THE EVALUATION OF AN ORGANOPHOSPHATE THERMOSETTING RESIN FOR USE IN A HIGH TEMPERATURE RESISTANT COMPOSITE

AND

A STUDY OF THE CHEMISTRY OF IONOMER CEMENTS.

BY

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Two different research projects are reported in this thesis. Both projects have been sponsored by The National Research and Development Corporation over a total period of four years.

This thesis is consequently presented in two parts:

Part 1 - The evaluation of an organophosphate thermosetting resin for use in a high temperature resistant composite.

Part 2 - A study of the chemistry of ionomer cements.

SYNOPSIS

Two different research projects were investigated for this thesis, which has consequently been presented in two parts.

PART 1

An attempt has been made to improve the high temperature performance of phenol-formaldehyde thermosets by modification of their structure with inorganic phosphate groups.

Transesterification of tri-phenyl phosphate with resorcinol has given a resorcinol phosphate resin, which cured with hexamethylenetetramine. A pilot scale batch of this resin has been made and used in high temperature stability studies.

Post-cured resorcinol phosphate resin-chrysotile asbestos (30:70) moulded bars retained 59.5% of their flexural strength after ageing at 523K for 1000 hr in air. Similar phenol-formaldehyde composite bars aged under identical conditions retained only 5.3% of their initial flexural strength. The utility of the resorcinol phosphate resin composite as a commercial product is limited, since the bars had a much lower initial flexural strength (30.85 MNm^{-2}) than the phenol-formaldehyde resin composite bars (108.5 MNm^{-2}).

Thermogravimetry and isothermal heating studies have indicated that the degradation of resorcinol phosphate resin was greatly accelerated by chrysotile asbestos, which may catalyse a bond re-organisation process that has been tentatively proposed as a mechanism for the fragmentation of the resin.

PART 2

Recently an ionomer dental cement (ASPA), prepared from aqueous poly(acrylic acid) and an ion-leachable aluminosilicate glass, has been developed. The system has been extended by studying other aqueous polymers. The factors influencing the gelation and the properties of the set cements have been examined. Poly(carboxylic acids)with hydrophobic, or no pendant substituents were found to be the most satisfactory polymers for preparing water stable cements.

To study the influence of the nature of the cation and polymer structure on the gelation and water stability of ionomer cements, a wide range of metal oxide-polyacid products have been studied. The formation of water stable cements depended markedly on the type of oxide and polyacid employed and appeared to involve factors such as the co-ordination geometry and radius of the cation and the nature of the cation-polyanion bonding in the matrix. A comparison between the water stabilities of ASPA cement and poly(acrylic acid)-CaO,Al_2O_3, or $Al(OH)_3$ cements has shown that the chemistry of ASPA cement is more complex than has been hitherto reported.

Stability constants have been determined for Ca^{2+} and Cd^{2+} with poly(acrylic acid) and ethylene-maleic acid copolymer by a potentiometric titration method developed by Gregor and modified by Mandel and Leyte. The stability constants obtained in 1.0M $NaNO_3$ at 298.2 ± 0.2K were:

for poly(acrylic acid), with Ca^{2+}, $\log b_{1\,PAA}^{Ca^{2+}} \sim -3.35$

with Cd^{2+}, $\log B_{av\,PAA}^{Cd^{2+}} = -2.30$

for ethylene-maleic acid copolymer,with Ca^{2+}, $\log b_{1\,EMA}^{Ca^{2+}} \sim -4.05$

with Cd^{2+}, $\log B_{av\,EMA}^{Cd^{2+}} = -1.95$

The $\log b_1$ values probably had little precise meaning, although to a first approximation,

$$\log b_{1\ \mathrm{PAA}}^{\mathrm{Ca}^{2+}} > \log b_{1\ \mathrm{EMA}}^{\mathrm{Ca}^{2+}}$$

The determined stability constants have been used with limited success in predicting the water stabilities of the corresponding metal oxide-polyacid cements.

PART 1

THE EVALUATION OF AN ORGANOPHOSPHATE THERMOSETTING RESIN FOR USE IN A HIGH TEMPERATURE RESISTANT COMPOSITE.

INDEX

1 INTRODUCTION

1.1. General Introduction.

Advances in technology are often limited by inadequacies in the properties of available materials. For example the development of modern high speed aircraft and missiles has demanded materials which combine high temperature resistance and a high strength to weight ratio. This demand has to some extent been met by extensive research in polymer science and technology and much has been discovered about the chemical structure of polymers in relation to high temperature resistance.

Some applications where high temperature resistant materials are required include the following:

Ablation shields on space craft, where polymers that burn to a highly insulating char residue have been developed.

Missile components, such as rocket motor housings, where materials of high strength to weight ratio are advantageous.

Diamond abrasive wheels, in which the wear of the wheel surface is induced by high temperature degradation of the resin binder by the heat generated during grinding processes.

Racing car and motorcycle brake lining binders, which are subjected to high temperatures developed from braking at high speed.

Flame retardant textiles and insulating foams, which do not release imflammible volatiles at high temperatures.

Heat resistant paints and coatings, for example transformer wire coatings, in which electrical energy losses may produce much heat.

High temperature resistant polymers are specialised products and their cost is usually high.

Rosato[1] has classified various polymer types into an approximate order of increasing high temperature resistance (diagram 1.1.1.). Polymers in zone 5 of Rosato's diagram have fairly good high temperature resistance and, with the exception of poly(tetrafluoroethylene), are low in price. Above zone 5 high temperature resistance increases, but the cost of the polymers increases markedly. The adoption of polymers from zones 6 and 7 for a particular application may therefore be restricted by their cost. Polymers in zone 8 are not, as yet, commercially important.

It is therefore evident that in the development of high temperature resistant polymers commercially viable products must combine, as far as it is possible, a high temperature resistance with relatively low cost.

The cost of a product containing a polymer also depends upon its production cost. For example, aromatic poly(imides) require higher processing temperatures and times than conventional thermosetting, or thermoplastic polymers and are consequently more expensive to fabricate. Ease of processing is a very important factor in deciding the commercial usefulness of a polymer. Thus, poly(p-phenylene) (I) has exceptionally good high temperature resistance but does not soften below about 1070 K[*][2] (under zero applied load) and is therefore of no commercial interest. Slight chemical modification of an intractable polymer may improve its processability, but almost invariably to the detriment of its thermal or thermo-oxidative stability; for example poly(2,6-dimethylphenylene oxide) (II) has a lower softening point (495 under zero applied load[3]) than poly(p-phenylene) but a much lower thermo-oxidative resistance.

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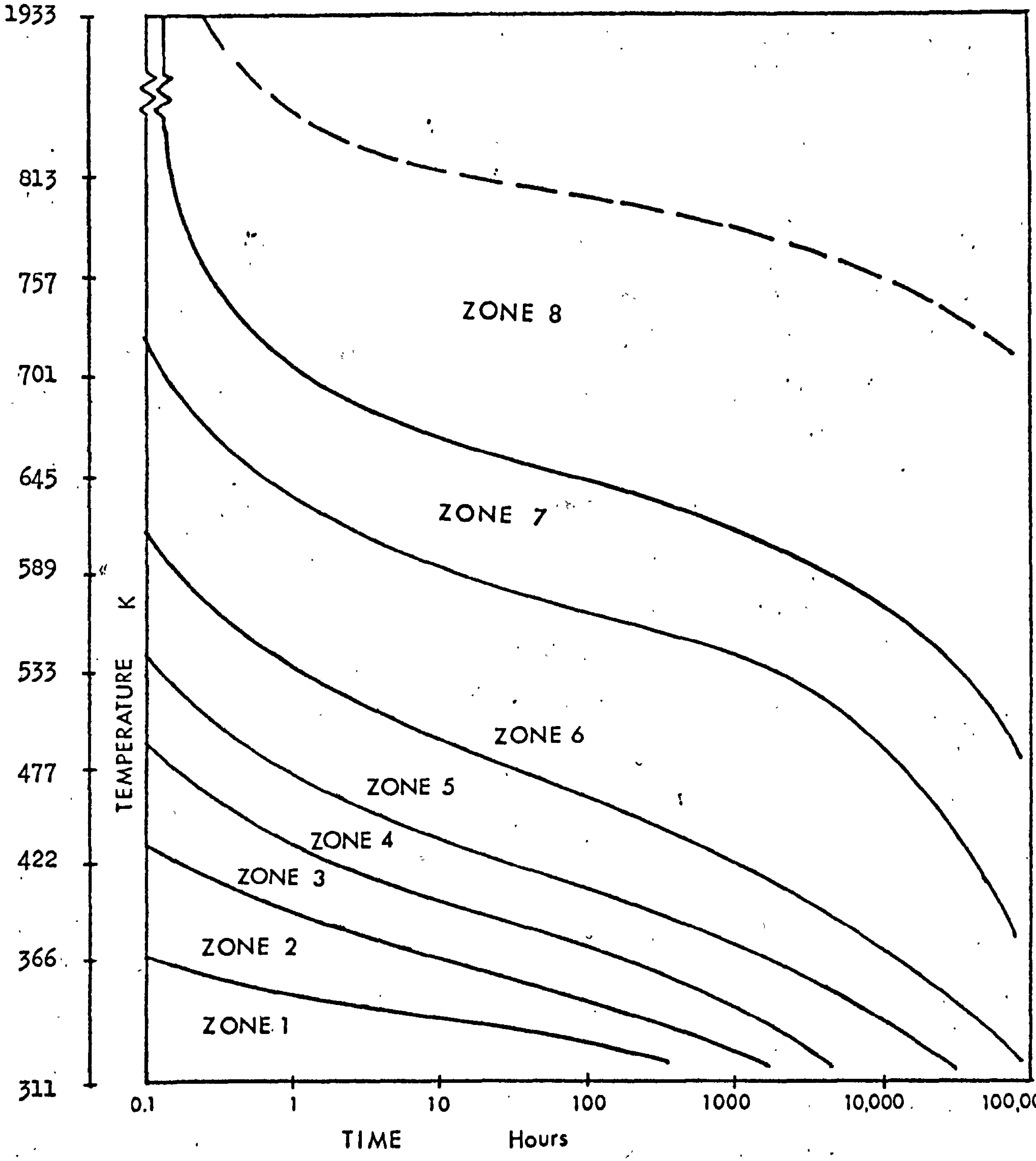
[*] *All temperatures in the text are in degrees Kelvin. The letter K will therefore be omitted from this point onwards.*

Diagram 1.1.1.

HOW PLASTICS PERFORM ON THE BASIS OF TEMPERATURE AND TIME.
Retaining 50 percent of mechanical or physical properties.
Tested at temperature in air.



ZONE	EXAMPLES
1	Acrylic , U.F.
2	Acetal , polyamide.
3	C.T.F.E.
4	Alkyd , P.P.O.
5	Epoxy, P.F., P.T.F.E.
6	Polybenzimidazole , silicone.
7	Polyimide .
8	Modern developments based on rigid

1.2. Factors contributing to the high temperature resistance of polymers.

Two basically different processes determine the high temperature resistance of polymers, both of which are dependent upon structural features of the macromolecular chains and the groups of atoms that exist in the polymer structure.

The first process is physical and reversible in nature and represents a 'softening' of the polymer with increase in temperature. Two fundamental physical property changes of this type are the glass transition temperature, Tg and the melting point, Tm of a polymer.

Tg is the temperature at which a polymer changes from a rigid glassy state to a flexible elastic state. This change is called a second order transition and the value of Tg depends upon the rate of heating or cooling of a polymer and upon the load applied to the polymer. When a polymer is cooled to its Tg the motion of the segments in the polymer macromolecules is 'frozen' and the polymer becomes rigid.

Tm is the temperature at which crystalline regions in a polymer disappear. No long chain polymer is wholly crystalline in structure so that sharp melting points are not possible. Tm represents the upper limit of a melting point range and is defined by the relationship.

$Tm = \frac{\Delta H}{\Delta S}$. It is a first order transition.

ΔH is the enthalpy of fusion, i.e. the heat absorbed to break down a crystalline structure.

ΔS is the entropy of fusion and is related to the molecular order, structure symmetry and chain flexibility.

In addition to Tg and Tm values various arbitrary softening points are also used to describe the behaviour of polymers on heating.

Two examples are the heat distortion temperature and the Vicat softening point, which are used as references for estimating the temperature limit of structural stability of polymers.

Korshak[4] has used the term 'heat'stability to describe the high temperature resistance of polymers in terms of the physical changes that take place with rising temperature. This term will be used in this thesis.

The second process, which effects high temperature resistance of polymers, is chemical in nature and involves the breaking of primary chemical bonds in the macromolecules. These chemical alterations of the macromolecules are permanent for organic polymers. During chemical breakdown volatile fragments may be released from a macromolecule, or alternatively a bond rearrangement may occur leading to, for example, cross-linking or cyclisation. Fragmentation leads to a lowering of the molecular weight of a polymer and a loss of mechanical strength, whilst cross-linking may increase the mechanical rigidity. A superimposition of these two processes may give the impression that a polymer is undergoing no chemical change on heating, although eventually one process will predominate and changes in mechanical properties will be observed.

Chemical breakdown at high temperature can occur by bond dissociation, or in air by oxidation. Korshak[5] has used the term 'thermal'stability to describe the resistance to thermal bond dissociation and 'thermo-oxidative' stability to describe resistance to oxidation at high temperatures. Both of these terms will be used in this thesis.

Thermal and thermo-oxidative stability are temperature and time dependant. This is well illustrated by the maximum service temperature of epoxide resins, which is 350-400 for 25000 hours' exposure, but is markedly increased to 410-520 for only 200 hours' exposure[6].

Thermal and thermo-oxidative stability are often defined in terms of the temperature and time at which a defined value in weight or mechanical strength property change is reached.

1.3. Some methods for measuring the high temperature resistance of polymers.

1.3.1. Heat stability.

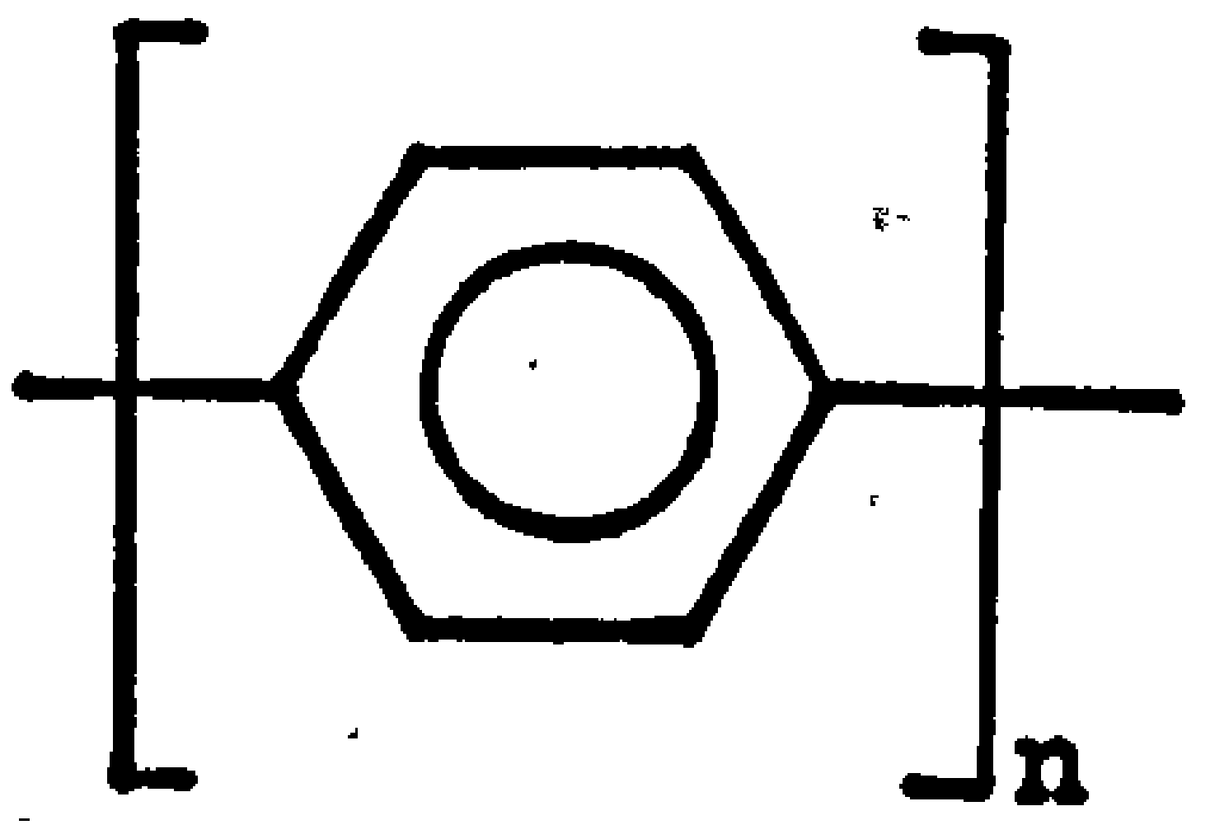
Tg and Tm can be determined from differential scanning calorimetry.

Tg, which is a second order transition and is therefore temperature and time dependent, is usually detected by the onset of an endothermic deviation representing a rate of increase of enthalpy with temperature. If the polymer is crystalline a well defined endothermic peak occurs at a temperature higher than Tg and represents the first order transition, Tm.

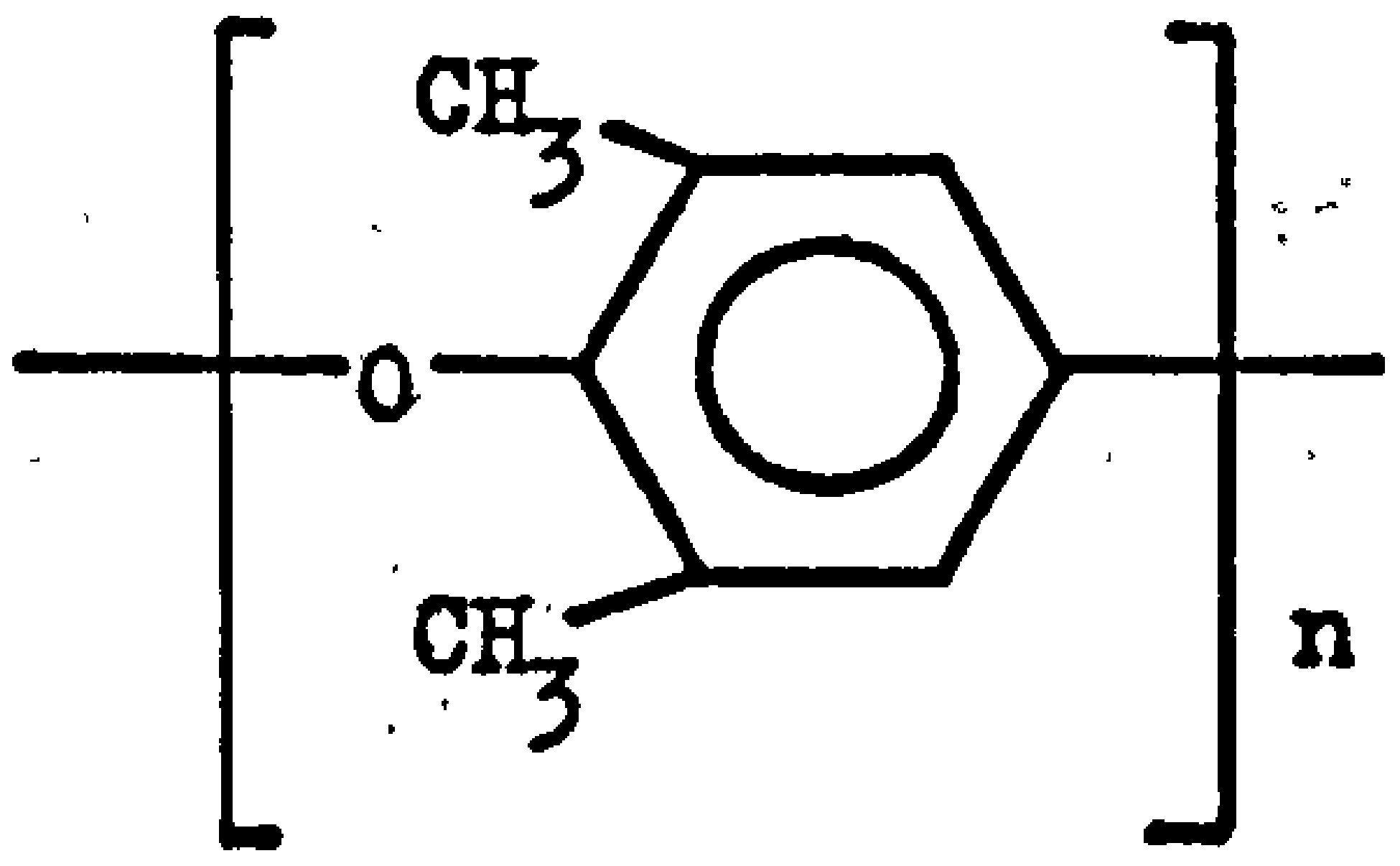
Arbitrary penetration and deflection methods are also widely used to determine the softening properties of polymers. Examples are the Vicat and the heat distortion temperatures,[7,8] where polymers are subjected to testing under constant load at a fixed rate of heating.

1.3.2. Thermal and thermo-oxidative stability.

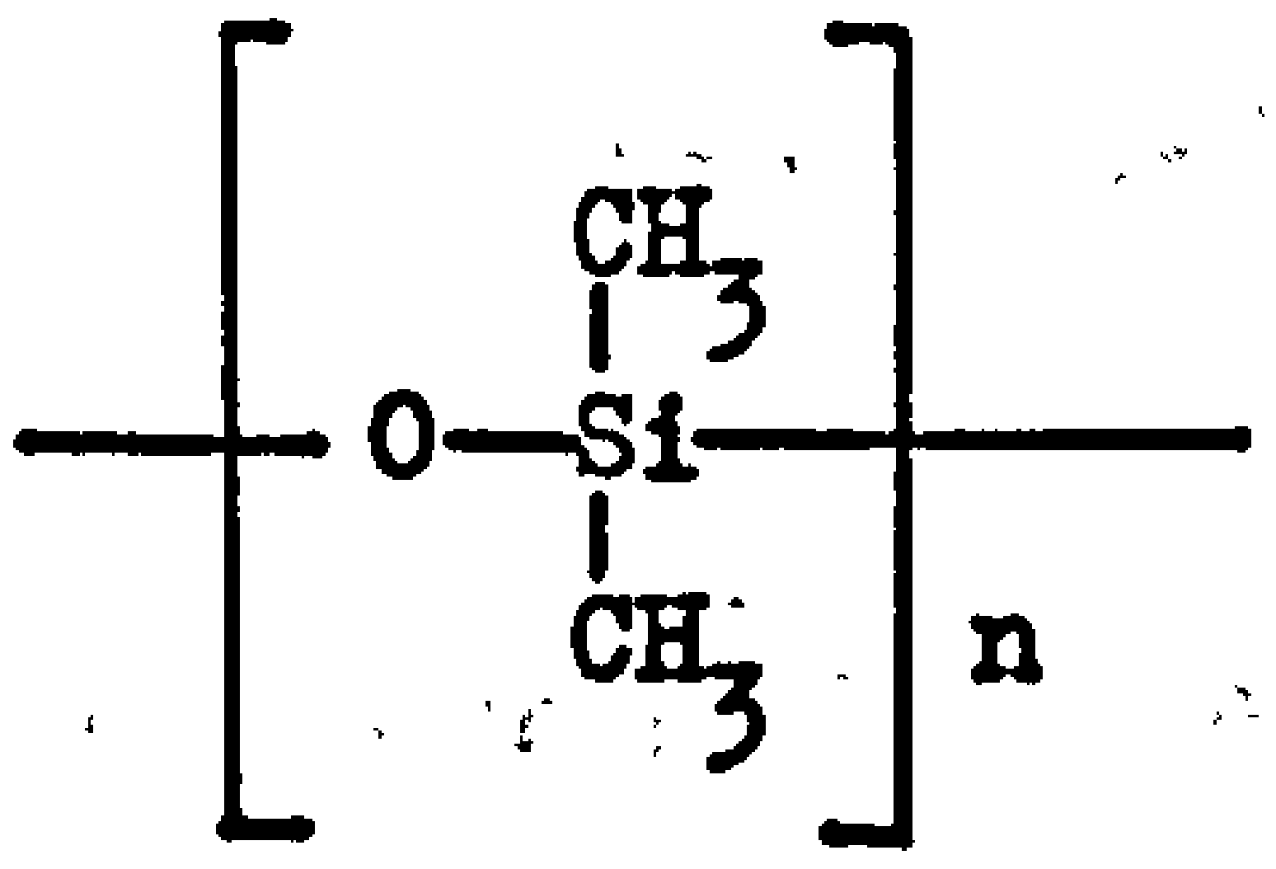
Thermogravimetry is widely used as a rapid method for comparing the thermal and thermo-oxidative stability of polymers. Samples are heated at a constant rate of temperature increase and weight losses monitored automatically as a function of temperature (diagram 1.3.2.1.). Arbitrary points on the thermogravimetric curves are used to define the stability of the polymer, such as To and Tx. To is the temperature at which rapid weight loss begins and Tx the temperature at which x% of the polymer weight has been lost. Since Tx occurs on a part of the curve where degradation has already started, its validity in comparing the thermal and thermo-oxidative stabilities of polymers must be viewed with caution. Some polymers contain a lower percentage of organic material than others, for example poly(dimethylsiloxane) (III) can be completely degraded with only a 20% loss in



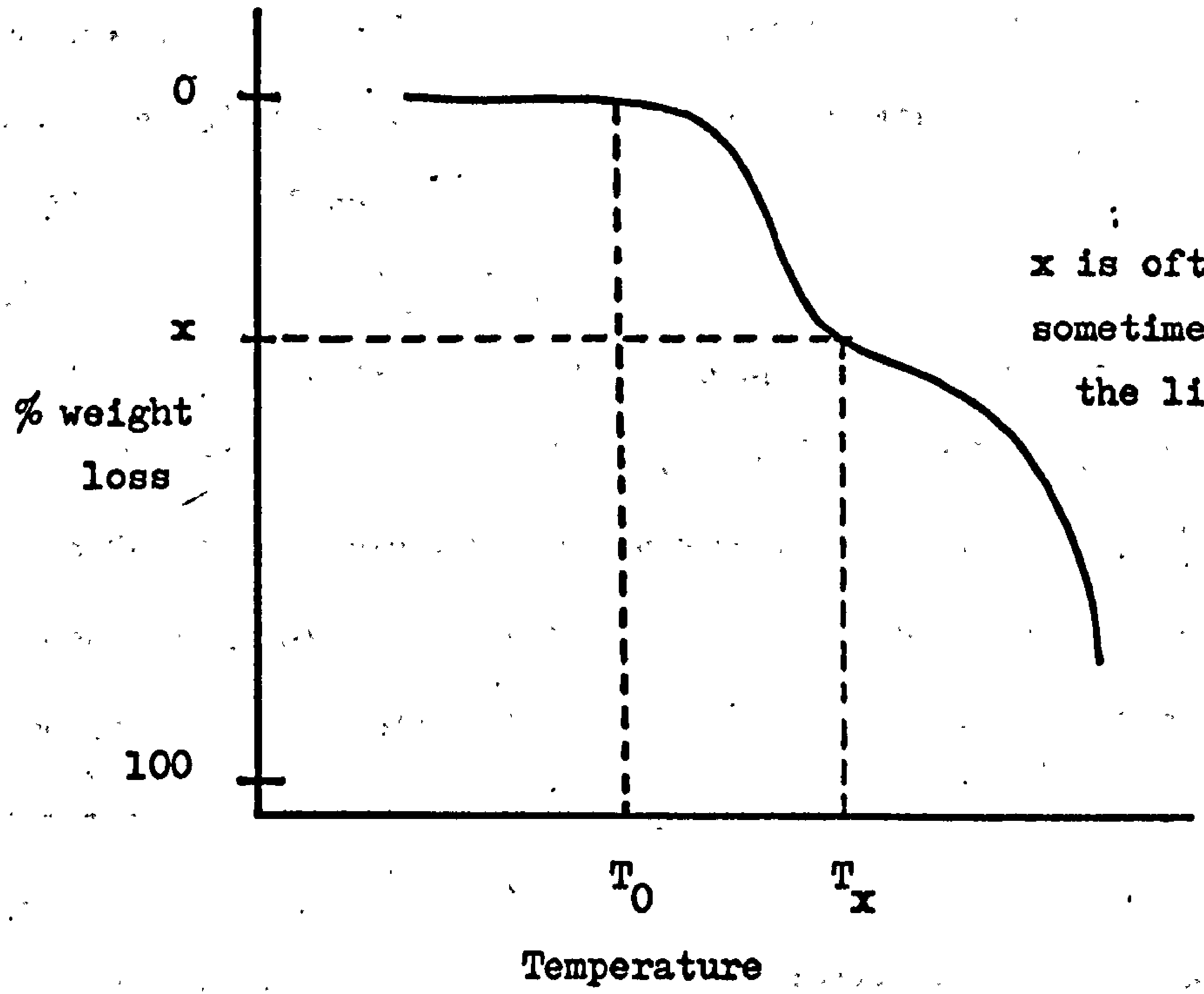
(I) Poly(p-phenylene).



(II) Poly(2,6-dimethyl phenylene oxide)



(III) Poly(dimethyl siloxane).



x is often 10% and sometimes 50% in the literature.

Diagram 1.3.2.1.

A Thermogravimetric Curve.

weight.

Isothermal weight loss determinations are also widely used and often give lower values for the degradation temperatures of polymers than the dynamic technique.

Thermal stability can be separated from thermo-oxidative stability by heating in inert atmospheres. In air, or oxygen, thermo-oxidative degradation very often precedes thermal degradation, which usually requires a substantially higher activation energy to occur.

Derivative thermogravimetry is useful in detecting thermo-oxidation, since the process is exothermic in nature.

Measurement of the change in mechanical properties, such as flexural strength and modulus, with ageing at high temperature is also used to describe the thermal and thermo-oxidative stability of polymers, especially thermosetting resins and "ladder" polymers, where chemical decomposition often takes place before the polymer significantly softens.

1.3.3. Applicational evaluations.

Although properties such as Tg and Tm may define the absolute limits of usefulness of a polymer, arbitrary softening points and information from thermogravimetry are of limited value. A polymer destined for a particular application must be evaluated by preparing the required components from the polymer and then testing these components in the thermal environments they are likely to encounter in use.

Polymers may be subjected to conditions where factors such as creep and distortion may limit their useful working life. Thermal expansion may also produce problems, especially where two different materials are in contact.

The loss in mechanical properties by chemical degradation is a process which can determine the suitability of a polymer for use in components operating at elevated temperatures under stress.

Electrical properties, such as resistance and dielectric constant, may irreversibly deteriorate as a result of use at temperatures high enough to produce chemical breakdown of the polymer.

1.4. The description of high temperature resistance.

The phrase "thermal stability" is often used in describing polymer systems in a loose and general sense that is of limited usefulness. Statements such as, "the polymer is thermally stable at 500", or "the polymer has high thermal stability," are abundant in the literature on high temperature resistant polymers. Nothing of any real practical value is conveyed in such statements. For a more meaningful description, having first stated the type of high temperature resistance i.e. heat, thermal or thermo-oxidative stability, the following information should also be stipulated where appropriate:

The property change measured.

The temperature to which the polymer has been exposed or the heating rate applied.

The time of exposure at the test temperature.

The temperature at which a measurement, e.g. flexural strength, was taken.

The atmosphere, or surroundings of the sample during heating.

The method and apparatus employed.

In a general sense high temperature resistant polymers are polymers that have a continuous service temperature above at least 475 in air. Heat, thermal and thermo-oxidative resistance are encompassed in this general description. In 1970 much research was aimed at producing polymers with long term service temperatures between 475 and 675.[9]

In engineering applications, the maximum long term service temperature is that to which a polymer can be exposed for a requisite period of time (often continuously) without any significant alteration in mechanical properties, or with an acceptable decline in mechanical properties.

Modification of a polymer may significantly alter its maximum service temperature, for example the heat resistance may be lowered by plasticisers or increased by reinforcing fillers.

1.5. Structural features influencing the heat stability of polymers.

Tg is a measure of the ability of a polymer chain to rotate about the constituent chain bonds, i.e. depends upon the flexibility of the chain.

In linear polymers the rotation about the bonds in the chain backbone is hindered by steric interactions of substituent groups. The inclusion of unsubstituted atoms into the polymer backbone tends to lower the Tg by separating the substituted atoms and thereby reducing the energy barrier to rotation. For example, the presence of oxygen atoms in a polymer backbone increases the chain flexibility, as is illustrated by comparing the Tg of poly(ethylene) with that of poly(formaldehyde) (table 1.5.1.). Introducing rings, such as phenylene groups, into a polymer backbone will stiffen the chain by hindering rotation, so that more thermal energy is needed to set the chain in motion. Thus, poly(phenylene oxide) has a much higher Tg than poly(formaldehyde) (table 1.5.1.) and poly(p-phenylene) (I) is completely intractable.

With asymmetrical polymer chains an additional restriction to rotation is imposed by steric effects. The presence of non-polar side groups increases Tg and the effect is accentuated with increase in the bulkiness of the groups. This effect is illustrated by comparing poly(ethylene), poly(propylene) and poly(styrene) (table 1.5.1.). Superimposed on this group size factor are effects of polarity and the intrinsic flexibility of the pendant group itself. An increase in cohesion between the polymer chains, by ion-dipole interactions or hydrogen bonding, increases Tg. Thus polar groups tend to increase Tg when compared with non-polar groups of similar size, as can be seen by comparing poly(propylene) with poly(vinylchloride) and poly(acrylonitrile) (table 1.5.1.). The effect of side chain flexibility on Tg can be seen by comparing poly(methyl acrylate), poly(ethyl acrylate) and poly(butyl acrylate) (table 1.5.1.).

Cross-linking also restricts chain rotation and increases Tg. Thus, poly(imidazopyrrolone) (IV), which is a "ladder" polymer and thermoset polymers, such as phenolics, are intractable.

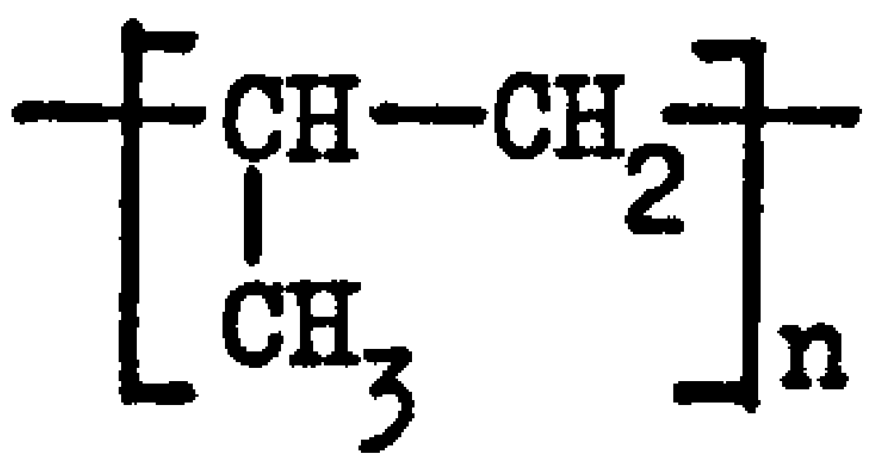
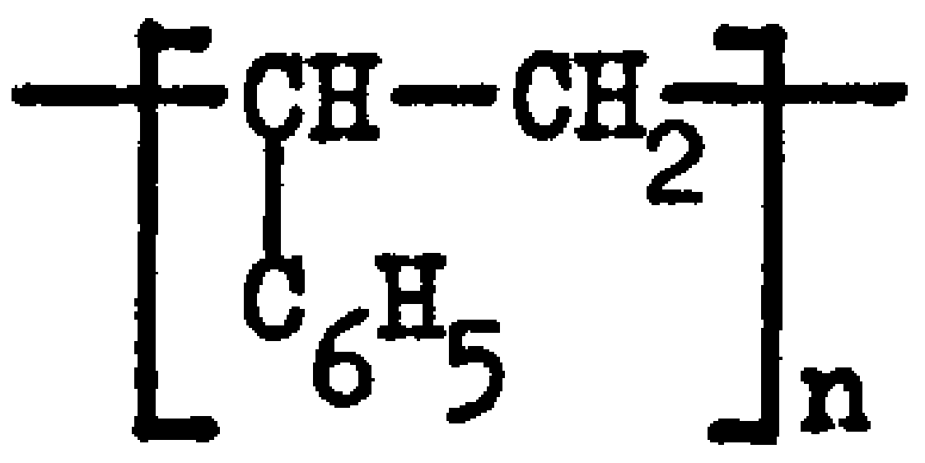
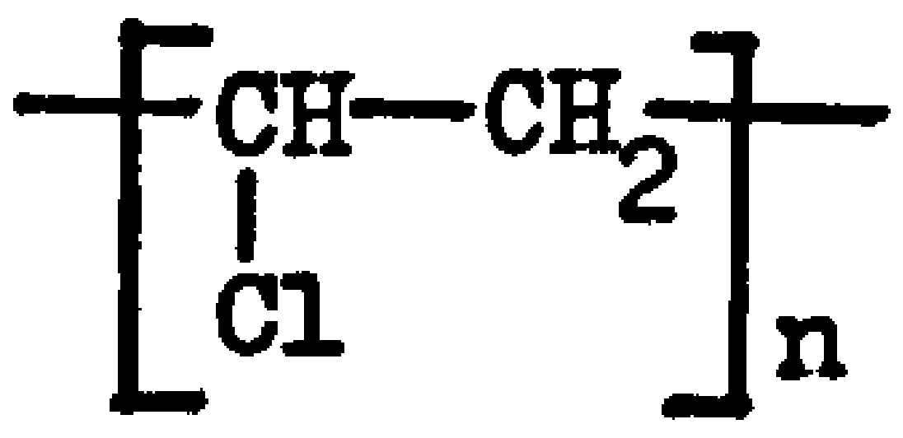
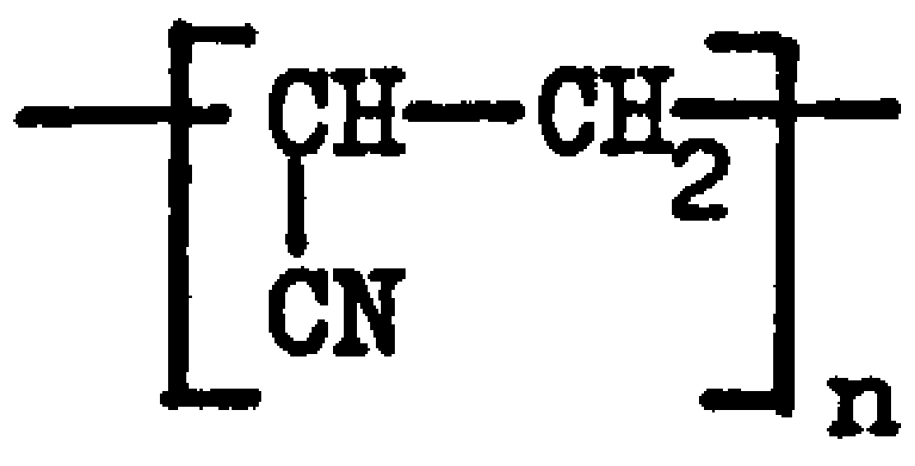
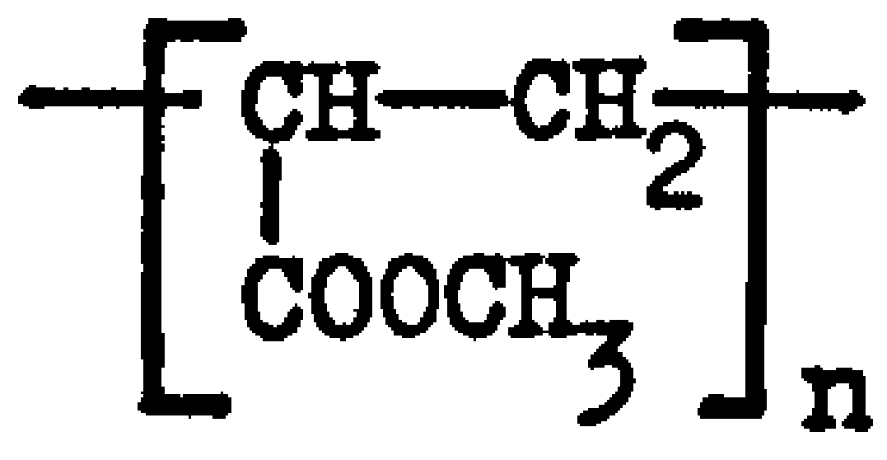
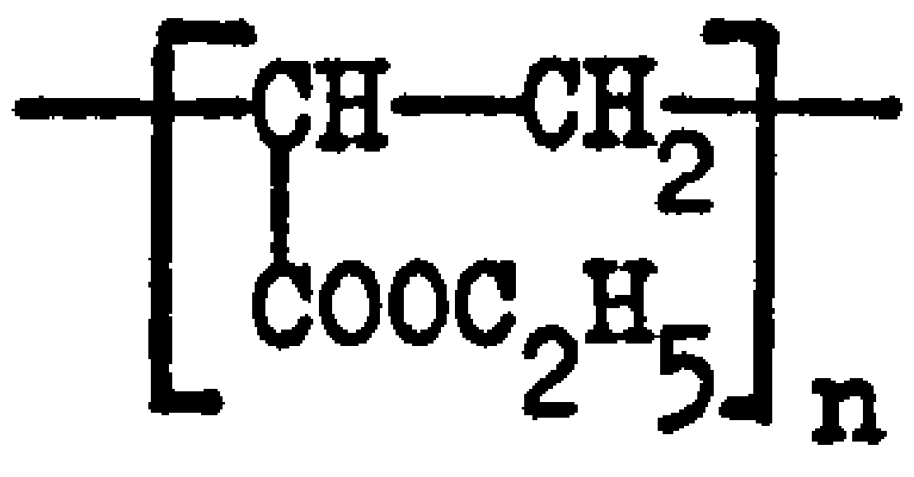
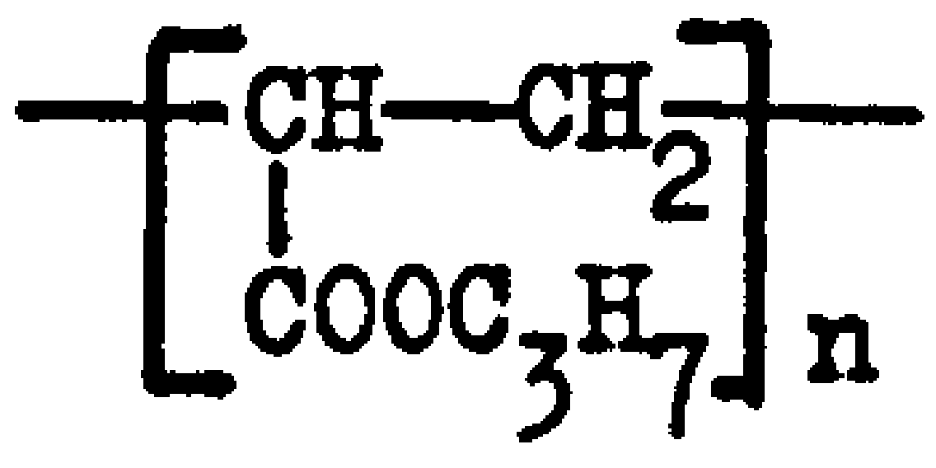
Tm is dependent upon structural effects in a polymer that tend to enhance the ordering, or crystallisation, of the polymer chains.

Ion-dipole interactions and hydrogen bonding between polar groups in a polymer increase inter-chain cohesion and increase Tm. Thus, poly(formaldehyde) has a higher Tm (448) than poly(ethylene) (Tm = 383), due to the increase in chain cohesion conferred by the oxygen atoms in the polymer chains.[10] The very high melting points of aliphatic poly(amides) (V)can be attributed to extensive inter-chain hydrogen bonding which gives the polymer high crystallinity. The incorporation of phenylene rings into a polymer backbone also increases the tendancy for the polymer to crystallise.

The presence of bulky non-polar side chains tends to hinder the ordering of the chains in atactic polymers and tend to lower Tm.

Table 1.5.1.

T_g values for various polymers.[11,12,13]

POLYMER	REPEAT UNIT	T_g
Poly(ethylene)	$\left[CH_2-CH_2 \right]_n$	253
Poly(propylene)	 $\left[CH(CH_3)-CH_2 \right]_n$	257
Poly(styrene)	 $\left[CH(C_6H_5)-CH_2 \right]_n$	353
Poly(formaldehyde)	$\left[CH_2-O \right]_n$	213
Poly(phenylene oxide)	$\left[C_6H_4-O \right]_n$	356
Poly(vinyl chloride)	 $\left[CH(Cl)-CH_2 \right]_n$	354
Poly(acrylonitrile)	 $\left[CH(CN)-CH_2 \right]_n$	378
Poly(methyl acrylate)	 $\left[CH(COOCH_3)-CH_2 \right]_n$	279
Poly(ethyl acrylate)	 $\left[CH(COOC_2H_5)-CH_2 \right]_n$	249
Poly(butyl acrylate)	 $\left[CH(COOC_3H_7)-CH_2 \right]_n$	218

1.6. Structural features influencing the thermal and thermo-oxidative stability of polymers.

1.6.1 Thermal stability.

The strength of a chemical bond puts an upper limit on the vibrational energy that molecules can possess without bond rupture. Atomic vibrations take place by absorption of thermal energy and the maximum amount of energy that two bonded atoms can absorb before dissociating is defined as the bond dissociation energy. Bond dissociation energies are documented, but tend to vary from author to author. Table 1.6.1.1. lists some bond dissociation energies between various atoms.

Absolute values of bond energies do not alone determine the thermal stability of a polymer. Secondary bonding by ion-dipole interaction between polar groups or by hydrogen bonding may also contribute to thermal stability, for example hydrogen bonding energies can provide up to the equivalent of 10% of the bond dissociation energy of the C-C bond. Factors tending to lower the thermal stability of bonds include steric over-crowding, activated groups (such as activated methylene groups) and chain irregularities. Wright and Lee[17] have demonstrated the limited applicability of bond dissociation energies by comparing experimental and calculated degradation temperatures for poly(ethylene). The calculated degradation temperature was determined from the Arrhenius equation, taking the activation energy as equivalent to the bond dissociation energies and using typical values for the collision number and probability factor. Taking a rate of degradation of 1% min^{-1} the calculated degradation temperature was found to be considerably higher than that found in practice.

Wolfes[18] has studied the dissociation energies of bonds between atoms in various polymers and has suggested that for

Table 1.6.1.1.

Bond dissociation energies[14,15,16]

BOND	BOND ENERGY (kJ $mole^{-1}$)
C-N	306
C-C (aliphatic-aromatic)	346
C-C (aliphatic)	347.5
C-C (aromatic)	410
C-H (aliphatic)	413
O-H	425
C-O (phenolic)	448
C-H (aromatic)	467
P-O	342
Si-O	451
B-O	473
Ti-O	670

thermally stable polymers the bonds energies in the macromolecular chains should not be less than 375 kJ $mole^{-1}$. For example, aromatic C-C links in polymers have a very high thermal stability.

Bond energies are calculated by assuming that the bonds dissociate homolytically. However, many bonds, such as P-O and C-O are polar and possess some ionic character. Electronegativities (table 1.6.1.2.) can be employed in estimating the degree of ionic character in bonds[19]. If the difference in electronegativities of two atoms forming a bond is less than about 1.7 then the bond can be considered to be predominantly covalent and a value higher than about 1.7 indicates that the bond is mainly ionic (table 1.6.1.3.).

Van Wazer[20] has made some important generalisations about the nature of inorganic bonds, compared to organic bonds. The breaking of bonds in organic polymers is usually associated with degradation processes involving charring and the elimination of volatiles at high temperatures. In inorganic polymers the fission of primary bonds gives rise to different processes. This point is illustrated by molten glass in which there is a very rapid exchange of parts between and within the molecules, but the system remains at equilibrium and does not degrade at high temperature in the presence of oxygen.

