sample injection system and a differential RI detector. The thermogravimetric studies were carried out on a Du Pont thermogravimetric analyser model 951 in nitrogen atmosphere at a heating rate of 20 ^{o}C min^{-1} with a sample weight of 5-10 mg. The limiting oxygen index data were determined by using a Stanton Red Croft LOI equipment of Model FTA-7101. Boron estimation was done spectrophotometrically using quinalizarin as the chromotropic reagent.

6.2.3 Synthesis

The triaryl borates were synthesised by transesterification reaction with trimethyl borate. A typical procedure for the preparation of tricardanyl borate (TCB) is as follows. Cardanol (0.03 mol, 9 g) and dry benzene (100 ml) were taken in a 250 ml R.B. flask fitted with a reflux condenser. The solution was stirred magnetically and the temperature was maintained at 60^{o}C. To this, trimethyl borate (0.01 mol, 1.04 g) was added and the reaction was continued for 3 hs. The solvents were stripped off and the product was dried in vacuum at 60^{o}C. Triphenyl borate (TPB) also was synthesised by the same procedure.

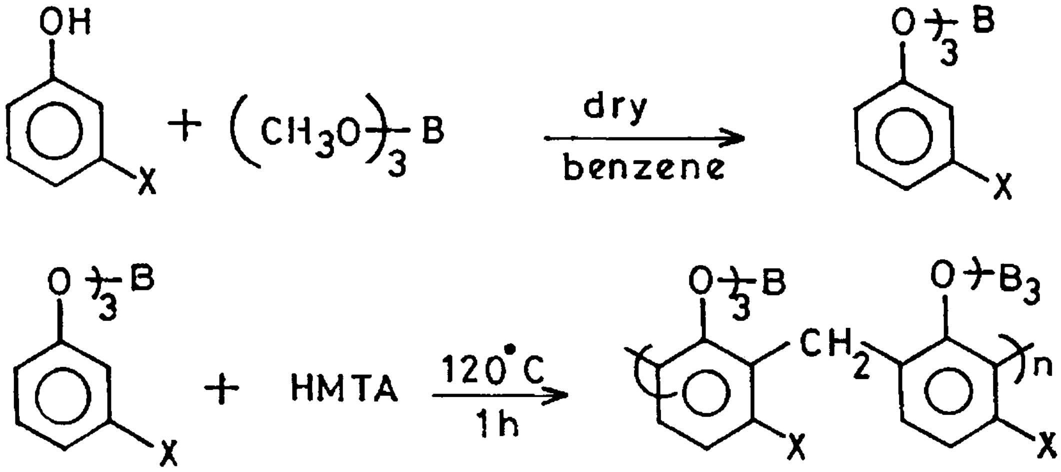
The triaryl borate obtained was polymerised with hexamethylenetetramine (HMTA). A typical polymerisation procedure is as follows. Tricardanyl borate (0.01 mol, 9.08 g) and HMTA (10 weight % to that of TCB, 0.91 g) were taken in a 100 ml R.B. flask and heated at 120^{o}C for 1 h to get tricardanyl borate-formaldehyde. TPBF was prepared by the similar procedure.

6.3 RESULTS AND DISCUSSION

The triaryl borates of cardanol and phenol as well as their formaldehyde condensates were prepared as illustrated in Scheme 6.1.

Tricardanyl and triphenyl borates (TCB and TPB) were synthesised by transesterification reaction with trimethyl borate in dry benzene. The yellow coloured liquids obtained are hygroscopic in nature. The yields were about 90%. The IR spectral data of TCB and TPB are given in Table 6.1. Their

IR spectra exhibited the characteristic B-O-C stretching vibrations at 1360 cm^{-1}. The characteristic bands of aliphatic side chain of cardanol were observed at 1620 and 2946 cm^{-1} (C=C and C-H for TCB). The absence of C-OH protons at δ 5.0 support the formation of the ester. The values of 1.2% for the TCB and 3.8% for TPB for boron contents are in agreement with the theoretical values of 1.21 and 3.8% respectively for the triesters. The ^{1}H NMR chemical shift values of TCB and TPB are given in Table 6.2.