Less is known about catenation between inorganic atoms than carbon atoms. In inorganic macromolecules the bonding is more complex, for example with elements from the third period of the periodic table 3d orbitals may be involved to give a $(d\text{-}p)\pi$ contribution to the bonding.

1.6.2. Thermo-oxidative stability

Since most high temperature resistant polymers are used in air, thermo-oxidative stability is very important technically and consideration of this aspect of degradation usually predominates

Table 1.6.1.2.

Pauling electronegativities.[19]

B	2.0
Al	1.5
C	2.5
Si	1.8
P	2.1
O	3.5
Ti	1.6

Table 1.6.1.3.

Ionic character of bonds.[15]

BOND	ELECTRONEGATIVITY DIFFERENCE OF ATOMS.	% IONIC CHARACTER*
B-O	1.5	43
Al-O	2.0	63
Si-O	1.7	51
C-O	1.0	22
P-O	1.4	39
Ti-O	1.9	59

* *Amount of ionic character* $= 1-\exp.\left[\frac{1}{4}(X_a - X_b)^2\right]$.

X_a *and* X_b *are Pauling electronegativities. The true ionic character may be much lower in cases where dative* π *bonding can occur.*

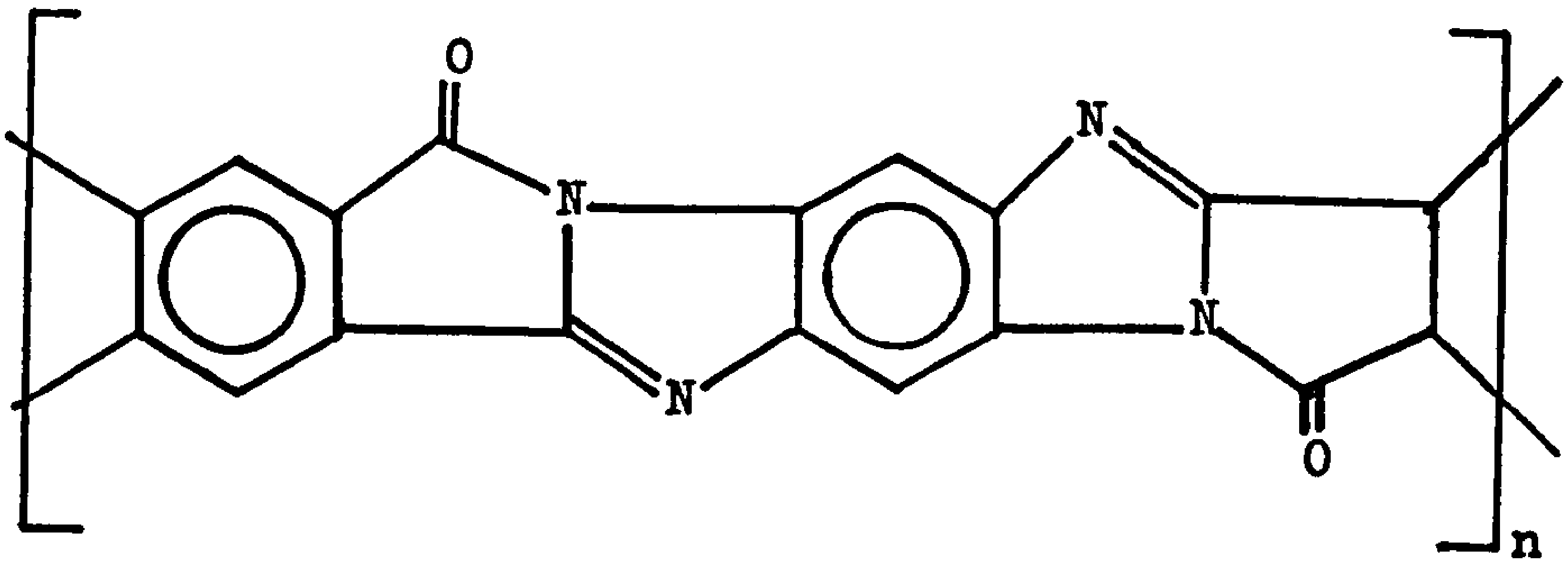
over thermal stability. Most organic groups in polymers are susceptible to thermo-oxidation. Phenolic hydroxyl groups are readily oxidised, even at moderate temperatures, to form quinone structures. Aliphatic C-H bonds are also susceptible to oxidation, especially at tertiary carbon atoms. Ketones and hydroperoxide groupings often form and hydroperoxide groups themselves are thermally unstable, dissociating into radicals. Thus, poly(propylene) is more readily oxidised than poly(ethylene) at high temperature, with the formation of hydroperoxide groups at the tertiary carbon atom[21] (VI).

The incorporation of aromatic carbocyclic or heterocyclic rings into a polymer main chain considerably enhances thermo-oxidative stability. In these systems, which are highly resonance stabilised, hydrogen atoms are very firmly bound and cannot split off as hydroperoxide radicals. Such polymers resist oxidation up to 675-875.[22] Poly(p-xylylene) (VII), for example, has a higher thermo-oxidative resistance than poly(ethylene) (VIII), whilst poly(benzyl)(IX) is more resistant than either of these polymers[23].

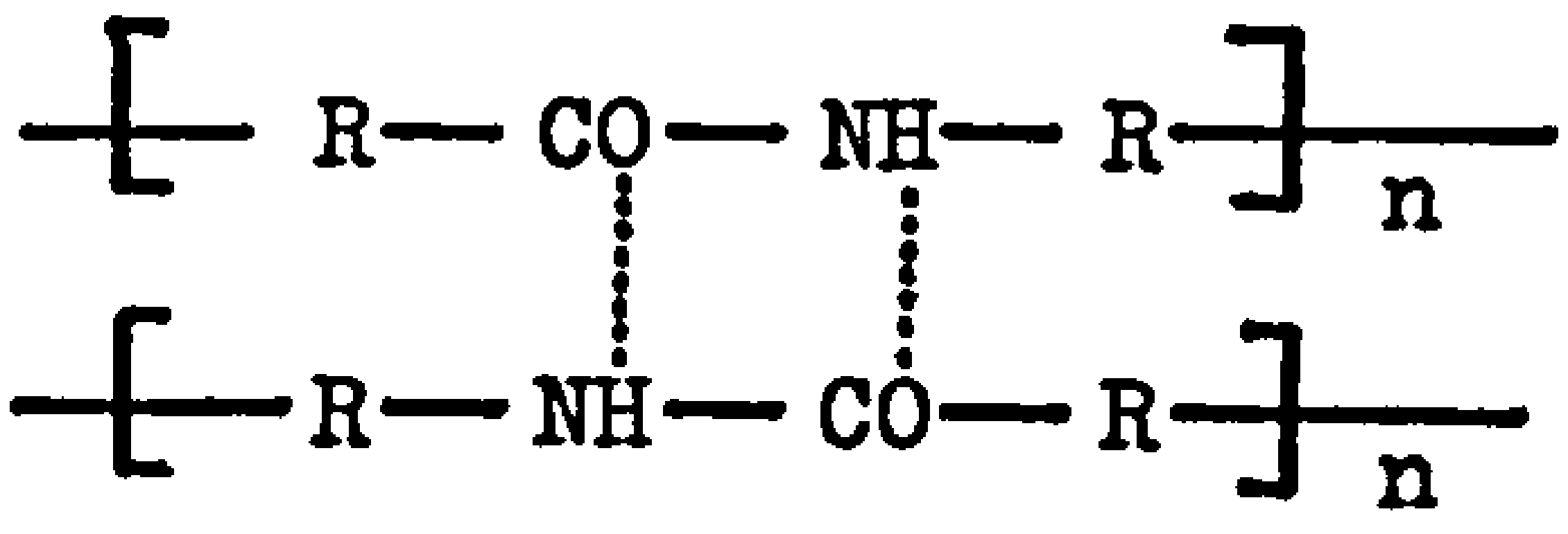
Inorganic atoms may also enhance thermo-oxidative resistance. Poly(tetrafluoroethylene) (X) has exceptionally high thermo-oxidative stability when compared to poly(ethylene) (VIII). It is important that the inorganic atoms in a polymer are in their highest oxidation state otherwise thermo-oxidative attack could take place at the inorganic atom.

1.6.3. Network structures.

Linear organic polymers with a "ladder" structure, such as poly(imidazopyrrolone) (IV)are less likely to undergo fragmentation by chemical bond scission than polymers with a single -C-C- macromolecular backbone. Fragmentation necessitates the scission

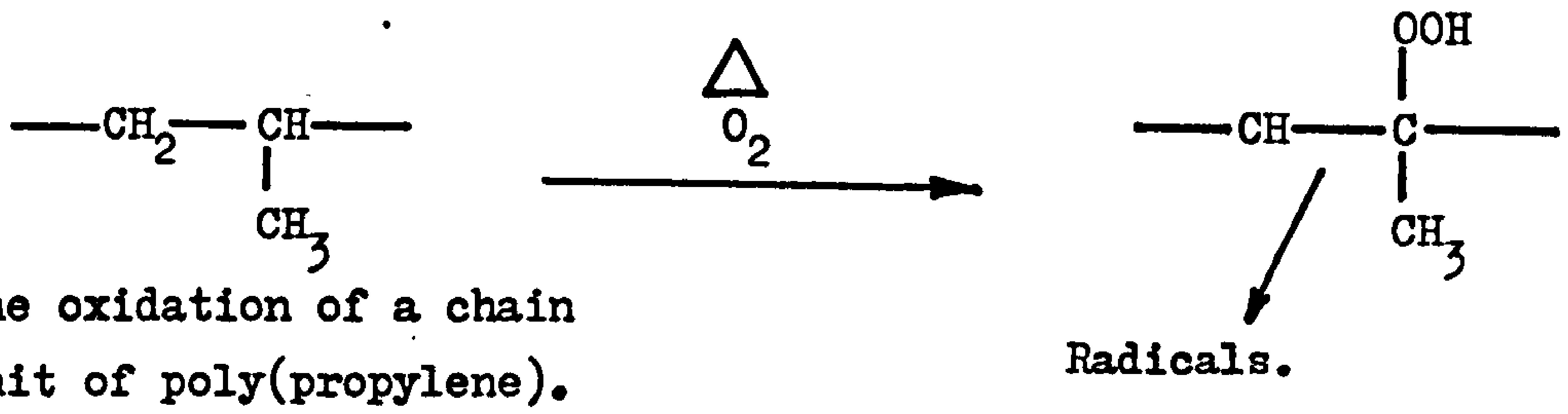


(IV) Poly(imidazopyrrolone).

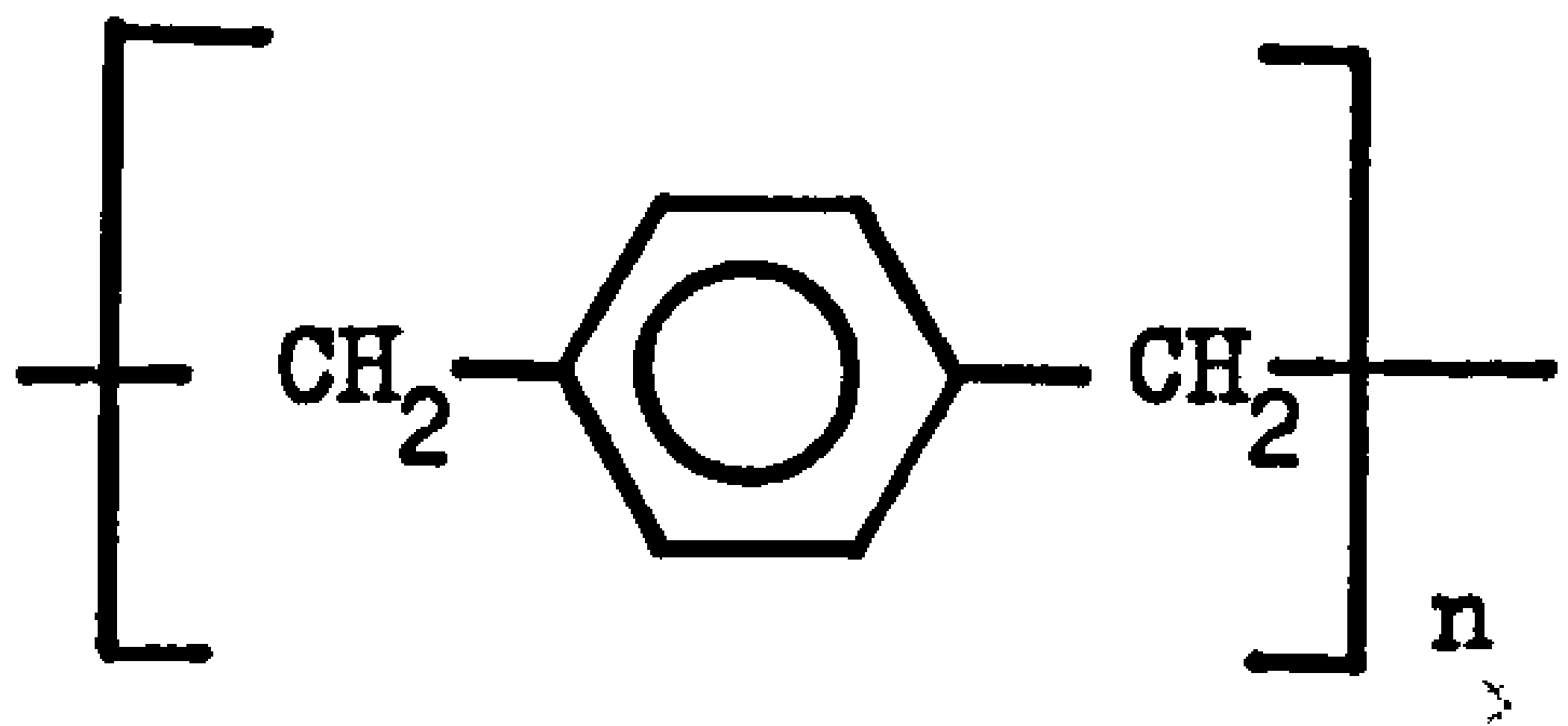


$$-\!\!\left[R-CO-NH-R \right]_n\!\!- \qquad -\!\!\left[R-NH-CO-R \right]_n\!\!-$$

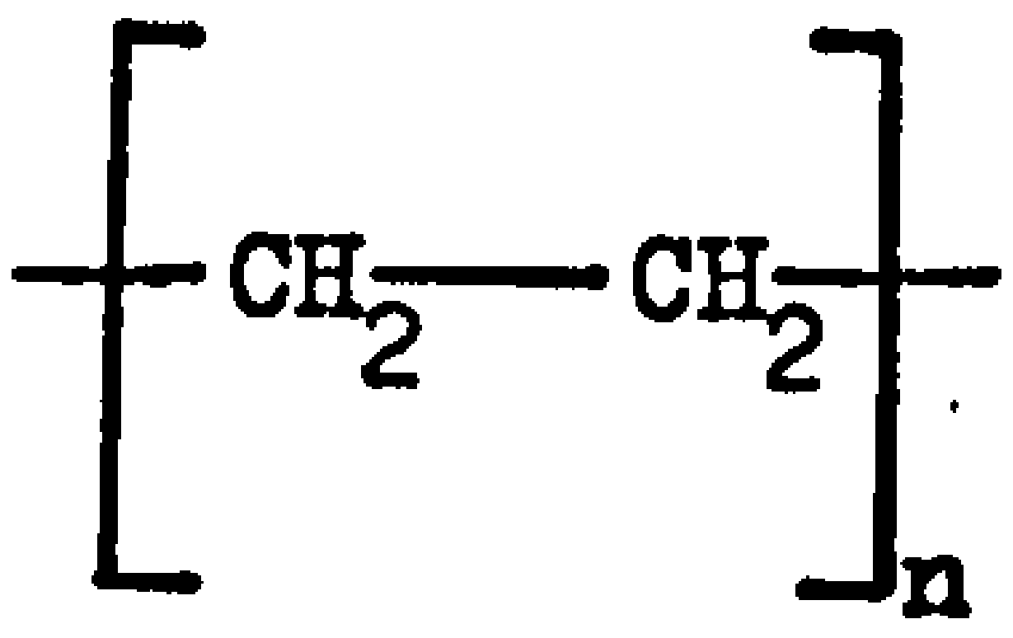
(V) Hydrogen bonding in aliphatic poly(amides).



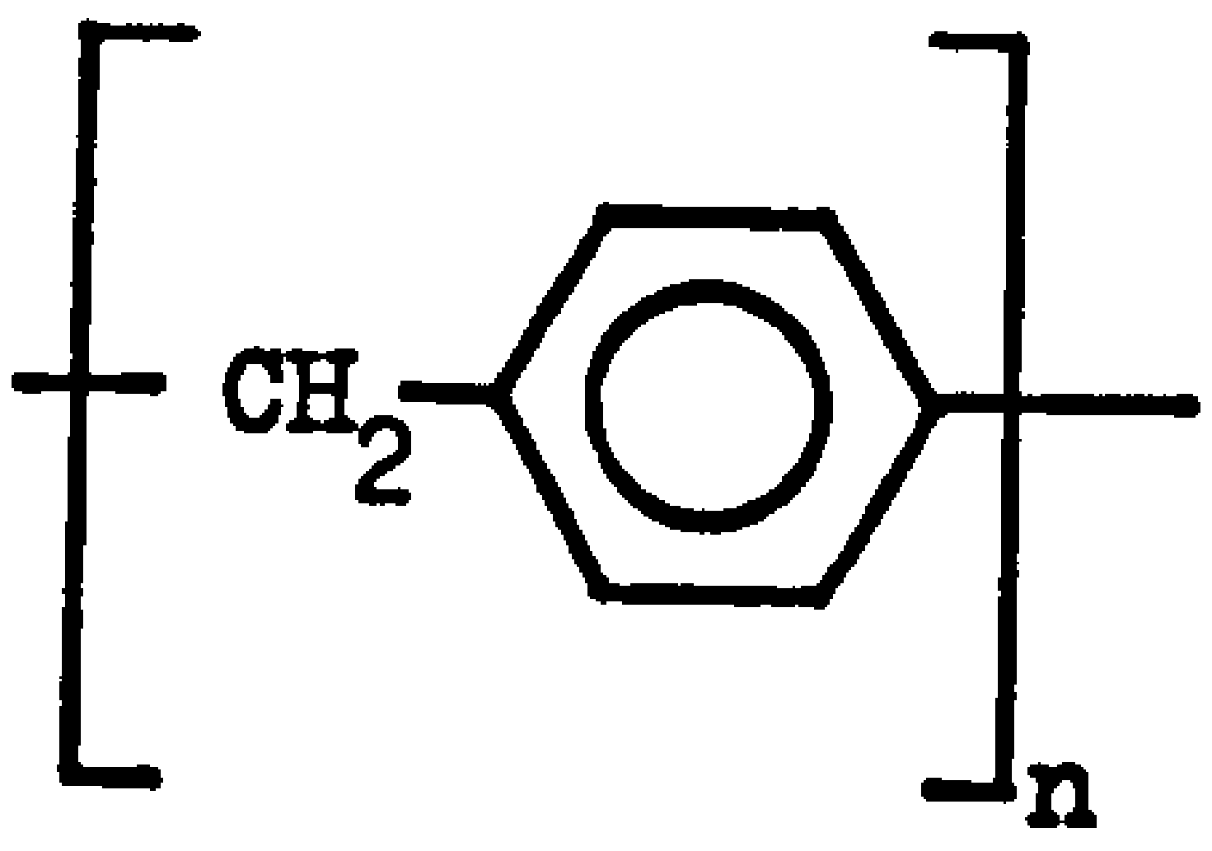
(VI) The oxidation of a chain unit of poly(propylene).



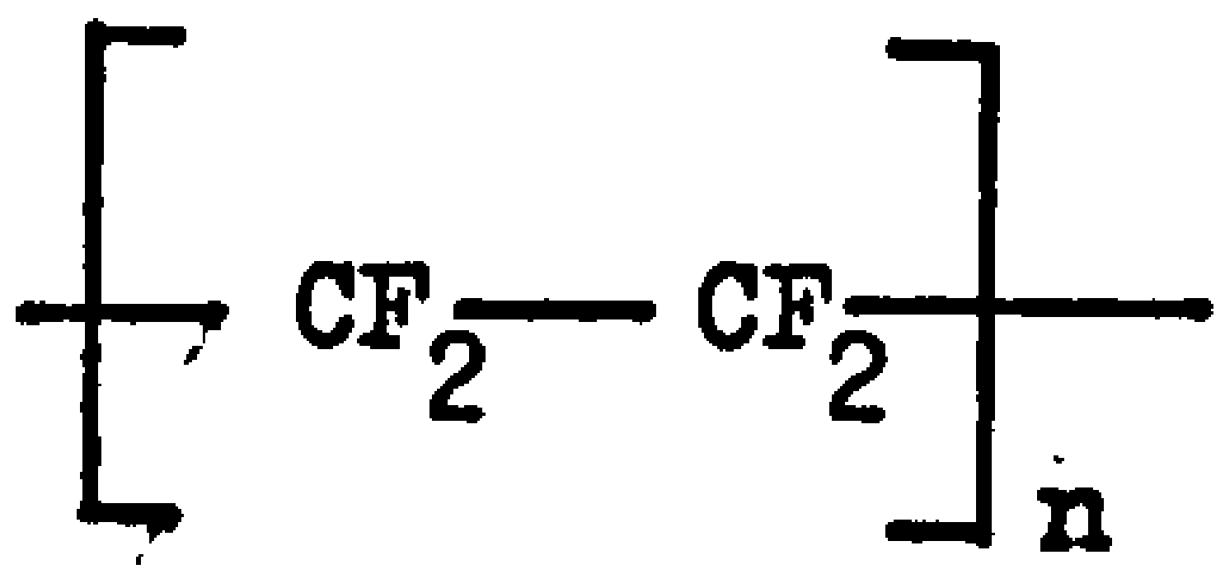
(VII) Poly(p-xylylene).



(VIII) Poly(ethylene).



(IX) Poly(benzyl).



(X) Poly(tetrafluoroethylene).

of two bonds within the same ring in the polymer main chain, which has been shown to be statistically less favoured with respect to scission of two bonds in different rings[24]. Thus, although thermal or thermo-oxidative degradation may occur, their effect on the mechanical properties of the polymer may be delayed. There is also the possibility that chain scission at one point in a ring may activate another part of the same ring to thermal or thermo-oxidative degradation, in which case fragmentation may occur rapidly.

Similar arguments apply to polymers with a three dimensional network of atoms, i.e. thermosets. The cross-linking of a thermosetting polymer also gives rise to another effect. Whilst in an uncured state the various groups of atoms in a thermosetting polymer are free to vibrate when they absorb thermal energy. Bond stretching and group wagging modes of vibration can occur, which dissipate the absorbed thermal energy. If a chemical bond absorbs too much thermal energy then its restoring force per unit displacement (or force constant) will be insufficient to prevent the two oscillating atomic nuclei from dissociating. By cross-linking the resin the various groups of atoms present will be held rigidly and thermal energy dissipation by wagging modes will be reduced. The bond stretching modes will then receive more thermal energy and the bonds will tend to dissociate at earlier stages than if they were a part of a freely vibrating discrete molecule.

1.7. General features of high temperature resistant polymers.

Most high temperature resistant organic polymers are composed of a high proportion of resonance stabilised aromatic rings and often have "ladder" or three dimensional network structures. Consequently, these polymers are very rigid and are often insoluble in most solvents.

Table 1.7.1. shows some examples of high temperature resistant polymers.

The linear polymers are usually very difficult to process, since they will only flow under high temperatures and pressures, or may not even flow at all. Temperatures in excess of 700 may be necessary[25] to fabricate these polymers (e.g. the sintering of poly(imides)). The insolubility of many high temperature resistant polymers limits their use in coatings, for example poly(phenylene sulphide) (table 1.7.1.) is insoluble in all organic solvents below 475[26].

Thermosetting polymers, such as Xylok resin (table 1.7.1.) are much easier to process than the linear high temperature resistant polymers by virtue of their initial tractability at fabricating temperatures and pressures. Disadvantages encountered with many thermosetting resins are that volatiles are released during the curing reaction and often a long post-cure is required to drive off these volatiles and thereby complete the cross-linking reaction.

There is very extensive literature available on high temperature resistant polymers and in the main thermosetting polymers have received less attention than the linear types.[27,28,29,30,31]

Table 1.7.1.

Some high temperature resistant polymers.

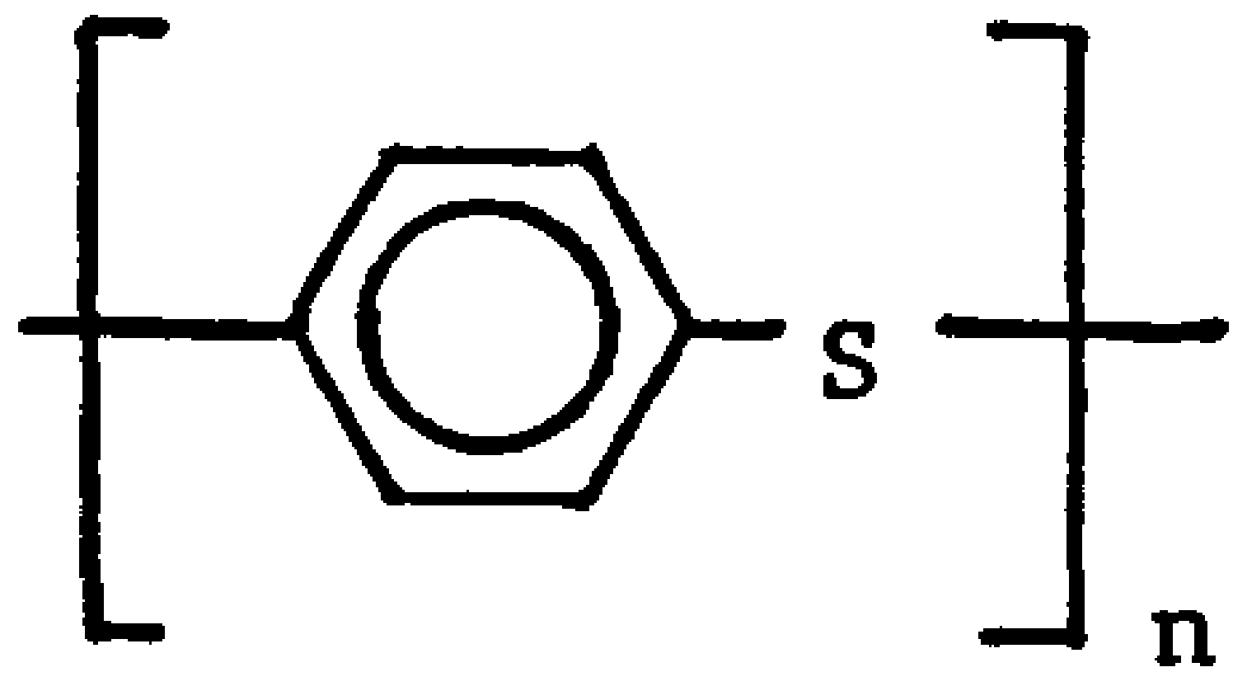
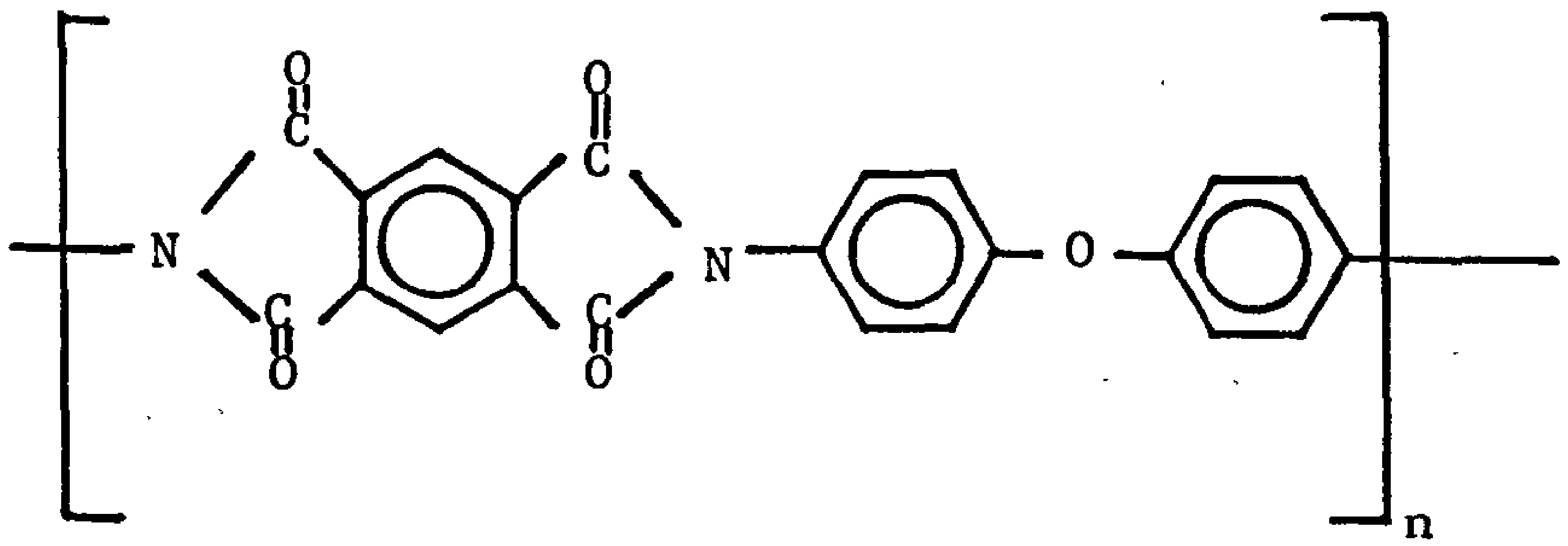
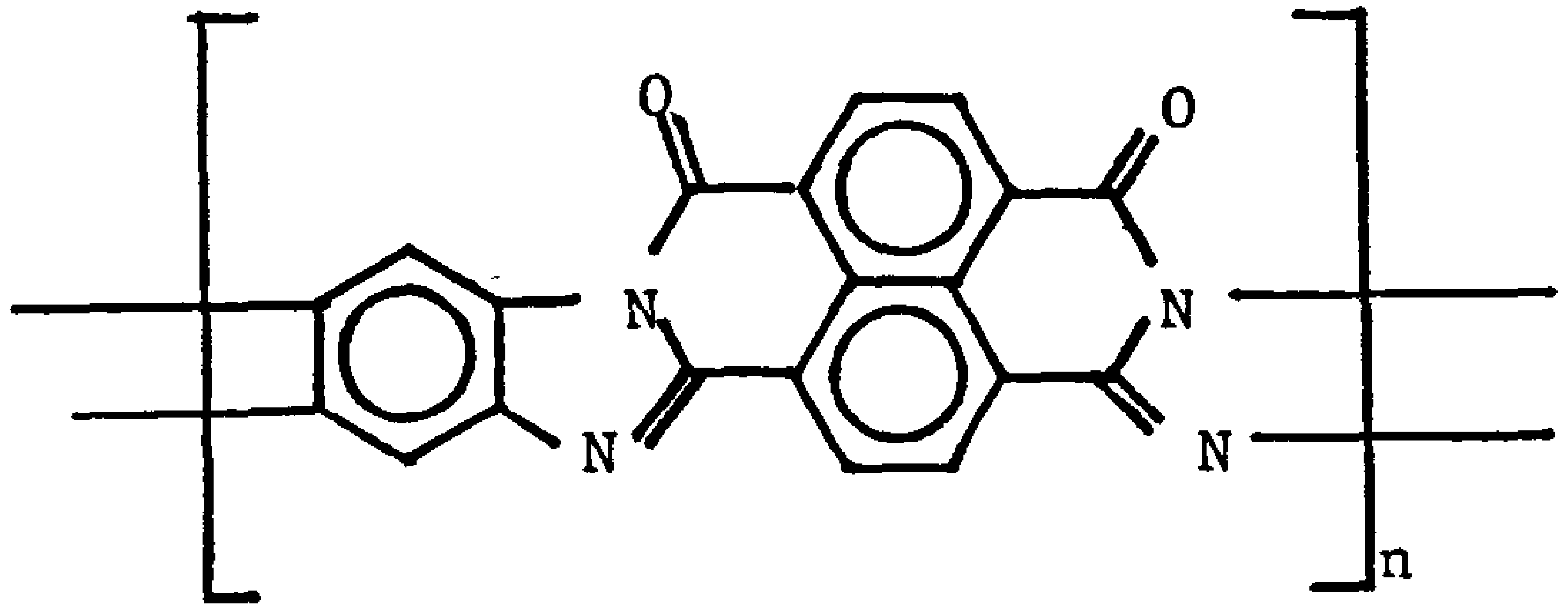
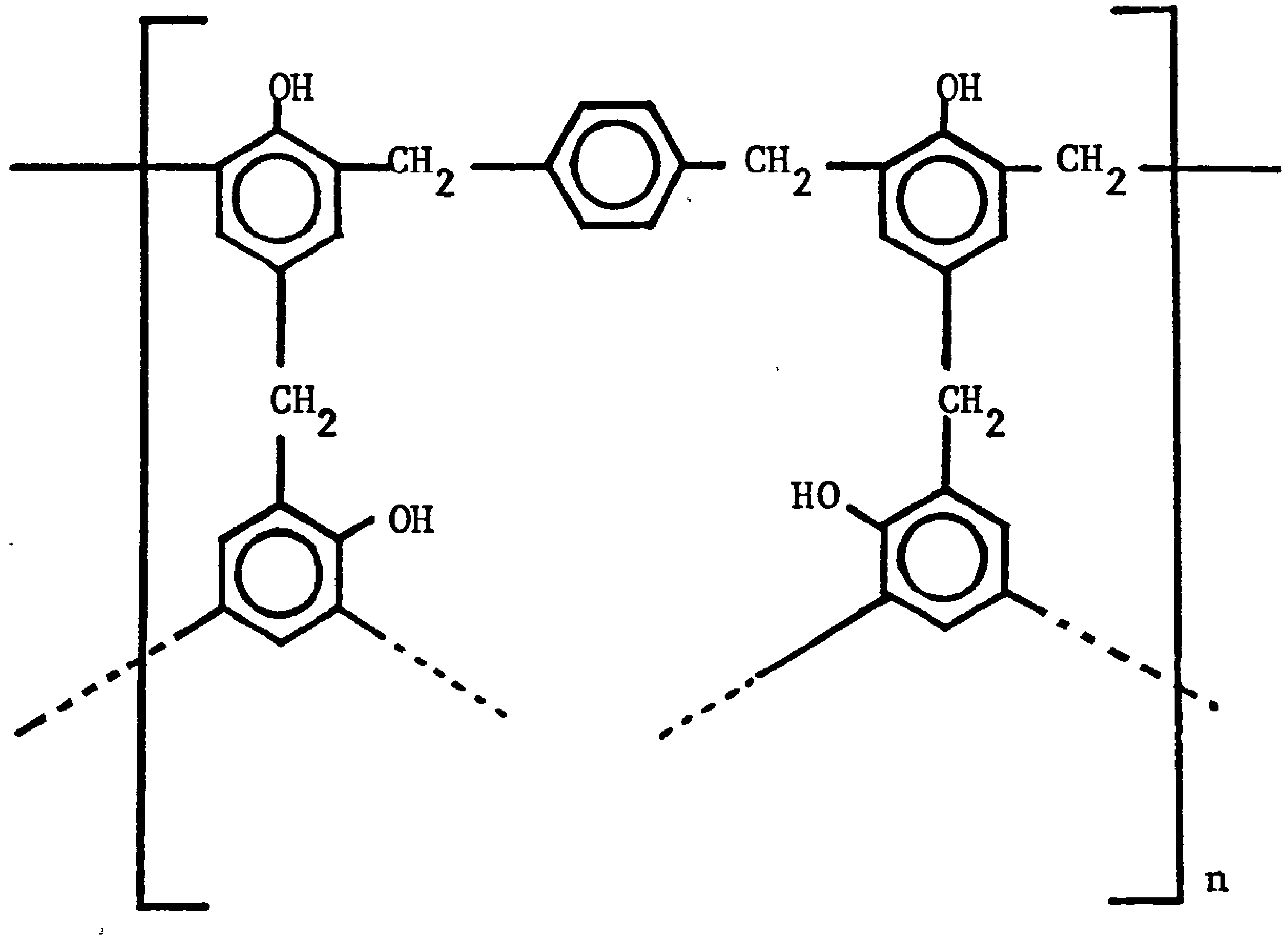
NAME	STRUCTURE	TYPE
Poly(phenylene sulphide)		Linear
Poly(N,N′-(p,p′-oxydiphenylene pyromellitimide)) (Poly(imide))		Linear ("step-ladder")
Poly(bis-benzimidazobenzophenanthrolein) (BBL)		Linear ("ladder")

Table 1.7.1. (continued).

NAME	STRUCTURE	TYPE
Phenol-p,p′-dimethoxyxylylene resin cured with hexamine. (Xylok resin*)	 - - - - ≡ Methylene bridges.	3-D network (thermoset).

---

* Manufactured by Albright and Wilson Ltd.

1.8. Organophosphorus Polymers.

1.8.1. General introduction.

There are two large groups of organophosphorus polymers. Group 1, where the phosphorus containing moiety is pendant to the main chain of the polymer.

Group 2, where the phosphorus atoms are a part of the main chain of the polymer.

Group 1 includes addition polymers of ethylenically unsaturated phosphorus containing monomers and polymers prepared by phosphorylating substituent groups on synthetic or naturally occurring organic polymers. The addition polymers are the most important member of this group and the first example was prepared by Toy et. al.,[32] who polymerised diallylaryl phosphonate (XI) to a hard, glassy, high temperature resistant product. Many hundreds of unsaturated organophosphorus monomers have been reported to polymerise and much information is available in the literature.[33-35]

Group 2 are the most important organophosphorus polymers from the point of view of high temperature resistance and includes poly(amides), poly(esters), poly(urethanes), poly(phosphazenes), polymers containing phosphorus and other inorganic elements in the main chain and certain co-ordination polymers, all of which are described in the literature.[33-35].

A large number of structurally related poly(esters) have been reported (table 1.8.1.1.) and of these only the poly(phosphates) will be discussed in detail.

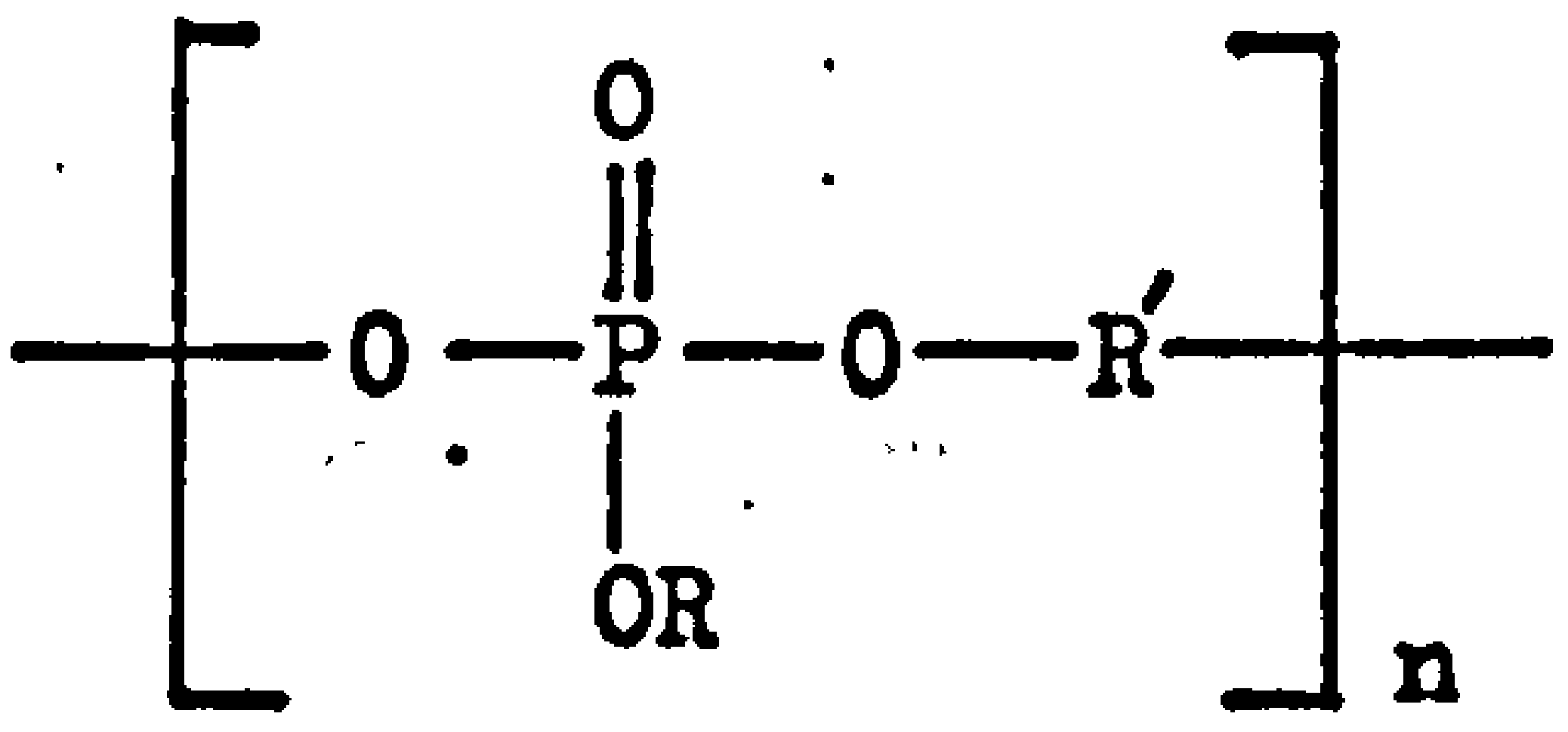
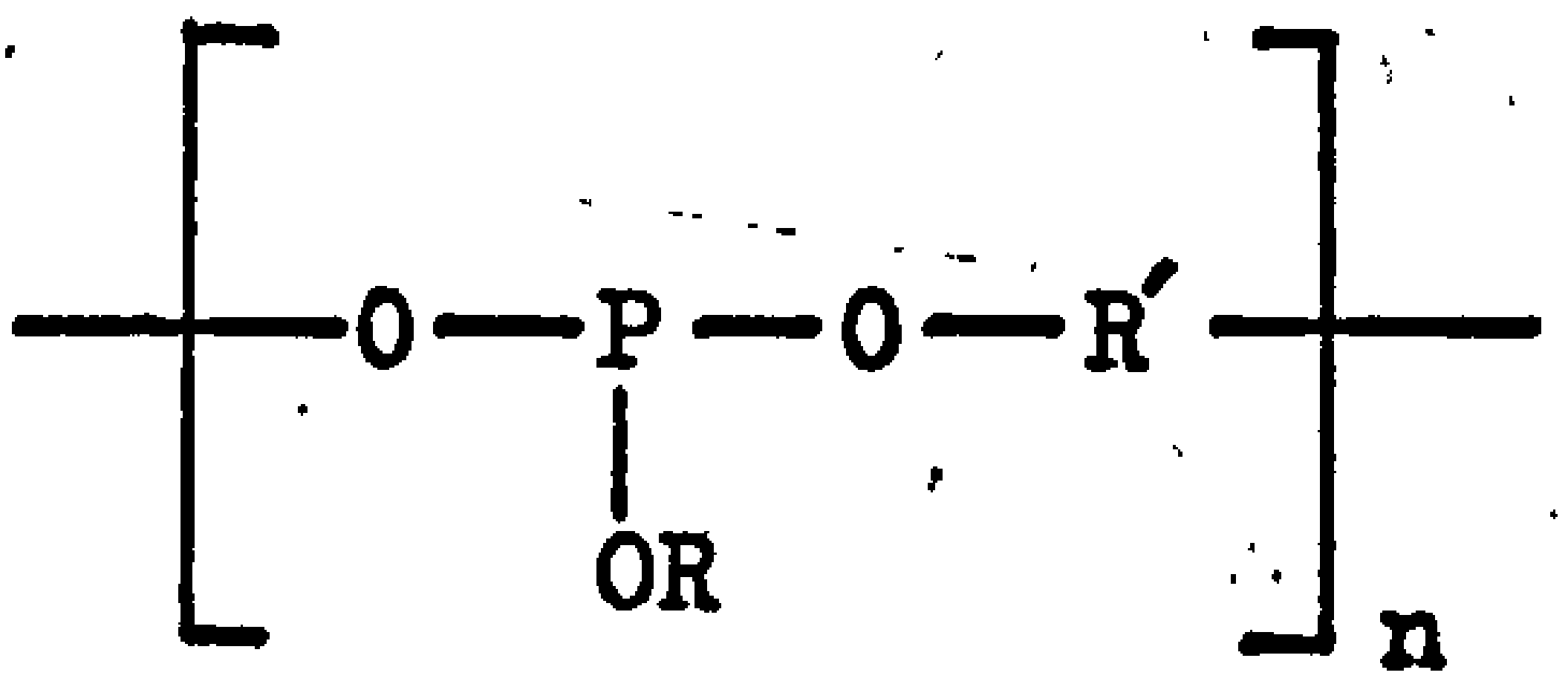
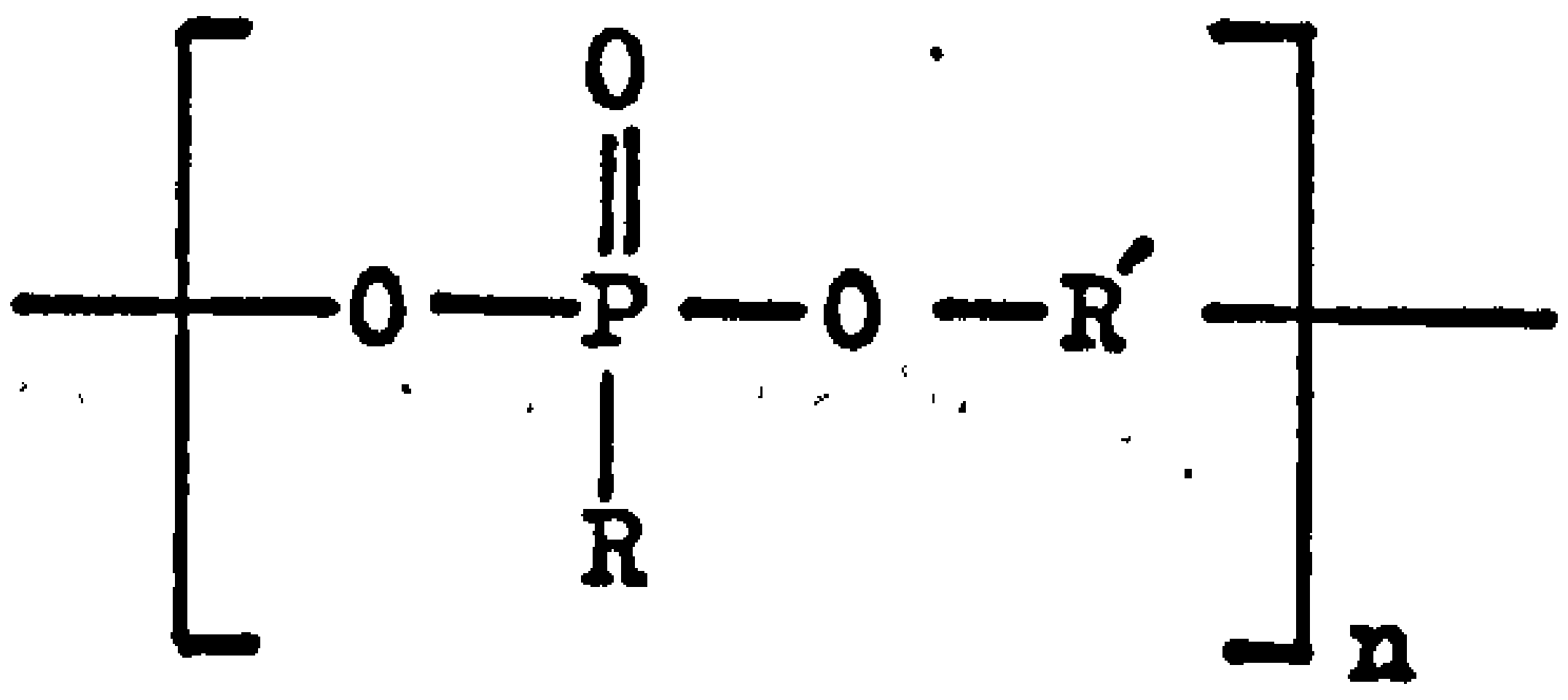
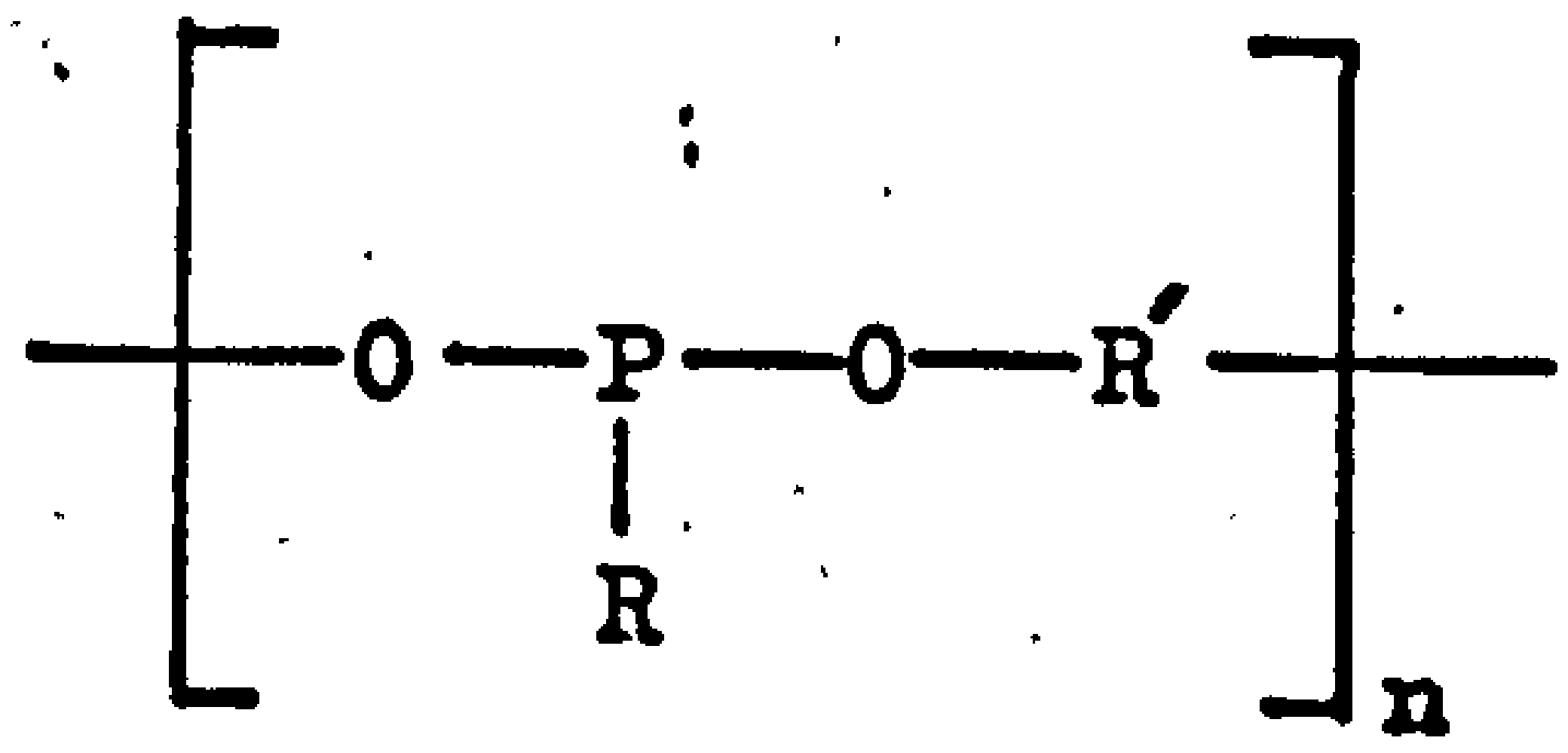
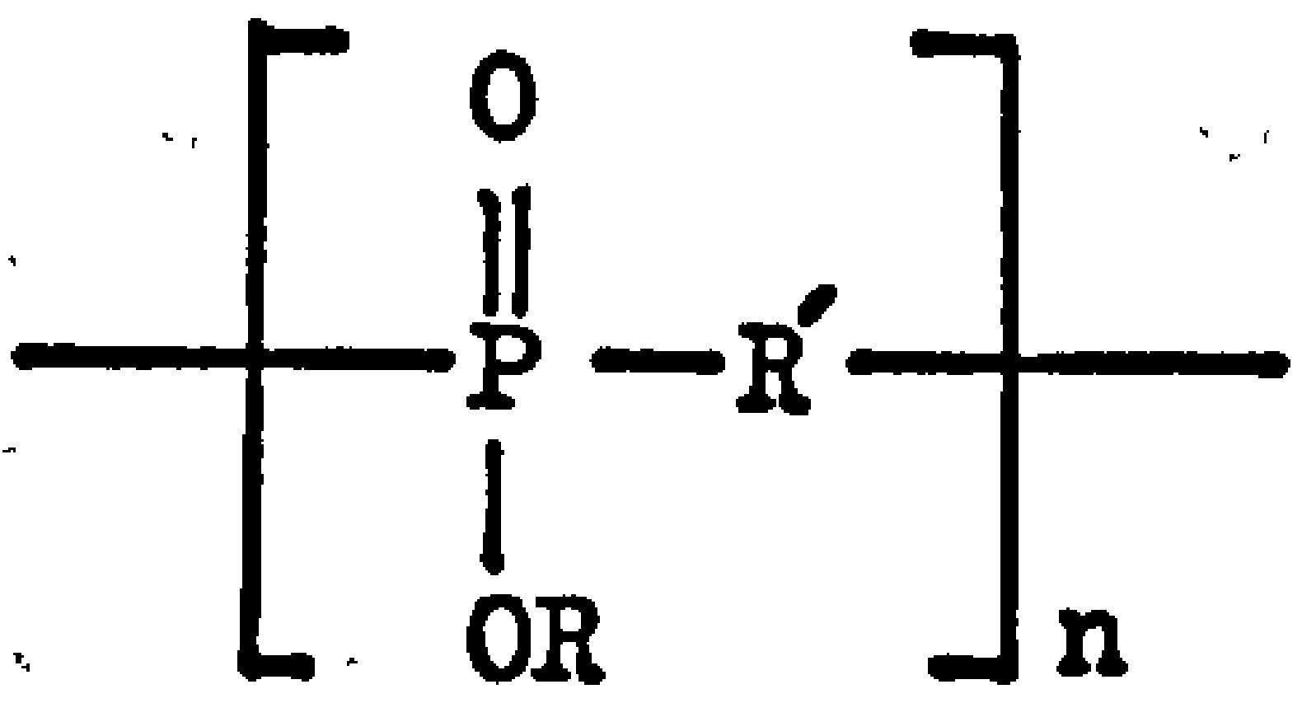
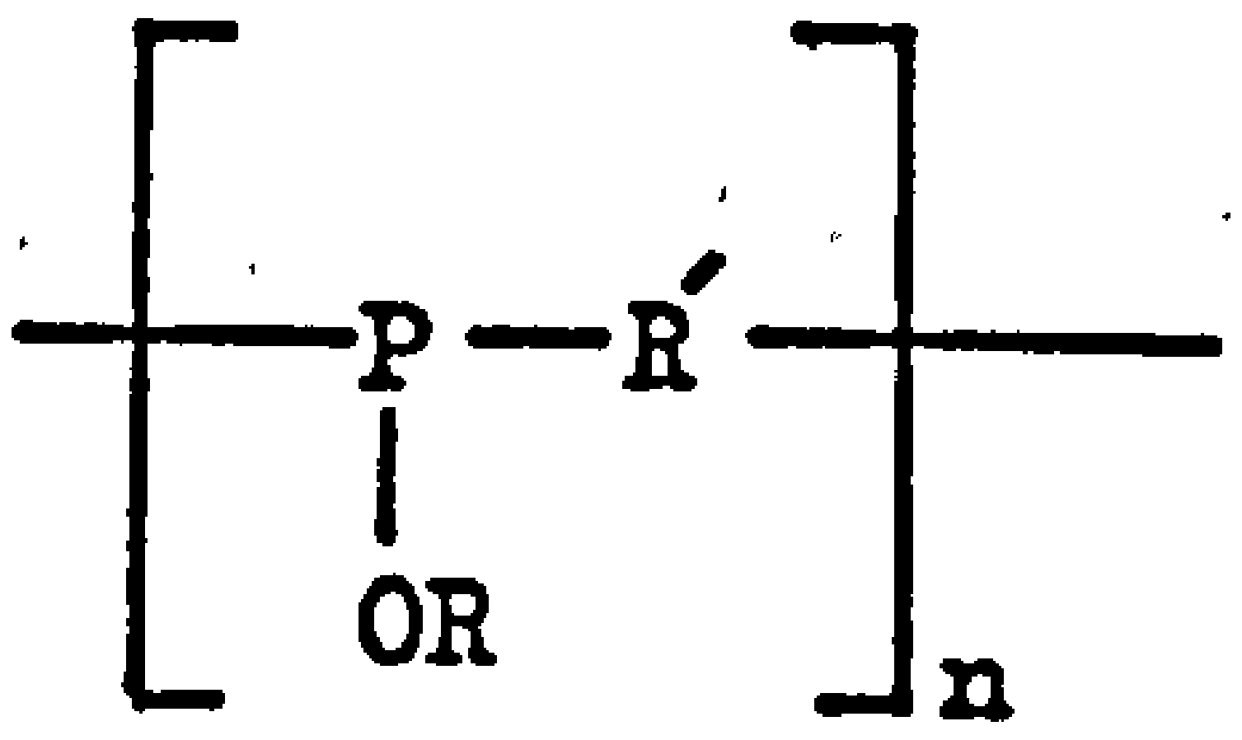
1.8.2. Poly(organophosphates).

Perhaps the most successful of the organophosphorus polymers, poly(organophosphates) were extensively researched by I.C.I. Ltd. in the 1950's. Many patents were published, mostly in the mid-1950's.[36-40]

Poly(organophosphates) are prepared from organophosphorodichloridates

Table 1.8.1.1.

Poly(esters) containing phosphorus in the main chain.

POLYMER	STRUCTURAL UNIT
Poly(phosphates)	 $\left[-O-\overset{\overset{O}{\|}}{\underset{\underset{OR}{\mid}}{P}}-O-R'-\right]_n$
Poly(phosphites)	 $\left[-O-\underset{\underset{OR}{\mid}}{P}-O-R'-\right]_n$
Poly(phosphonates)	 $\left[-O-\overset{\overset{O}{\|}}{\underset{\underset{R}{\mid}}{P}}-O-R'-\right]_n$
Poly(phosphonites)	 $\left[-O-\underset{\underset{R}{\mid}}{P}-O-R'-\right]_n$
Poly(phosphinates)	 $\left[-\overset{\overset{O}{\|}}{\underset{\underset{OR}{\mid}}{P}}-R'-\right]_n$
Poly(phosphinites)	 $\left[-\underset{\underset{OR}{\mid}}{P}-R'-\right]_n$

and diols or dihydric phenols (XII).

With aliphatic diols and aliphatic phosphorodichloridates the reaction proceeds at high rate, but seven side reactions occur,[41] namely,

a. Phosphorodichloridates act as mild chlorinating agents for alcohols, (XIII (i)).

b. $O{=}\overset{/}{\underset{\backslash}{P}}{-}OH$ groups are formed, (XIII (i)).

c. These acid groups react with -O-R side groups with cross-linkage by anhydride formation, (XIII (ii)).

d. The -O-R side groups are able to react with the phosphorodichloridate with anhydride formation, (XIII (iii)).

e. Under strongly acid conditions, traces of water which are mostly contained in the glycol used, will hydrolyse the P-Cl, P-OR or $P{-}OR'$ bonds to P-OH.

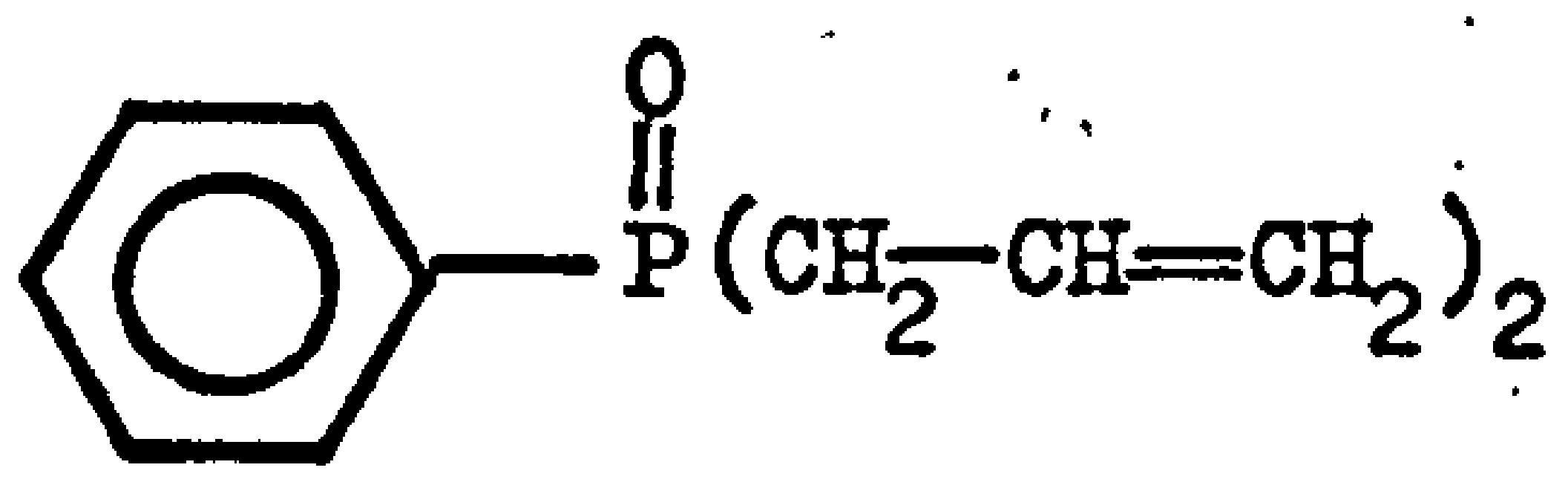
f. Ethylene glycol (and poly(ethylene glycols)) are condensed to 1,4-dioxan by the HCl evolved, (XIII (iv)).

g. In the presence of bases, monomeric cyclic phosphates are formed, especially from 1,2-, or 1,3-diols (XIII (v)).

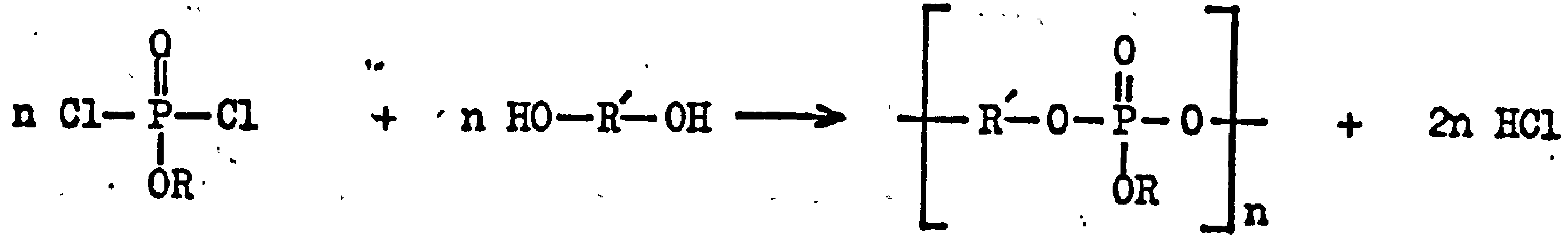
These side reactions prevent the formation of poly(organophosphates) with molecular weights above about 2000. With dihydric phenols side reactions a, b, c, f and g do not occur and side reactions d and e can be eliminated by using aromatic phosphorodichloridates.

The polymerisation reaction can be performed in the melt phase,[36] by heating the monomers in an inert solvent with a hydrogen chloride acceptor,[36] or by an interfacial method using aqueous alkali as a hydrogen chloride acceptor.[42]

Poly(esters) have also been prepared by heating bis-phenols, phenols and phosphoryl chloride together[43] and by reacting dihydric phenols with imidazole derivitives of phosphorus[44] (XIV), or with phosphoric triamide[45] (XV).

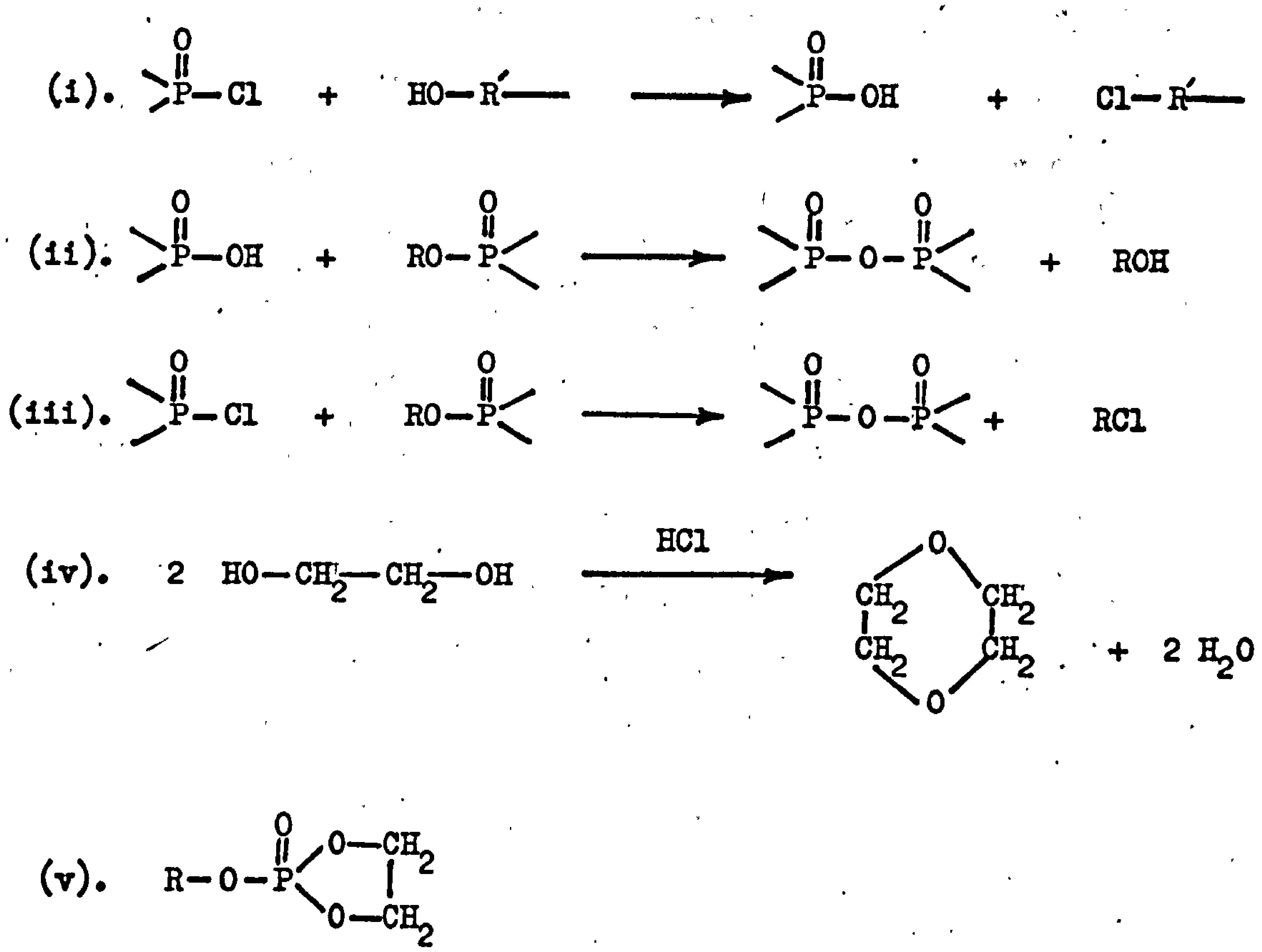


(XI) Diallylphenyl phosphonate.



R,R′ = alkyl,aryl.

(XII) The preparation of a poly(organophosphate)



(XIII) Side reactions and products in the preparation of poly(organophosphates).

Another method of preparing poly(organophosphates) is by transesterification (XVI) but has received less attention. Up to 1966, transesterification of tri-alkyl and tri-aryl phosphates with glycols had not been characterised in detail.[41] Aromatic phosphate esters are reported to be difficult to transesterify,[45] although tri-phenyl, tri-cresyl and tri-xylyl phosphates are reported to undergo transesterification with phenols in the presence of catalysts (e.g. sodium hydroxide).[46]

Direct reaction between orthophosphoric acid and alcohols or phenols only leads to partial ester formation, because of the comparatively low reactivity of the P-OH groups.[47]

Aliphatic poly(organophosphates) are hydrolytically unstable, whereas the aromatic poly(esters) resist hydrolysis.[41] I.C.I's poly(organophosphates) were aromatic and reached a developmental stage in commercial success as "Phoryl" resins (XVII).

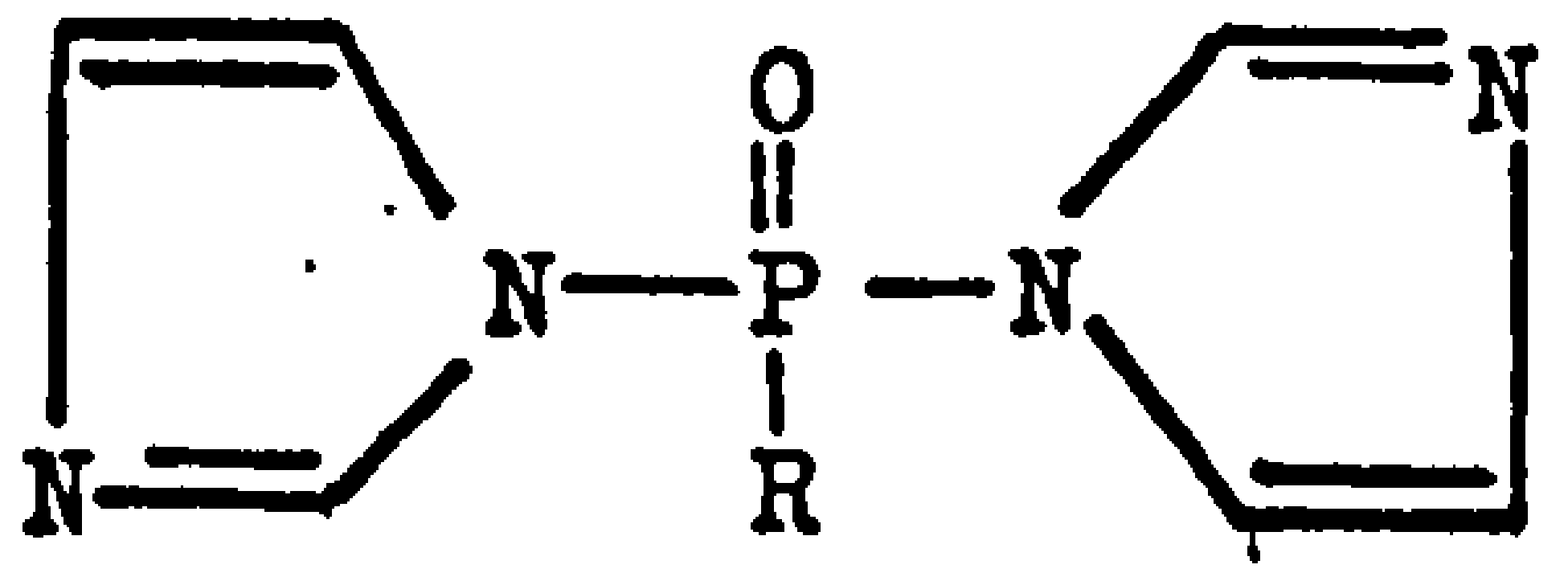
1.8.3. The properties of "Phoryl" resins.

I.C.I. Ltd. once made a range of "Phoryl" resins with different substituents on the phenyl side chains (XVII).

Generally, these resins were stable in water and in cold dilute acids and alkalis. The resins were soluble in many solvents (e.g. benzene) and were attacked by concentrated mineral acids and strong aqueous alkalis.[48]

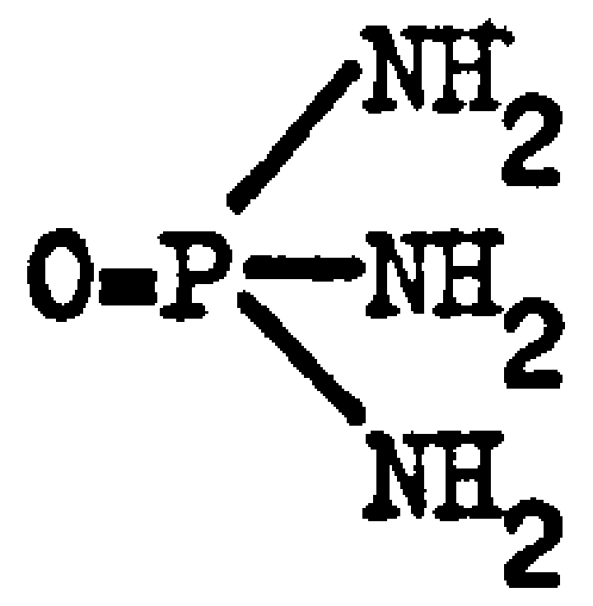
"Phoryl" resins were thermoplastic, although certain patents described methods of hardening the resins. These methods were heating with paraformaldehyde,[38] or lead monoxide (1.5% added),[37] or even simply heating the resin alone to 575 for several minutes.[38] None of these reactions was characterised.

The information on the high temperature resistance of "Phoryl" resins is very scanty and vague. They have been reported to withstand 373 for two weeks[49] and to be stable when heated to 573.[37]



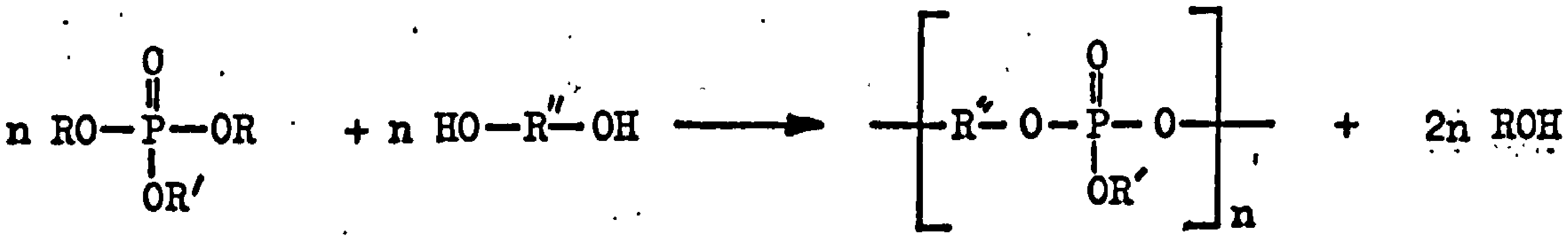
R = aryl, or aryloxy.

(XIV)



Phosphoric triamide.

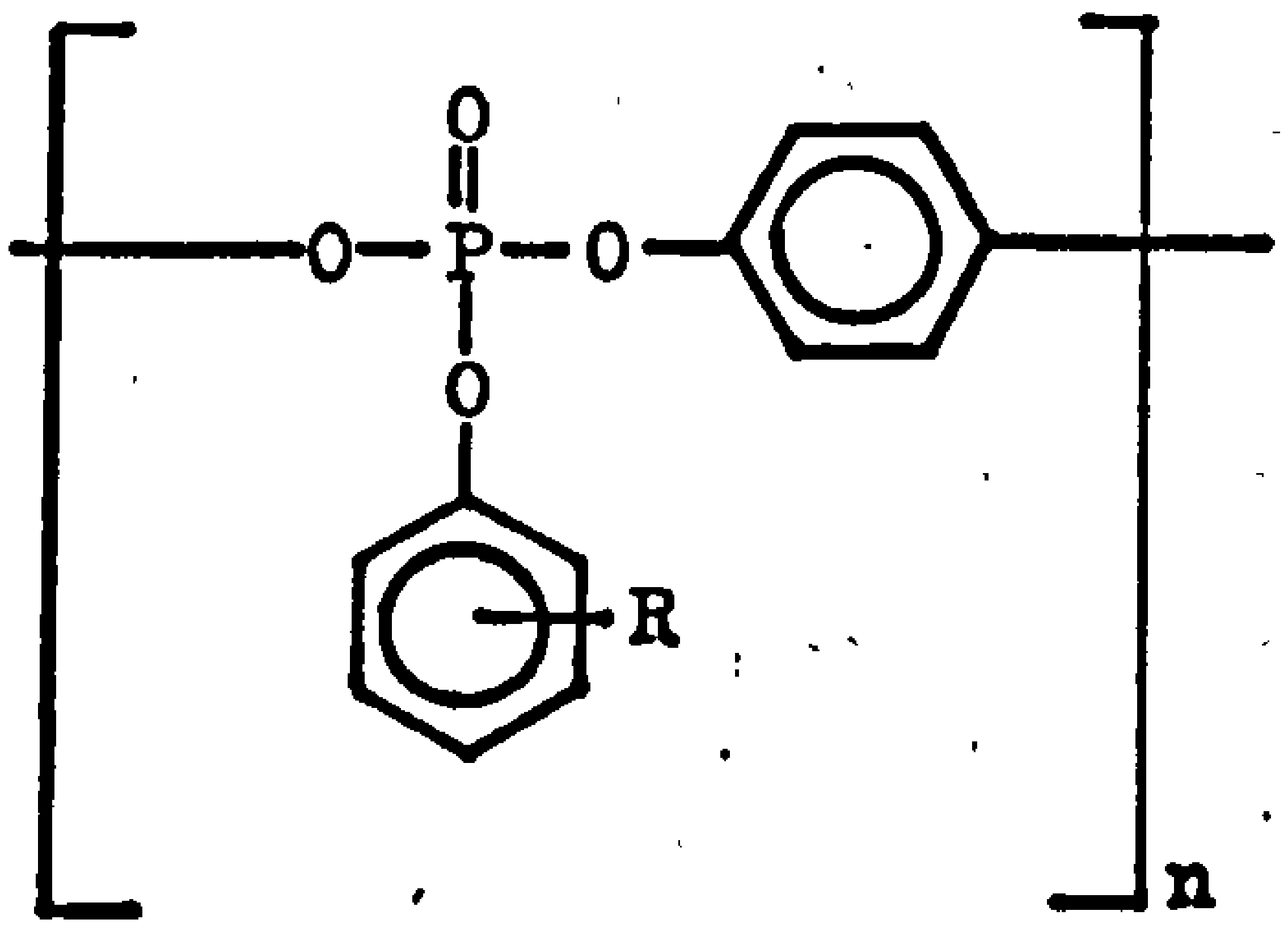
(XV)



$$n\,RO-\overset{O}{\underset{OR'}{P}}-OR + n\,HO-R''-OH \longrightarrow \left[-R''-O-\overset{O}{\underset{OR'}{P}}-O-\right]_n + 2n\,ROH$$

R, R′, R″ = aryl, or alkyl.

(XVI) The preparation of a poly(organophosphate) from a tri-organophosphate ester by transesterification.



R = H, phenyl,
substituted phenyl,
alkyl, or halogens.

(XVII) "Phoryl" resin.

I.C.I. Ltd. eventually abandoned "Phoryl" resins, probably because of their low softening points ($< 390^{50}$) and inadequate heat hardening properties.

1.8.4. Thermosetting organophosphate polymers.

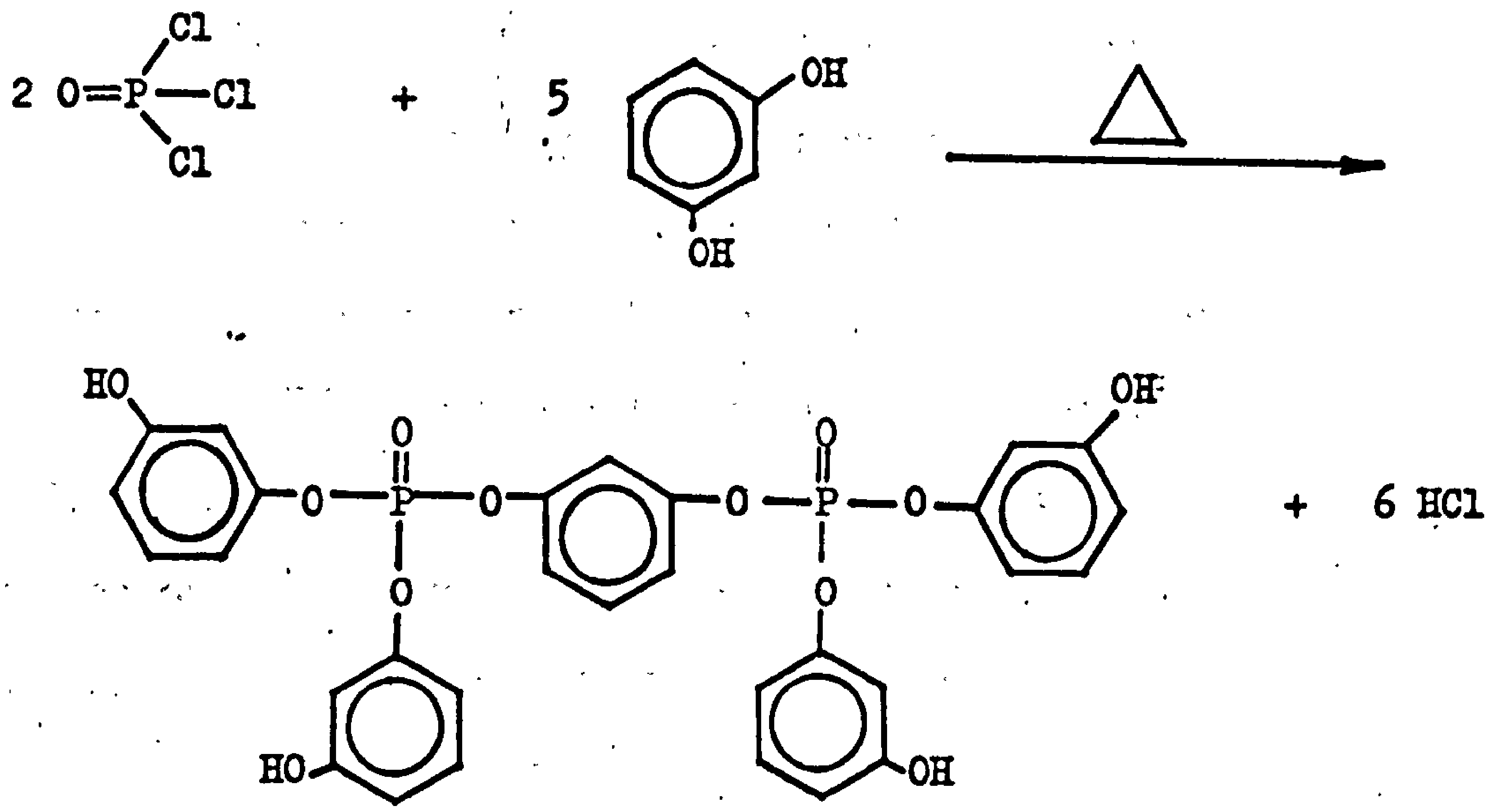
Over about the last twenty years Redfarn and Bedford, consultant polymer chemists, have been investigating organophosphate and organoborate polymers with a view to preparing high temperature resistant plastics with useful mechanical properties. Thermosetting organophosphate and organoborate polymers have been prepared and some reported.[51] The resins contained phenolic hydroxyl groups and were cured by formaldehyde donors, such as paraformaldehyde and hexamethylene tetramine (hexamine).

The organoborate polyesters gave cured products that were hydrolytically unstable and therefore of no commercial value, whilst the organophosphate polyesters resisted hydrolysis.

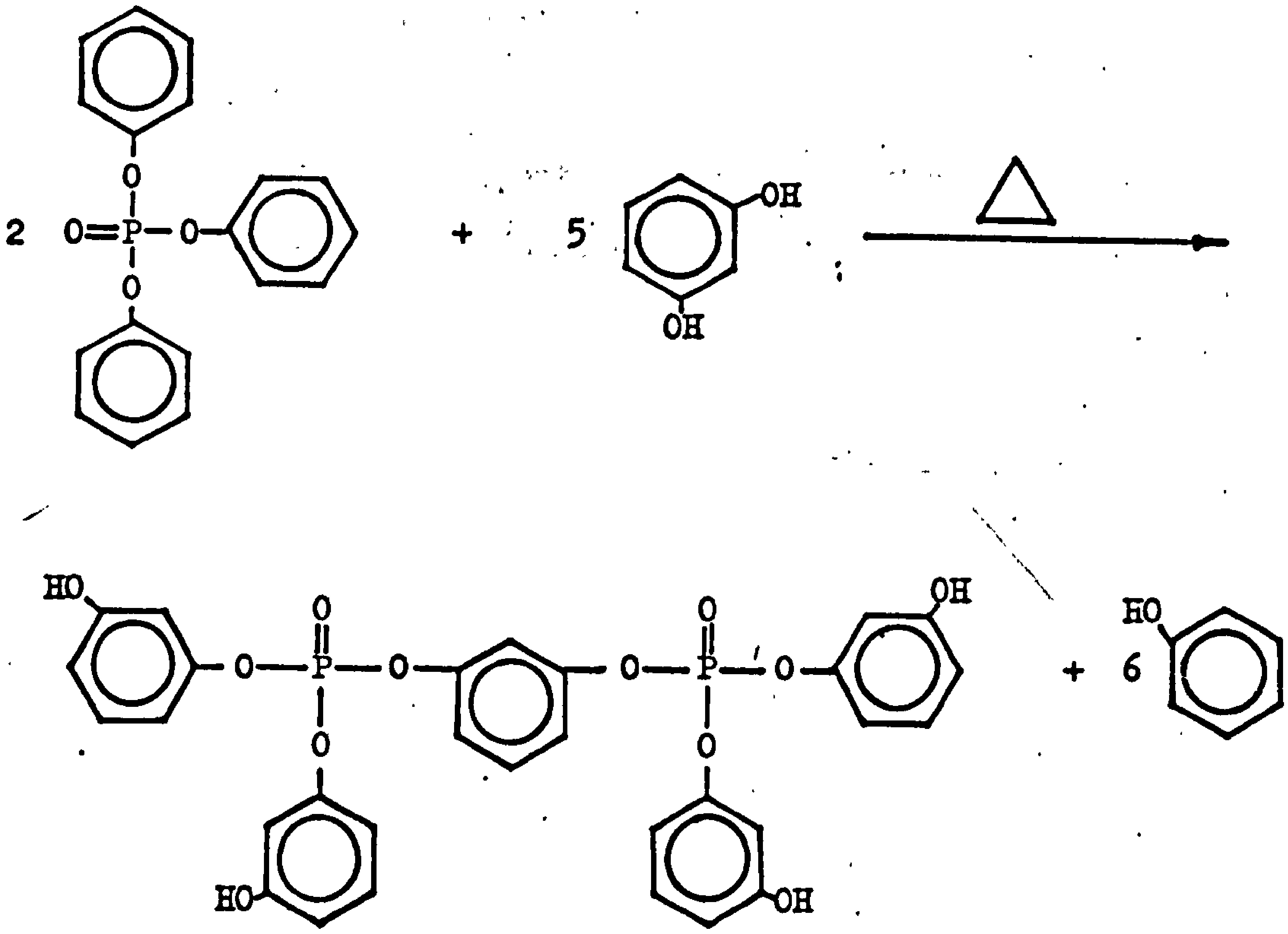
Generally, the organophosphate polyesters were prepared from an inorganic phosphoric acid or polyhalide thereof, or phosphoryl chloride, by heating with a polyhydric phenol in the melt phase or in solution. The resins contained some free unreacted phenolic hydroxyl groups (e.g. $\underline{\overline{\text{XVIII}}}$) to activate the benzenoid rings present for subsequent curing with formaldehyde donors. The use of dihydric phenols may be expected to minimise the chances of side reactions occurring.

Copious evolution of hydrogen chloride during the preparation of the resins and the difficulty in removing all traces of hydrogen chloride from the product is a disadvantage with this method of preparation.

Redfarn[52] adopted a new approach to the preparation of the resins by employing a transesterification reaction (e.g. $\underline{\overline{\text{XIX}}}$). Phenol is evolved as a by-product and is preferable to hydrogen



(XVIII) The preparation of a thermosetting organo-phosphate resin from phosphoryl chloride and resorcinol.



(XIX) The preparation of a thermosetting organo-phosphate resin from tri-phenyl phosphate and resorcinol by transesterification.

chloride, since traces of phenol in the product will also react with formaldehyde donors.

A suitable dihydric phenol is resorcinol, which will react readily with tri-phenyl phosphate at high temperature in the presence of a condensation catalyst. A resorcinol: tri-phenyl phosphate ratio of 5:2 gives an excellent resin, whose idealised structure is shown, (XIX). Increasing this ratio to 3:1 would theoretically not yield a polymer and decreasing it below 5:2 would lower the ratio of hydroxyl: phosphate groups present in the resin, which would lower the potential cross-link density in the cured resin. Resorcinol is meta hydroxy substituted and therefore has a high reactivity towards formaldehyde donors.

Both resorcinol and tri-phenyl phosphate are commercially available and are relatively inexpensive, which makes them attractive as raw materials.

Until the advent of Redfarn's patent[51] no satisfactory curing organophosphate polymers had been reported.

1.9. Discussion of the predicted high temperature resistance of cured resorcinol phosphate resin.

1.9.1. Introduction.

The idealised structure of resorcinol phosphate resin prepared from tri-phenyl phosphate and resorcinol (mole ratio = 2:5) and cured with hexamine is shown (XX).

The presence of $-CH_2-NH-CH_2-$ cross-links is not considered in this discussion, although it is possible they may occur to some extent.

To assess contributions to the high temperature resistance of the cured resin each part of its structure will be theoretically evaluated separately. The moieties present are:

Aromatic rings.

Phenolic hydroxyl groups.

$\equiv$ P-O-C aromatic.

$\equiv P=O$

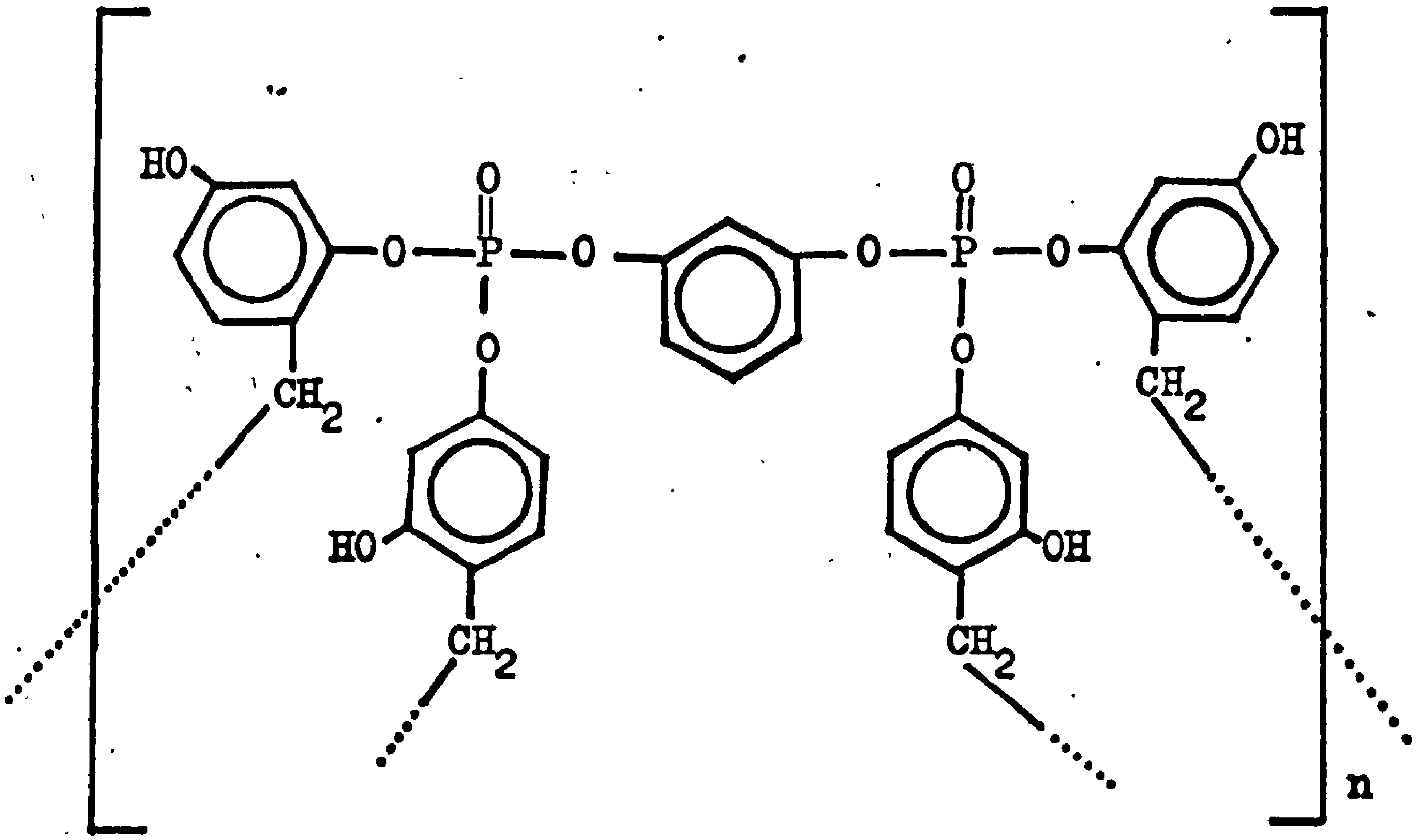
$-CH_2-$ (methylene bridges).