Where X = H or $C_{15}H_{27}$

Scheme 6.1

The ^{11}B NMR spectra of TCB and TPB indicated singlets at δ -18.17 and at δ -0.17 respectively for the boron present in the compounds.

TCB and TPB were polymerised with hexamethylenetetramine to get soluble and fusible resins which were further crosslinked with additional amounts of HMTA at a temperature of 130-

$140^{\circ}C$ to get cured products. The linear resins were characterized by gel permeation chromatography to get the molecular weight averages. The number average molecular weight ($\overline{M}n$) values of TCBF and TPBF are 2450 and 1500 respectively and are given in Table 6.3. The dynamic TGA curves of the cured products are given in Figure 6.2.

The thermal stabilities and thermal degradation kinetics are presented in Table 6.4. The present study compares the thermal behaviour of TCBF and TPBF with those of CF and PF resins. The parameters studied are the temperature corresponding to initial decomposition (T_i) 25% weight loss ($T_{1/4}$) and the char yield at $600^{\circ}C$ (C_y). Comparison of these values in Table 6.4 shows that the boron containing polymers are having higher thermal stability over that of the nonmodified ones at high temperature (say above $400^{\circ}C$). It can be seen that boration brings down the T_i values from 390 to 250 for TPBF and from 360 to 170 for TCBF. On the other hand the $T_{1/4}$ and C_y values have increased considerably. The $T_{1/4}$ values have increased from 515 to 540 for TPBF and from 410 to 420 for TCBF. Similarly, C_y values have increased from 62 to 71 for TPBF and from 11 to 18 for TCBF. The LOI values of the polymers given in Table 6.4 shows that upon boration flame retardancy has increased from 19 to 25 and 35 to 38 for TCBF and TPBF respectively. The major effect of boron compounds in improving the flame resistance of phenolic resins might most probably their action in the condensed phase [3]. It is generally thought that these boron compounds retard flammability through both a surface coating effect and as substances which smoother flame [3]. Formation of the large amount of char and high LOI of TPBF and TCBF are in support of a condensed phase mechanism. Surface coating might promote char formation and thereby reduce the amount and rate of diffusion of combustible volatiles to the ignition zone [3]. The borate esters would be expected to enhance the char-formation decomposition reactions as well as the retention of the boric oxi surface coating during high temperature exposure of the phenolic mass. The low values of char yield and $T_{1/4}$ (18% and 420°C) for TCBF in comparison to those of TPBF (71% and 540° C) can be understood from the presence of thermally labile aliphatic side chain in cardanol.

The thermal decomposition kinetic parameters (energy of activation E and order of thermal decomposition reaction n) (Table 6.4) were calculated by the modified Anderson and Freeman method [17]. The polymers showed activation energies in the range 30-40 kCal/mol. Fractional orders in the range of 0.75 to 0.95 were observed for the degradation reactions. It can be seen that the TPBF has a higher E value of 40 kCal/mol than that of TCBF (32 kCal/mol). This is in agreement with the observed thermal stabilities of the polymer.

Table 6.1: Infrared absorption frequencies of TCB and TPB (Wavenumber cm^{-1})

TCB	TPB	Assignment
685 (S)	660 (S)	Out-of-plane bending of C-H bonds of aromatic rings
725 (W)	720 (W)	
790 (S)	800 (S)	
1020 (W)	1010 (W)	In-plane bending of C-H bonds of aromatic rings
1070 (M)	1060 (M)	
1360 (S)	1360 (S)	B-O-C stretching
1460 (S)	1440 (S)	C=C ring stretching
1590 (S)	1590 (S)	
1620 (S)	-	C=C aliphatic stretching
2940 (S)	-	Aliphatic C-H stretching
3040 (M)	3040 (M)	Aromatic C-H stretching

Table 6.2: ^{1}H NMR spectral data for TCB and TPB

Sample	Description of peaks, multiplicity and peak assignment
TCB	δ 0.9 (T, Me)
	1.3 (M, CH_2)
	1.8-2.1 (M, allyl)
	2.2-2.5 (M, benzyl)
	2.6-2.8 (M, diallyl)
	5.2-5.4 (M, vinyl)
	6.5-7.0 (M, aryl) ppm
TPB	δ 6.7-7.0 (M, aryl) ppm