1.9.2. Aromatic rings.

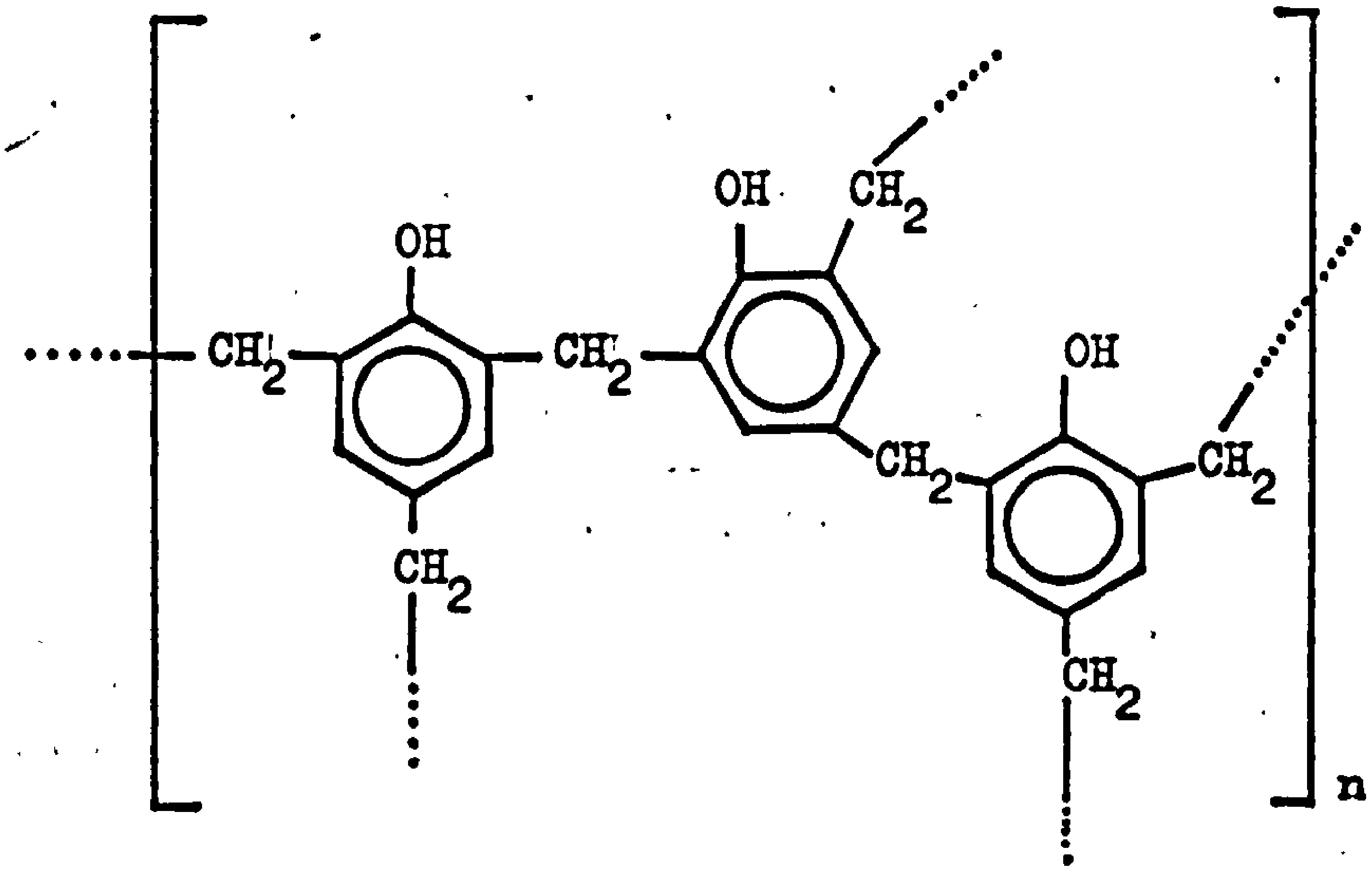
The aromatic rings in resorcinol phosphate resin are a part of the backbone of the polymer structure and would be expected to have high thermal and thermo-oxidative resistance (see sections 1.6.1. and 1.6.2.).

1.9.3. Phenolic hydroxyl groups.

The presence of substituents on an aromatic ring may tend to lower the thermal and thermo-oxidative stability of the structure. Madorsky and Straus[53] compared the high temperature stabilities of poly(p-phenylene) (I) and a cured phenol-formaldehyde resin (XXI) by thermogravimetry and found that poly(p-phenylene), which has no substituents on the benzene rings, had a higher



(XX) The idealised structure of a hexamine cured resorcinol phosphate resin.



(XXI) The idealised structure of a hexamine cured phenol-formaldehyde resin.

resistance to degradation than the cured phenolic resin, which has hydroxyl and methylene substituent groups.

Resorcinol phosphate resin is cured at about 475. In conventional two stage phenolic resins curing is effected at about 430 and at temperatures of 475 some decomposition may also occur to form quinone methide structures (XXII). Similar reactions cannot be precluded in the curing of resorcinol phosphate resin at 475.

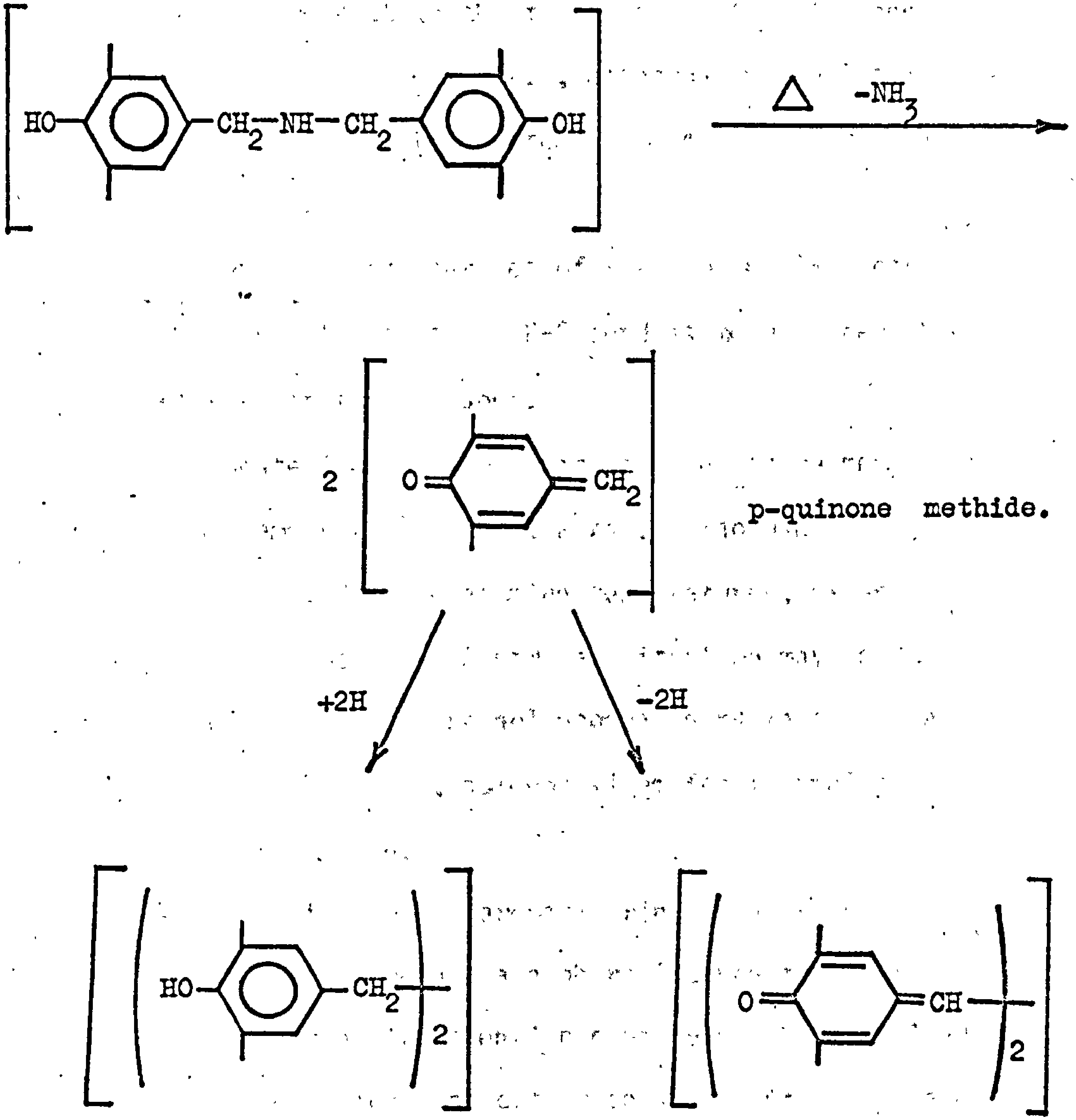
Quinone structures are also known to occur in the thermo-oxidative breakdown of cured phenolic resins (XXIII) after ageing in air at 473 and have been detected by infra-red spectroscopy.[55]

From the point of view of the resistance to bond dissociation the thermal stability of the phenolic hydroxyl group would be expected to be high, since the O-H and C-O bond energies are very high (table 1.6.1.1.). In the thermal breakdown of cured phenolic resins loss of -OH groups, as detected by the evolution of benzene or alkyl benzenes, does not occur below about 725[55].

There is a possibility that etherification may occur between phenolic hydroxyl groups on the resin at high temperatures, although the rigidity of the cross-linked resin structure would minimise the likelihood of this happening. Any phenolic ether links produced would serve to aid cross-linking and would be expected to have good thermal and thermo-oxidative stability (c.f. commercial poly(imides), such as Kapton H film,[56] which contains diphenylene ether groups (table 1.7.1.) and can be used continuously in air at 525).

1.9.4. P-O-C aromatic groups.

There is little information on the high temperature stability of this group.



(XXII) The formation of p-quinone methides and their possible reaction products in a two stage phenolic resin. (o-Quinone methides may also be formed).[54]

Thermogravimetry has shown that "Phoryl 3" resin, which has 4-octylphenyl groups pendant to the main chain[21] (XVII), does not degrade below 550 (see section 3.5.2.), although in the literature "phoryl" resins are reported to be stable up to 575 under unspecified conditions.[37]

Comparison of the bond energies of the C-O and P-O bonds (table 1.6.1.1.) indicates that the P-O bond is more susceptible to thermal rupture than the C-O bond.

As the phosphate link is inorganic, bond exchange mechanisms may occur at high temperature. Thus, although inorganic poly(phosphates) do not degrade at high temperatures, extensive bond exchange probably occurs. A similar situation may be true for the phosphate links in resorcinol phosphate resin i.e. the phosphate groups may be labile, but not sites for thermal or thermo-oxidative degradation.

Although bonded to organic aromatic rings the P-O-C bonding may be expected to retain a high resistance to thermal degradation. For example, tri-phenyl phosphate may be distilled at 683 without decomposition, indicating considerable short term stability.[57]

1.9.5. P=O groups.

This group is present in inorganic phosphates, which withstand extremely high temperatures without decomposition, although bond exchange processes will involve this group. The phosphorus atom in compounds containing the P=O group is in its ultimate oxidation state of +5. No oxidation of the phosphate links in resorcinol phosphate resin would be expected, even if the resin were pyrolysed to red heat.

1.9.6. $-CH_2-$ (methylene) bridges.

The presence of methylene cross-links in cured resorcinol phosphate resin will impart considerable rigidity to the resin structure i.e. the heat resistance of the cured resin would be expected to be very high.

Methylene bridges form a major part of the structure of cured phenol-formaldehyde resins. It is reasonable to assume that the high temperature stability of the methylene bridges in a cured phenol-formaldehyde resin would be similar to that of the methylene bridges in cured resorcinol phosphate resin.

Mass spectrographic analysis of the high temperature degradation products of phenol formaldehyde resin has shown that chemical breakdown occurs primarily at the methylene bridges. Three stages of breakdown have been identified[58]:

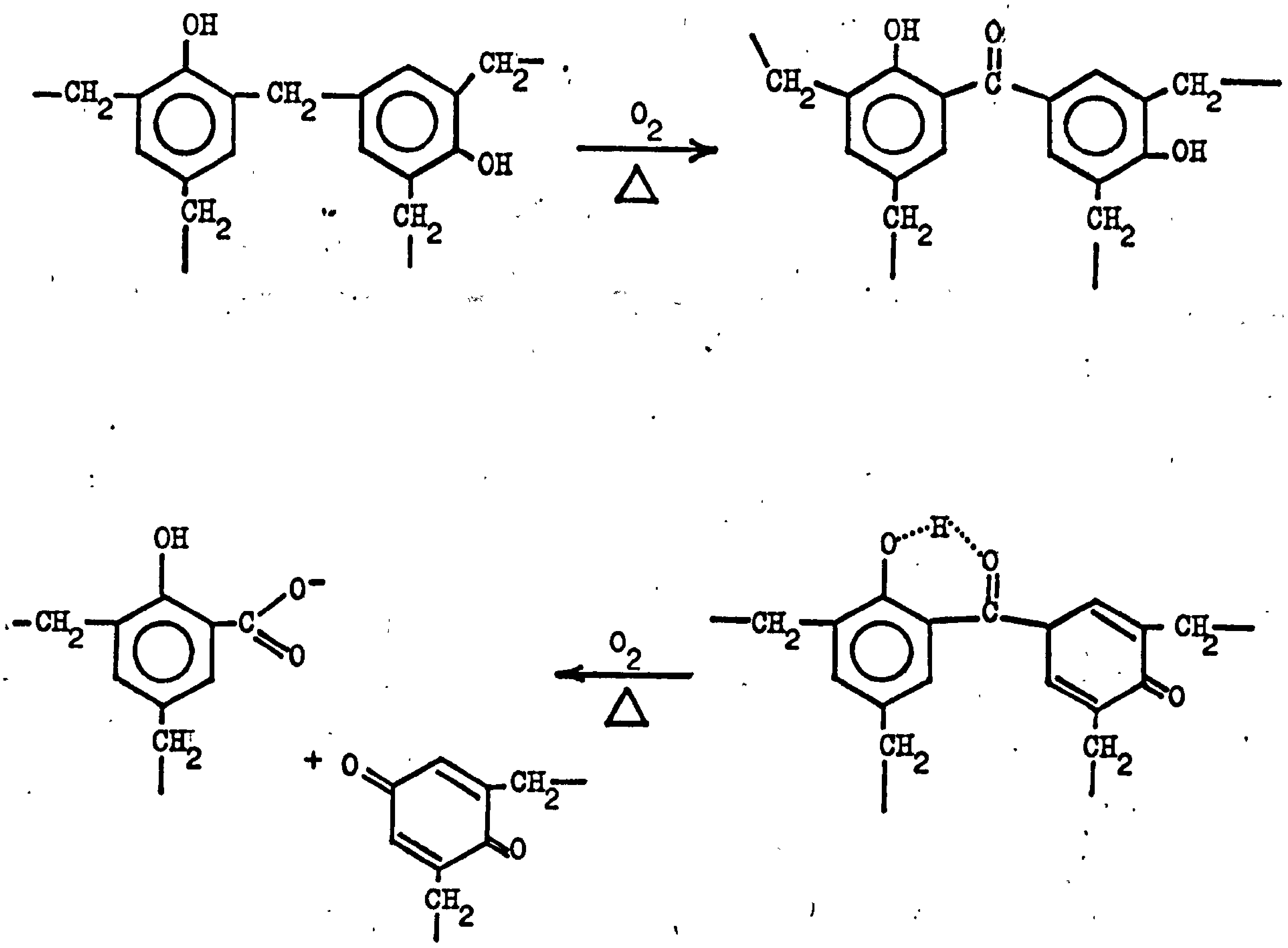
1. Up to 725. Post-hardening and oxidation, leading to loss of water and formaldehyde.

2. 725 - 875. Oxidation, leading to the evolution of carbon dioxide, carbon monoxide and water. Thermal bond dissociation, leading to phenol and homologues of phenol.

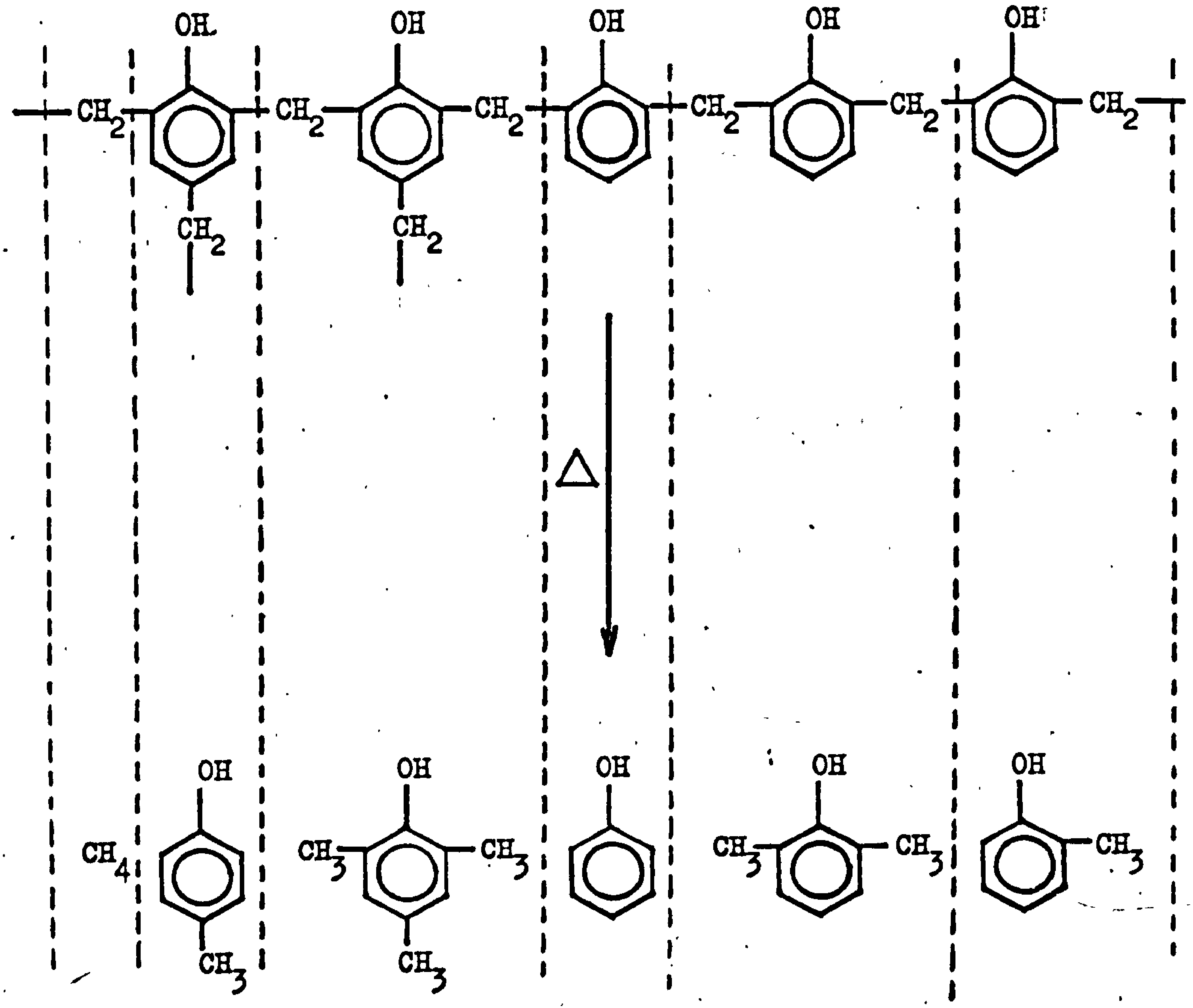
3. Above 875. Coke formation, accompanied by loss of carbon dioxide and hydrogen by thermal and thermo-oxidative degradation.

Mechanisms have been proposed for the thermal[58] and thermo-oxidative[59] degradation of cured phenol-formaldehyde resins (XXIII and XXIV) and thermo-oxidation is the predominant mode of breakdown between 495 and 1275.[55]

Thermo-oxidation may therefore be expected to be a major contributor to the degradation of cured resorcinol phosphate resin at temperatures above about 475. Oxidation of the methylene bridges would be expected to occur initially with subsequent breakdown of the resin structure by a mechanism similar to that occurring in phenol-formaldehyde resin (XXIII). At temperatures above about 725 thermal breakdown of the methylene bridges may also be expected. Oxygenated, carboxylated and alkylated low



(XXIII) The thermo-oxidative degradation of phenol-formaldehyde resin.



(XXIV) The thermal degradation of phenol-formaldehyde resin.

molecular weight aryl phosphates may be among the degradation products formed.

The maximum service temperatures for cured phenol-formaldehyde resins are variously reported. Techel[60] has suggested that conventional phenol-formaldehyde resins can withstand 475 for several years. Many other sources report indefinite service at 450, several hundred hours' service at 475 and only a few hours service above 475. The modified phenolic resin, Xylok 210 resin (table 1.7.1.), which also contains methylene bridges, is reported to operate at 525 for at least 1000hr.[61] Possibly the reduced number of hydroxyl groups per benzene ring in the cured Xylok resin reduces the number of sites in the structure that can be oxidised by the mechanism (XXIII) (see section 3.3.9.).

By comparison with the performance of these phenolic resins it is reasonable to expect cured resorcinol phosphate resin to be serviceable for extended periods at up to 525, since in these resins a considerable number of phosphate links are present in addition to the thermo-oxidatively unstable methylene bridges. i.e. cured resorcinol phosphate resin can be considered as a cured phenol-formaldehyde resin in which a high proportion of methylene links have been replaced by phosphate links. From the point of view of thermo-oxidation the phosphate links may be expected to be considerably more stable than methylene bridges. By comparison with cured phenol-formaldehyde resin the predominant and primary cause of degradation in resorcinol phosphate resin would probably be thermo-oxidation.

1.10. The objectives of the research.

The objective of this work was to prepare high temperature resistant thermosetting organophosphate resins, which could be moulded at temperatures $\leqslant$ 475 using conventional equipment common to the processing of phenol-formaldehyde resins. Special emphasis was placed on the use of readily available commercial monomers in an attempt to keep the cost of the resins at a competitive level.

From the earlier work of Redfarn, the most suitable method for preparing thermosetting organophosphorus resins was considered to be that of transesterification between tri-organo phosphate esters and polyhydric phenols to produce polymers containing phenolic hydroxyl groups.

After the adoption of a suitable resin system and curing agent the evaluation of the high temperature resistance of moulded composite test pieces was considered necessary to provide the first step in assessing the commercial viability of the material. A programme was therefore contrived to involve the pilot scale synthesis of the resin, the preparation of a large batch of moulding powder from the resin compounded with chrysotile asbestos, the moulding of the composite into test specimens and finally the isothermal ageing of the mouldings in air at 525 with subsequent testing for loss in weight and changes in flexural strength.

A product of high temperature resistance sufficient to place it in zone 6 of Rosato's chart (diagram 1.1.1.) was considered a desirable prerequisite for the commercial exploitation of the system.

2. EXPERIMENTAL DETAILS

2.1. The preparation of resins by the transesterification of polyhydric phenols with tri-phenyl phosphate

2.1.1. Introduction

In an attempt to prepare a range of thermosetting organo phosphate resins by transesterification certain polyhydric phenols have been heated with tri-phenyl phosphate in the presence of a catalyst.

The reactants were heated in a flask, fitted with a still head, air condenser and receiver. Transesterification is an equilibrium process and in order to aid the completion of the reaction slightly reduced pressure was applied to the distillate receiver to facilitate the removal of phenolic by-products from the reactant melt. The reactants were heated rapidly to the reaction temperature and usually there was a short induction period before a phenol distilled over. A slight excess of up to 10% by weight of the polyhydric phenol was employed to allow for slight losses carried over in the distillate.

Induction and reaction times for these preparations were taken from the time the melt temperature reached 475.

2.1.2. The preparation of resorcinol phosphate resin

Materials:	16.3g Tri-phenyl phosphate (0.05 mole)	
	15.1g Resorcinol (0.125 mole +10%)	
	0.2g Zinc oxide	
Conditions:	Max.melt temperature	~ 560
	Max.still head temperature	~465
	Induction period	~ 40 min
	Reaction time (total)	~3 hr

Product: A soft, clear, brown resin was obtained, which cured readily when heated with 10% of added hexamine. The resin was soluble in acetone, alcohol, aqueous sodium hydroxide, aqueous ammonia and other organic solvents, but was insoluble in water.

Distillate:	Yield	12.5 g	
	Resorcinol content	~13.6% (~1.7g)	
	Expected yield of distillate	14.1g phenol 1.4g resorcinol	15.5g

2.1.3. Attempted preparation of a hydroquinone phosphate resin

Materials: 16.3g Tri-phenyl phosphate (0.05 mole)
15.1g Hydroquinone (0.125 mole + 10%)
0.2g Zinc oxide

Conditions:	Max.melt temperature	555
	Max. still head temperature	480
	Reaction time (total)	3hr 20 min

Under these conditions the mixture was a homogeneous liquid, but hydroquinone was sublimed from the melt.

Product: A non-resinous, pale brown liquid resulted, containing unchanged hydroquinone.

Distillate:	Yield	7.0g	
	Hydroquinone content	8.9% (0.6g)	
	Expected yield of distillate	14.1g phenol 1.4g hydroquinone	15.5g

A weighed sample of the distillate was extracted with benzene to give two fractions. One fraction was soluble in benzene and the other was insoluble. The insoluble fraction, which was hydroquinone, was dried and weighed to determine the proportion of hydroquinone in the distillate.

2.1.4. Attempted preparation of a di(hydroxyphenyl) sulphone phosphate resin

Materials:	16.3g Tri-phenyl phosphate	(0.05 mole)
	33.4g Di(hydroxyphenyl) sulphone	(0.125 mole + 7%)
	0.2g Zinc oxide	
Conditions:	Max.melt temperature	575
	Max.still head temperature	440 (generally 325-340)
	Total reaction time	7.5 hr

The mixture became homogeneous at about 510 and distillation began at about 555. After 7.5 hr the melt suddenly frothed up, white vapours were evolved and distillation became more rapid.

Product: A hard, dark, brittle solid was obtained, which softened at about 370 and had an odour of phenolic ethers. In boiling water the product became "spongey" and disintegrated. After standing the product in cold water for 12 hours SO_2 gas was detected. With 10% added hexamine the product did not cure when heated at about 435 on a hot plate.

The solid product was only partially soluble in hot 10% caustic soda and in warm acetone, but dissolved in 0.880 ammonia solution.

Distillate:	Yield	13.9g	
	Expected yield of distillate	14.1g phenol	
		2.2g di(hydroxyphenyl) sulphone	16.3g

The fresh warm distillate had an odour of SO_2 gas.

2.1.5. Attempted preparation of a phloroglucinol phosphate resin

Materials: 16.3g Tri-phenyl phosphate (0.05 mole)

12.8g Phloroglucinol dihydrate (0.075 mole + 5%)

0.1g Zinc oxide

The reactants were ground together before heating.

Conditions:

Max.melt temperature	575
Max.still head temperature	385
Reaction time (total)	3hr 40min

Product: A black solid and a dark, non-resinous liquid resulted.

Distillate:

Yield	3.2g	
Expected yield of distillate	2.3g water 14.1g phenol 0.5g phloroglucinol	16.9g

The preparation was repeated on a larger scale with stirring under nitrogen, keeping the melt temperature below 550. A similar two phase, non-resinous product was obtained, together with a deep yellow two phased distillate (probably a phenol/water mixture).

2.1.6. Attempted preparation of a pyrogallol phosphate resin

Materials: 16.3g Tri-phenyl phosphate (0.05 mole)

14.8g Gallic acid monohydrate (0.075 mole + 5%)

0.2g Zinc oxide

Conditions: Two runs, a and b, were carried out at different temperatures.

	a	b
Max.melt temperature	~ 595	~ 515
Max.still head temperature	436	431
Induction period (hr)	1.5	-
Reaction time (total) (hr)	4.5	2.75

Products: Both runs, a and b, gave non-resinous, soft, black solid products. The product from run b gave a brown solution when washed in hot water and the washed material was infusible at about 455

Distillates:

	a	b
Yield(g)	9.8	6.3

Expected yield of distillate for runs a and b.	14.1g phenol 1.3g water 0.5g pyrogallol	15.9g

2.2 Resin preparation by transesterification with tri-alkyl phosphates

2.2.1. Introduction

The method used in these preparations was similar to that used with tri-phenyl phosphate, unless otherwise stated, but the air condenser was replaced by a Liebig condenser.

Reaction times were measured from the commencement of heating of the materials, unless otherwise stated.

2.2.2. The preparation of resorcinol phosphate resin from tri-methyl phosphate

Materials:	35g Tri-methyl phosphate	(0.25 mole)
	76g Resorcinol	(0.628 mole + 10%)
	1.1g n-butyl titanate	

Conditions:	Max. melt temperature	465	Slow reaction	525
	Max. still head temperature	335	so	365
	Reaction time up to		then heated	
	the max. melt temperature (hr)	3.25	thus	4

Product: A dark brown resin resulted, which was a brittle solid when cool. The resin melted in boiling water and was soluble in acetone. With 10% added hexamine the resin cured in about 25 seconds at 450 on a hot plate.

Distillate: A few ml of distillate were collected. The liquid had a phenolic and an ethereal odour and tests showed phenolic compounds to be present.

2.2.3. The preparation of resorcinol phosphate resin from tri-n-butyl phosphate

Materials:	13.3g Tri-n-butyl phosphate	(0.05 mole)
	13.8g Resorcinol	(0.125 mole + 10%)
	0.3g n-butyl titanate	

Conditions:	Max. melt temperature	465	No apparent reaction. Cooled and reheated thus:	485
	Max. still head temperature	325		365
	Reaction time up to and at the max. reaction temperature (hr)	1.33		2.75

Product: A brown, brittle, fusible resin was obtained, which cured readily with 10% added hexamine at about 455 on a hot plate.

Distillate: A few ml of a two phased liquid were collected. The distillate had a pungent odour not exactly similar to that of butanol.

2.2.4. The preparation of resorcinol phosphate resin from tri-octyl phosphate

Materials: 10.9g Tri-octyl phosphate (0.025 mole)
7.6g Resorcinol (0.0625 mole + 10%)
~0.25 ml n-butyl titanate

Conditions:	Max. melt temperature	465	No apparent reaction, so temperature raised thus:	535
	Max. still head temperature	325		385
	Reaction time up to the max. reaction temperature (hr)	1.25		0.6

Product: A dark brown, brittle, fusible resin was obtained, which cured in 18 seconds with 10% added hexamine at about 445 on a hot plate.

Distillate: A few ml of a two phased liquid were collected. The distillate had an ethereal odour and contained at least three distillable fractions.

2.2.5. Attempted preparation of di(hydroxyphenyl) sulphone phosphate resin from tri-methyl phosphate

Materials: 7.0g Tri-methyl phosphate (0.05 mole)
34.4g Di(hydroxyphenyl) sulphone (0.125 mole + 10%)
20 ml 1,4 - dioxan
0.2g Zinc oxide

1,4 - dioxan solvent was added to achieve a homogeneous solution, since the di(hydroxyphenyl) sulphone was very bulky compared to the tri-methyl phosphate.

Conditions: The solution was heated at a temperature under 373 for 1hr 45min and then refluxed for two hours. Half the solvent was distilled off and then the mixture heated for one hour up to 450.

Product: A non-resinous, wet, crystalline material resulted.

Distillate: 10 ml of distillate were collected, which was probably entirely 1,4-dioxan.

2.2.6. Attempted preparation of pyrogallol phosphate resin from tri-n-butyl phosphate and gallic acid

Materials: 106.4g Tri-n-butyl phosphate (0.4 mole)
118.4g Gallic acid monohydrate (0.6 mole + 5%)
1.2g Zinc oxide

Conditions: The reactants were heated, with stirring, under nitrogen. As the temperature was raised water was initially evolved and at about 445 frothing began as CO_2 was produced. The frothing continued throughout the reaction.

Max.melt temperature	505
Max.still head temperature	397
Reaction time after the onset of frothing	50 min

Product: A black, brittle solid product resulted. In boiling water the product softened and a small fraction dissolved to give a brown solution. A sample of the product gave a rubbery material when heated at about 460 with 10% added hexamine for 1 minute, but the product material was not stable in boiling water.

Distillate:	Yield	33.3g	
	Expected yield of distillate	11.25g water 89g butanol 18.8g pyrogallol	119g

A two phased distillate was obtained, with a clear yellow upper layer and a white, cloudy lower portion. The liquid had a pungent "butyl" odour. At least three distillable fractions were present in the yellow phase, which was also found to contain phosphorus compounds.

2.3. Attempted preparation of a di(hydroxyphenyl) sulphone phosphate resin using phosphoryl chloride

Materials: 6.25g Di(hydroxyphenyl) sulphone (0.025 mole)
1.54g Phosphoryl chloride (0.01 mole)
1,4 - dioxan

Conditions: A solution of phosphoryl chloride in 1,4-dioxan was carefully added over a period of 1 hour to a refluxing solution of di(hydroxyphenyl) sulphone in 1,4-dioxan. The mixture was further refluxed for 2 hr 40 min. HCl gas was evolved throughout the reaction. At the end of the heating time the effluent gases were tested for SO_2, which was found to be present.

Product: A dark, almost black, solution resulted, together with some black solid. After removal of the 1,4 - dioxan a black, tacky, non-resinous mass was obtained, which melted at about 475-495. The product was soluble in hot water and in 10% aqueous sodium hydroxide. With 10% added hexamine the product thickened slightly, but did not cure, on a hot plate at 495. A stiff rubbery product was, however, obtained by heating the product at 475 with a little α,α'-dimethoxyxylylene and a trace of $ZnCl_2$ catalyst.

2.4. The effect of catalysts on the reaction between tri-phenyl phosphate and resorcinol

Mixtures of tri-phenyl phosphate (1 mole %) and resorcinol (2.5 mole % + 10%) with various catalysts were heated under distillation conditions with slightly reduced pressure applied to the apparatus. Reaction times were estimated roughly from the time the reactants had reached 475 to the time when 12.5 g of distillate had been removed. The reaction temperature employed was 555-560.

2.5. The study of potential curing agents for resorcinol phosphate resin.

Small samples of resorcinol phosphate resin, prepared from tri-phenyl phosphate (1 mole %) and resorcinol (2.5 mole % + 10%), were heated and spatulated with various compounds on a hot plate. The hot products were examined for signs of curing, decomposition or the evolution of volatiles.

2.6. Examination of the hydrolytic and high temperature stability of resorcinol phosphate resin cured with iso-propyl titanate

2.6.1. Hydrolytic stability

Materials: 2g Resorcinol phosphate resin
0.9 g Iso-propyl titanate
0.5 g Chrysotile asbestos
The resin was prepared from tri-phenyl phosphate (1 mole %) and resorcinol (2.5 mole % +10%).

Method: The materials were thoroughly mixed and then cured at about 445 for 30 minutes to give a hard, brittle brown pellet. On boiling in water for 10 minutes the pellet disintegrated to a sticky resin and asbestos.

2.6.2. High temperature stability

Materials: 2 g Resorcinol phosphate resin*
1.1 g Iso-propyl titanate.

Method: The iso-propyl titanate was stirred into the melted resin and the mixture spread onto glass slides. After heating in air at 455-475 for 116 hours a hard, black, brittle solid was obtained. Duplicate samples showed a weight loss of 33.75% and 33.95% after heating.

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* *The same resin as described in section 2.6.1.*

2.7. The examination of the composition and structure of resorcinol phosphate resin

2.7.1. Fractional distillation of the distillate from the resin preparations

Weighed portions of the phenolic distillate were fractionally distilled and the vapours evolved at up to 463 collected. The residue was then cooled and reheated to collect any further small fractions distilling over at up to 463. Assuming the distillate to be phenol (b.pt. 454) and the residue resorcinol (b.pt. 549), the resorcinol content of the prepared resin was estimated and expressed in terms of a tri-phenyl phosphate: resorcinol ratio.

2.7.2. Solvent extraction of the resin with acetone

Solvent extraction with acetone was carried out on the prepared resins to determine the amount of insoluble material present. Carefully prepared resins dissolved completely in acetone, whereas over reacted products gave a dark brown residue after extraction. One resin, which had been prepared at too high a temperature and was a dark, brittle solid with an odour of phenolic ethers, gave about 20-25% insoluble matter on extraction with acetone.

Only resins which were completely soluble in acetone were used in the experimental work.

2.7.3. The steam distillation and toluene extraction of the resorcinol phosphate resin blend

2.7.3.1. Steam distillation:

A weighed amount of the resorcinol phosphate resin blend was steam distilled for several hours and the distillate extracted with ether. After removal of the ether a trace residue of phenolic compounds was obtained, which weighed less than 0.5% of the total resin weight.

2.7.3.2. Extraction with toluene:

A weighed amount of the resorcinol phosphate resin blend was refluxed with 25 ml of toluene for 2 hours and the solvent was then decanted. After further refluxing with 50 ml. of toluene for 30 minutes and again decanting the combined extracts were evaporated to dryness. A yellow-brown resinous residue resulted, which weighed 1.8% of the total resin weight. The residue contained phosphorus compounds and cured when heated with hexamine.

2.7.4. Infra-red spectroscopy

Samples of the dried resin were ground with KBr. and pressed into discs. Spectra were recorded from the discs using a Unicam SP200 Infra-Red Spectrophotometer.

The spectra were interpreted by using published tables[62,63] and by comparison with infra-red spectra from the literature[64,65] and from model compounds.

2.7.5. N.M.R. spectroscopy

A sample of resorcinol phosphate resin was dried in acetone solution over anhydrous $MgSO_4$. After evaporating off the acetone in a warm oven a small specimen of the dried resin was dissolved in deuteroacetone and the N.M.R. spectrum recorded, using a Varian T60 N.M.R. spectrophotometer. D_2O exchange was carried out on the same sample and the N.M.R. spectrum was again recorded.

2.7.6. Quantitative analysis of resorcinol phosphate resin for % P content and molecular weight determination

The phosphorus content and molecular weight of a sample of resorcinol phosphate resin were determined at The Division of Chemical Standards at The National Physical Laboratory, Teddington, Middlesex.

2.8. Thermogravimetry

Thermosetting resin samples were ground or mixed with curing agent and heated on a hot plate to obtain cured specimens. After grinding to a coarse powder the specimens were post cured by heating in an oven at a suitable temperature to expel residual volatiles and ensure complete reaction.

Before testing, the thermoset resins and other samples were ground to pass through a 149-125 µm sieve. Approximately 80 mg samples of the finely ground powders were placed in a Stanton TR-02 Thermogravimetric Balance and heated at a rate of increase in temperature of 4-4.5 Kmin^{-1} to obtain thermogravimetric curves. Blank runs, using Al_2O_3, were also carried out to obtain a buoyancy correction curve, which was used to correct the thermogravimetric curves of the tested samples. In all cases about 80 mg of Al_2O_3 was used with the reference thermocouple in the thermogravimetric balance.

2.9. The large scale synthesis of resorcinol phosphate resin for high temperature stability studies

Materials: 1630g Tri-phenyl phosphate (5 mole)
1512.5g Resorcinol (12.5 mole +10%)
15g Zinc oxide

Method: The reactants were heated together in a 51 flanged reaction vessel, fitted with a short, lagged reflux column attached to a long air condensor. The mixture and apparatus was flushed with O_2 free N_2 before and throughout the reaction. During the transesterification process the still head temperature was kept as close to 454 (the b.pt. of phenol) as possible to minimise resorcinol loss. The still head temperature was found to increase with

1. increase in stirrer speed,
2. increase in nitrogen flow through the apparatus,
3. increase in lagging around the reflux column and
4. decrease in the length of the reflux column.

After preparing the resins they were washed by paddling with six successive 1.5 - 21 volumes of boiling water, decanting after each aliquot. The resin was then dried by heating at about 400 until effervescence had practically ceased.

Two batches of resin were prepared (a and b) and the conditions are shown in table 2.9.1.

A resin blend was prepared from products a and b and a commercially prepared resorcinol phosphate resin.

Table 2.9.1.

Preparation of resorcinol phosphate resin.

Batch	a	b
Reaction time (hr)*	5	4
Induction time (hr)**	1.75	1
Time to reach 475 (hr)	1.5	2
Still head temp.	455-485	455-460
Flask temp.	540	540
Reflux column used	Empty	Filled with ceramic cylinders
Distillate yield (kg)	1.32	1.459
Resorcinol content of distillate (%)	22.6	24.5
Resin yield (kg)	1.5-1.6	1.2
Resin cured with hexamine	Yes	Yes
Estimated ratio of triphenyl phosphate: resorcinol.	1:2.2.	1:2.1

** and ** Time from point when reactants reached 475 to point*

*when * the reaction was ceased.*

*and ** the distillation began.*

Thus a mixture of

1.13 kg of resin a.

1.20 kg of resin b.

2.00 kg of commercially prepared resin*

were melted together and thoroughly blended.

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*ex. *Hilton Davies Chemicals Ltd. Tri-phenyl phosphate: resorcinol ratio reported to be 1:2.5.*

2.10. The effect of cross-linking on the high temperature stability of resorcinol phosphate resin

Two test samples were prepared in duplicate as follows:

Two approximately 5 g samples of resorcinol phosphate resin blend were placed in two Petri dishes, which had been dried to constant weight.

A solution of 3 g of resorcinol phosphate resin blend and 0.3 g hexamine in 4 ml of absolute alcohol and 1 ml of water was divided into two aliquots and placed in Petri dishes, which had been dried to constant weight.

The samples were gently raised to about 330 for a short period, followed by longer heating at about 395.

After this pre-ageing treatment, which cured the resin containing hexamine, the samples were subjected to isothermal heating in stages at 460, 520 and 560 in air.

At suitable intervals the samples were cooled in a desiccator and weighed.

2.11. The evaluation of the high temperature stability of resorcinol phosphate resin and P-F novolak resin composites.

2.11.1. The preparation of moulding materials:

Materials:

120 g	Resorcinol phosphate resin blend, or P-F novolak resin.
308 g	5R-21 grade chrysotile asbestos
12 g	Hexamine
2 g	Magnesium hydroxide.

Milling: Milling was carried out on a two roll mill for 4-5 min to obtain a hide. The resorcinol phosphate resin composite was milled at 343-348 and the P-F novolak composite at 338-343. Moulding powder was prepared by disintegrating the cooled hides to pass through a 1190 µm sieve.

5 batches of the resorcinol phosphate resin composite and 4 batches of the P-F novolak resin composite were made.

The flow properties of the composites: The flow properties of the prepared moulding powders were determined using flow discs.[66] An average of 4 measurements of the thickness of the centres of each of the resulting composite discs was taken.

The flow properties of the P-F novolak composite batches were very similar and the batches were blended together. Similarly, the resorcinol phosphate resin composite batches were also blended together.

2.11.2. Moulding of the resin-asbestos composites.

29.2 g portions of dried moulding powder were cold preformed by compression moulding in a test bar mould. The preformed bars were then compression moulded in the same mould at 46.3 MNm^{-2} pressure to give rectangular bars, measuring 11.43 x 1.27 x approximately 0.953 cm.[7] The P-F novolak resin composite bars were made by moulding at 433 ± 5 for 6 minutes and the resorcinol phosphate resin composite moulded at 473 ± 5 for 15 minutes.

2.11.3. Long term testing of the resin-asbestos composites at 525.

6 P-F novolak resin composite bars and 6 resorcinol phosphate resin composite bars were set aside for testing with no prior heat treatment.

36 weighed bars of each type of composite were post cured for 48 hours; at 445 for the P-F novolak resin-asbestos bars and 475 for the resorcinol phosphate resin-asbestos bars. 6 bars of each type of composite were then removed for testing.

The remaining post cured bars were weighed and then heated at 525, removing 6 bars of each type of composite after about 50, 100, 200, 500 and 1000 hours had elapsed. The bars were cooled in a desiccator prior to testing.

Flexural strength measurements[7] were made with a Hounsfield Tensometer with jaws of 10.16 cm span at a constant rate of loading. An average of 6 values was taken per test.

2.11.4. Control tests on cured resorcinol phosphate resin alone and chrysotile asbestos alone at 525.

Moulded bars were prepared by heating an intimate mixture of resorcinol phosphate resin blend and 10% hexamine in a mould at 475 for 15 to 30 minutes under light pressure. The brittle mouldings were broken into sections measuring approximately 3 x 1.3 x 0.95 cm and post cured at 475 for 48 hours, during which time they softened and hardened to irregular shapes. After cooling the specimens were weighed.

Weighed samples of chrysotile asbestos, compacted to bars approximately 11.4 x 1.3 x 1 cm in size, were heated at 475 for 48 hours and then one sample was removed, cooled and weighed.

The cured resorcinol phosphate resin and preheated asbestos samples were then heated at 525 and samples were removed for weighing at the same intervals as were the moulded resin composite bars.

All samples were cooled to room temperature in a desiccator before weighing.

2.11.5. Pyrolysis of resorcinol phosphate resin - chrysotile asbestos composite moulded bars.

4 weighed moulded bars were heated in a furnace under the following conditions:

16 hr at	475
+ 3 hr up to and at	675
+50 min up to and at	875
+1 hr 30 min up to and at	1075
+overnight slowly cooling from 1075	

At 675 much smoke was evolved from the bars. The bars reached dull red heat at 875 and red heat at 1075. After cooling overnight in the furnace the samples were still hot and were cooled finally to room temperature in a desiccator before weighing.

The pyrolysed bars were pale brown with black central cores and possessed cracks and surface blisters.

2.12. The materials used in the experiments.

The materials employed in the experimental work were as follows:

Tri-phenyl phosphate - ex. Geigy (U.K.) Ltd. - Plasticiser grade $\geqslant 98\%$ pure.

Resorcinol - ex. L.B. Holliday and Co. Ltd. - Commercial grade, 99% pure.

Hydroquinone - ex. Dr. Redfarn's Laboratory - Reagent grade.

Di(hydroxyphenyl) sulphone - ex. Yorkshire Chemicals Ltd. 70% 4,4'-isomer and 30% 2,4'-isomer, 97% pure.

Phloroglucinol - ex. Whiffen and Sons Ltd. - Technical grade.

Gallic acid - ex. The British Dyewood Co. Ltd. - Technical grade.

Zinc oxide - ex. Lewis and Burrows Ltd. - B.P. grade.

Tri-methyl phosphate - ex. BDH Ltd. - Technical grade.

Tri-n-butyl phosphate - ex. Geigy (U.K.) Ltd. - Technical grade.

Tri-octyl phosphate - ex. Dr. Redfarn's Laboratory - Technical grade.

α,α'-dimethoxyxylylene - ex. Albright and Wilson Ltd. Technical grade, 70% α,α'-isomer and 30% other isomers.

Xylok 225 resin - ex. Albright and Wilson Ltd. Commercial two stage thermosetting resin.

P-F novolak resin - ex. James Ferguson and Sons Ltd. Nestorite No. 1. phenol-formaldehyde resin.

Hexamine - ex. Griffin and George Ltd. - Reagent grade.

Chrysotile asbestos - ex. Cape Universal Ltd. 5R-21 grade fibre.

Phosphoryl chloride - ex. B.D.H. Ltd. Reagent grade >98% pure.

1,4-dioxan - ex. Griffin & George Ltd. Reagent grade.

n-butyl titanate - ex. Laport Industries Ltd. - Commercial sample.

iso-propyl titanate - ex. Titanium Intermediates Ltd. - Commercial sample.

Potassium bromide - ex. B.D.H. Ltd. - Spectroscopic grade.

Magnesium hydroxide - ex. Brunel University - Reagent grade.

Phoryl 3 resin - ex. I.C.I. Ltd. No longer commercially available.

Dicyandiamide - ex. Dr. Redfarn's Laboratory - Reagent grade.

Thiourea - ex. Dr. Redfarn's Laboratory - Reagent grade.

Hydroxylamine - ex. Dr. Redfarn's Laboratory - Reagent grade.

Oxamide - ex. Griffin and George Ltd. - Reagent grade.

Melamine - ex. Dr. Redfarn's Laboratory - Commercial grade.

Guanidine carbonate - ex. Judex (General Chemical and Pharmaceutical Co. Ltd.) A.R. grade.

Hydrazine - ex. Whiffen & Sons Ltd. - 40% w/w aqu.soln.

Lead monoxide - ex. Harrington Bros. Ltd. - Reagent grade.

Lead dioxide - ex. Dr. Redfarn's Laboratory - 96-98% pure.

Cupric benzoate - prepared at Dr. Redfarn's laboratory.

Potassium ferricyanide - ex. Griffin and George Ltd. - Reagent grade.

Aluminium iso-propoxide - ex. Kaylene Chemicals Ltd. - Reagent grade.

Ferrocene - ex. Koch Light Laboratories Ltd. - ≥95% pure.

Diphenyl dichlorosilane - ex. Hopkins and Williams Ltd. - Technical grade.

Activated alumina - ex. Laporte Industries Ltd. - Commercial sample.

Ferric chloride, cobalt chloride, zinc chloride, aluminium chloride

- ex. Dr. Redfarn's Laboratory - Reagent grades.

Stannic chloride - ex. BDH Ltd. - Anhydrous reagent grade.

Cupric thiocyanate - ex. Hardman and Holden Ltd. - Reagent grade.

p-toluene sulphonic acid - ex. Griffin and George Ltd. - Reagent grade.

3. RESULTS AND DISCUSSION

3.1. The preparation of organophosphate resins.

3.1.1. Introduction

Tri-alkyl and tri-aryl phosphates are commercially available materials. Some applications of these esters include plasticisers for polymers, for example tri-xylyl phosphate in poly(vinyl chloride) and tri-phenyl phosphate in cellulose acetate, and the use of tri-butyl phosphate in solvent extraction. Alkylaryl phosphate esters, such as tri-tolyl phosphate (XXV) are considered unsuitable for preparing high temperature resistant polymers, since any unreacted residual alkylphenyl moieties remaining in the resin structure would be potential sites for thermo-oxidation. For this reason the only aryl phosphate ester used throughout this work is tri-phenyl phosphate, because of the high thermo-oxidative stability of the benzenoid nuclei, which are free from easily oxidisable organic substituents.