Table 6.3: GPC data of TCBF and TPBF

Sample	$\bar{M}$n	$\bar{M}$w	D
TCBF	2450	5070	2.07
TPBF	1500	3150	2.1

Table 6.4: Thermal stabilities and thermal degradation kinetics in N_2

Sample	T_i	$T_{1/4}$	C_y	LOI	E	n
TCBF	170	420	18	25	32	0.75
TPBF	250	540	71	38	40	0.9
CF	360	410	11	19	29	0.85
PF	390	515	62	35	36	0.80

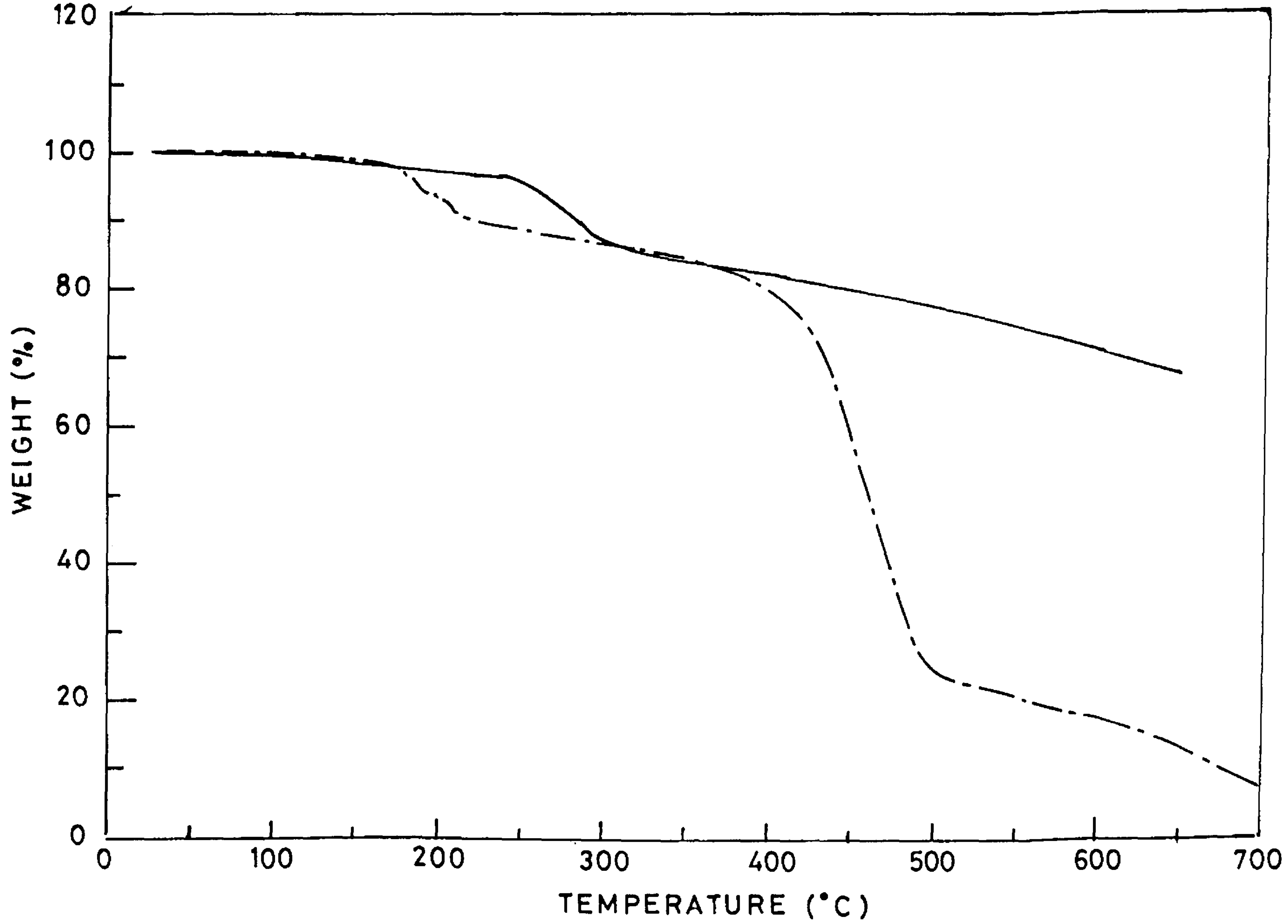


FIG. 6.2. Thermogravimetric traces of —— TPBF & —·— TCBF

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CHAPTER 7

EFFECT OF MCPA AND MPPA MONOMERS AND POLYMERS ON THE THERMAL AND FLAMMABILITY CHARACTERISTICS OF POLYETHYLENE

7.1 INTRODUCTION

Synthesis, characterization, thermal and flammability behaviour of phosphorus, bromine and boron containing FR monomers and polymers of cardanol and phenol have been described in the preceeding chapters. Previous reports indicate that FR polymers are more effective than their monomer counterparts [1-3]. This is because the polymer will not bloom, or migrate to the surface or leach out and so they are considered to be more advantageous [1-3] than the simple FR compounds. In the present work a series of FR monomers and polymers were synthesised and characterised, but their relative effectiveness can be evaluated only if they are added to a polymer to be made flame resistant. Polyethylene was selected for this study because, it was shown in an earlier experiment carried out at the Regional Research Laboratory, Trivandrum, that when phosphorylated CNSL prepolymer (PCNSL-containing only 8% P) was added to PE, its LOI showed an incredible increase from 18 to 24.5 [4]. Moreover, blends of PCNSL with PE were totally compatible [4]. This steep rise in LOI values is yet to be understood, but possible contribution from antioxidant activity of PCNSL to decelerate the thermooxidative decomposition of PE can be suspected.