Tri-alkyl phosphates are more reactive towards nucleophilic attack than tri-aryl phosphates and would be expected to undergo transesterification more readily and at lower temperatures than their aromatic analogues. Resin preparations at lower temperatures may thus be possible with some polyhydric phenols that tend to decompose or self condense at high temperatures. A disadvantage with tri-alkyl phosphates is that incomplete reaction with polyhydric phenols will leave alkyl substituents in a product resin's structure and these remaining aliphatic ester groups would be potential sites for thermo-oxidation and hydrolysis. Side reactions are almost certain to occur when tri-alkyl phosphates are heated with polyhydric phenols, since the aliphatic phosphate esters are known to act as alkylating reagents for alcohols[67] and phenols[68]. Acidic groups are likely to be present in the structures of resins prepared from tri-alkyl phosphates as a result of these side reactions (XXVI).

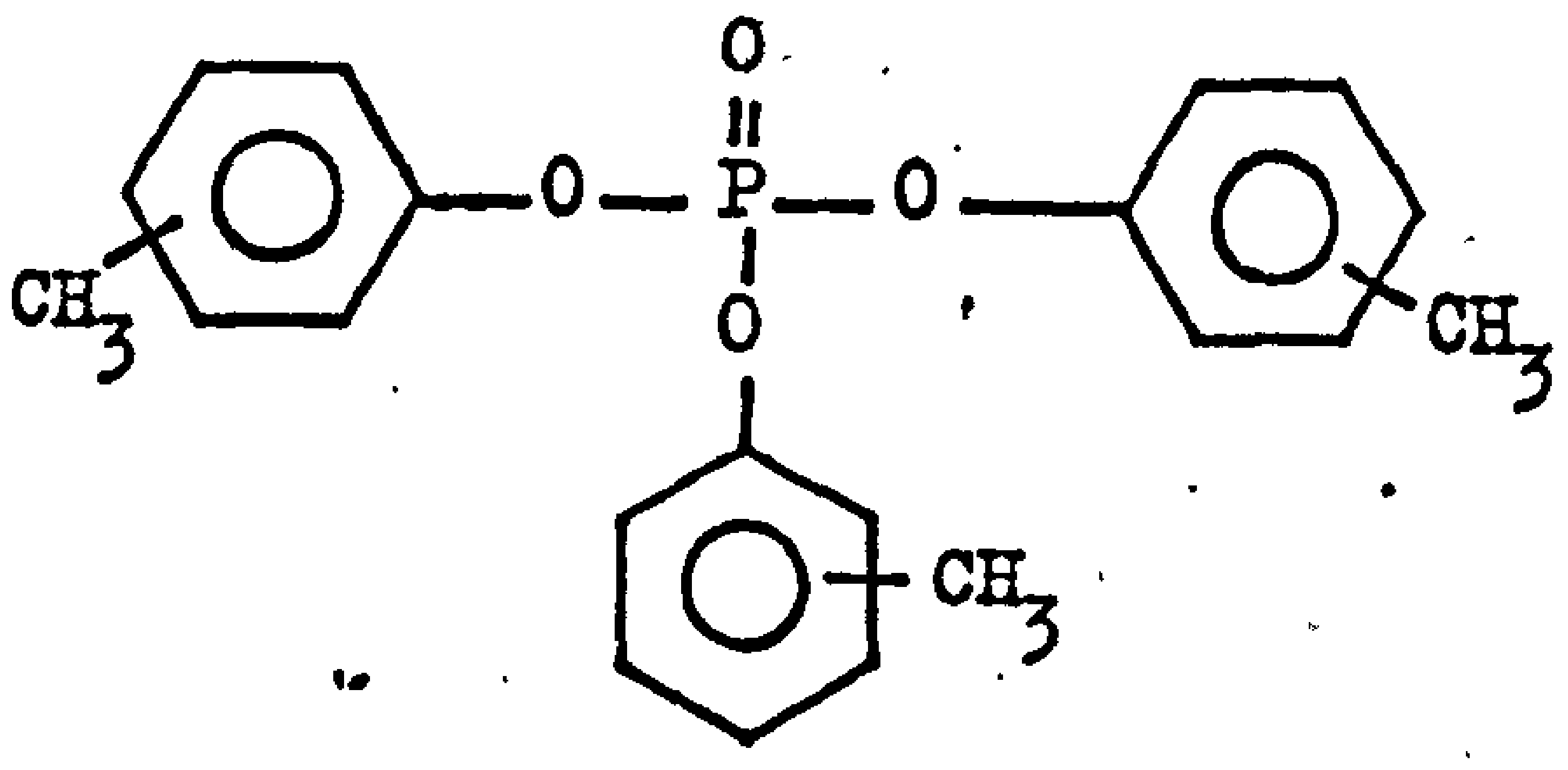
Several polyhydric phenols, such as resorcinol and hydroquinone, are commercially available chemicals. The resins produced by transesterification of tri-organo phosphates with polyhydric phenols are formulated so as to give structures containing benzenoid rings with one or more hydroxy substituents. From the point of view of curing these resins with formaldehyde donors the structure of the polyhydric phenol is important. Phenolic hydroxyl groups activate a benzenoid ring towards electrophilic substitution by formaldehyde donors, directing the reaction at the ortho-and para-positions. In this sense resorcinol is the most preferred dihydric phenol and phloroglucinol the most reactive tri-hydric phenol.

With dihydric phenols the resins are formulated to give linear polymers (XXVII). Tri-hydric phenols may give cyclic structures with tri-organophosphates with the possibility of "step ladder" polymers (XXVIII). Ring formation in this way would be desirable from the point of view of preparing high temperature resistant polymers (see section 1.6.3.), although products of this kind may be intractable and impossible to process (see section 1.5.). An alternative to cyclisation is the formation of linear polymers (XXIX), which may react further to produce cross-linked structures.

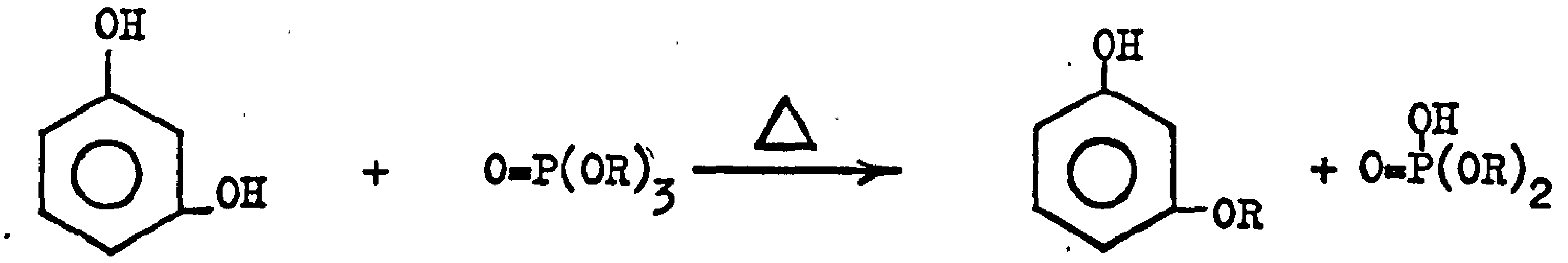
3.1.2. The Preparation of Resorcinol phosphate resins.

3.1.2.1. Transesterification of resorcinol with tri-phenyl phosphate.

The reaction between tri-phenyl phosphate and resorcinol (mole ratio 2:5) proceeds smoothly and is the only satisfactory reaction as yet found.

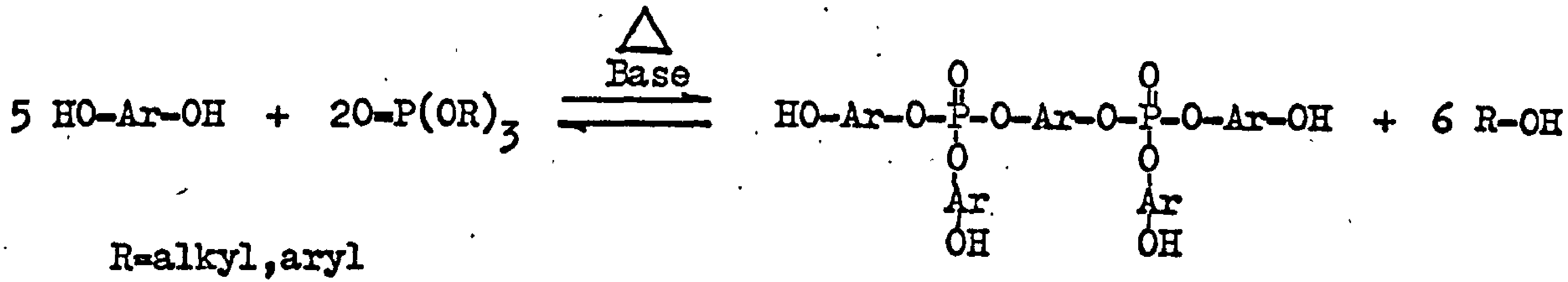


(XXV) Tri-tolyl phosphate.



R=alkyl

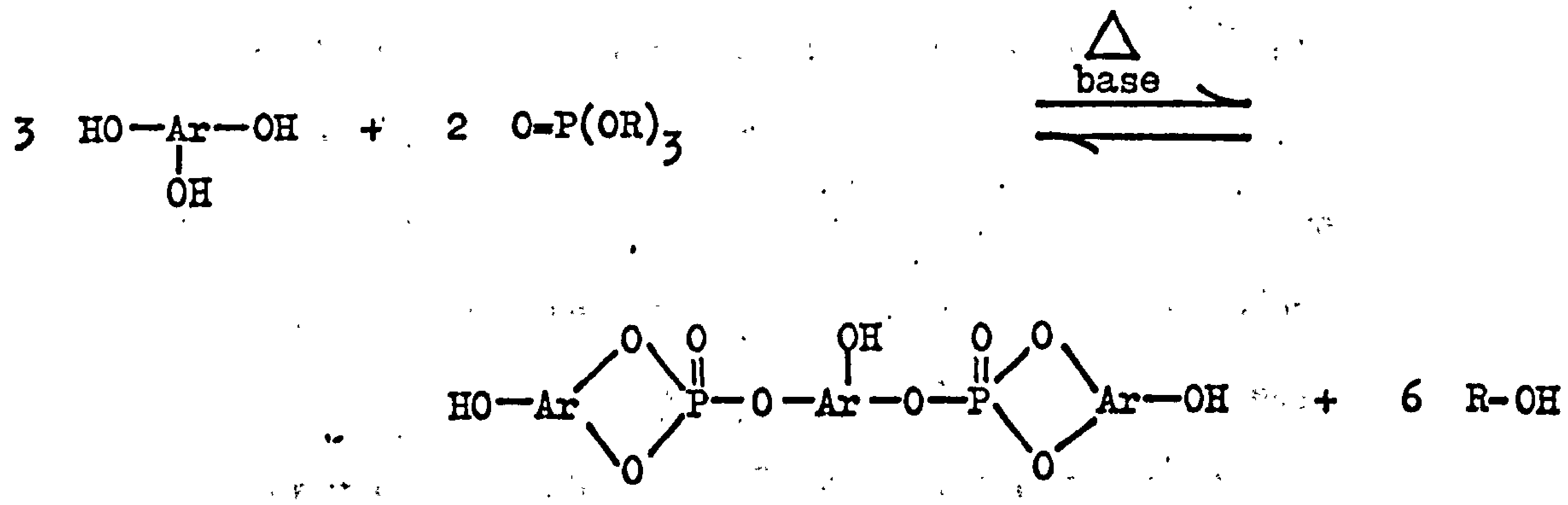
(XXVI) Ether formation by reaction of a di-hydric phenol and a tri-alkyl phosphate.



$$5\,HO\text{-}Ar\text{-}OH + 2O{=}P(OR)_3 \;\overset{\Delta}{\underset{}{\overset{\text{Base}}{\rightleftharpoons}}}\; HO\text{-}Ar\text{-}O\text{-}\overset{O}{\underset{\underset{\underset{OH}{Ar}}{O}}{\overset{\|}{P}}}\text{-}O\text{-}Ar\text{-}O\text{-}\overset{O}{\underset{\underset{\underset{OH}{Ar}}{O}}{\overset{\|}{P}}}\text{-}O\text{-}Ar\text{-}OH + 6\,R\text{-}OH$$

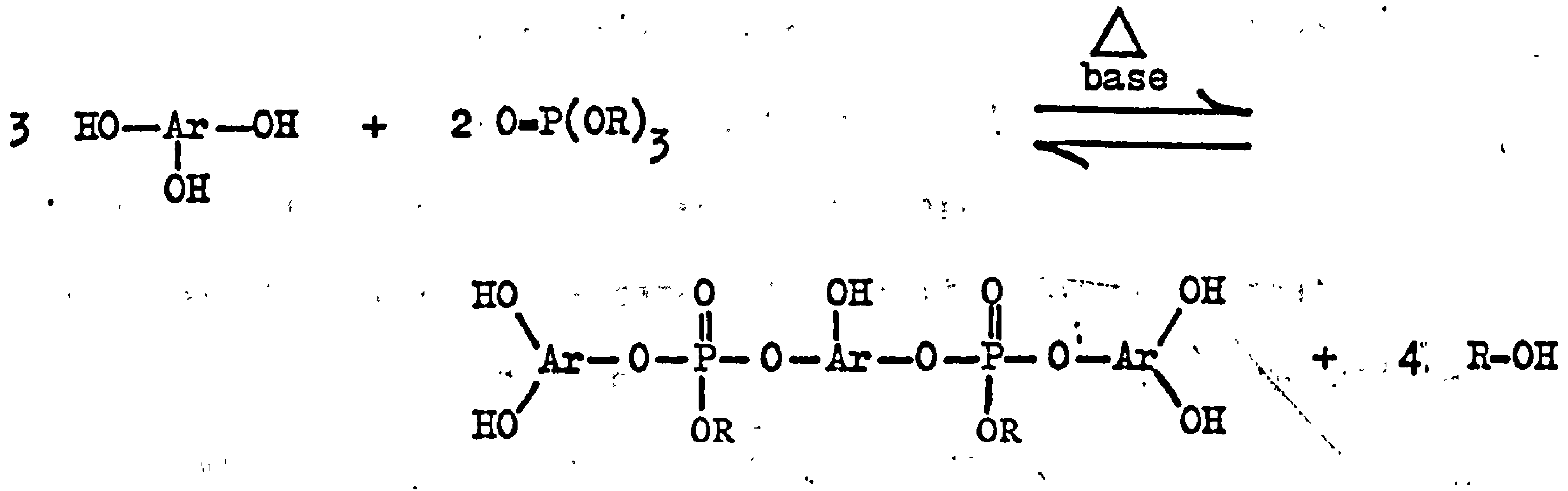
R=alkyl,aryl
Ar=aryl

(XXVII) General reaction scheme for the preparation of resins from di-hydric phenols and tri-organophosphates.



R=alkyl,aryl. Ar=aryl.

(XXVIII) The formation of cyclic structures with tri-hydric phenols.



R=alkyl,aryl. Ar=aryl.

(XXIX) The formation of linear polymers with tri-hydric phenols.

The idealised reaction product (XIX) is probably not formed, since the distillate from the reaction contains more resorcinol than the 10% excess allows for losses.

By-reactions take place at reaction temperatures which are above about 560. Over reacted products may be recognised by an odour of phenolic ethers, which may be a result of the condensation of resorcinol or phenol (or both) (XXX) and by the presence of highly coloured acetone insoluble material, which may be due to some cross-linking of the polymer molecules by self condensation or condensation with resorcinol.

3.1.2.2. Transesterification catalysts.

Table 3.1.2.2.1. shows the efficiencies of some catalysts in the reaction between resorcinol and tri-phenyl phosphate.

Bases are known to catalyse transesterification reactions and the results in table 3.1.2.2.1. show that ZnO and $Zn\ (OH)_2$ are both effective catalysts. Freshly prepared $Zn\ (OH)_2$ shows no improvement over ZnO as a catalyst, for it is probable that the hydroxide is dehydrated to the oxide at the reaction temperature. The base catalysed resins are soluble in acetone.

Alkyl titanates have been reported to be transesterification catalysts[69], but n-butyl titanate is not as effective as ZnO in catalysing the preparation of resorcinol phosphate resin and gives rise to a product that is partially soluble in acetone. There is a possibility that the n-butyl titanate reacts with phenolic compounds during the preparation of the resin to give some acetone insoluble material.

In the absence of catalysts the reaction does not proceed to completion, even after heating at 550-560 for 6 hours.

Table 3.1.2.2.1.

Transesterification catalysts for the reaction between tri-phenyl phosphate and resorcinol (mole ratio 2:5)

Catalyst (approx. % of reactants' weight)	Approx. reaction time (hr)
½% ZnO	3
1% ZnO	3.75
½% $Zn(OH)_2$ (freshly prepared)	3.25
½% n-butyl titanate	6
None	6*

*Incomplete conversion to resin.

3.1.2.3. Transesterification of resorcinol with tri-alkyl phosphates.

Tri-alkyl phosphates react with resorcinol to form resins. It is unlikely that the idealised reaction product (XXVII) occurs, since side reactions take place. For example, tri-methyl phosphate and tri-octyl phosphate react with resorcinol to give distillates possessing strong ether-like odours. At least three distinct fractions are present in the distillate from the reaction with tri-octyl phosphate. Also, the resin prepared from tri-methyl phosphate and resorcinol gives acidic extracts with hot water. Although detailed analyses of the resins and distillates have not been carried out it is evident that transesterification is not the only reaction occuring in the preparation of these polymers. Whatever the structures are of the resins obtained, they cure readily when heated with hexamine.

The reaction temperatures required to prepare resins from tri-alkyl phosphates and resorcinol are lower than the temperature employed to prepare a resin from tri-phenyl phosphate and resorcinol in the presence of n-butyl titanate as catalyst. However, since side reactions occur when the aliphatic phosphates are used, the extent of transesterification cannot be estimated by weighing the distillate evolved during the reaction and the apparent reaction temperatures employed may be determined by the production and distilling over of by-products from the side reactions. Satisfactory comparisons of the reaction temperatures required with tri-alkyl phosphates and tri-phenyl phosphate with resorcinol cannot therefore be made.

3.1.3. The preparation of hydroquinone phosphate resin.

Hydroquinone is isomeric with resorcinol, yet with a similar formulation as the resorcinol phosphate resin a polymer cannot be prepared by reaction with tri-phenyl phosphate, even at about 555.

A major disadvantage with hydroquinone is that it readily sublimes over into the condenser during the heating of the reactant melt and so the stoichiometry of the reaction is altered.

3.1.4. The preparation of di(hydroxyphenyl) sulphone phosphate resin.

3.1.4.1. Introduction

Di(hydroxyphenyl) sulphone is a bis-phenol in which the phenolic rings are connected by a sulphone group (XXXI). Di-phenylene sulphone groups are found in many high temperature resistant polymers[70], consequently di(hydroxyphenyl) sulphone is attractive as a monomer for preparing thermosetting phosphate resins. Three methods of preparation of di(hydroxyphenyl) sulphone phosphate resin have been attempted, but none was successful.

3.1.4.2. Transesterification of di(hydroxyphenyl) sulphone with tri-phenyl phosphate.

Phenol is evolved when di(hydroxyphenyl) sulphone is heated with tri-phenyl phosphate in the presence of ZnO catalyst. There is also a possibility that some di(hydroxyphenyl) sulphone (b.pt. = 523) is carried over with the phenol in the distillate. The process is difficult to control, since even after maintaining at a constant 573 for 40 minutes, a sudden vigorous reaction can take place.

Decomposition of the di(hydroxyphenyl) sulphone appears to occur, since the product possesses an odour of phenolic ethers and SO_2 is evolved during the reaction. Di(hydroxyphenyl) sulphone alone decomposes at 525-575 in air with the evolution of phenol and the formation of a black resinous product. Consequently, the reaction product obtained by heating tri-phenyl phosphate and di(hydroxyphenyl) sulphone at up to 573 may be a mixture of compounds formed by transesterification and decomposition reactions. The fact that the product does not cure with hexamine indicates a loss of phenolic hydroxyl groups during the resin preparation, although alternatively it is possible that the electron withdrawing effect of the sulphone grouping deactivates the benzenoid rings to such an extent that electrophilic attack by formaldehyde donors is made difficult.

3.1.4.3. Transesterification of di(hydroxyphenyl) sulphone with trimethyl phosphate.

In order to lower the reaction temperature and thus to prevent decomposition of the di(hydroxyphenyl) sulphone, transesterification with tri-methyl phosphate has been attempted.

At a temperature of about 450, which is below the boiling point of tri-methyl phosphate (470), no reaction takes place.

3.1.4.4. Condensation of di(hydroxyphenyl) sulphone with phosphoryl chloride.

Following the unsuccessful attempts to prepare a resin from di(hydroxyphenyl) sulphone and tri-organo phosphates by transesterification a low temperature solution polymerisation was attempted, using phosphoryl chloride in place of organophosphate esters.

When di(hydroxyphenyl) sulphone and phosphoryl chloride are refluxed in 1,4-dioxan both HCl and SO_2 are evolved. The production of SO_2 indicates that the di(hydroxyphenyl) sulphone is decomposed under the reaction conditions. A non-resinous product is obtained, which is not reactive towards hexamine at about 495.

3.1.5. The preparation of phloroglucinol phosphate resin by transesterification of phloroglucinol with tri-phenyl phosphate.

The reaction between phloroglucinol and tri-phenyl phosphate (mole ratio 3:2) is probably complex and does not proceed to completion, even at up to about 575.

Phloroglucinol is reported to self condense to phloroglucide at 603-627[71] (XXXII). This reaction may be catalysed by the presence of ZnO, which can behave as a condensation catalyst. The high hydroxyl functionality of phloroglucide may give rise to cross-linking during the resin preparation. Etherification may also occur between phenolic hydroxyl groups to produce cross-linked products. A control test on phloroglucinol alone showed that when heated it melts and then, at about 595, resolidifies.

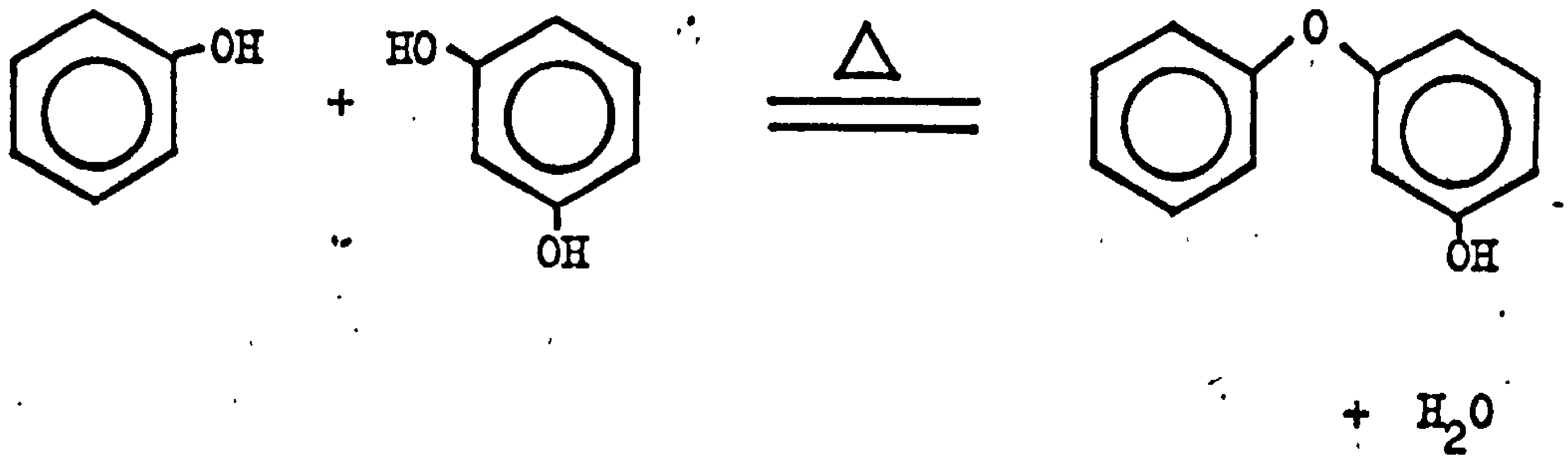
The black, non-resinous product produced when phlorogluncinol is heated with tri-phenyl phosphate supports the view that some kind of cross-linking takes place, or that perhaps self condensation products of phloroglucinol result. Even in the absence of oxygen a black solid product is obtained. Ring formation would seem unlikely to occur since the ring structures (XXVIII) would be strained because of the meta-orientation of the hydroxyl groups on the phloroglucinol.

3.1.6. The preparation of pyrogallol phosphate resin.

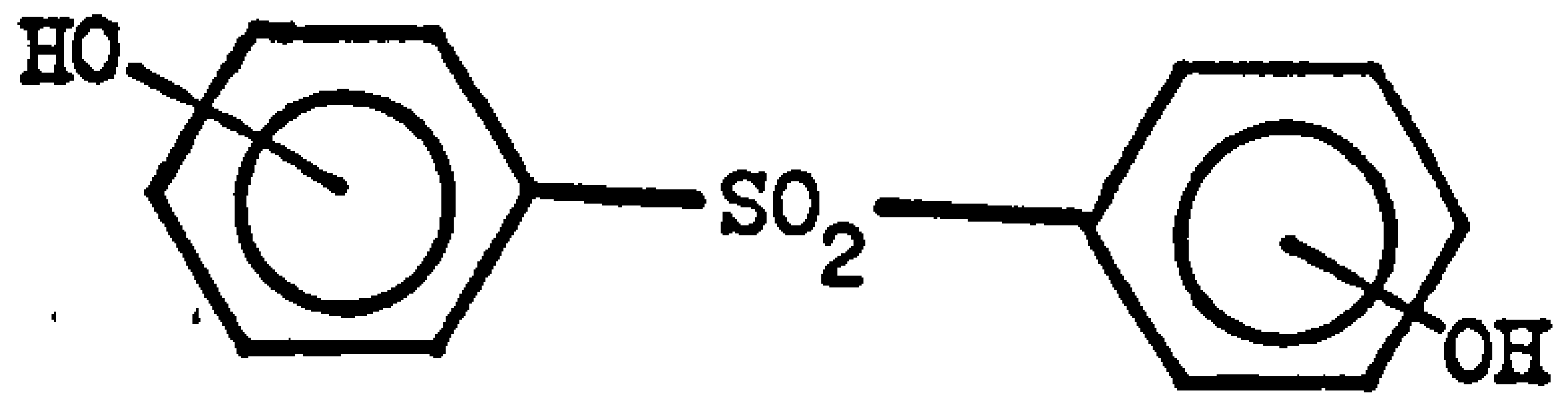
3.1.6.1. The reaction of gallic acid with tri-phenyl phosphate.

For this reaction gallic acid is used instead of the more expensive pyrogallol. Gallic acid loses water of crystallisation at 373 and decarboxylates with the evolution of CO_2 at its melting point of 526-527[72] (XXXIII). The decarboxylation temperature is lowered to 448 in the presence of water and an alkaline oxide catalyst[72].

Complex reactions probably occur when tri-phenyl phosphate and gallic acid are heated together. Self condensation of the pyrogallol formed may occur to give compounds with high hydroxyl group functionality, which may give rise to cross-linked resin products. Etherification may also take place between hydroxyl groups in a resin structure to give cross-linked species.

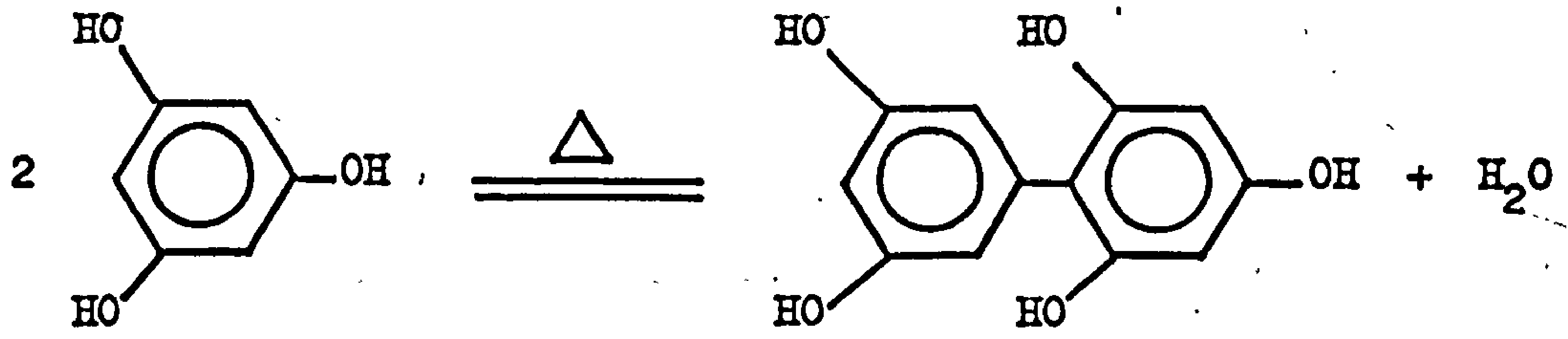


(XXX) Condensation of phenols in over-reacted resorcinol phosphate resin.



(XXXI)

Di(hydroxyphenyl)sulphone.



(XXXII) The formation of phloroglucide.

(XXXIII) The decomposition of gallic acid to pyrogallol.

When gallic acid is heated with tri-phenyl phosphate (mole ratio 3:2) a black solid results, which may be cross-linked resin material, self condensation products of pyrogallol, or a mixture of both. Cyclic structures may also be present, since the 1,2,3- orientation of phenolic hydroxyl groups may allow the formation of stable rings (XXVIII). Only two adjacent hydroxyl groups per pyrogallol molecule would be expected to take part in ring formation with tri-phenyl phosphate but the remaining hydroxyl group may tend to inhibit this ring formation by steric hinderance.

3.1.6.2. The reaction of gallic acid with tri-butyl phosphate.

Gallic acid and tri-butyl phosphate (mole ratio 3:2) react to give a black, partially water soluble product of unknown composition. The nature of the distillate evolved during the heating indicates that by-reactions occur. Although the product obtained cures when heated with hexamine, the cured material is not stable in water.

3.1.7. Summary and conclusions:-

Of the various polyhydric phenols studied only resorcinol is suitable as a monomer for preparing organophosphate thermosetting resins. The most satisfactory results are obtained with resorcinol and tri-phenyl phosphate, since with tri-alkyl phosphates side reactions occur.

Resorcinol phosphate resin is prepared easily, is convenient to handle and cures rapidly when heated with hexamine. For these reasons the resin is considered suitable for evaluation as a useful high temperature resistant thermosetting polymer.

3.2. The effect of cross-linking on the high temperature stability of resorcinol phosphate resin.

Table 3.2.1. shows the weight losses observed after preheating uncured and hexamine cured resorcinol phosphate resins and then ageing at 460, 520 and 560 in air.

The results clearly demonstrate that the high temperature stability of resorcinol phosphate resin is considerably enhanced by cross-linking with methylene bridges. At 460 the effect of cross-linking is especially pronounced and slowly declines with increasing temperature.

Uncured resorcinol phosphate resin is not a high temperature resistant polymer, as can be seen by the extremely high weight losses at a temperature as low as 460. At this temperature, over 92 hours, approximately 40% of the theoretical organic content of the resin is lost.

The high temperature stability of cured resorcinol phosphate resin may therefore be mainly governed by the decomposition of the polymer backbone.

Table 3.2.1.

The high temperature stability of cured and uncured resorcinol phosphate resin in air.

HEATING CONDITIONS		SAMPLE	
Temperature	Time (hr)	Resorcinol phosphate resin	Resorcinol phosphate resin + 10% hexamine
Pre-ageing treatment		Weight loss %	
∿ 330 393 ± 3	∿ 2) * ∿55)	1.72, 1.56 (Mean 1.64)	- -
∿330 393 ± 3	∿3) + ∿41)	- -	- -
Heat ageing		Cumulative weight losses on preheated samples %	
460	92	30.53, **29.66 (Mean 30.10)	3.43, 5.65 (Mean 4.5)
518 ± 3	146	49.95, 50.23 (Mean 50.09)	10.86, 12.69 (Mean 11.78)
558 ± 5	456	57.83, 58.93 (Mean 58.38)	19.16, 19.53 (Mean 19.35)

* Still very slowly losing weight.

\+ At constant weight.

** The resin hardened to a brittle solid under these conditions.

3.3. Alternative curing agents for resorcinol phosphate resin.

3.3.1. Introduction:

Several compounds have been evaluated as potential curing agents for resorcinol phosphate resin, as alternatives to hexamine, with a view to improving the thermal stability of the cross-links in the cured resin.

Table 3.3.1.1. shows the results obtained. Reaction temperatures and times are only approximate. The tests applied are simple and are designed only to ascertain whether a cure can be effected at practically useful temperatures and times.

There are two possible reaction sites on resorcinol phosphate resin, namely the aromatic rings and the phenolic hydroxyl groups. The benzene rings in the resin are activated towards electrophilic substitution at the ortho- and para- positions to the phenolic hydroxyl groups. Phenolic hydroxyl groups will undergo condensation reactions with acid chlorides and transesterification reactions with esters. The acidity of these hydroxyl groups may also give rise to salt formation with basic inorganic compounds. Phenols also undergo oxidative coupling reactions in the presence of suitable oxidants.

The various types of potential curing agents studied will now be discussed, giving reasons for their choice and some speculation as to the reactions taking place.

3.3.2. Curing with hexamine.

A very rapid cure is obtained with hexamine. The disadvantages of methylene cross-links in the structure of phenolic resins and resorcinol phosphate resin are discussed in section 1.9.6.

3.3.3. The self curing of resorcinol phosphate resin:

On very long heating at about 525 the resin will self cure, probably by etherification of the phenolic hydroxyl groups. The

Table 3.3.1.1.

A study of curing agents with resorcinol phosphate resin

Compounds tested with the resin*	Heating conditions		Products and comments.
	Temp.	Time	
None	525	Prolonged	Brittle solid
5% hexamine	455	60 sec	Cures to a brown solid.
7.5% hexamine	455	26 sec	
10% hexamine	455	19 sec	
10% dicyandiamide	475	5 min	No cure) Copious
20% dicyandiamide	475	13¼ min	Rubbery cure) Alkaline) vapours
40% dicyandiamide	475	14 min	Rubbery cure) evolved)
Resin alone	475	16¼ min	No cure
Thiourea	-	-	No cure
Hydroxylamine	-	-	No cure
10% oxamide	445 and 525	-	No cure
10% melamine	445 and 525	-	No cure
Guanidine carbonate	495	Prolonged heating	Rubbery cure. Copious fuming and effervescence.
Hydrazine	525	-	Cured. Copious fumin
10% PbO	445	3 min	Rubbery cure) much
20% PbO	495	1½ min	Rubbery cure) fuming
PbO_2	-	-	Violent reaction, flashes of flame.
10% cupric benzoate	475 and 525	10 min	) No cure
10% ($Mg(OH)_2$ + $K_3Fe(CN)_6$ 1:1 by volume).	455	5 min	)
10% n-butyl titanate	525	3¼ min	Cured to a yellowy brown rubbery mass, hardening on prolonge heating. Copious evolution of "butyl" vapours.
15% n-butyl titanate	525	1⅔ min	
20% n-butyl titanate	525	1½ min	
30% iso-propyl titanate	445	10 min	No cure.

Table 3.3.1.1. (continued)

Compounds tested with the resin*	Heating conditions		Products and comments.
	Temp.	Time	
35% iso-propyl titanate	445	-	Fairly rapid cure. Soft product.
40% iso-propyl titanate	445	-	Rapid cure. V. rubbery product.
45% iso-propyl titanate	445	-	Rapid cure. V. rubbery product.
50% iso-propyl titanate	445	-	Immediate cure. Rubbery product.
50% iso-propyl titanate, heated at once	475	-	Immediate cure.
50% iso-propyl titanate, stood 15 min in air before heating.	475	-	Slow, incomplete cure.
40% aluminium iso-propoxide	475 and 525	-	No cure.
10% ferrocene	465	1-2 min	No cure
10% ferrocene + a little $AlCl_3$	465	10 min	
10% ferrocene + a little activated Al_2O_3.	445	5 min	
α,α'-dimethoxyxylylene (designated X)	455-465	2 min	No cure or partial cure.
X + ZnO, PbO, Na_2SO_3, NH_4-OH, oxalic acid, or $Mg(OH)_2$	455-465	1-2 min	No cure.
X + p-toluene sulphonic acid	455-465	-	Rapid cure. Rubbery product, hardening on prolonged heating.
X + $AlCl_3$, $FeCl_3$, $CoCl_2$, $ZnCl_2$, Cu $(SCN)_2$ or H_3PO_4.	455-465	-	Rapid cure.
Diphenyl dichlorosilane	475	< 1 min	Rapid cure. Rubbery solid, hardening on prolonged heating. HCl evolved.

* % = % of resin weight.

conditions required are far too extreme to be of practical use.

3.3.4. Cross-links containing C-N bonds:

In air the primary cause of breakdown of methylene cross-links is thermo-oxidation (section 1.9.6.). The introduction of cross-links containing only inorganic C and N, or C, O (or S) and N atoms may be expected to lead to an increase in thermo-oxidative stability, compared to organic hydrocarbon cross-links. A decrease in thermal stability would, however, be expected with C-N bonds compared to C-H bonds as is illustrated by their respective dissociation energies (table 1.6.1.1.).

Several compounds containing $-NH_2$ or $=NH$ groups have been heated with resorcinol phosphate resin, but none are useful curing agents. Hydrazine, guanidine carbonate and dicyandiamide will cure resorcinol phosphate resin, but at the same time acrid, copious fumes are evolved, which are very undesirable. With thiourea, oxamide, melamine and hydroxylamine no reaction takes place.

The nature of the curing reactions occuring is not known.

3.3.5. Curing with lead monoxide:

Lead monoxide, which has been reported as a curing agent for "Phoryl" resins[37] (section 1.8.3.), will cure resorcinol phosphate resin. Much fuming and probably decomposition occurs during the reaction. It is possible that a lead salt is produced by neutralisation of the oxide by the acidic phenolic hydroxyl groups on the resin. Lead dioxide appears to vigorously oxidise the resin.

3.3.6. Curing by oxidative coupling:

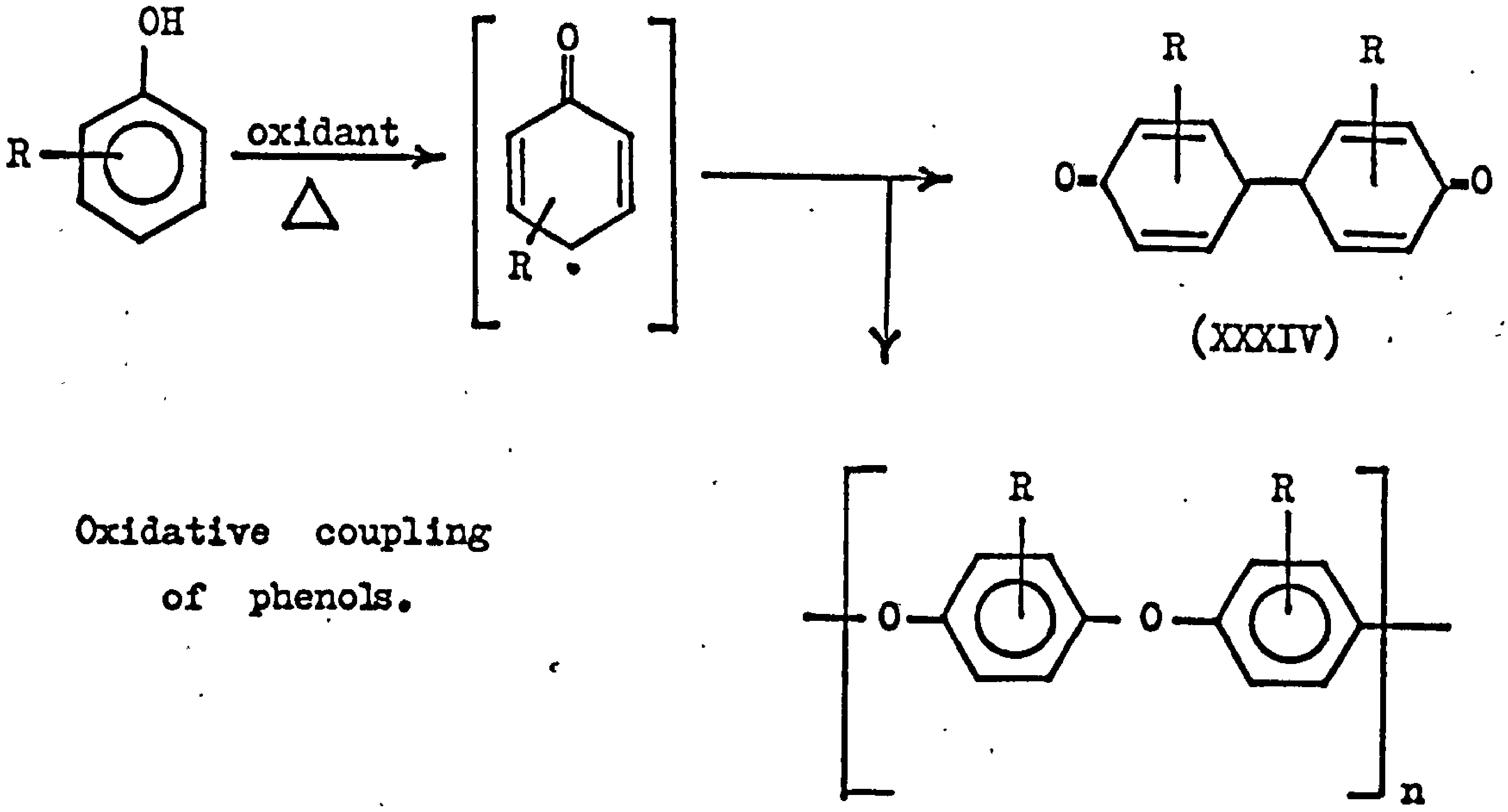
Cupric benzoate has been reported as an oxidant and catalyst for oxidative coupling in fused phenols at 393-498[73] and alkaline potassium ferricyanide has been used at lower temperatures in solution as an oxidative coupling reagent[74]. Compounds containing structures of the type (XXXIV) or (XXXV) can be formed. Oxidative coupling between the phenolic groups on the resorcinol phosphate resin would be expected to give rise to ether cross-links or the direct bonding of aromatic rings between different resin molecules. Cross-links of these types should have high thermal and thermo-oxidative stability, since these diphenylene and diphenylene oxide structural units are found in high temperature resistant polymers, such as polyimides[75] (table 1.7.1.).

In spite of the potential of oxidative coupling as a curing mechanism, no cross-linking reaction can be effected by heating resorcinol phosphate resin with cupric benzoate or alkaline potassium ferricyanide.

3.3.7. Curing with alkyl titanates.

Alkyl titanates react readily with resorcinol phosphate resin, probably by condensation with the phenolic hydroxyl groups (XXXVI). Large amounts of the alkyl titanates are required to effect a complete cure of the resin. A serious disadvantage with alkyl titanates is their susceptibility to hydrolysis in moist air. Table 3.3.1.1. shows that the effectiveness of iso-propyl titanate as a curing agent is considerably reduced after only 15 minutes' exposure to air before heating with the resin.

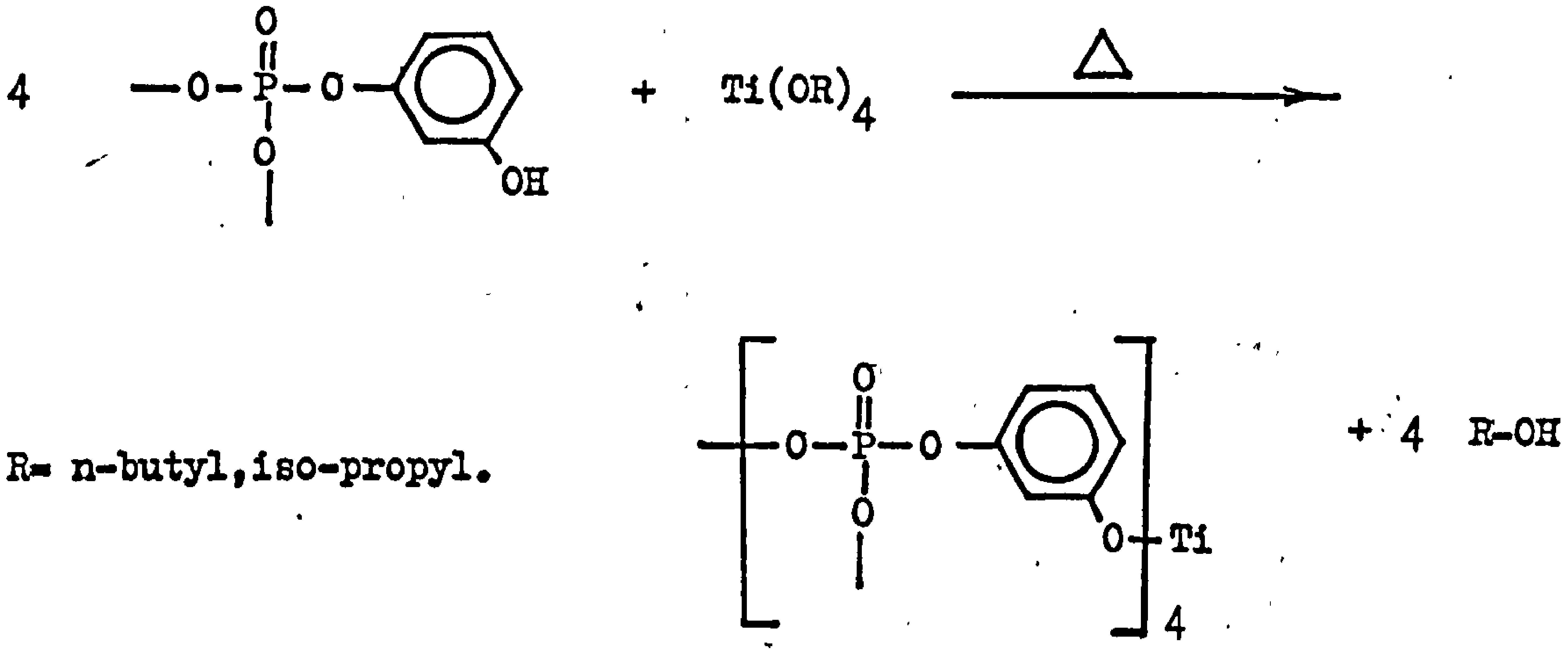
Although Ti-O-C cross-links offer a high resistance to thermo-oxidative attack the Ti-O bonding is predominantly ionic (table 1.6.1.3.) and may be expected to be labile at elevated temperatures (see section 1.6.1.). The ionic character of the Ti-O bond renders it susceptible to nucleophilic and electrophilic attack as is evidenced by the poor hydrolytic stability of resorcinol phosphate resin cured with iso-propyl titanate. A



(XXXIV)

(XXXV)

Oxidative coupling of phenols.



R= n-butyl,iso-propyl.

(XXXVI) The reaction between resorcinol phosphate resin and alkyl titanates.

sample of resorcinol phosphate resin cured with 27% by weight of iso-propyl titanate shows a weight loss of nearly 34% after 116 hours at 453-473. The poor high temperature stability of the cured resin may be a result of considerable reorganisation of bonds within the network structure such as (XXXVII) or(XXXVIII).

No reaction occurs when aluminium iso-propoxide is heated with resorcinol phosphate resin, which contrasts the behaviour of iso-propyl titanate.

3.3.8. Curing with ferrocene.

Ferrocene has been reported to condense with "A" stage phenolic resins at 423-443 in the melt phase in the presence of Friedel Crafts catalysts[78]. Reactions with carbinols at 393-423 in the melt phase with added zinc or aluminium chloride have also been reported[79].

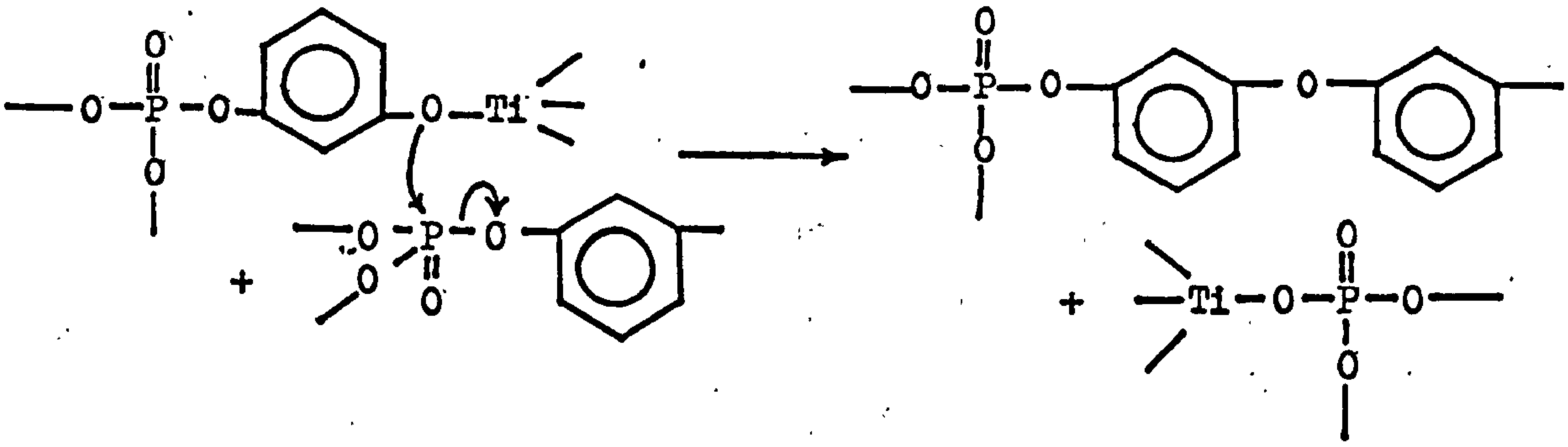
Ferrocene is a sandwich organo metallic compound with two aromatic cyclopentadienyl rings complexed by an iron atom and is attractive as a potential curing agent for resorcinol phosphate resin.

Aromatic rings are known to possess good high temperature stability and the semi-inorganic nature of the compound may enhance its resistance to thermo-oxidation.

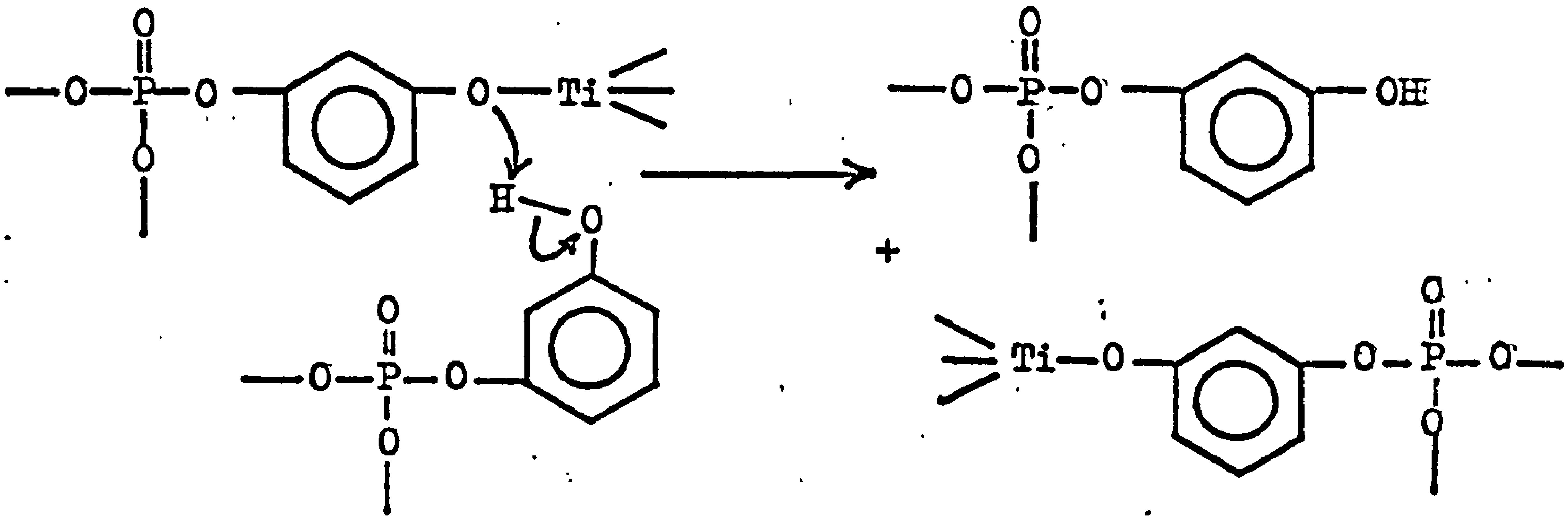
However, in the presence of Friedel Crafts catalysts, such as activated Al_2O_3 and $AlCl_3$, no reaction can be effected by heating ferrocene and resorcinol phosphate resin together, even at up to 465.

3.3.9. Curing with α,α'-dimethoxyxylylene:

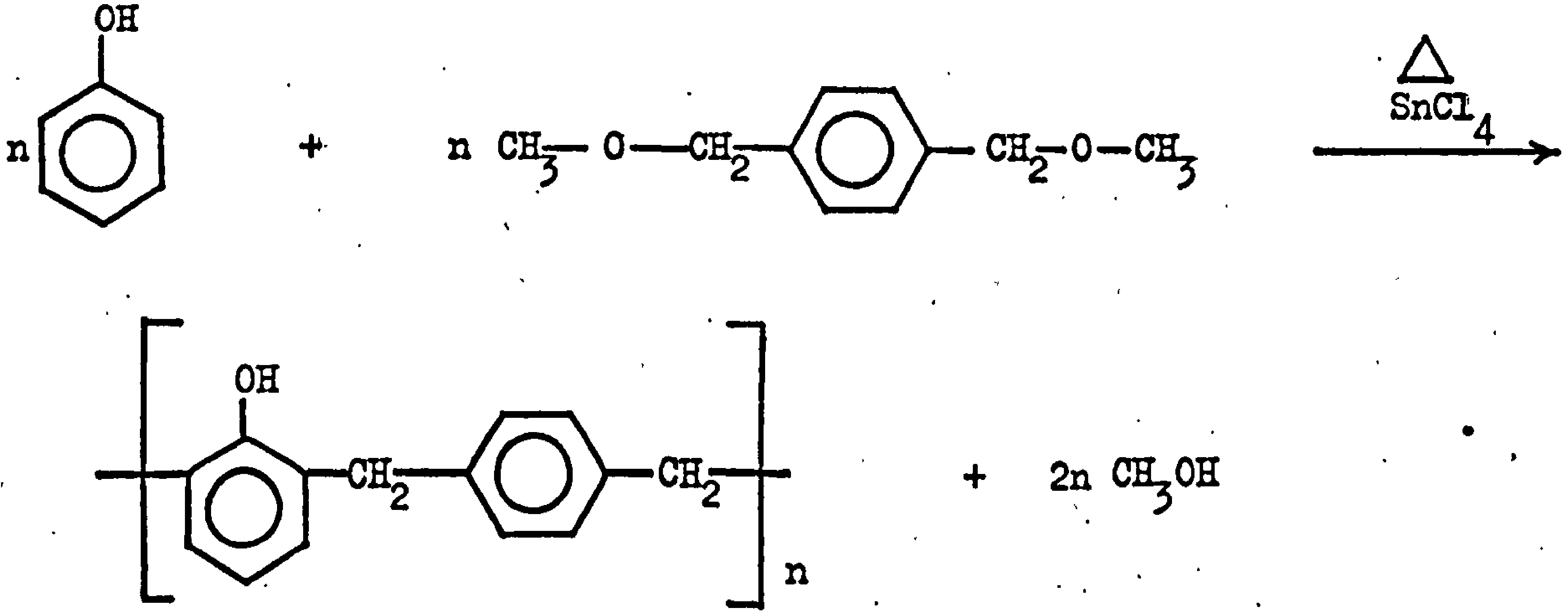
α,α'-dimethoxyxylylene is known to condense with phenols in the presence of Friedel Crafts catalysts to produce resins such as Xylok resin (XXXIX). Electrophilic attack at positions ortho- and para- to the hydroxyl group of the phenolic compound would be expected to occur.



(XXXVII)



(XXXVIII)



(XXXIX) Friedel-Crafts reaction between phenol and α,α'-dimethoxyxylylene.

The potential of α,α'-dimethoxyxylylene as a curing agent lies in the fact that it introduces aromatic rings without hydroxyl substituents into the resin structure. Hexamine introduces methylene bridges which are linked by two phenolic residues in the resin. Jeffreys[59] has suggested that the thermo-oxidative breakdown of the methylene links in cured phenolic resins involves a cyclic transition state involving phenolic hydroxyl groups (XXIII). When α,α'-dimethoxyxylylene is condensed with phenols structures are formed in which methylene groups are linked by one phenolic residue and one phenylene group. Consequently, the probability of the formation of a cyclic transition state during the thermo-oxidation of these methylene links is reduced by a half compared to the methylene groups in a hexamine cured phenolic resin. This reasoning may explain the enhanced thermal stability of Xylok resin compared to conventional phenolic resins (see section 1.9.6.).

Table 3.3.1.1. shows that resorcinol phosphate resin is cured readily by α,α'-dimethoxyxylylene in the presence of certain catalysts. Only Friedel Crafts catalysts are successful in effecting the reaction. Condensation catalysts such as ZnO, Na_2SO_3, NH_4OH, oxalic acid and $Mg(OH)_2$, which can be used in phenolic resin preparation, are unsuitable.

Copious fuming during the curing reaction is a disadvantage with α,α'-dimethoxyxylylene. The fumes are lachrymatory, consequently the milling of a resin containing this curing agent would therefore be difficult. Also, the cured resin tends to be rather rubbery. The curing reaction may also be complicated by the fact that in the presence of catalyst α,α'-dimethoxyxylylene self condenses.

3.3.10. Curing with diphenyldichlorosilane.

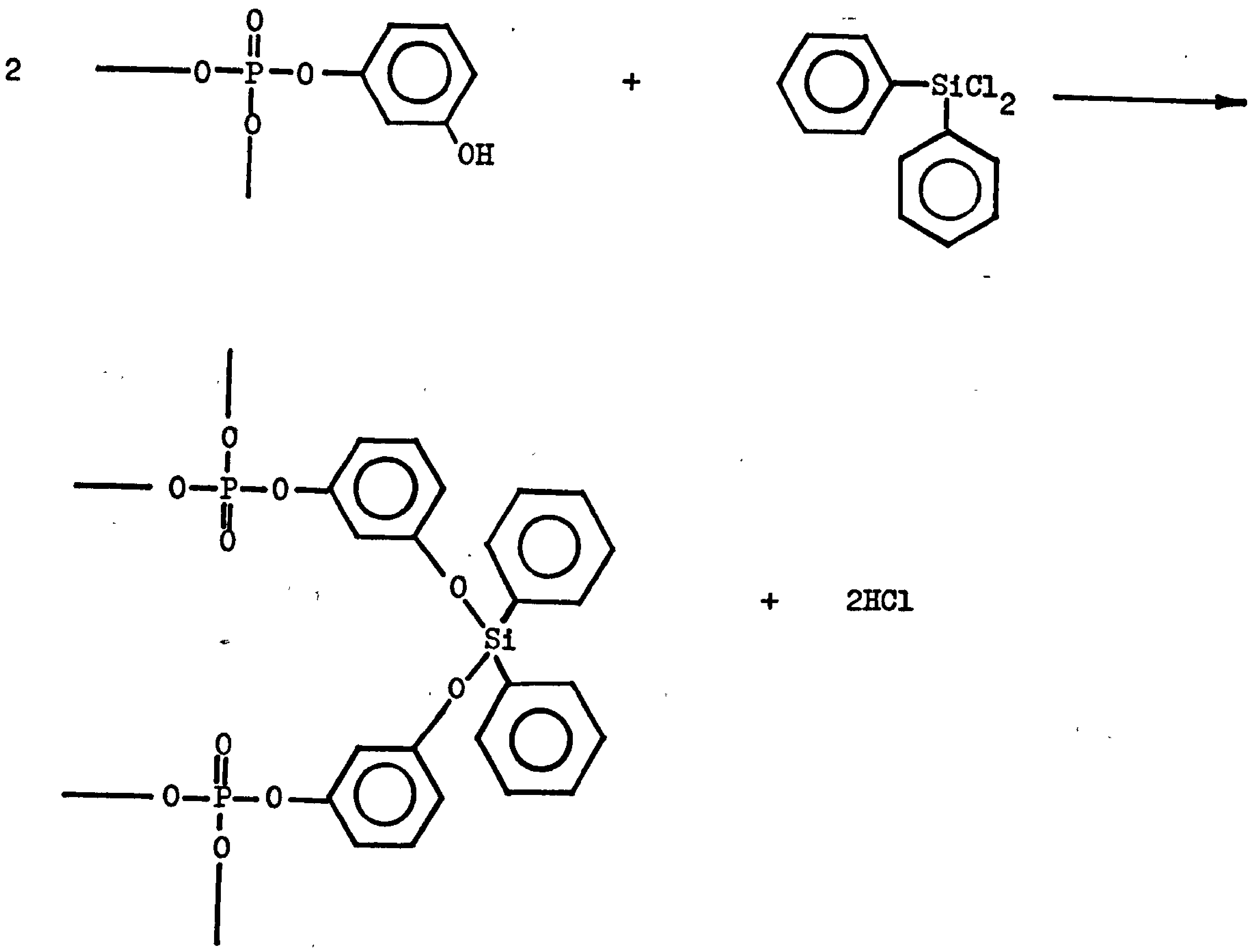
Chlorosilanes react readily with hydroxylated compounds with the evolution of HCl and a rapid cure is obtained when resorcinol phosphate resin is heated with diphenyldichlorosilane, presumably due to the formation of siloxane bridges (XL).

The siloxane bridge may be predicted to possess a high resistance to thermo-oxidation since it is inorganic in nature and the pendant phenyl groups are only oxidised above about 675[80].

Diphenyldichlorosilane is not considered as a suitable curing agent for resorcinol phosphate resin, since HCl is evolved during the reaction and the product is hydrolytically unstable.

3.3.11. Summary and conclusions:

Of the various potential curing agents studied and found to react, only α,α'-dimethoxyxylylene appears to be suitable as an alternative to hexamine, but it suffers from disadvantages such as excessive fuming during reaction and a rubbery cure. For these reasons hexamine has been chosen as the curing agent for resorcinol phosphate resin in the evaluation of the high temperature resistance of the polymer.



(XL) Siloxane bridge formation.

3.4. Examination of the composition and structure of the blended resorcinol phosphate resin used in the high temperature stability studies.

3.4.1. Estimation of the composition of the resin by fractional distillation of the reaction distillates.

The resin blend is composed of three resorcinol phosphate resins. The resorcinol content of each resin is estimated roughly by analysis of the distillates from their preparations.

An approximate calculation to determine the composition of the resin blend is given below:

Weight of resin	Tri-phenyl phosphate: resorcinol ratio	% of total blend
1200 g	1 : 2.1	28
1130 g	1 : 2.2	26
2000 g	1 : 2.5	46

Hence, the tri-phenyl phosphate: resorcinol ratio in the blend is:

$0.28 \times 1 + 0.26 \times 1 + 0.46 \times 1$ tri-phenyl phosphate:

$0.28 \times 2.1 + 0.26 \times 2.2 + 0.46 \times 2.5$ resorcinol

i.e. Tri-phenyl phosphate: resorcinol 1:2.3.

3.4.2. The steam distillation and toluene extraction of the resorcinol phosphate resin blend.

Steam distillation removes only a trace of phenolic compounds from the resin, which illustrates that the hot water washing process employed in purifying resorcinol phosphate resin is very efficient.

Toluene extraction yields less than 2% of a resinous material, which cures with hexamine. It is probable that the residue is similar to the main bulk of the resin, since it contains phosphorus and does not possess a phenolic odour. Since tri-phenyl phosphate dissolves in toluene it is apparent that virtually all of this monomer reacts with resorcinol during the transesterification reaction.

3.4.3. Infra-red spectroscopy.

The infra-red spectrum of the resorcinol phosphate resin blend is shown (spectrum 3.4.3.1.) and plausible band assignments are given in table 3.4.3.1.

A band at 1080 cm^{-1} suggests the presence of ether groups in the resin, but the possibility of other absorption bands (and fingerprint bands) in this region prevents a definite assignment to be made.

3.4.4. N.M.R. Spectroscopy.

Spectrum 3.4.4.1. is that of the resorcinol phosphate resin blend in deuteroacetone. The signal at $\delta = 8.1$ arises from the presence of phenolic hydroxyl groups and is confirmed by D_2O exchange (spectrum 3.4.4.2.). The signal corresponding to the aromatic protons occurs between $\delta = 6.7 - 7.4$. Small signals at $\delta = 2.1$ and 1.2 may be due to trace impurities of acetone and water.

From the N.M.R. spectrum of the resin the approximate aromatic proton: hydroxyl proton ratio is 7.5:1.

3.4.5. The % phosphorus content and molecular weight of the resorcinol phosphate resin blend.

Analysis of the resorcinol phosphate resin blend gave a % phosphorus content of 9.17 ± 0.03 and a number average molecular weight of 702 ± 7.

3.4.6. Summary and interpretation of the analysis of the resorcinol phosphate resin blend.

An approximate assessment of the ratio of tri-phenyl phosphate: resorcinol in the resin, as determined by analysis of

Spectrum 3.4.3.1. The infra-red spectrum of resorcinol phosphate resin.

Spectrum 3.4.4.1. The N.M.R. spectrum of resorcinol phosphate resin.

Spectrum 3.4.4.2. The N.M.R. spectrum of resorcinol phosphate resin after D_2O exchange.

Table 3.4.3.1.

The infra-red spectrum of resorcinol phosphate resin blend.

Band cm^{-1}	Type	Plausible assignments
3350	Strong	-O-H stretch
1930,1850	Weak	Aromatic C-H overtone & combination bands.
1600,1490	Strong	Aromatic C-C in plane deformations
1280	Strong	P=O
1240	Shoulder	Phenolic C-O stretch
1140	Strong	P-O-C stretch
1080	Medium	Aromatic C-H, or aromatic C-O (ether) stretch.
1000	Strong	P-O-C stretch.
690-865	Various	Aromatic C-H out of plane deformations.

the reaction distillates, indicates that the idealised resin structure (XIX) is not strictly valid for the molecules present. However, this method of analysis fails to take into account any unreacted resorcinol remaining in the resin. Residual resorcinol in the resin is removed by washing with water, in which it is highly soluble.

Toluene extraction and steam distillation of the resin after scrubbing with hot water show the resin to contain little, or no tri-phenyl phosphate and only a trace of free phenols. The resin is considered pure enough for quantitative analysis.

Although the infra-red spectrum of the resin blend shows bands consistant with the proposed idealised structure (XIX), N.M.R. spectroscopy strongly suggests that other structures are present. The aromatic proton: hydroxyl proton ratio of about 1: 7.5, obtained from the N.M.R. spectrum of the resin shows that the number of hydroxyl substituted benzenoid rings present is considerably less than in the idealised structure (XIX), which has an aromatic proton: hydroxyl proton ratio of 1:5.

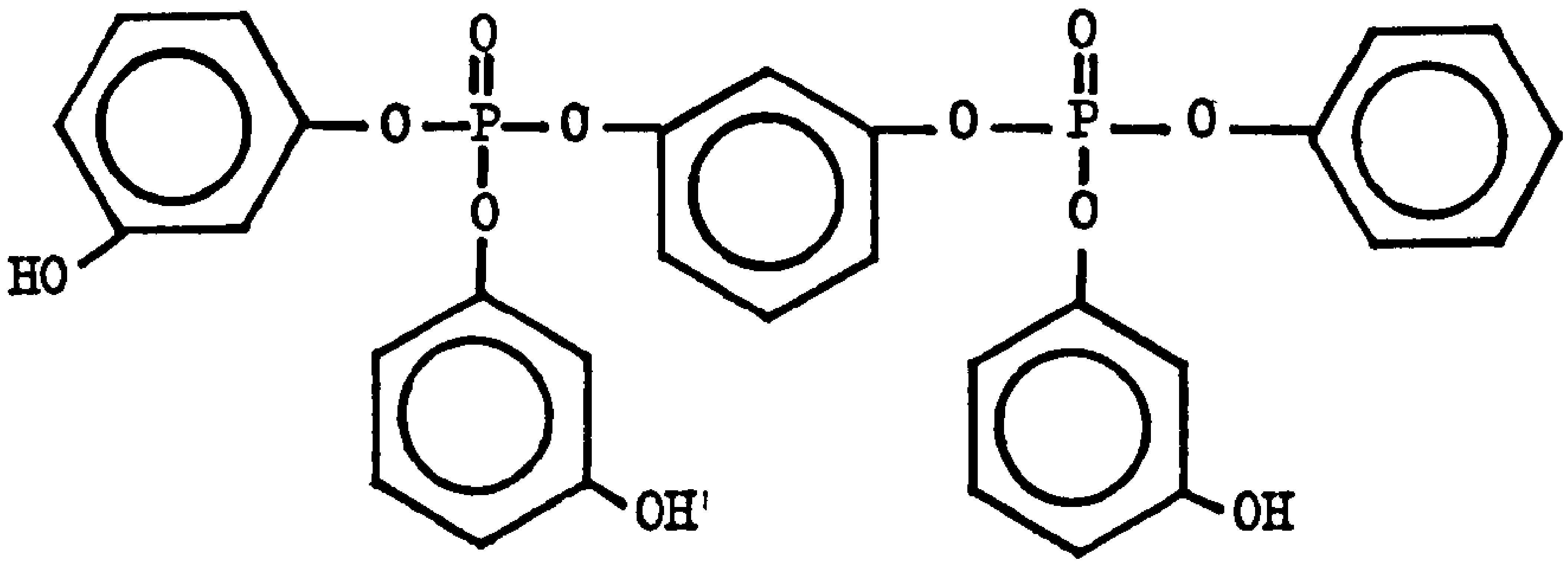
The phosphorus content of the resin is 9.17%, which is of the same order as expected from the idealised structure (XIX), i.e. 9.72%. The molecular weight, 702, of the resin is about 10% higher than the idealised structure's (638), which confirms the presence of higher polymers probably containing more than 2 phosphate moieties.

On the basis of the N.M.R., % phosphorus content and molecular weight evidence no single structure can be drawn to satisfy all the data obtained, indicating a mixture of several species is actually present. A structure can be drawn (XLI), which very roughly fits the experimental figures and which may be a predominant contributor to the polymer mixture.

Table 3.4.6.1.

Comparison of experimental and calculated data for the composition of resorcinol phosphate resin.

PROPERTY	EXPERIMENTAL RESULTS	CALCULATED RESULTS FOR STRUCTURE (XLI)
Tri-phenyl phosphate : resorcinol ratio.	~ 1:2.3	1:2.0
Aryl : hydroxyl proton ratio.	~7.5:1	7:1
% phosphorus content	9.17	9.97
Molecular weight ($\overline{Mn}$)	702	622



(XLI)

Table 3.4.6.1. shows the approximate correspondence between the experimental and the calculated data for the resin and the compound (XLI).

The closeness of structure (XLI) to the idealised structure (XIX) is sufficient to justify the use of the idealised structure, for convenience, in discussing the curing and high temperature stability of resorcinol phosphate resin.

3.5. The evaluation of the high temperature stability of resorcinol phosphate resin.

3.5.1. Introduction:

Isothermal heating and thermogravimetric analysis have been carried out on samples containing resorcinol phosphate resin in an attempt to gain an insight into the mode of high temperature degradation of the resin and its potential as a possible commercial product.

The resin used for all of these studies is the resorcinol phosphate resin blend, described in section 3.4.

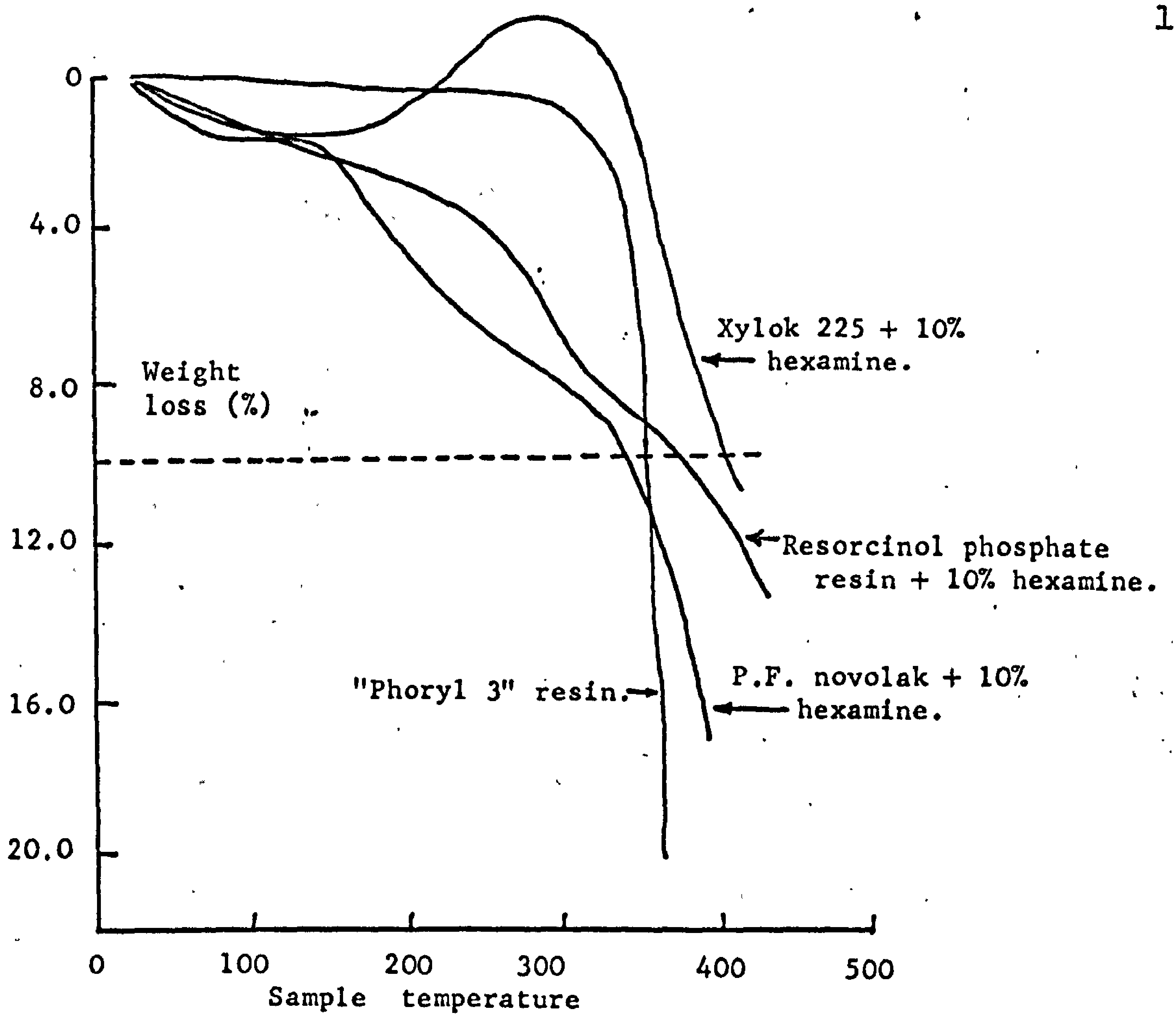
3.5.2. Thermogravimetry

The results from the thermogravimetry of various resin samples heated in air are shown in graphs 3.5.2.1. to 3.5.2.8. and table 3.5.2.1.

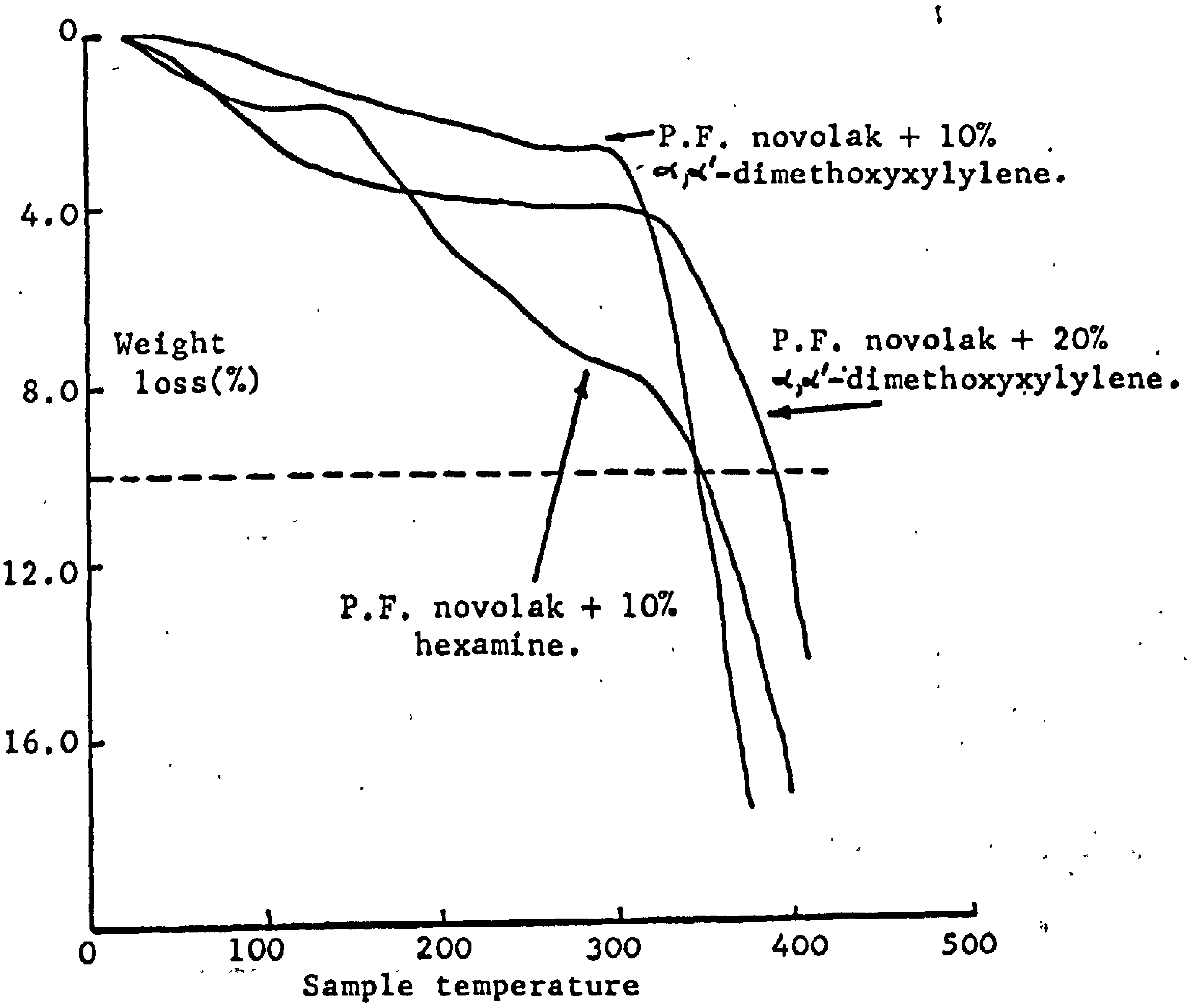
Resorcinol phosphate resin + 10% hexamine shows a continuous weight loss, similar to P-F novolak resin + 10% hexamine (graph 3.5.2.1.) and from the 10% weight loss temperatures shows only marginal improvement in high temperature stability over the cured P-F novolak resin.

Xylok 225 resin + 10% hexamine, a high temperature resistant phenolic resin, gives a thermogravimetric curve with a humped plateau up to about 575, followed by rapid degradation (graph 3.5.2.1.). The hump in the plateau may be due to the absorption of oxygen at high temperatures and appears to preceed the decomposition stage. The shape of the curve and the 10% weight loss temperature of 680 suggest that Xylok 225 resin + 10% hexamine has much better high temperature stability than resorcinol phosphate resin + 10% hexamine.

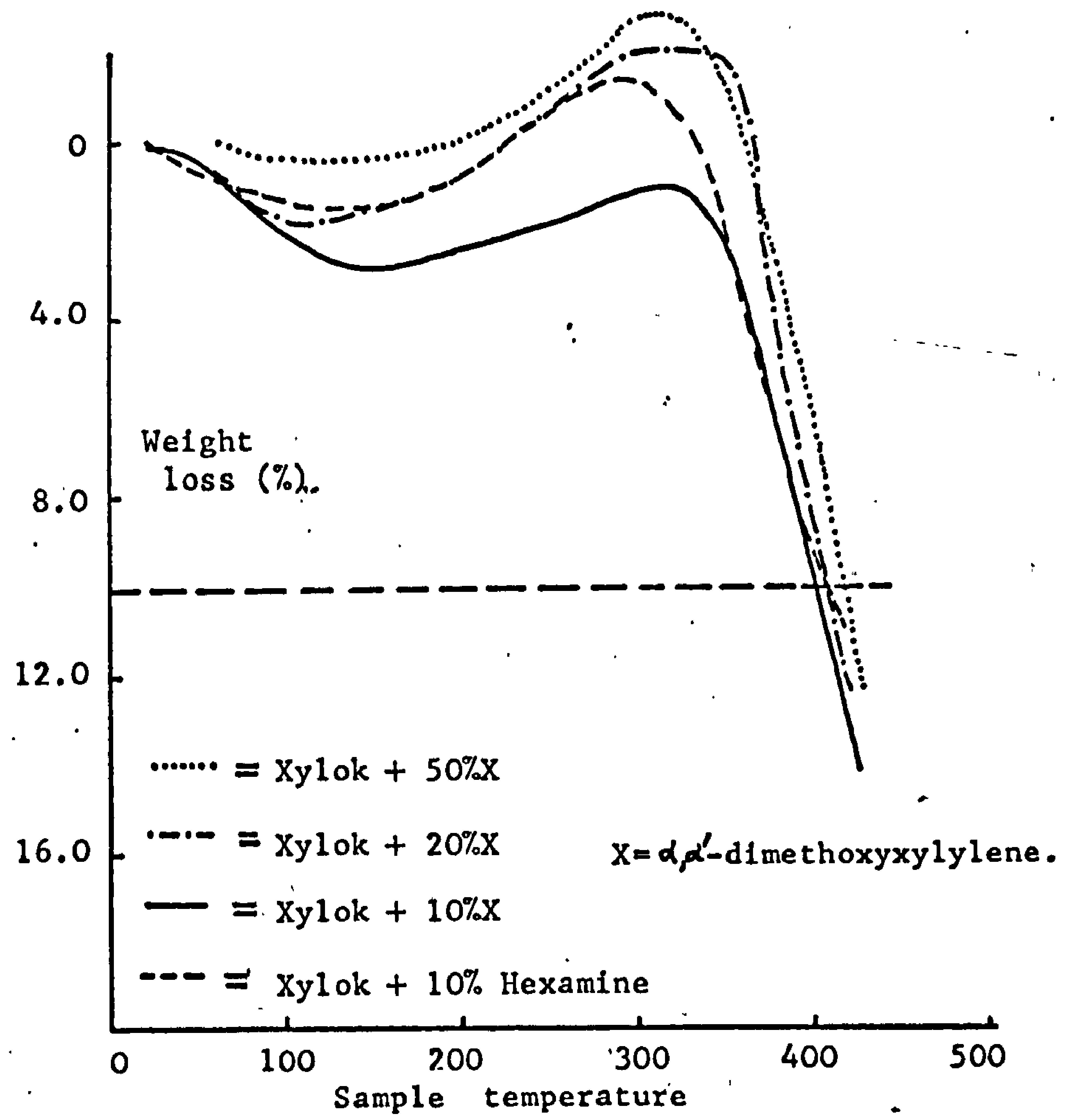
Graphs 3.5.2.2. to 3.5.2.4. show the effect of changing the curing agent from hexamine to α,α'-dimethoxyxylylene in P-F novolak, Xylok 225 and resorcinol phosphate resins.



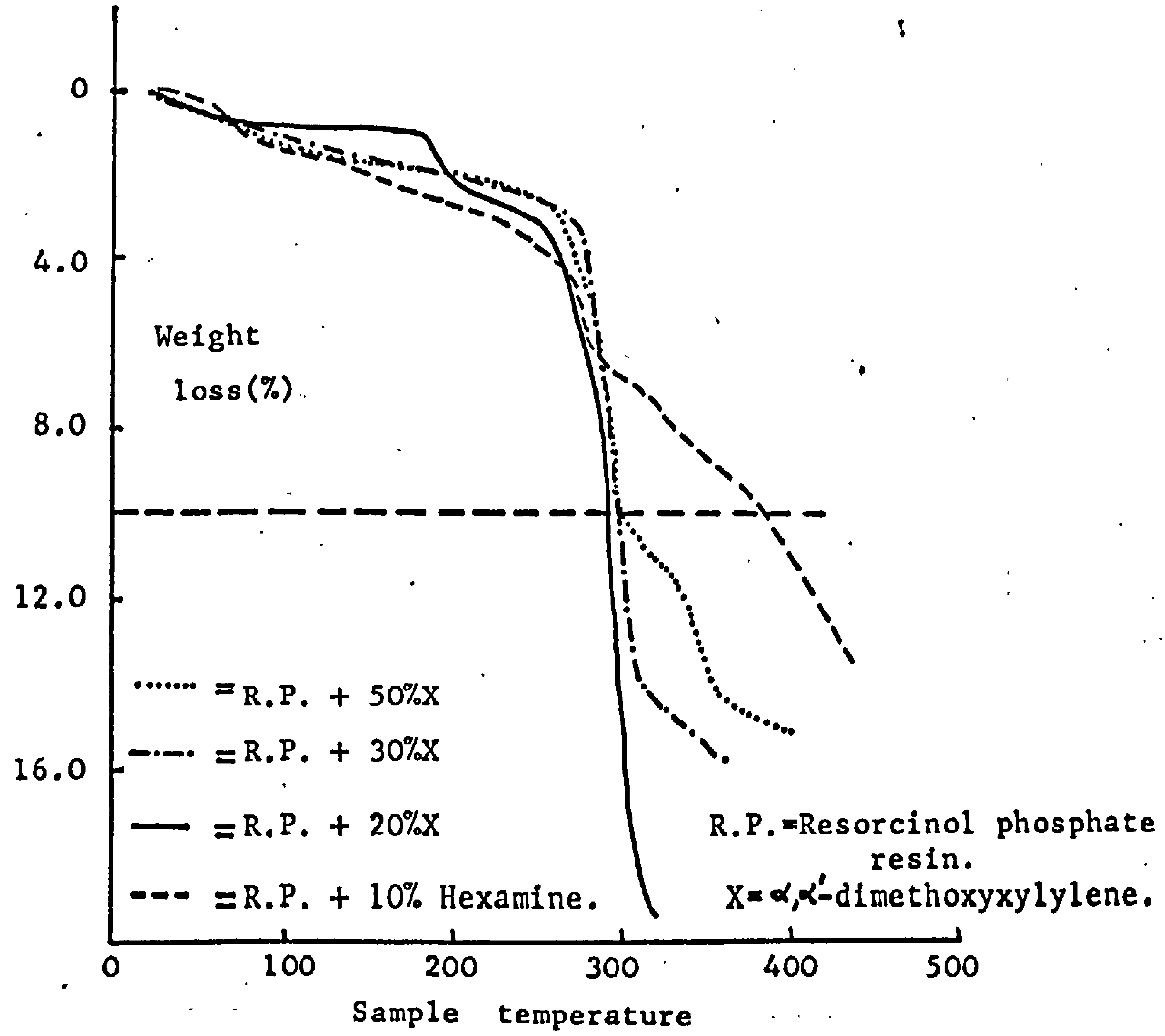
Graph 3.5.2.1.



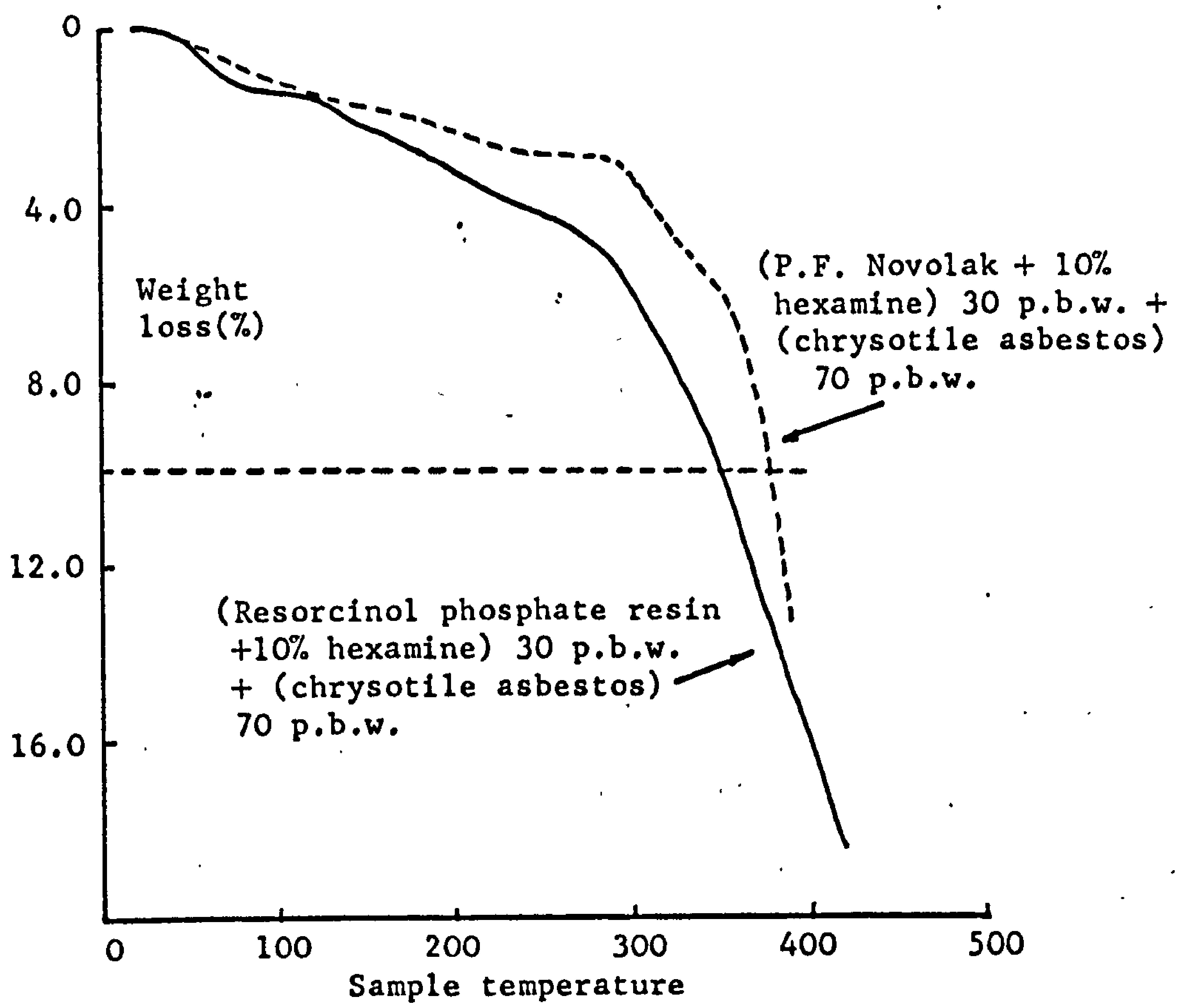
Graph 3.5.2.2.



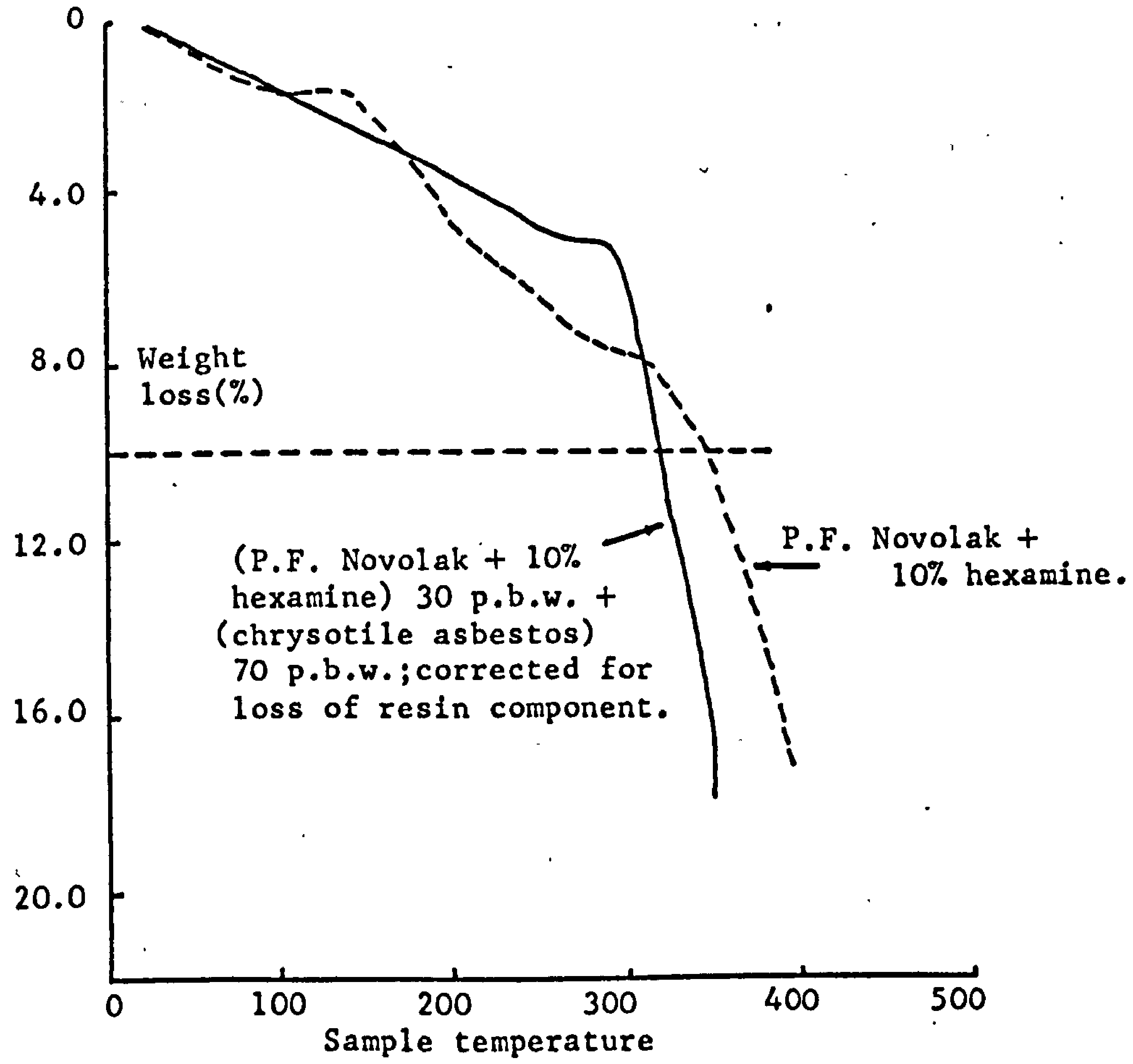
Graph 3.5.2.3.