The FRs prepared in the present work is also expected to behave in a similar way. To have a comparative study the corresponding phenolics were also blended with PE. Therefore this chapter deals with the evaluation of the flame retardant and thermal characteristics of the polymeric FRs vis-a-vis the monomeric FRs when used in a polymer such as PE.

7.2 EXPERIMENTAL

7.2.1 Materials

Polyethylene of grade Indothene 16 MA 400 was purchased from IPCL, India. PF resin was prepared as reported in chapter 4 (4.2.3). MCPA, MPPA, MCPAF and MPPAF were prepared as given in chapters 3 and 4 and were used for the blending studies.

7.2.2 Measurements

The thermogravimetric studies were carried out on a Dupont thermogravimetric analyser model 951 in nitrogen atmosphere at a heating rate of $20^{\circ}C\ min^{-1}$ with a sample weight of 5-10 mg. The LOI data were determined by using a Stanton Redcroft LOI equipment of model FTA-7101. Scanning electron microscopic studies were done using a JEOL 35 C Microscope. Blending studies were carried out using Brabender Plasti-Corder Model PLE 651.

7.2.3 Blending studies

A typical blending procedure is given below. The temperature was adjusted at $120^{\circ}C$ and rotor speed was kept at 25 rpm. 40 g of PE and 10 g of MCPA were mixed in the measuring mixer, through the loading chute in minimum time. The torque developed was noted and the torque vs time graph was plotted. The mixing was continued for 20 min. The polymer was taken out from the mixer and used for further studies.

7.3 RESULTS AND DISCUSSION

MCPA, MCPAF, MPPA and MPPAF were blended with PE and their effect on thermal and flammability characteristics of PE were investigated. Fig. 7.1 shows the torque vs time plots obtained for PE and PE-MCPA blend. The final mixing torque observed is 4 Nm which is quite low when compared to 7.5 Nm for PE indicatinng that the system exhibits better processability and compatibility. The SEM pictures given in Fig. 7.2 show that MCPA is more compatible and miscible with PE than the phenolics. The formation of an intimate blend with MCPA could be understood from the presence of C_{15} aliphatic side chain.