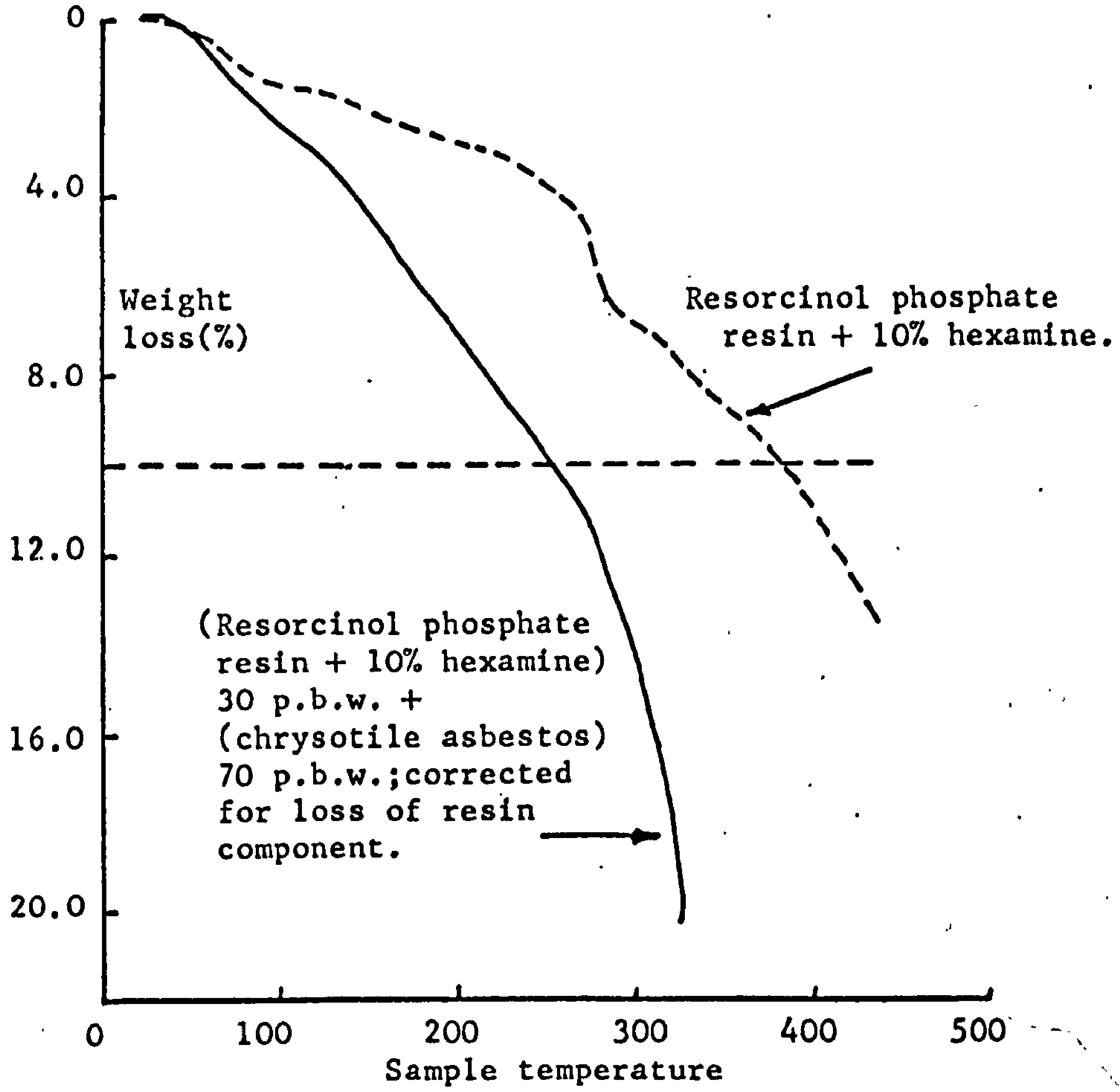
Graph 3.5.2.4.



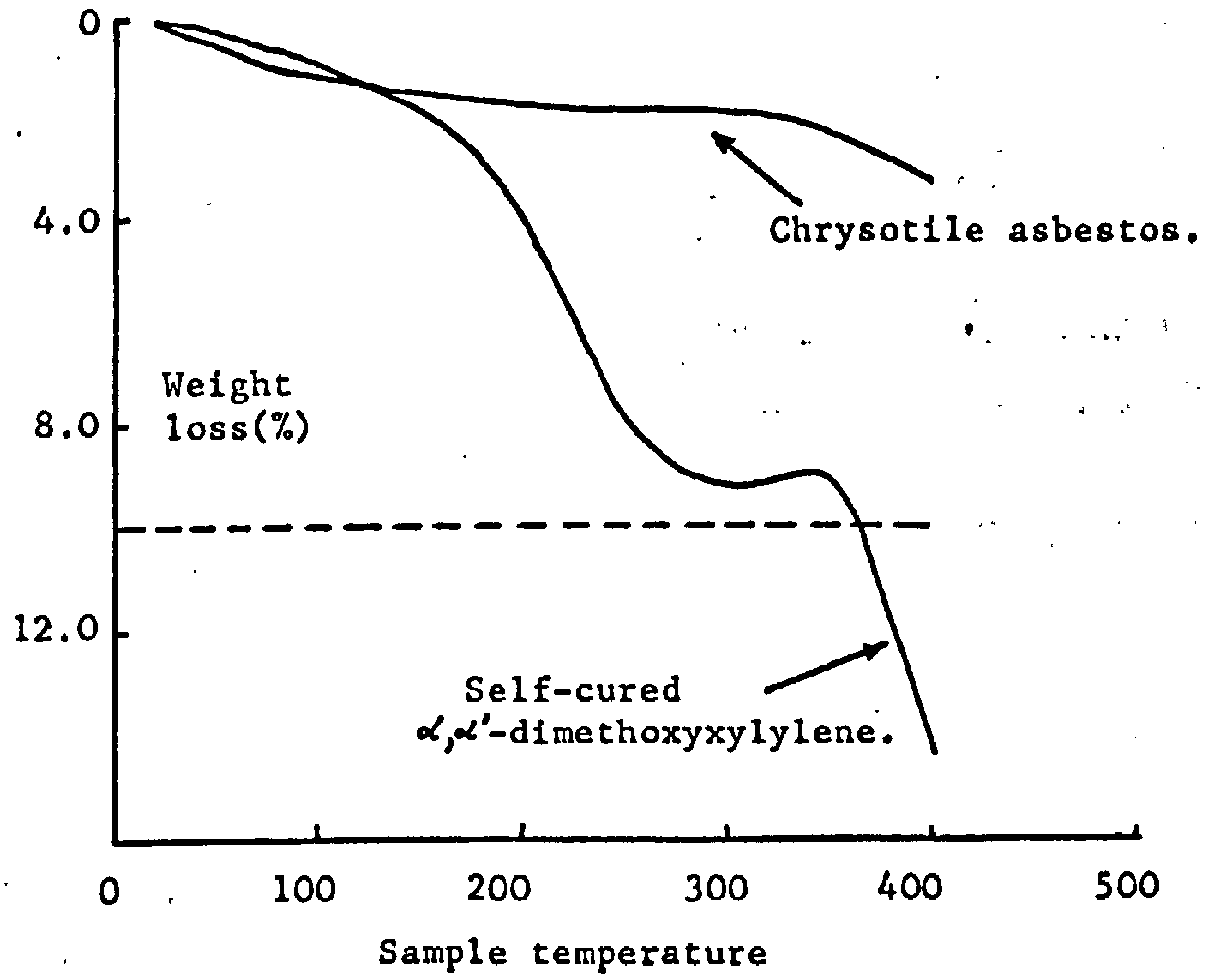
Graph 3.5.2.5.



Graph 3.5.2.6.



Graph 3.5.2.7.



Graph 3.5.2.8.

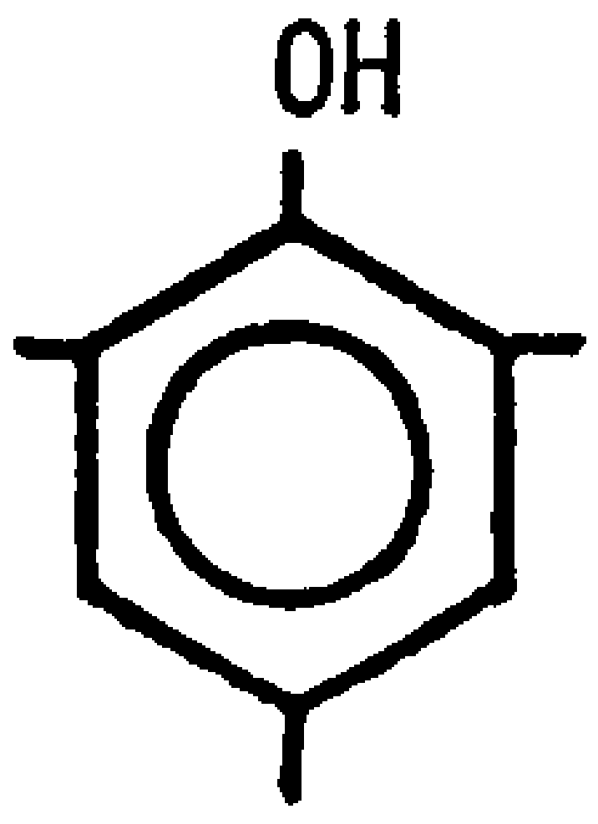
Table 3.5.2.1.

10% weight loss temperatures

Graph No.	Samples.	10% Wt. loss temp.
3.5.2.1	Resorcinol phosphate resin + 10% hexamine	655
3.5.2.1	P-F Novolak resin + 10% hexamine	620
3.5.2.4	Resorcinol phosphate resin + 20% X	565
	+ 30% X	575
	50% X	575
3.5.2.2	P-F Novolak resin + 10% X	620
	20% X	660
3.5.2.1	Xylok 225 resin + 10% hexamine	680
3.5.2.3	Xylok 225 resin + 10% X	675
	20% X	685
	50% X	690
3.5.2.8	Self Cured X	590
3.5.2.1	Phoryl 3 resin	630
3.5.2.5	(Resorcinol phosphate resin + 10% hexa) +(chrysotile asbestos) 3:7	625
3.5.2.5	(P-F Novolak resin + 10% hexa) + (chrysotile asbestos) 3:7	655
3.5.2.7	(Resorcinol phosphate resin + 10% hexa) + (chrysotile asbestos) 3:7 adjusted for loss of the organic material present only.	530
3.5.2.6	(P-F Novolak resin + 10% hexa) + (chrysotile asbestos) 3:7 adjusted for loss of the organic material present only	595
3.5.2.8	Chrysotile asbestos % wt. loss at 675	3.2

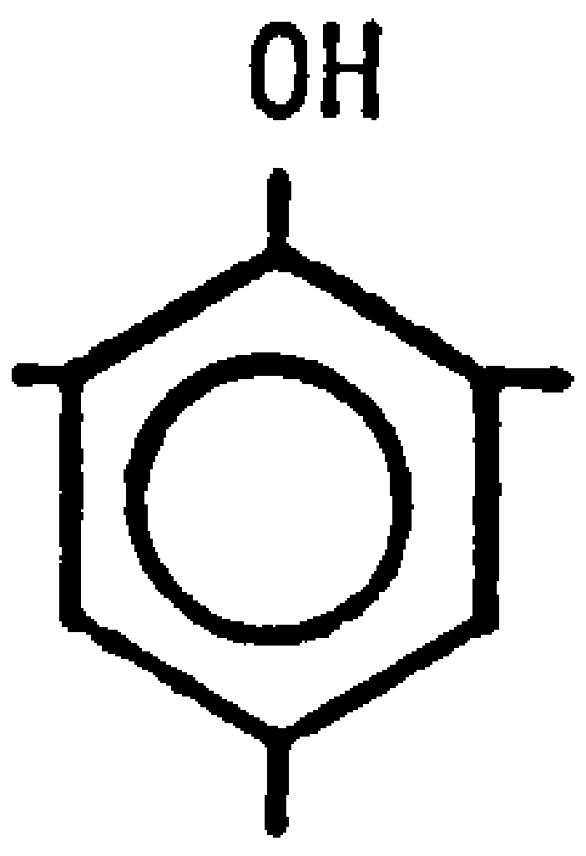
X = α,α'-dimethoxyxylylene

A hexamine cured P-F resin has a structure based entirely on



and $-CH_2-$ units.

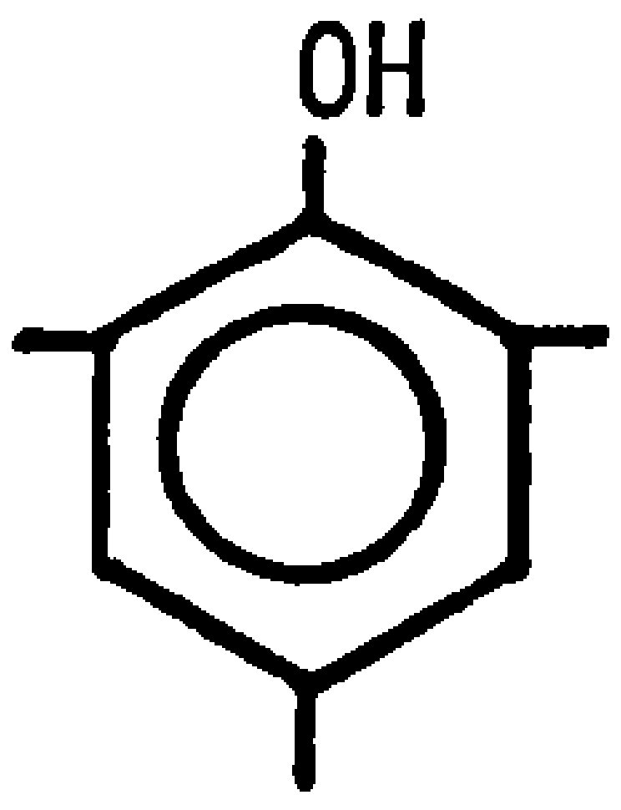
An α,α'-dimethoxyxylylene cured P-F novolak resin and a hexamine cured Xylok 225 resin have structures based on



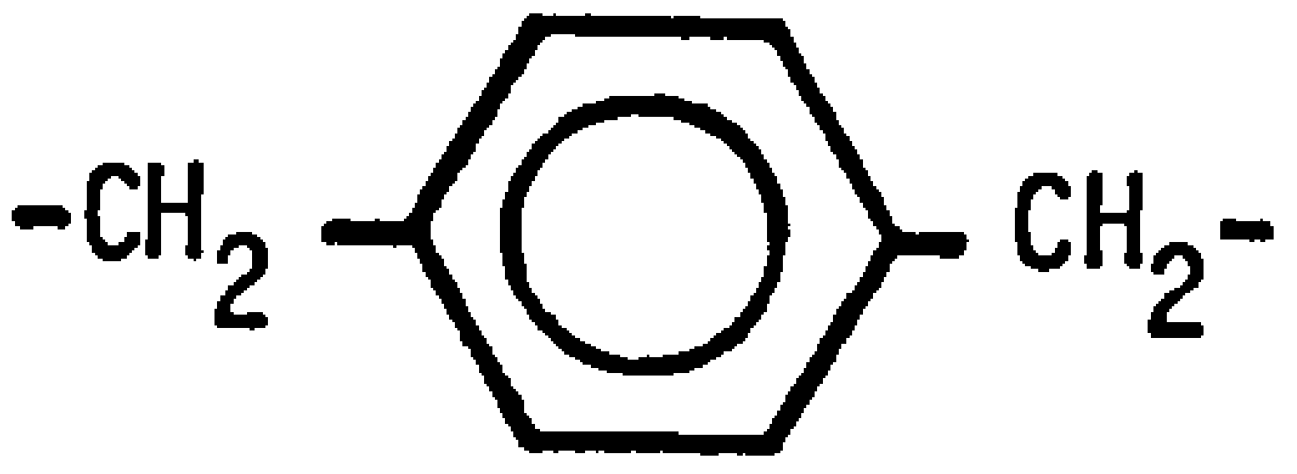
units linked by $-CH_2-$ and

groups.

An α,α'-dimethoxyxylylene cured Xylok 225 resin has a structure based on



units linked by



groups.

Comparing the shapes of the curves in graphs 3.5.2.2. and 3.5.2.3. it can be seen that replacement of hexamine by α,α'-dimethoxyxylylene increases the length of the plateau before rapid weight loss occurs; e.g. for P-F novolak and Xylok 225 resins the maximum plateau temperatures are:

P-F novolak + 10% hexamine	410	Graph 3.5.2.2.
P-F novolak + 10% or 20% α,α'-dimethoxyxylylene	575-595	
Xylok 225 + 10% hexamine	575	Graph 3.5.2.3.
Xylok 225 + 10,20 or 50% α,α'-dimethoxyxylylene	595-625	

The degrees of cross-linking between the resins cured with hexamine and with α,α'-dimethoxyxylylene, assuming complete reaction of all the curing agent used, are not comparable. 1 mole of cross-linking groups can be theoretically obtained from 18.7g of hexamine, whereas 166g. of α,α'-dimethoxyxylylene are required to produce 1 mole of cross-links.

Thus, even if 50% of the resin weight of α,α'-dimethoxyxylylene is used as the curing agent, the theoretical cross-link density would be less than that obtained by employing 10% of the resin weight of hexamine. Despite the lower degrees of cross-linking obtained with α,α'-dimethoxyxylylene, the use of this curing agent still gives thermosets of much improved high temperature stability compared to the hexamine cured products. The possible reason for the improvement of the high temperature stability of these resins when α,α'-dimethoxyxylylene is used as a curing agent has been discussed in section 3.3.9.

Interestingly, self cured α,α'-dimethoxyxylylene (graph 3.5.2.8.) has lower high temperature resistance than the resins in which it is a curing agent.

Comparing resorcinol phosphate resin cured with hexamine and α,α'-dimethoxyxylylene (graph 3.5.2.4.) it can be seen that both thermosets show a gradual initial sloping plateau, followed by a rapid weight loss. The onset of this rapid loss in weight occurs at about 535 with the hexamine cured resin and 525-545 with the α,α'-dimethoxyxylylene cured resins. Thus, the expected increase in the temperature of the onset of rapid weight loss, by changing the curing agent from hexamine to α,α'-dimethoxyxylylene, does not occur with resorcinol phosphate resin. These results indicate that the degradation of resorcinol phosphate resin is not dependent upon the curing agent and suggest that the commencement of rapid weight loss is controlled by the breakdown of other parts of the cured resin's structure, probably the -P-O-C bonds. However, the thermogravimetric curve of "Phoryl 3" resin (XVII)shows the beginning of a rapid loss in weight at 570 (graph 3.5.2.1.), indicating that P-O-C bonds should at least be stable up to this temperature in air.

Comparison of moulded resin + chrysotile asbestos composites (finely powdered for this work) shows that the composite containing P-F novolak resin + 10% hexamine has a higher 10% weight loss temperature than the composite containing resorcinol phosphate resin + 10% hexamine (graph 3.5.2.5., table 3.5.2.1.). This contrasts with the results obtained for the hexamine cured resins in the absence of asbestos.

For these composites the weight loss due to the asbestos component is determined from the thermogravimetric curve of chrysotile asbestos (graph 3.5.2.8.) and an estimate made of the % weight loss of the resin components in the composites (graphs 3.5.2.6. and 3.5.2.7.). It can be seen that P-F novolak resin + 10% hexamine gives a thermogravimetric curve similar to P-F novolak resin + 10% hexamine in the presence of chrysotile asbestos (graph 3.5.2.6.): the presence of asbestos lowers the 10% weight loss temperature by about 25 (table 3.5.2.1.).

Graph 3.5.2.7. shows that resorcinol phosphate resin + 10% hexamine in the presence of chrysotile asbestos gives a thermogravimetric curve showing a much more rapid weight loss than resorcinol phosphate resin + 10% hexamine alone. The presence of asbestos lowers the 10% weight loss temperature by 125 (table 3.5.2.1.).

These results indicate strongly that chrysotile asbestos has a detrimental effect on the high temperature stability in air of P-F novolak and resorcinol phosphate resins cured with 10% hexamine. However, with resorcinol phosphate resin + 10% hexamine this effect is so great that it appears that the asbestos actually attacks and decomposes the resin at elevated temperatures.

3.5.3. Isothermal ageing studies at 525.

3.5.3.1. The preparation of moulding powders.

The resorcinol phosphate resin - chrysotile asbestos composite can be milled to a hide in a similar manner to a commercial phenol formaldehyde resin composite.

Table 3.5.3.1.1. shows the conditions employed in determining the flow properties of the moulding powders obtained and table 3.5.3.1.2. gives the flow disc thicknesses obtained for each resin-asbestos composite batch prepared.

3.5.3.2. The preparation of moulded test bars.

Resorcinol phosphate resin-chrysotile asbestos composite can be moulded in the same way as a conventional phenol-formaldehyde resin composite, although a slightly higher mould temperature is required and the moulding time is about three times that of the conventional phenol-formaldehyde resin composite.

3.5.3.3. The evaluation of the high temperature resistance of the resorcinol phosphate resin-chrysotile asbestos composite moulded bars.

The results from the isothermal ageing studies are shown in graphs 3.5.3.3.1. to 3.5.3.3.4.

Graph 3.5.3.3.1. shows the weight losses of the post cured moulded bars aged at 525. Up to 800 hours' ageing in air. The composite containing the resorcinol phosphate resin shows a higher weight loss than the P-F novolak resin composite.

Graph 3.5.3.3.2. shows the flexural strength changes of moulded bars after post curing, followed by ageing at 525 in air. As expected post curing the P-F novolak resin composite bars gives an increase in flexural strength, but surprisingly the resorcinol phosphate resin composite bars suffer a significant drop in flexural

Table 3.5.3.1.1.

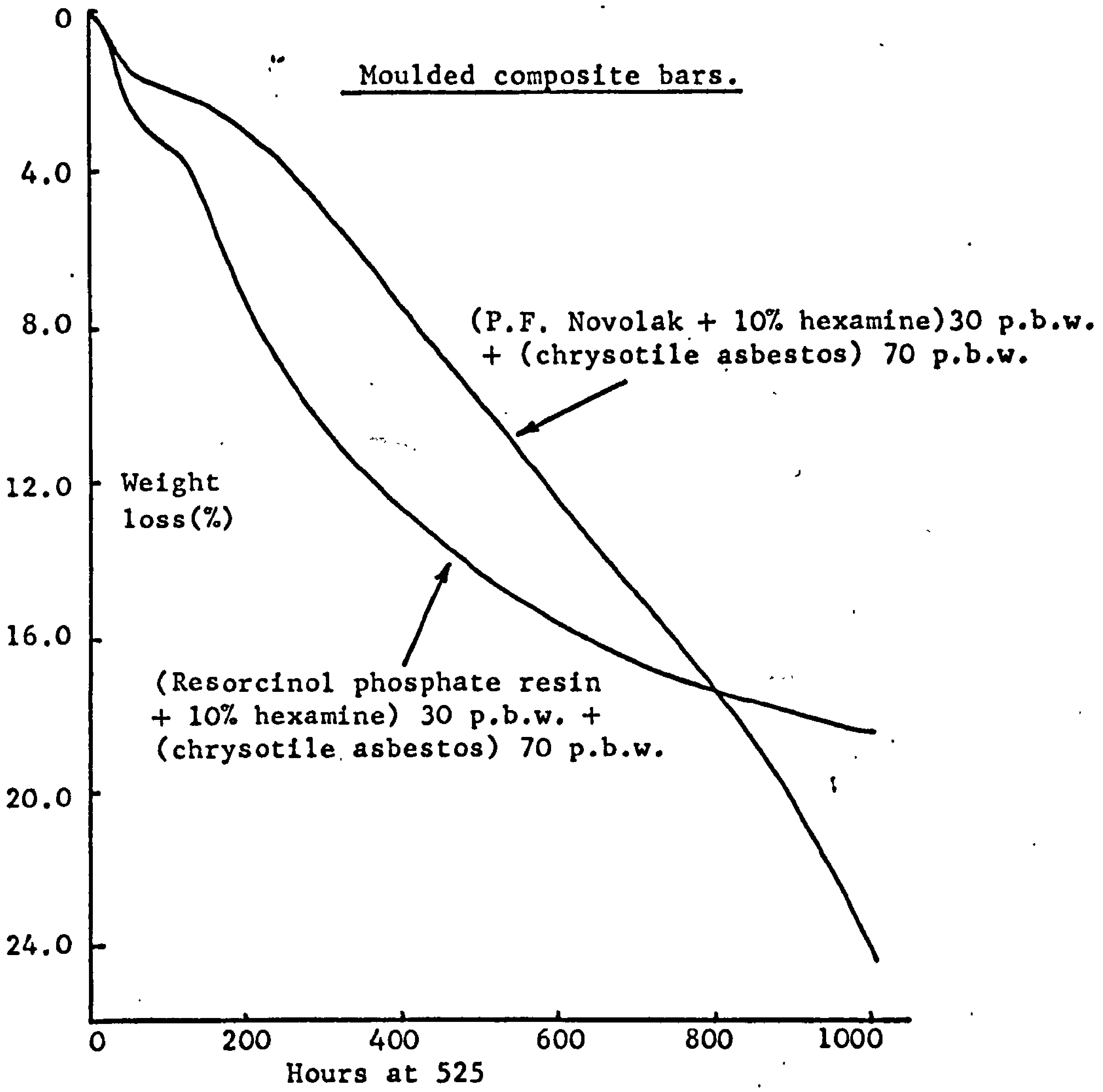
Flow disc method for determining the flow properties of moulding materials.

Discs' diameter (cm)	15.24
Discs' temperature (K)	435-445
Load applied on discs (Mg)	4.064
Sample weight (g)	16

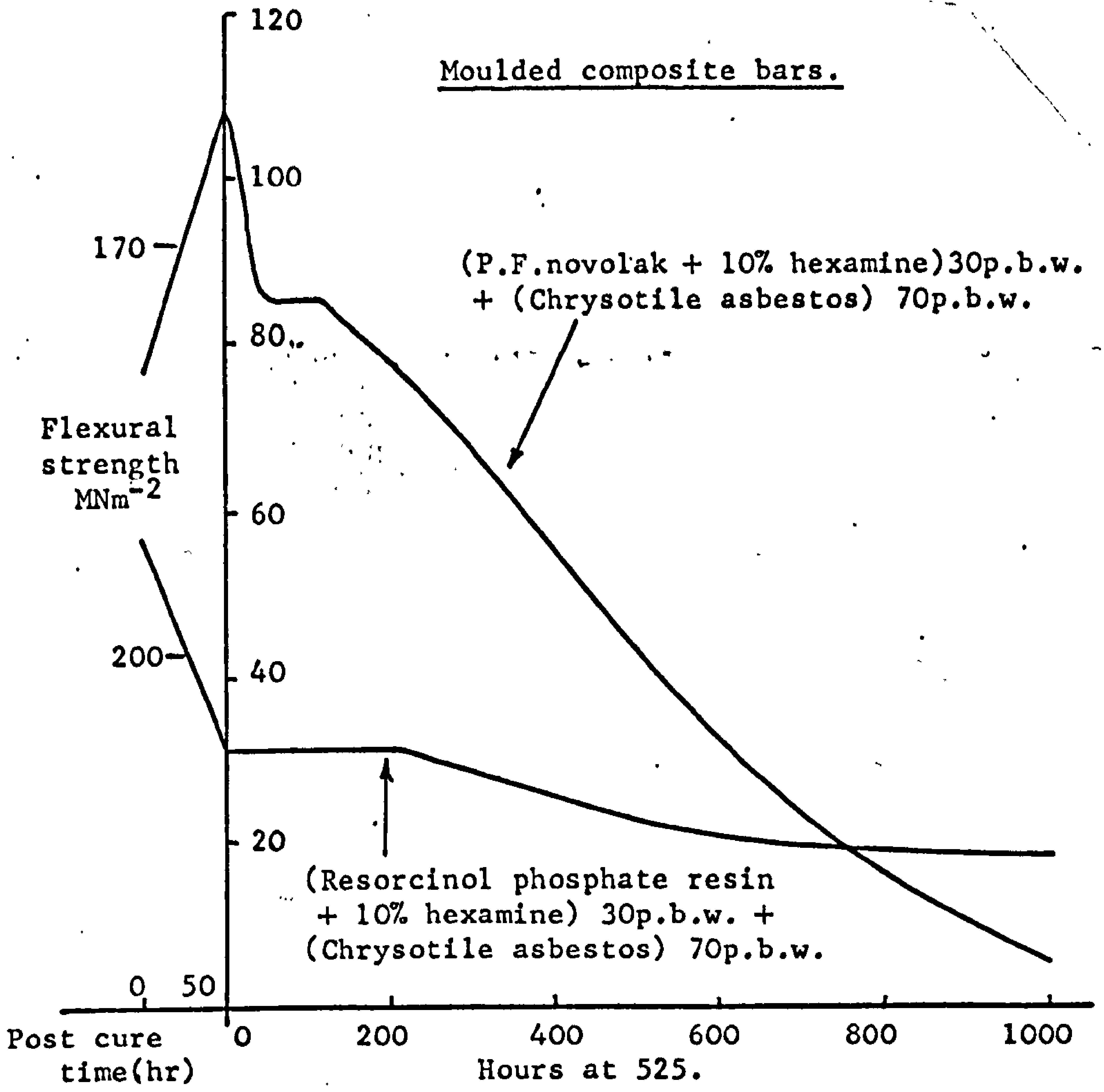
Table 3.5.3.1.2.

Flow disc thickness of batches of resin-asbestos composites.

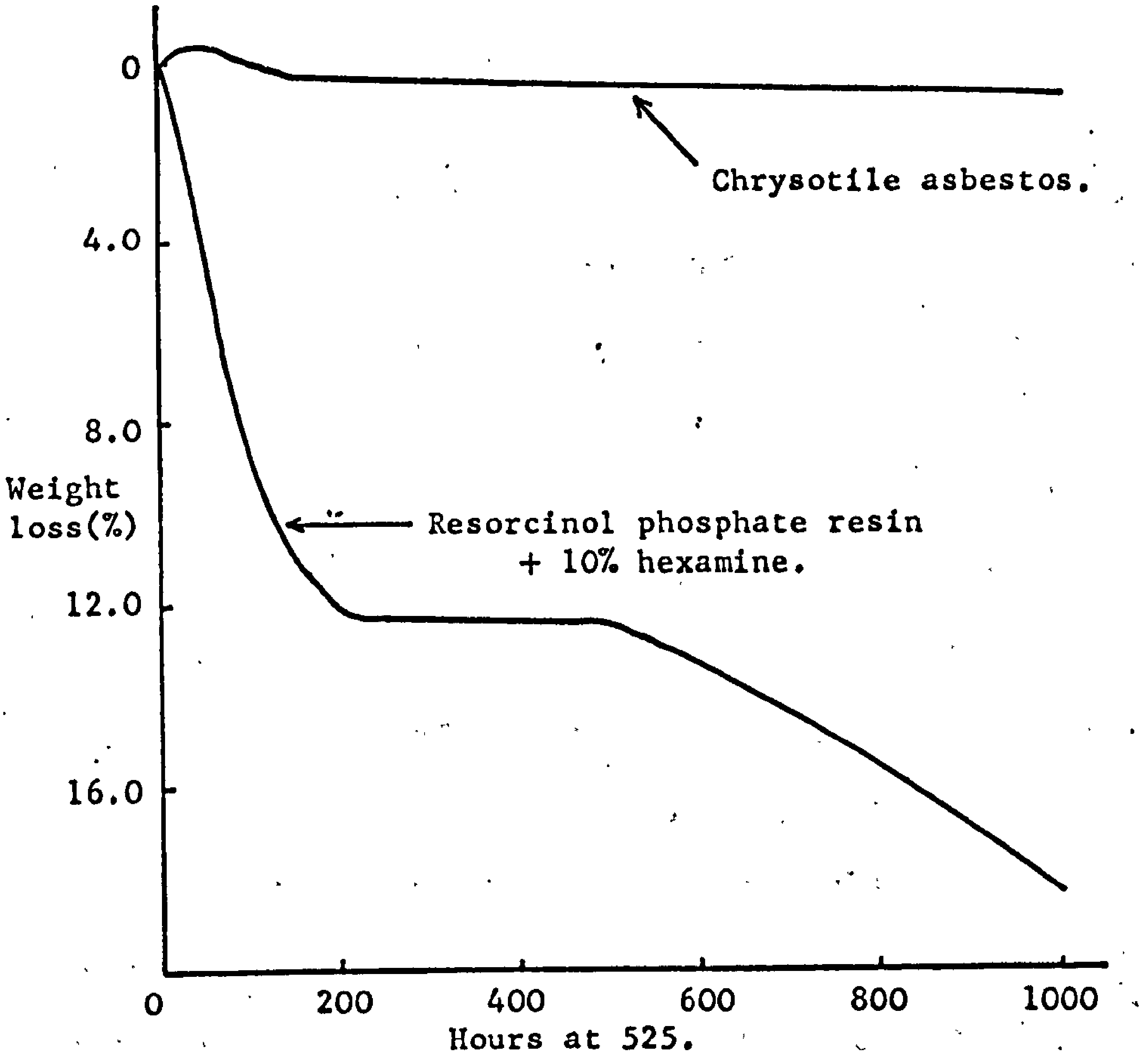
P-F novolak composite (mm)	Resorcinol phosphate resin composite (mm)
1.91	1.34
1.78	1.25
1.70	1.40
1.78	1.45
	1.42


Moulded composite bars.
0
4.0
8.0
12.0
16.0
20.0
24.0
Weight loss(%)
(P.F. Novolak + 10% hexamine)30 p.b.w. + (chrysotile asbestos) 70 p.b.w.
(Resorcinol phosphate resin + 10% hexamine) 30 p.b.w. + (chrysotile asbestos) 70 p.b.w.
0
200
400
600
800
1000
Hours at 525

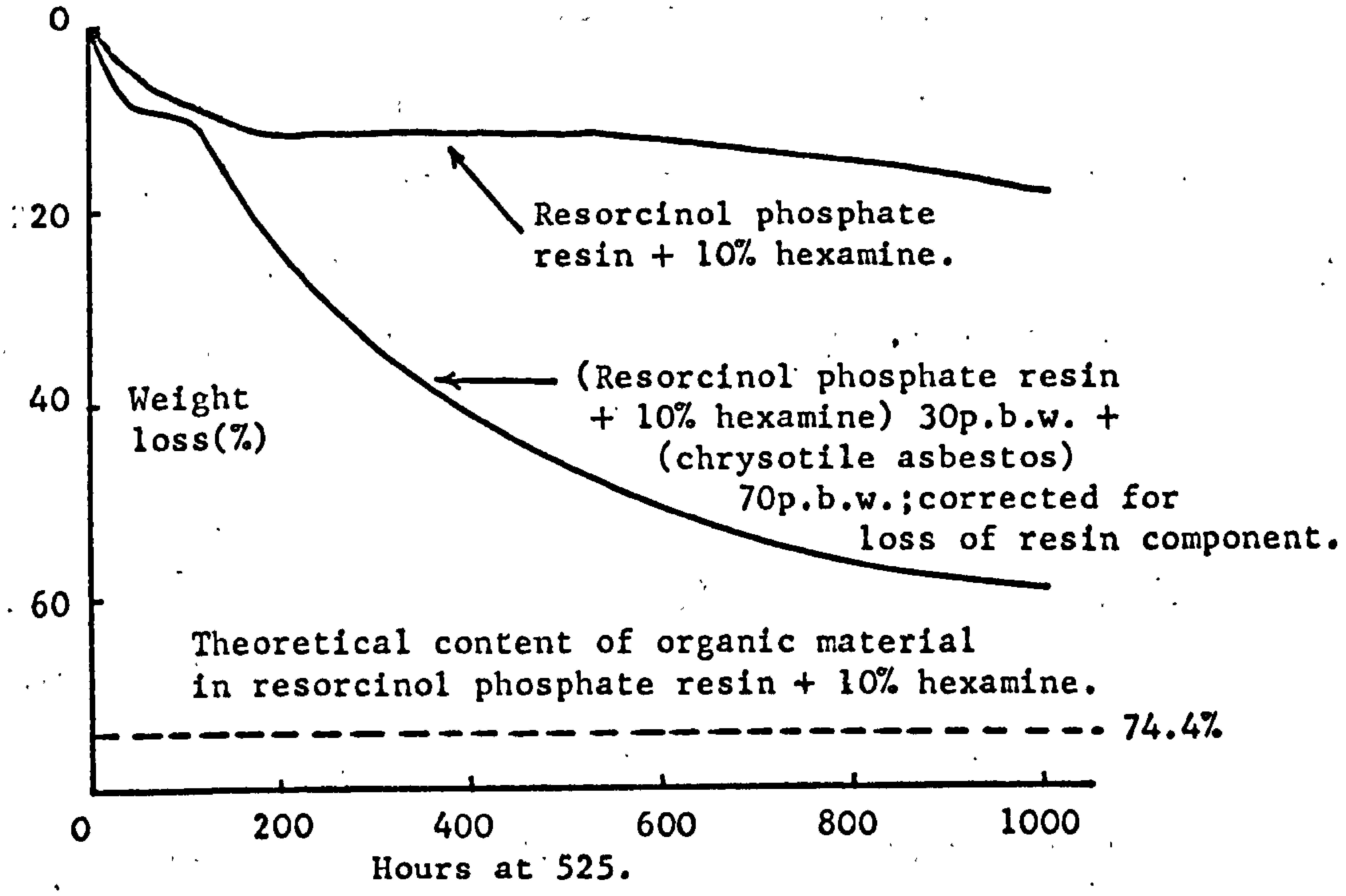
Graph 3.5.3.3.1.


Moulded composite bars.
120
100
80
60
40
20
170
200
Flexural strength MNm^{-2}
(P.F.novolak + 10% hexamine)30p.b.w. + (Chrysotile asbestos) 70p.b.w.
(Resorcinol phosphate resin + 10% hexamine) 30p.b.w. + (Chrysotile asbestos) 70p.b.w.
0
50
Post cure time(hr)
0
200
400
600
800
1000
Hours at 525.

Graph 3.5.3.3.2.



Graph 3.5.3.3.3.



Graph 3.5.3.3.4.

strength on post curing.

At 525 in air the P-F novolak resin composite bars undergo a rapid decline in flexural strength over 1000 hours, retaining only 5.3 % of their flexural strength after post curing. In comparison the resorcinol phosphate resin composite keeps 59.5 % of its flexural strength after post curing when aged in air for 1000 hours at 525. In-spite of the better retention of flexural strength at 525 of the resorcinol phosphate resin composite specimens, their initial flexural strength after post curing is disappointingly low, being only 28.4% of that of the P-F novolak resin composite bars.

Graph 3.5.3.3.3. shows the weight losses of samples of cured resorcinol phosphate + 10% hexamine and chrysotile asbestos. Both samples had been preheated at 475 for 48 hours before ageing at 525. The weight loss of the cured resin is about 19% after 1000 hours at 525 and that of the asbestos negligible at less than 1%.

Graph 3.5.3.3.4. shows the weight loss of resorcinol phosphate resin + 10% hexamine, preheated at 475 for 48 hours, compared with the estimated weight loss of the resorcinol phosphate resin + 10% hexamine in the post cured moulded bars. It is apparent that the presence of chrysotile asbestos greatly accelerates the degradation of resorcinol phosphate resin. After 1000 hours at 525 the cured resin alone loses only 18.3% of its weight, compared to a weight loss of about 60% for the resin in the asbestos composite. This behaviour is in line with thermogravimetric evidence.

3.5.4. Pyrolysis of resorcinol phosphate resin-chrysotile asbestos composite moulded bars.

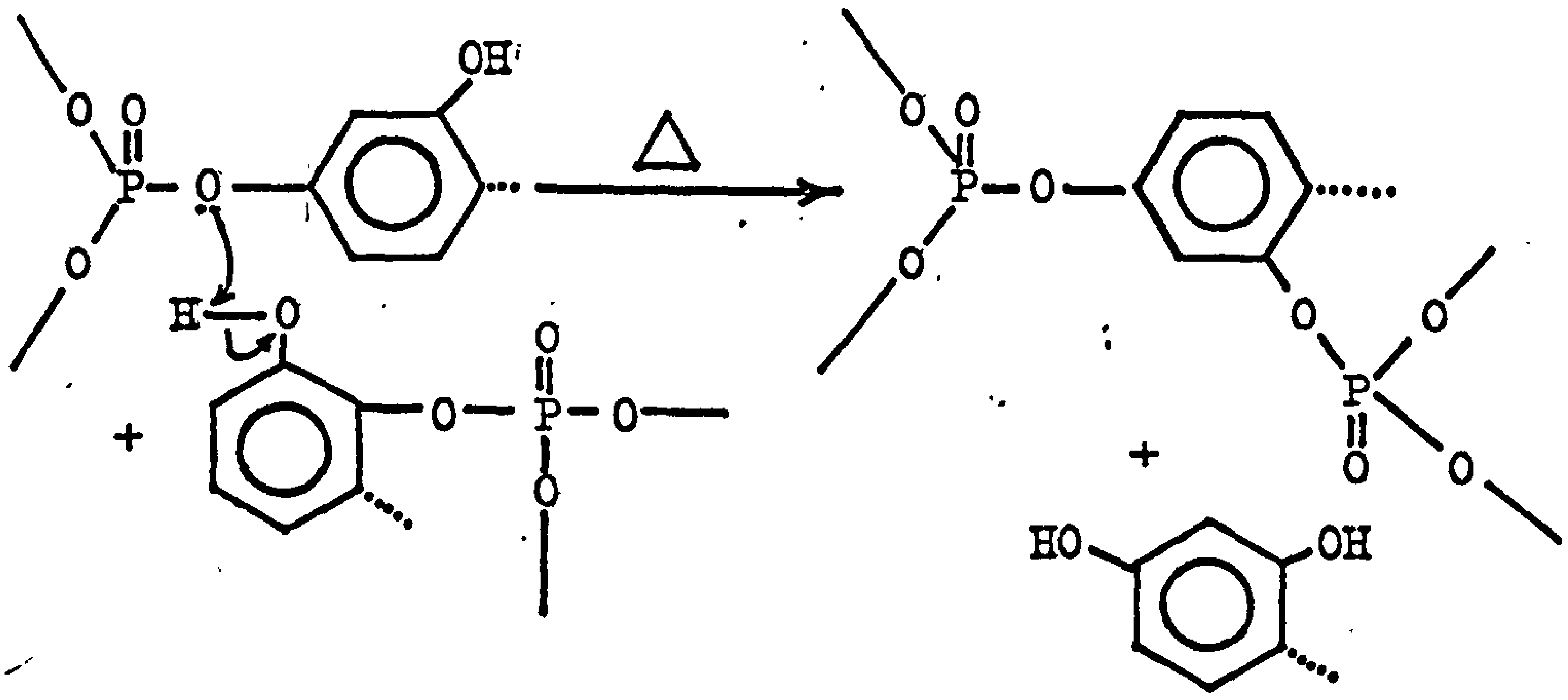
Resorcinol phosphate resin + 10% hexamine and chrysotile asbestos composite moulded bars have been heated in stages up to about 1075. The specimens lose 30% of their weight during the pyrolysis. Assuming the asbestos contains about 13%[81] of water, the theoretical weight loss for water and organic material from the composite is about 30%.

Even though apparently all of the organic content of the composite is lost during heating to about 1075 the bars remain coherent and have a residual flexural strength at room temperature of the order of 10-11 MNm^{-2}. It is possible that the inorganic phosphate residues remaining after removal of the organic material combine with the asbestos to form a coherent mass. Chrysotile asbestos undergoes structural re-organisation at 1085 to the non-fibrous crystalline olivine mineral.[81] A transformation of this type may occur when resorcinol phosphate resin and chrysotile asbestos composite is pyrolysed and may also account for the coherent nature of the heated bars.

3.5.5. Summary and conclusions.

Although moulded composites of resorcinol phosphate resin + 10% hexamine and asbestos show good retention of flexural strength at 525, their initial flexural strength is considerably lower than that of a comparable conventional P-F novolak resin + 10% hexa and asbestos composite. This deficiency in initial mechanical strength is too great for the resorcinol phosphate resin composite system to be a commercially viable product.[82]

Chrysotile asbestos is undesirable as a filler in resorcinol phosphate resin, since it accelerates the high temperature degradation of the resin. It is possible that the alkaline magnesia content of the asbestos causes hydrolysis of the P-O-C bonds in the resin at 525, or alternatively it may catalyse a thermal reorganisation of the inorganic phosphate links to degrade the resin structure (XLII).



.... = cross links

(XLII) Thermal re-organisation of bonds in resorcinol phosphate resin.

4. SUGGESTIONS FOR FUTURE WORK.

These studies have shown that resorcinol phosphate resin is easily prepared and processed, but decomposes rapidly at 525. Preliminary thermogravimetry has suggested that thermal breakdown may occur at the P-O-C bonds in the resin.

To ascertain the mode of thermal or thermo-oxidative degradation of the cured resin a fuller understanding of the fragmentation taking place is required. Some approaches that may be useful in determining the products formed when the resin is heated are:

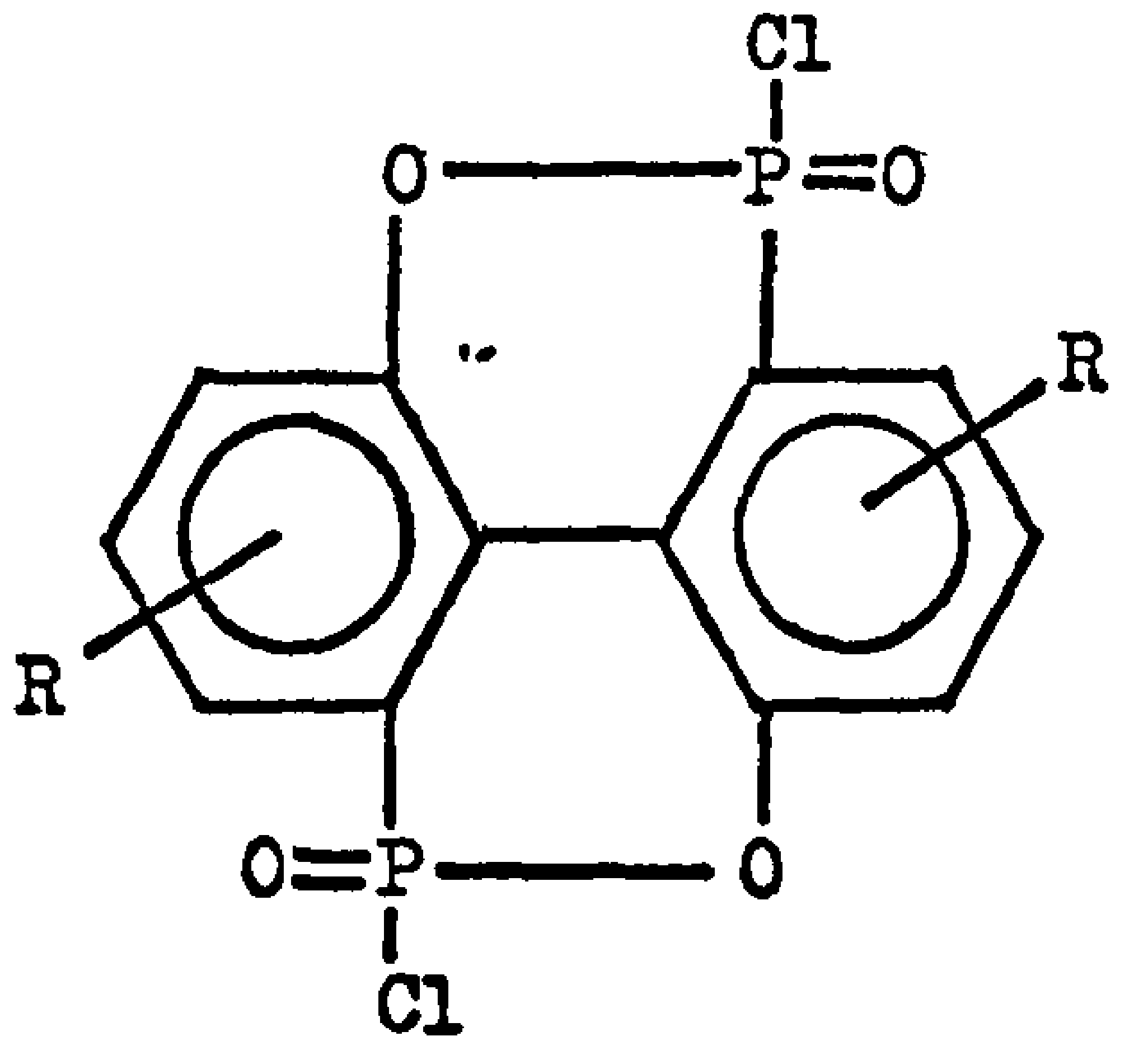
1. Destructive distillation of the resin in air or nitrogen, followed by chromatographic, spectroscopic and chemical analysis of the distillate.
2. Isothermal heating of the cured and uncured resin in air and in nitrogen, using a pyrolysis unit connected to a mass spectrometer.
3. Long term refluxing of model compounds, such as tri-phenyl phosphate, with air and with nitrogen passing through the liquid, followed by chromatographic and chemical analysis.