The thermal stability of the polymers (Ti-initial decomposition temperature, $T_{1/4}$ temperature corresponding to 25% weight loss and C_y - the char yield at $500^{\circ}C$) are given in Table 7.1. It can be seen that Ti, $T_{1/4}$ and C_y values have increased considerably for the blends than those for PE. Thus Ti values have increased from 385 of PE to 400, 410 and $420^{\circ}C$ for PE-MCPA, PE-MCPA linear blend and PE-MCPA cured blend. The Ti values are still higher for PE-MPPA and their polymers. The Ti values are 440^{0} C, 455^{0} C and 465^{0} C for PE-MPPA, PE-MPPAF (linear blend) and PE-MPPAF cured blend. But $T_{1/4}$ values and char yields are higher for MCPA systems. $T_{1/4}$ values have increased from 405^{0}C for PE to 480^{0}C for PE-MCPA blend. The $T_{1/4}$ values for the PE-MCPAF linear blend is 490^{0} C whereas that for PE-MCPAF cured blend is 495^{0}C. The $T_{1/4}$ values for phenolic systems are 470, 485 and 490^{0}C for the monomer, linear resin and the cured system respectively. Moreover the char yields also follow the same trend. The C_y for PE is 1.4% which has increased from 40 through 56 to 62 while going from MPPA monomer, MPPAF linear resin and MPPAF cured and for the cardanolics, the char yields have increased from 42 for MCPA to 59 for MCPAF linear blend and 65 for MCPAF cured blend. Thus, it can be seen that cardanolics improve the thermal stability of PE than phenolics.

The LOI values are also higher for the MCPA blends than MPPA blends. The values are 22.5, 22.5 and 23.0 for phenolics whereas they are 23.5, 24 and 24.5 for the cardanolics.

From these studies it can also be seen that the polymeric flame retardants are better than monomeric flame retardants in PE.

Table 7.1: Thermal stabilities and LOI values of PE blends

S.No.	Sample	Ti	$T_{1/4}$	C_y at 500^oC	LOI
1.	PE	385	405	1.4	18
2.	PE + MPPA	440	470	40	22.5
3.	PE + MPPAF (linear)	455	485	56	22.5
4.	PE + MPPAF (cured)	465	490	62	23.0
5.	PE + MCPA	400	480	42	23.5
6.	PE + MCPAF (linear)	410	490	59	24
7.	PE + MCPAF (cured)	420	495	65	24.5

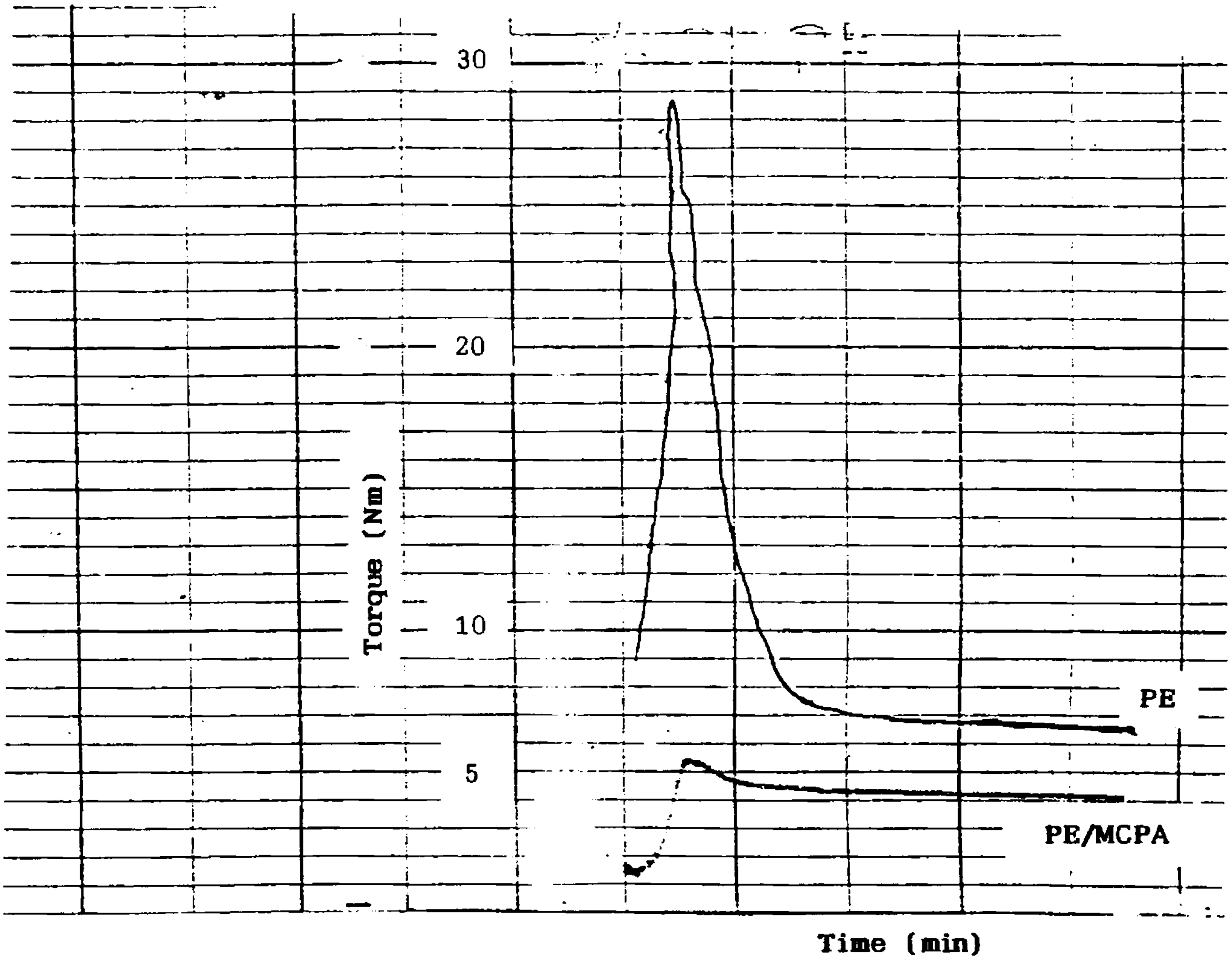
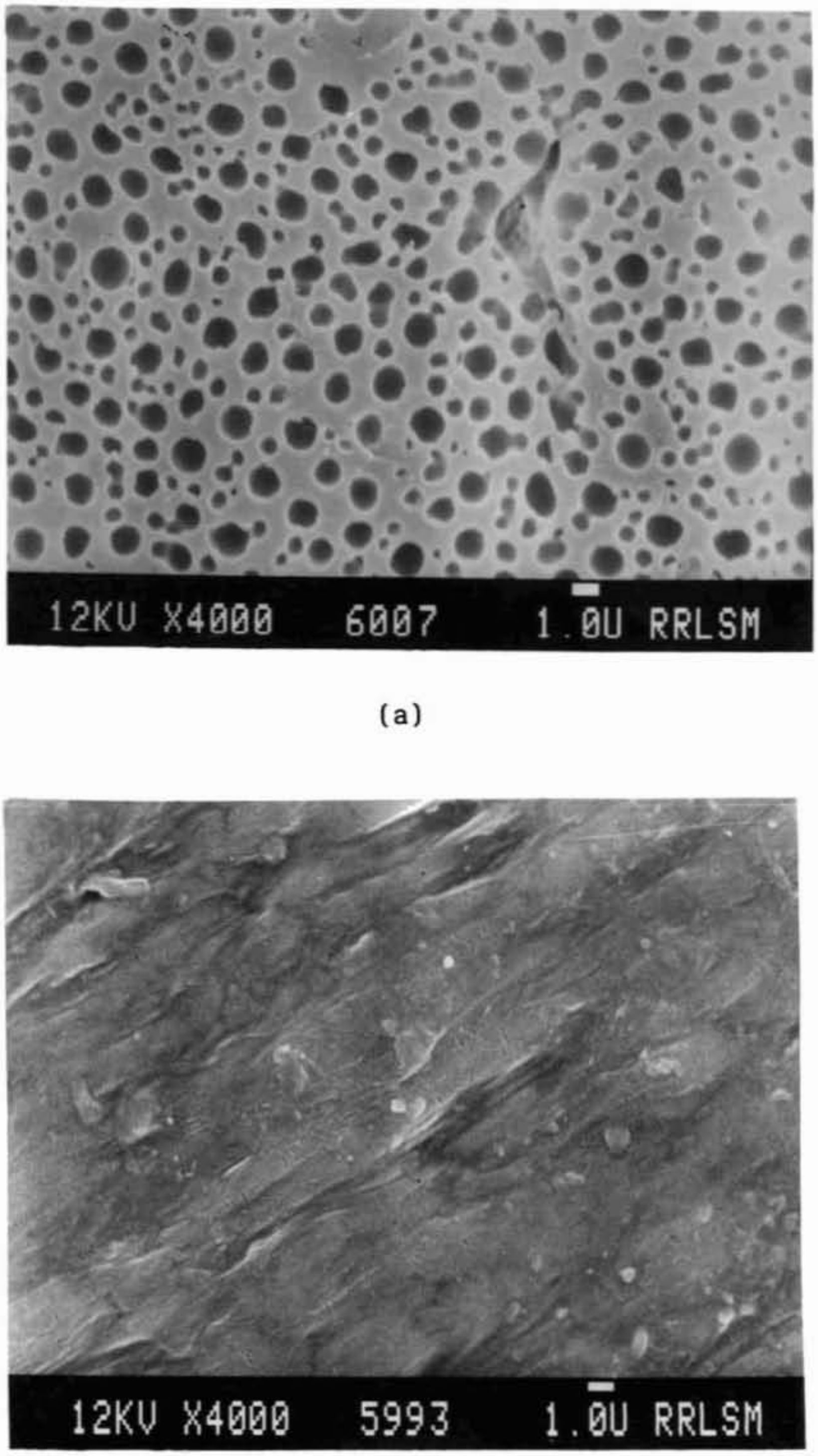


Fig. 7.1: Torque vs time plots for PE and PE/MCPA blend



(a)

(b)

Fig. 7.2: SEM pictures of (a) ~~PE,~~ PE/MPPA (b) PE/MCPA blend

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SUMMARY AND OUTLOOK

Flame retardation of polymeric materials involves use of flame retardant (FR) compounds as an additive or as a reactive component. The efficiency of the FR compound is thought to be enhanced when the FR elements are built into the structure of the polymer. It is also reported that polymeric FRs function better than their monomeric counterparts. Owing to problems such as insufficient compatibility and miscibility, the use of FRs are restricted mostly to one FR for one polymer with a specific application. This could be solved by developing wide spectrum FRs with FR elements built into the monomeric structure having both hydrophobic and hydrophilic moieties in the same molecule and polymerising the modified monomer to a prepolymer (because at the polymer level, a higher loading of the FR will be needed. Moreover, it will be easier to process the prepolymer than the polymer and at the same time the drawbacks of common FR compounds such as blooming, migration, reduction in mechanical properties etc. will be overcome). The present work, therefore, concerns mainly with the synthesis and characterization with particular emphasis on thermal and flammability behaviour of FR monomers, prepolymers and polymers of two related monomers, phenol and cardanol both of which can easily be chemically modified with the latter having special structural features for transformation into wide spectrum FRs. The effect of three FR elements phosphour[illegible]and boron (because they are reported to enhance the thermo-oxidative resistance of phenolics) and bromine (because a thermoset cardanolic polymer containing phosphorus and bromine was shown earlier at the Regional Research Laboratory, Thiruvananthapuram, to exhibit ablation behaviour) were studied and the effectiveness of FR monomer vs prepolymer and wide spectrum FR was evaluated with respect to a polymer such as polyethylene.

Phosphorus was introduced in the first set of experiments by simple phosphorylation of the hydroxyl group of cardanol and phenol to get the mono-phosphates which were then condensed with formaldehyde or hexamine to prepare prepolymers and polymers. The bromo derivatives of the monomers and polymers were also prepared. The products were chatacterized by IR, ^{1}H NMR, ^{13}C NMR and GPC. Thermogravimetric and LOI studies indicated that incorporation of phosphorus enhanced thermal stability and flame retardancy of both cardanolic and phenolic (phosphorus was found to enhance the thermo-oxidative resistance of phenolics, in particular) polymer. On the other hand, bromine while raising their LOI values surprisingly affected the stability of phenolics adversely. In the case of cardanolics, thermal and flammability data point to a positive interaction (no synergism or additive effect was observed) between phosphorus and bromine in the condensed phase with phosphorus acting mostly in the condensed phase and bromine in the vapour phase. The lower thermal stability of cardanolics in comparison to phenolics was explained on the basis of the presence of the labile aliphatic side chain of cardanol.

In the second set of experiments, phosphorus was introduced through the preparation of phosphorodichloridates of 3-pentadecylphenol and brominated cardanol which were then interfacially condensed with dihydric phenols such as hydroquinone bisphenol, tetrabromobisphenol and phenol-phthalein to get the respective polyphosphates. The products were characterized by IR, ^{1}H NMR, ^{13}C NMR, ^{31}P NMR and GPC. TGA and LOI values of these polymers indicate that the thermal stability of the polymer derived from pentadecyl phenol are stabler than those derived from brominated cardanol. The highest stability was observed for the polymer containing the phenolphthalein moiety. The bromine containing polymers showed the highest LOI values. The thermal and flammability data suggest that flammability of these polymers is a function not only of phosphorus and bromine content, but also has direct relation to their thermal stability and structure.

Since boron is reported to effect behaviour similar to that of phosphorus, boron containing cardanolic and phenolic polymers were prepared and characterized. Thermal and LOI data indicated enhancement of thermal stability and reduction in flammability of both the systems on introduction of boron. The lower values of char yield for the boron containing cardanolic polymer in comparison to that of phenolic was explained on the basis of the presence of thermally labile aliphatic side chain in cardanol.

The thermal decomposition kinetic parameters (activation energy E and order of thermal decomposition reaction) were calculated and used to understand the mechanistic aspects of thermal decomposition of all the polymers.

The effect of polymeric/prepolymeric FR vs monomeric FR was studied by blending some of the above polymers with polyethylene and evaluating the thermal and flammability behaviour of the blend. The results positively indicated that polymeric/prepolymeric FRs are much superior to monomeric FRs. The polymeric/prepolymeric FRs in addition exhibited better processability and compatibility than their monomeric counterparts. Moreover, the cardanolic FR polymers were easier to process than that of the phenolic prepolymers indicating that cardanolics may function as wide spectrum flame retardants. However, this aspect has to be confirmed by blending with other polymers.

The present investigation shows that:

1. Introduction of phosphorus and boron enhances the thermo-oxidative resistance of phenolic polymer. The problem of gelation and lower phosphorus and boron contents in the polymer could be overcome by introducing these elements at the monomer stage. Thus phosphorus and boron modified polymers show prospects as thermally stable polymers.

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2. Introduction of phosphorus and bromine into cardanolic polymers have enhanced their thermal stability and reduced flammability considerably. In an earlier experiment at the Regional Research Laboratory, Thiruvananthapuram, it was shown that thermoset cardanolic polymer containing phosphorus and bromine exhibit the property of ablation. The present data on thermal and flammability of the model compounds studied here might contribute to further understanding on the ablation phenomenon.

3. Cardanolic FR prepolymers showed better compatibility and processability indicating their possible use as wide spectrum FRs. Use of wide spectrum FRs may solve problems associated with the conventional FRs and also will reduce cost considerably.

4. Comparative evaluation of polymeric/prepolymeric FR vs monomeric/simple FR compounds shows that polymeric/prepolymeric FRs of cardanol and phenol function better than their monomeric counterparts. So FR prepolymer of cardanol and phenol show prospects as good FRs.

5. Studies on cardanol based polyphosphates showed that flammability of these polymers is not only dependent on phosphorus and bromine contents, but also has direct relation to thermal stability and structure.

Further work in this line could lead to a quantitative correlation of parameters that control flammability of polymers.