Should the high temperature stability of the P-O-C linkage be found to be poor at 475-525 then there would be little point in incorporating such linkages in phenolic resins for use in this temperature range. Conventional phenolic resins satisfy most needs below 475.

Incorporation of P-O-C linkages into a two dimensional network structure may reduce fragmentation considerably. Recently some cyclic aryl phosphates have been reported,[83] for example (XLIII), which may condense with polyhydric phenols to produce "step ladder" polymers, for example (XLIV).

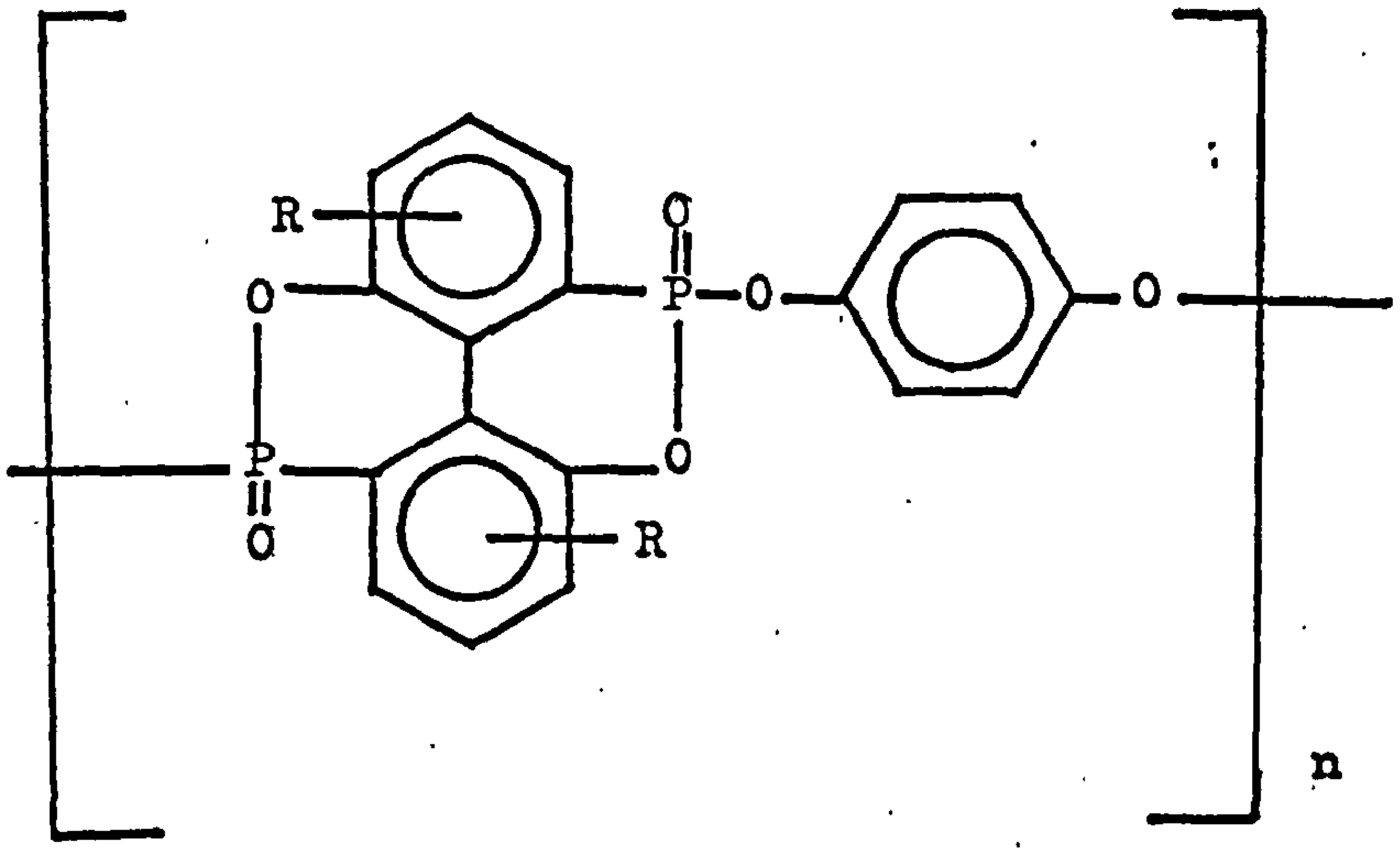
By choice of a suitable substituent on the aromatic rings of the cyclic phosphate monomers curing may be possible by hexamine or α,α'-dimethoxyxylylene.

The breakdown of resorcinol phosphate resin is accelerated appreciably by chrysotile asbestos at 525. Incorporating inert,



R=various substituents.

(XLIII)



R = various substituents.

(XLIV)

non-basic fillers such as an alkali free silica fibre mat, may give composites with acceptable heat ageing properties at 525. An insight into the mechanism of the high temperature breakdown of resorcinol phosphate resin in the presence of chrysotile asbestos may be gained by applying the methods (1,2 and 3) suggested for the cured resin alone.

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A.L. Reader 1972.

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PART 2

A STUDY OF THE
CHEMISTRY OF IONOMER
CEMENTS.

INDEX

1. INTRODUCTION

1.1. General Introduction

Cement materials, such as gypsum and clays, have been known for centuries and even the common, modern portland cement dates back to the early nineteenth century. Strictly speaking, the word cement includes a large range of materials, which can act as adhesives, binders, fillers and construction and grouting materials. All cements have one property in common, namely that they are worked whilst in a fluid, or semi-fluid state and then are left to set and harden. Plaster of Paris, portland cement, organic adhesives and cold curing thermosets, solders and dental amalgams and restoratives may all be classified as cements.

Recently a new class of cements based on ionomers has been developed. Ionomers are metal-polyanion salts, or complexes, formed by reacting organic polyacids with basic metal substances.

The applications of ionomer cements are, at present, confined mainly to dentistry and particularly as permanent restorative materials, adhesives and cavity liners. Ionomer cements combine a number of useful properties and may have considerable potential for uses outside the dental field.

One particular feature of ionomer cements is their ease of preparation. The chemical bonds between the metal ions and polyanions in ionomers have a high degree of ionic character and the formation of ionic bonds is usually rapid and can take place at low temperatures. Consequently, ionomer cements set rapidly at ambient temperatures.

Hardened ionomer cements resemble ceramic materials, in that they can have high compressive strengths, a hard finish and good resistance to solvents.

Despite these potentially valuable characteristics ionomer cements have not been extensively researched. Much of the existing knowledge on the chemistry and physics of these cements has stemmed from their use in dentistry. The field is therefore open for research and development in other applications, especially those involving cement composites.

1.2. The development of dental cements.

The use of chemical dental cements originated in the 1850's with the introduction of zinc oxychloride cements. These cements, which had poor cementing properties and were attacked by oral fluids, have long since been abandoned.[1]

Some 20-25 years later zinc phosphate cement was introduced and is still used in modern dentistry. This cement shows some improvement over zinc oxychloride cements, but still suffers from serious shortcomings. The cement has a low compressive strength and poor stability to oral fluids.[2] Its low initial pH can cause pulpal irritation when applied to a tooth cavity and when it has set there is very little adhesion between the cement binder and the tooth substance. The opacity of zinc phosphate cement is high and does not match tooth enamel. Zinc phosphate cement can be used for temporary restorations and as insulating bases for permanent restorations.[3] Some properties of zinc phosphate cement and other important dental cements are shown in table 1.2.1.

Dental silicate cements evolved at about the same time as zinc phosphate cement. Their compressive strength and translucency are considerably better than zinc phosphate cement, although the adhesion to tooth substances, the pulpal irritancy effect and resistance to oral fluids show no great improvement.[5] Dental silicate cement is the most widely used chemical dental cement and finds applications in non-stress bearing anterior restorations and for temporary crowns.[3] The cement cannot, however, be described as being permanent in these applications.

In the late 1880's, shortly after dental silicate cement appeared, zinc oxide-eugenol cement was introduced. This cement is bland towards tooth pulp, but has a low strength, high opacity, and is hydrolytically unstable. It is widely used in modern dentistry and finds application in insulating bases and temporary restorations.[3]

There then came a stagnation in the evolution of dental cements, which was revived some 70 years later by the modification of zinc oxide-eugenol cement with o-ethoxybenzoic acid and the modification of existing inorganic dental cements with polyacids. But it was not until another 10 years later that a significant contribution was made, namely the introduction of the first ionomer cement - zinc poly(carboxylate).

Zinc poly(carboxylate) cement[6] shows a significant improvement in adhesion to tooth substances when compared with the dental silicate and zinc phosphate cements. The initial pH of zinc poly(carboxylate) cement paste prior to application is higher than that of dental silicate and zinc phosphate and hence the cement is much less of an irritant.[3] Like zinc phosphate cement the opacity of zinc poly(carboxylate) cement is high.[4] The compressive strength of zinc poly(carboxylate) cement is about the same,[6] or slightly lower[7] than zinc phosphate cement and is considerably less than dental silicate or ASPA cements.

In dentistry zinc poly(carboxylate) cements are used mainly for insulating bases and luting cements.[3]

The latest development, closely following zinc poly(carboxylate) cement is ASPA cement,[8] which is related to dental silicate and zinc poly(carboxylate) cements. ASPA cement (Alumino silicate-polyacrylate) has a combination of the favourable properties found in its predecessors.[4] For example, it has a high compressive strength, good resistance to attack by oral fluids, a high initial pH and hence shows a very low irritancy to tooth substances, good adhesion to tooth substances and fairly good translucency. ASPA cement is very new and although it has reached a commercial stage in development it is not widely used as yet. Research and development is underway at the present time to further improve the system.

Diagram 1.2.1. shows the development of dental cements in chronological order, culminating with the new ASPA system. Some of the important cements in diagram 1.2.1. will be discussed briefly in section 1.3. and ASPA cement will be fully discussed in section 1.4.

Table 1.2.1.

Comparison of some of the properties of ASPA cement with other dental cements.[4]

PROPERTY*	ASPA cement (A)	ASPA cement (B)	Dental silicate cement	Zn poly(carb-oxylate cement	Zn phosphate cement	ZnO-eugenol cement(simple)	ZnO-eugenol cement (reinforced)
Powder: liquid ratio (g ml^{-1})	3.5	3.0	4.0	3.6	4.2	2.6	2.35
Volume fraction of powder (%)	56	52	62	40	43	32	30
Setting time (min)	4.5	4.5	3.75	3.25	4.25	(3.75)[a]	(3.75)[a]
Compressive strength (MNm^{-2}) 24 hr	213	196	226	85	128	13	39
7 day	-	222	246	-	-	-	-
Diametral tensile strength (MNm^{-2}) 24 hr	17	15	13	12	8	1.6[b]	3.5[b]
7 day	-	16	14	-	-	-	-

Table 1.2.1. continued

PROPERTY*		ASPA cement (A)	ASPA cement (B)	Dental silicate cement	Zn poly(carboxylate cement	Zn phosphate cement	ZnO-eugenol cement (simple)	ZnO-eugenol cement (reinforced)
Solubility and disintegration in water (%) 24 hr		0.3	0.3	0.5	0.04	0.02	0.1 (2.6)[c]	0.1 (1.5)[c]
Acid erosion at pH=4.0 at 310K (%)	24 hr	-	0.1	0.8	-	-	-	-
	7 day	-	0.3	3.9	-	-	-	-
pH Initial,	3 min	-	2.5	1.3	2.6	1.5	-	-
	24 hr	-	5.3	4.7	6.9	6.4	-	-

a. *The standard setting time differs from that used for other cements.*

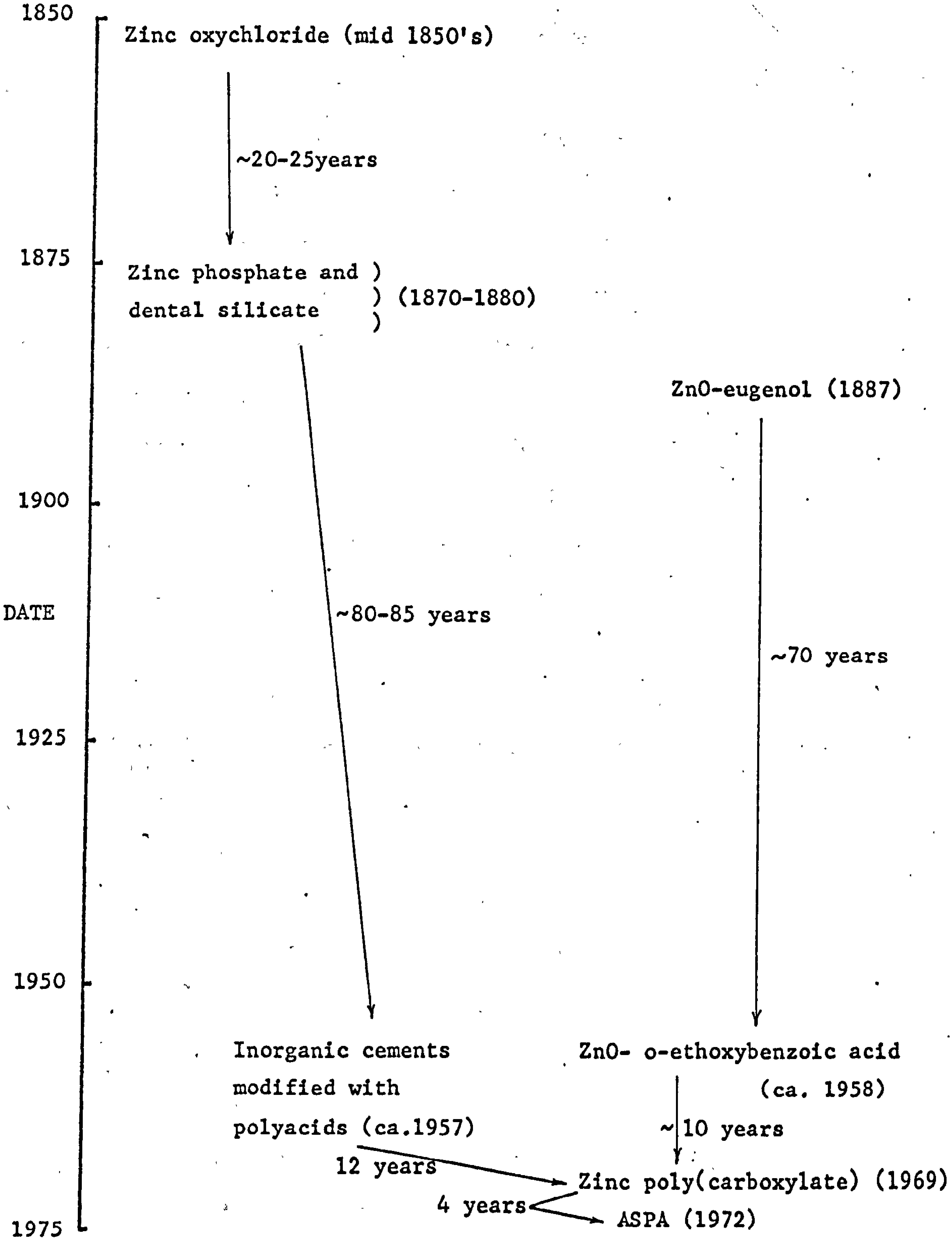
b. *Indicated values only. This test only strictly applies to brittle cements.*

c. *A best estimate for the actual disintegration in water.*

* *For test methods see reference 4.*

Diagram 1.2.1.

The developement of dental cements.



1.3. The nature of dental cements.

1.3.1. Metal phosphate cements.

Metal phosphate cements are prepared by mixing aqueous o-phosphoric acid with a powdered metal oxide or mixture of metal oxides. Kingery[9] has summarised the chemistry and properties of metal oxide -- o-phosphoric acid cold setting ceramics and has reported that only certain metal oxides give setting and coherent products. Acidic or chemically inert oxides (e.g. MoO_3 and Al_2O_3) do not react. Highly basic oxides (e.g. CaO and ZnO) react violently to give porous, friable cements with little cohesion. The reaction rate must be compatible with the organisation of the reaction products into a coherent mass. Many weakly basic, or amphoteric oxides react, but not all give setting cements. Set cements all contain mono- or di-basic phosphates and hydrogen bonding in these structures aids cohesion in the cement.

In dental cements thermally deactivated zinc oxide is used, usually with about 10% added magnesium oxide and traces of other oxides. The o-phosphoric acid solution contains small amounts of dissolved zinc and aluminium phosphates and about 36% w/w water.[10]

Metal phosphate cements have also found application as refractory materials.[9]

1.3.2. Dental silicate cement.

Dental silicate cements are prepared by mixing an ion-leachable aluminosilicate glass with o-phosphoric acid solution containing dissolved zinc and aluminium phosphates and about 40% w/w water. Ca^{2+} and Al^{3+} ions are leached from the surface of the glass particles by H^+ ions from the phosphoric acid. The glass particle surfaces are left coated with a siliceous hydrogel and the leached metal ions precipitate the phosphoric acid as insoluble (and possibly polymeric) metal phosphates. F^- ions are also leached from the glass. The cementing matrix of the products is believed to be a mixture of metal phosphates and fluorides in an amorphous condition.

The literature on dental silicate cements is extensive. Between 1967 and 1972, Wilson et. al. characterised the cement chemistry in detail.[5]

A modification of dental silicate cement is silicophosphate cement, in which the powder phase contains both aluminosilicate glass and zinc oxide.[11]

1.3.3. Zinc oxide-eugenol cement.

The chemistry of the setting of zinc oxide-eugenol cement was characterised by Smith[12] well over half a century after its introduction as a dental material.

Briefly, the setting of zinc oxide-eugenol cement is due to the concurrent sorption of eugenol by the zinc oxide and the formation of zinc eugenate by chemical reaction (I). The method of preparation of the oxide governs the balance between the physical and chemical aspects of the setting reaction. Zinc eugenate formation is catalysed by metal salts and will not form in the absence of moisture.

Brauer, White and Moshonas[13] have studied a wide range of organic acids with various metal oxides in an attempt to find alternatives to zinc oxide-eugenol cement. To obtain hard, coherent cements only acidic organic compounds will suffice (e.g. carboxylic acids, or acidic enols or phenols) and from the compounds tested o-ethoxybenzoic acid was the most successful. Only certain metal oxides were found to react and these were either basic or amphoteric (e.g. MgO,CaO,ZnO,CdO,HgO,PbO). Other oxides, some basic and some acidic, did not give setting cements (e.g. $CuO, Ag_2O, Al_2O_3, TiO_2, PbO_2, Bi_2O_3, MoO_3, MnO_2, Fe_2O_3, CoO$ and NiO). Cements prepared from CaO and MgO were less stable in water and had a lower compressive strength than the ZnO cement. With LiOH, $Ca(OH)_2, Sr(OH)_2, NaCl, MgCl_2, CaCl_2, PbCl_2$, Zn acetate, $ZnSO_4$, or Zn oxalate setting cements were not obtained with o-ethoxybenzoic acid, although a setting product was obtained with $HgCl_2$.

Nielsen[14] has investigated the cement forming ability of 39 organic chelating agents, including β-diketones, keto-esters, 2-methoxyphenols, salicylaldehyde and derivatives and 8-hydroxyquinoline, with various metal oxides. CuO, ZnO, CdO and Bi_2O_3 gave cements with at least one chelating agent, whereas $Al_2O_3, ZrO_2, Fe_2O_3, MnO_2, NiO$ and WO_3 did not form cements with any of the organic compounds. Only the Bi_2O_3-8-hydroxyquinoline product was considered suitable as a dental cement.

1.3.4. Metal poly(carboxylate) cements.

The most important example of this class of cements was patented by Smith in 1969[6] and is prepared by mixing an approximately 50% w/w aqueous solution of poly(acrylic acid) (PAA) with thermally deactivated zinc oxide powder. Additives, such as $MgO, Bi_2O_3, Ca_3(PO_4)_2$ and CaF_2, can be used with the zinc oxide.

During the mixing and setting of the cement an acid-base reaction takes place and the pH rises. The PAA is believed to dissolve some of the zinc oxide to form a product in which partially reacted zinc oxide particles are embedded in a hydrated zinc poly(acrylate) ionomer matrix. It is unlikely that all of the carboxyl groups react with the metal oxide.

Some cement products related to zinc poly(acrylate) are shown in table 1.3.4.1. and all have been developed specifically for dental use.

Table 1.3.4.1.

Cements related to zinc poly(acrylate) cement.

Polyacid phase	Inorganic phase	Cement preparation	References
Poly(acrylic acid) (aqueous)	Powdered ZnO + MgO	Simply mix	15
Poly(acrylic acid) (powder)	Powdered ZnO + silica powder (Aerosil)	Mix with water	16
Acrylic acid-itaconic acid copolymer (aqueous)	Mixtures containing e.g. ZnO,$ZnSO_4$, $Zn_3(PO_4)_2$,MgO,Al_2O_3, Bi_2O_3.	Simply mix	17
Poly(acrylic acid) or poly(methacrylic acid)	ZnO + MgO-phosphate cement and/or a silicate cement (e.g. dental silicate)	-	16
Poly(acrylic acid), poly(methacrylic acid), or other polyacids.	Mixtures containing e.g. ZnO,$ZnSO_4$, $Zn_3(PO_4)_2$,MgO,Al_2O_3, Bi_2O_3	Mix with H_3PO_4 solution alone, or with added polymerisable organic acids + initiators.	18
Poly(acrylic acid), poly(methacrylic acid), or other polyacids. Polymerised whilst mixed with inorganic phase, then powdered.	Mixtures containing e.g. ZnO,$ZnSO_4$, $Zn_3(PO_4)_2$,MgO,Al_2O_3, Bi_2O_3.	Mix with H_3PO_4 solution alone, or with added polymerisable organic acids + initiators.	18

1.4. ASPA cement.

1.4.1. Introduction:

ASPA cement is formed by reacting an ion-leachable aluminosilicate glass powder with aqueous PAA (∿50% w/w solution). The cement may be broadly considered as a hybrid between dental silicate and zinc poly(carboxylate) cements and indeed shows many of the favourable characteristics associated with these related products.

Acid erosion tests have shown ASPA to have a greater stability at pH=4.0 (a typical value for the limit of the acidity in the mouth) than dental silicate cement. In dental silicate cement the cementing matrix is composed of discrete (and possibly polymeric)phosphate units, which are ionically linked and are thus very susceptible to degradation. Phosphate polyhedra which are probably linked by aluminium ions will be attacked by acids to release individual acidic phosphate fragments. In ASPA cement the covalently bonded linear polyanion chains are not attacked by acids and will not degrade into fragments and thus ASPA is more resistant to acids than dental silicate cement.[4]

The irritancy of fresh ASPA cement when placed in a tooth cavity is less than dental silicate cement. Two factors are responsible. Firstly, the acid strengths of phosphoric acid and PAA are very different. In fresh dental silicate cement a pH=1.3 is developed prior to application, compared to pH=2.5 for ASPA. Secondly, the migration of PAA molecules through the tooth pulp will be hindered by the size of the molecule, chain entanglements and the fact that parts of the molecule may be bound to the cementing matrix. With the smaller phosphoric acid molecules migration would be less hindered.[4]

1.4.2. The composition of the glass:

The aluminosilicate glass[8] is prepared by heating mixtures of inorganic compounds at 1375K* for 2 hours, quenching in water,

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* *All temperatures in this thesis are in degrees K. From here onwards the letter K will be omitted.*

drying and then grinding and sieving to about 40µm particle size. Melt temperatures above 1475 are to be avoided, otherwise the cement working time will be drastically shortened. A typical glass formulation is shown in table 1.4.2.1. For dental applications a glass designated G200 is used, but its exact composition cannot be disclosed for patent reasons. The Al : Si ratio in the glass is vital when considering its reactivity with PAA. In fact, G200 glass was developed to give sufficient reactivity towards PAA, for the glasses used in dental silicate cements were developed for the much stronger phosphoric acid and were not reactive enough with PAA.

1.4.3. The composition of the poly(acrylic acid) solution:

PAA is readily prepared in aqueous solution, although a chain transfer agent is required to control the molecular weight.[8] Molecular weights of about 1×10^4 to 3×10^4 are suitable, but higher polymers tend to give solutions too viscous for satisfactory use. 45-50% w/w solutions are generally employed and are usually treated with stabilisers and additives before use. Methanol is a possible stabiliser and is reported to prevent the polymer solution gelling. Additives, such as tartaric acid, are employed to give cement mixes with good workability and sharp setting characteristics. Cements will still form in the absence of additives.

1.4.4. The mix composition:

The cement mix composition depends mainly upon the dental application, but powder: liquid ratios (P:L) of 1:2 to 1:3 g ml^{-1} are often employed. The components are spatulated for 1 minute on a glass block and then applied.

1.4.5. The chemistry of ASPA cement:

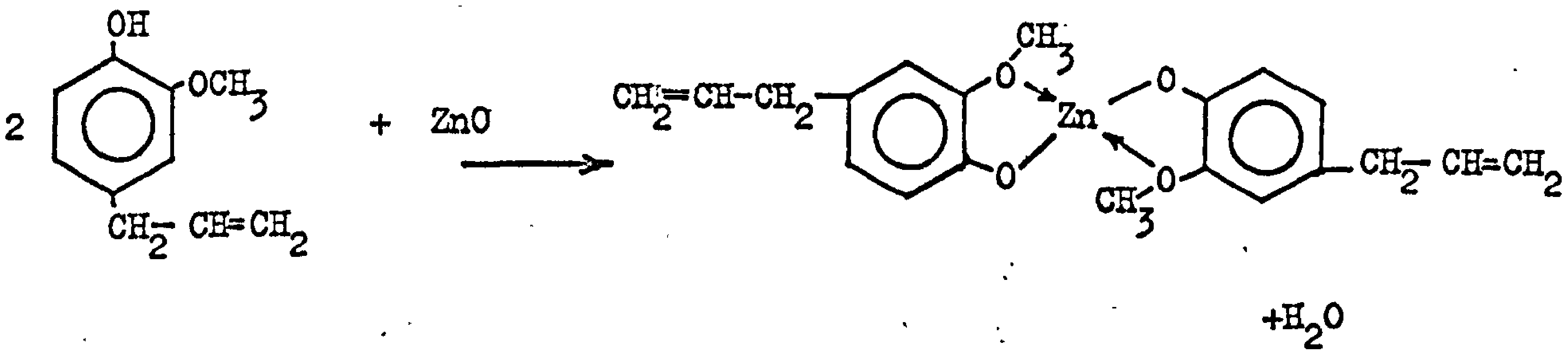
ASPA cement is a very recent invention, but despite this much work has been carried out to elucidate its chemistry.

The basic mechanism[19] for the reaction of the aluminosilicate glass with PAA is shown, (II). Protons from the PAA displace cations from the glass particles' surfaces to give a product consisting of a glass particle aggregate in a metal poly(acrylate) cementing matrix. Water present hydrates the matrix and may hydrate the siliceous hydrogel surface of the glass particles. The matrix is water insoluble and may be hydrogen bonded to the siliceous hydrogel surface of the glass particles.

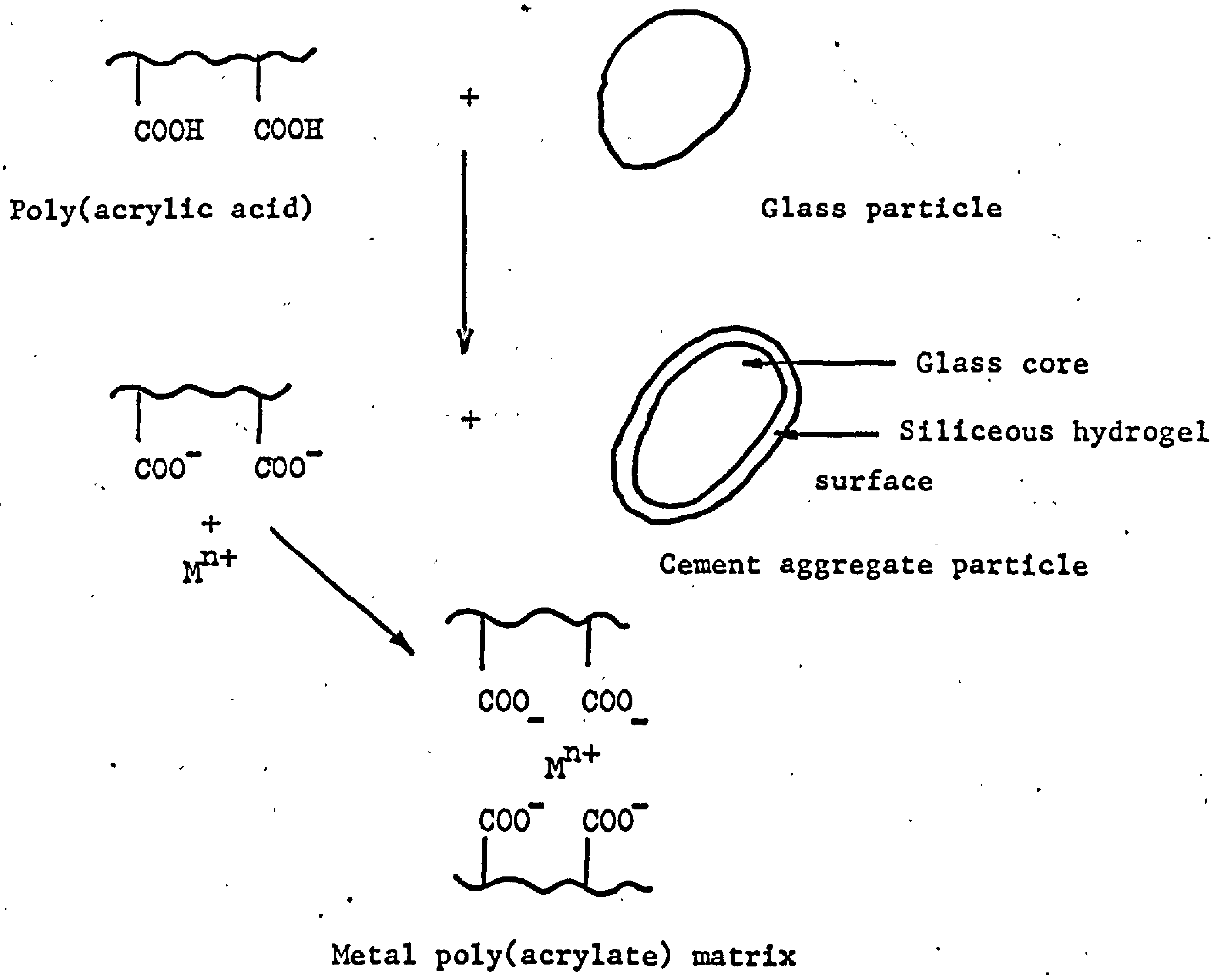
Extraction experiments on ASPA cements aged for various times have shown that ion leaching is very rapid. Probably most of the ions are leached out within 10 minutes at room temperature. In addition to Ca^{2+} and Al^{3+}, Na^{+}, F^{-} and PO_4^{3-} ions are leached into solution. Ca^{2+} and Al^{3+} are believed to be partially complexed as fluorides and phosphates. Excess Ca^{2+} and Al^{3+} ions are bound by the partially neutralised PAA to form the cementing matrix.[19]

Infra-red spectroscopy on cements of various ages[19] has shown that a rapid reaction takes place. In freshly prepared ASPA cements this is illustrated by formation of silica gel (band at about 1050 cm^{-1}) and the conversion of some carboxyl groups (band at 1700 cm^{-1}) to carboxylate groups (bands at 1500 to 1600 cm^{-1}). Over a period of 24 hours the carboxyl group band is reduced considerably, whilst the carboxylate group bands (at 1540 and 1600 cm^{-1}) are markedly enhanced.

By comparing the infra-red spectra of calcium and aluminium poly(acrylate) model compounds with the infra-red spectra of ASPA cements Crisp and Wilson found that calcium poly(acrylate) is rapidly formed in fresh ASPA cement, whilst aluminium poly(acrylate) does not form in appreciable amounts until after about 1 hour from mixing. The delayed formation of the aluminium poly(acrylate) has



(I) Zinc eugenate formation.



(II) Basic chemistry of ASPA cement formation.

been attributed to the unfavourable entropy associated with the orientation of three carboxylate groups around the tri-positive aluminium ion. Other factors may be the lower mobility of the highly solvated Al^{3+} ion and the difference in morphology of the cation sites in the G200 glass.

The setting reactions occurring in ASPA cement continue for at least 48 hours and are accompanied by an increase in compressive strength with time. Wilson[20] has suggested that the setting reaction may continue very slowly in hardened cements for several months, or even indefinitely.

The rate of reaction between the glass and the PAA not only depends upon the composition of the glass, but also (in the case of G200) the method of preparation and morphology of the glass.

1.4.6. The morphology of G200 glass:

The morphology of G200 glass depends to some extent on the temperature employed in its preparation.

Barry, Miller and Wilson[21] have shown that G200 glass, like the glass used in dental silicate cements, is phase separated. The degree and nature of phase separation depends upon the melting history of the glass and has a pronounced effect on the workability and setting time of the ASPA cements prepared from the glass. For example a G200 glass prepared at 1425 gives a satisfactory mix with PAA, whilst a G200 glass fused at 1575 gives a mix which rapidly becomes rubbery and unworkable.

Both G200 (1425) and G200 (1575) are phase separated into droplets dispersed in an amorphous matrix. X-ray analysis has shown the droplets to be almost entirely composed of calcium fluoride, whilst the glass matrix contains aluminium,silicon and calcium. At the boundary between the droplets and the matrix the aluminium: silicon ratio is higher than in the matrix. Optical and electron transmission microscopy have shown a fundamental difference between G200 (1425) and G200 (1575) glasses. In a glass prepared at 1425 incomplete melting of calcium fluoride occurs and the material contains massive inclusions of fluoride droplets (several microns across), which are non-uniformly dispersed. A glass prepared at 1575 contains no massive droplets, owing to a more complete melting of the mix.

Both glasses also contain small spherical droplets of calcium fluoride, which differ markedly with the melt temperature employed. For G200 (1425) the average size of the spherical droplets is 1.67 $\pm$ 0.83μm. (volume fraction $\sim$20%), whilst for G200 (1575) the droplets are slightly smaller at an average of 1.08$\pm$ 0.32μm. (volume fraction $\sim$19%). The degree of crystallinity within the calcium fluoride droplets differs considerably between the two glasses. In G200 (1425) most of the droplets are crystalline, or partly crystalline, whilst in G200 (1575) glass many of the droplets are entirely amorphous. It is the degree of crystallinity of the calcium fluoride droplets in the glass that controls its reaction rate with PAA. Where the droplets are mostly crystalline a slow acid leaching of Ca^{2+} takes place, but where the droplets are mainly amorphous a very rapid acid leaching of Ca^{2+} occurs and the PAA is quickly saturated with these ions. Thus, G200 (1425) gives a workable cement with PAA, whilst G200 (1575) glass does not. In addition to melt temperature other factors, such as melt cooling rate (which will be more rapid for G200 (1575) glass) probably affect the crystallinity of the glass.

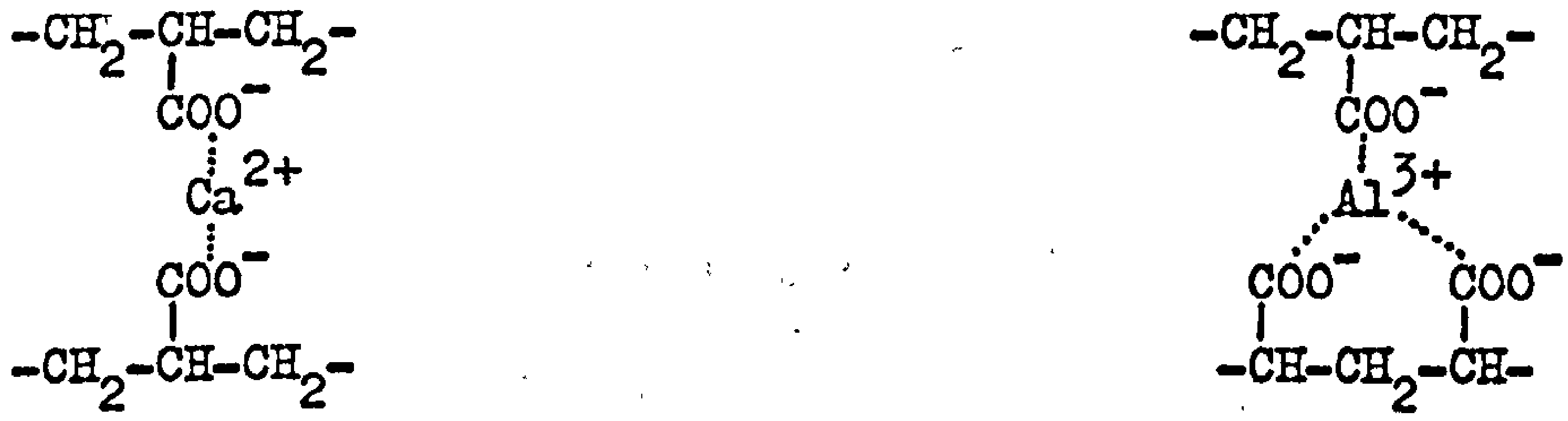
1.4.7. The morphology of the cement:

Barry, Miller and Wilson[21] have shown by optical microscopy that the microstructures of dental silicate and ASPA cements are similar, i.e. polygonal glass particles dispersed in a cementing matrix. Non-dispersive X-ray analysis has been used to study the element distribution in an ASPA cement prepared from G200 (1425) glass. The cement matrix contains about three times the proportion of calcium relative to either aluminium and silicon, in contrast to much lower ratios of calcium to aluminium and silicon present in the glass particle. Thus, in the cementing matrix bound calcium appears to predominate over bound aluminium ions by a factor of about three. The abundance of calcium in the cementing matrix is probably attributable to a preferential acid leaching of the amorphous droplets in the glass. Calcium and aluminium in the cementing matrix are believed to be present as salt bridges, or cross-links, between poly(acrylate) chains[21] (III).

Table 1.4.2.1.

A typical glass composition for ASPA cements[8].

SiO_2	1000	p.b.w.
Al_2O_3	618	"
Na_3AlF_6	730	"
$AlPO_4$	303	"
CaF_2	470	"
AlF_3	174	"



(III) Postulated salt bridges in the cementing matrix of ASPA cement.

1.5. Other ionomer materials.

A very important class of ionomer materials are ionomer resins, such as Surlyn A (Du Pont). These ionomer resins are prepared by neutralising a partially carboxylated poly(alkene) with basic metal salts. For example, a typical ionomer resin is prepared by milling an ethylene-methacrylic acid copolymer (containing 1-10% acidic co-monomer) with 20-80% of the copolymer weight of water soluble oxides, hydroxides or other basic salts of sodium, potassium, magnesium or zinc.[22,23]

The ionic bonds in the ionomer resin are thermally labile, so that at ambient temperature the resin is rigid (like a thermoset) and at elevated temperatures softens (like a thermoplastic). There is much controversy over the morphology of ionomers, but generally the metal cations in the resin are thought to be located in domains dispersed throughout an aliphatic hydrocarbon matrix. The size of these domains is not known with certainty and diameters of 0.5-1.0nm to 10-50nm have been suggested. Several morphological models have been proposed.[24-27]

Ionomer resins are transparent and have excellent resistance to many solvents and oils. The gas permeability of ionomer resin films is very low. Applications for ionomer resins include food packaging foils, oil and grease resistant films and mouldings, stress-crack and solvent resistant bottles and electrical component casings.

An interesting modification has been reported using portland cement as the inorganic phase in ionomer resins.[28,29] Partially carboxylated poly(alkenes) are milled with portland cement to obtain a composite, which can be cured at 373-473 in water or steam. The cured composite has a higher stiffness and yield strength than the unfilled copolymer and has been suggested as suitable for wire coatings and high temperature resistant products.

Portland cement is predominantly a mixture of calcium silicates ($3\ CaO.SiO_2$ - 39%; $2\ CaO\ SiO_2$ - 30%) with some tetracalcium alumino ferrite ($4\ Ca.O.\ Al_2O_3.Fe_2O_3$ - 11%), tricalcium aluminate ($3\ CaO.Al_2O_3$ - 11%), free lime (1.7%) and other minor components.[30] Thus, in these portland cement modified resins the carboxylate groups on the polymer chains are probably neutralised by Ca^{2+} ions (which are abundant in portland cement) and possibly by Al^{3+}(and Fe^{3+})ions. This composite is therefore probably related to ASPA cement in respect of the cross-linking ions present, differing in degree of cross-linking and the reaction medium.

Polyacids have been employed in countless applications with inorganic substances capable of providing cross-linking metal ions, or providing an adsorbant surface for the polyacid macromolecules. Table 1.5.1. shows a few reported products.

Table 1.5.1.

Products between organic polyacids and inorganic substances.

Polymer*	Inorganic phase	Products and uses	Example refs.
MA -AA copolymer MA-MAA copolymer	Cement and mortar	Cements and mortars with improved durability	31
PAA and PAA salts	Plaster of Paris	Modified plasters with reduced water absorption properties.	32
Various organic polyacids	Various, suspended particles in water	Deflocculants, fluocculants. Glaze additives and thickening agents.	33,34
Various organic polyacids	Soils	Soil stabilisers and strengtheners	35
AA-2-ethylhexyl acrylate co-polymer powder	ZnO alone, or with steel rovings. CaO and PbO.	Compression moulded high strength composites. Moulded at high temp. and pressure.	36,37
Various organic polyacids	Metal salts	Cast films or compression mouldings for medical uses and for photographical filters, fibres and catalysts.	38
Various organic polyacids	Polybases	Ionenes	39
PAA	$CaCl_2$	Anti-scaling agent for oil wells	40
PAA	phenyl tin (and silicon) chlorides.	Cross-linked products produced by a base catalysed interfacial method.	41

Table 1.5.1. (continued)

Polymer*	Inorganic phase	Products and uses	Example refs.
PAA salts	Al^{3+},Mn^{2+}, Co^{2+},Pb^{2+}	Polymerisation catalysts. Levelling agents for laquers.	42
AA-AA esters copolymers	Cd^{2+},Zn^{2+}, Cu^{2+},Ni^{2+}	Aqueous resinous coatings	43
Various organic polyacids, partially cross-linked	Various cations	Ion exchange resins	44
Partially hydrolysed acrylate polymers	Al,Zn,Ni salts	Additives to poly-(propylene) fibres	45
AA or MAA ester-AA or MAA or ICA copolymer emulsions.	Oxides, hydroxides or basic salts of polyvalent metals.	Coatings for soft asbestos-cement products.	46
VE-MA copolymer	$Ca(OH)_2$	Surgical splinting bandages.	47

*AA≡acrylic acid; MA ≡ maleic acid; MAA ≡ methacrylic acid.

ICA≡itaconic acid; VE ≡ vinylmethyl ether.

1.6. General survey of polyacid - metal ion interactions.

1.6.1. Introduction to polyacids:

Polyacids are macromolecules having many ionisable acidic groups. Table 1.6.1.1. shows some common polyacids.

Polyacids are often water soluble, dissociating into aquated protons and aquated macromolecular anionic species. They are neutralised by alkalis and bases to form salts, which may be water soluble. In aqueous solution the anionic macromolecular chains tend to attract the counterions (aquated cations) by virtue of the high localised electron density on the pendant ionised acid groups. Oosawa[48] identifies four regions in which the counterions may exist:

1. Site bound counterions, localised at specific anionic groups on the macromolecule.
2. Counterions bound in the cylindrical region occupied by the macroanion chain. These counterions are mobile.
3. Counterions bound in the spherical volume occupied by the random macroanion coil as a whole. These counterions are also mobile.
4. Counterions lying outside the sphere of coulombic attraction of the macroanion chain. These counterions exist freely in solution.

Addition of neutral salts to polyacids, or polyacid salt solutions screens the electrostatic effect of the macroanions and increases the activity coefficient of the free counterions in solution. Thus, addition of a neutral salt to a polyacid solution results in an apparent marked increase in strength of the polyacid. This principle can be exploited in titrating polyacids, since in the presence of neutral salts sharper end points are obtained. The titration behaviour of a polyacid depends upon the nature of the

Table 1.6.1.1.

Some common polyacids

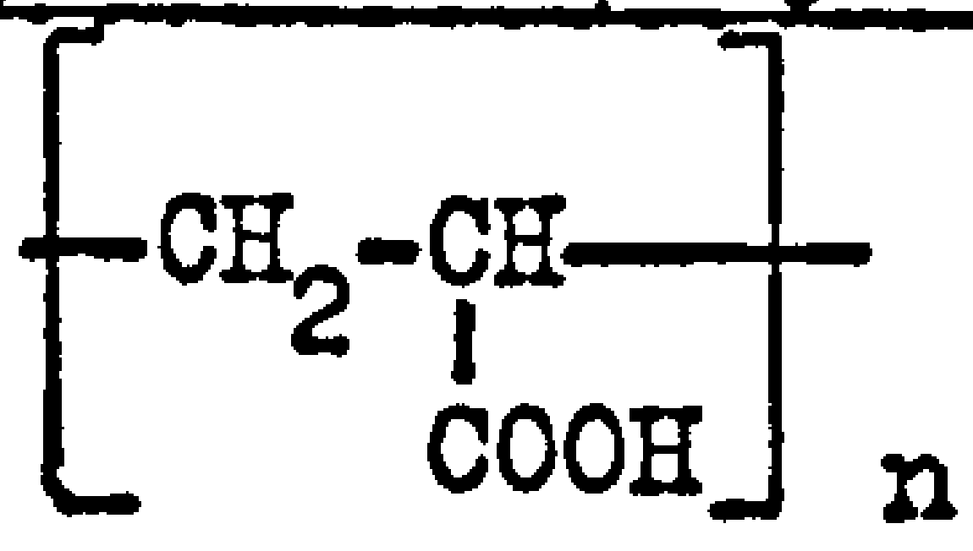
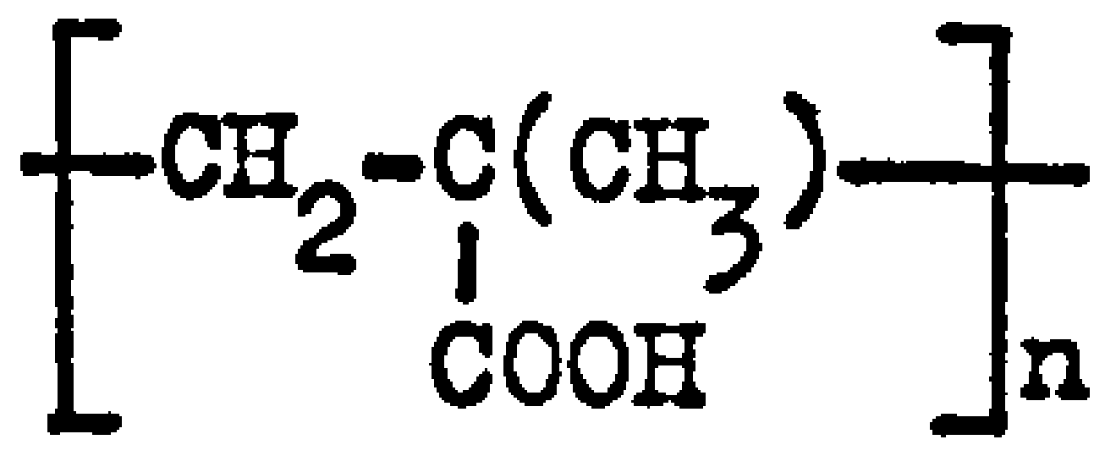
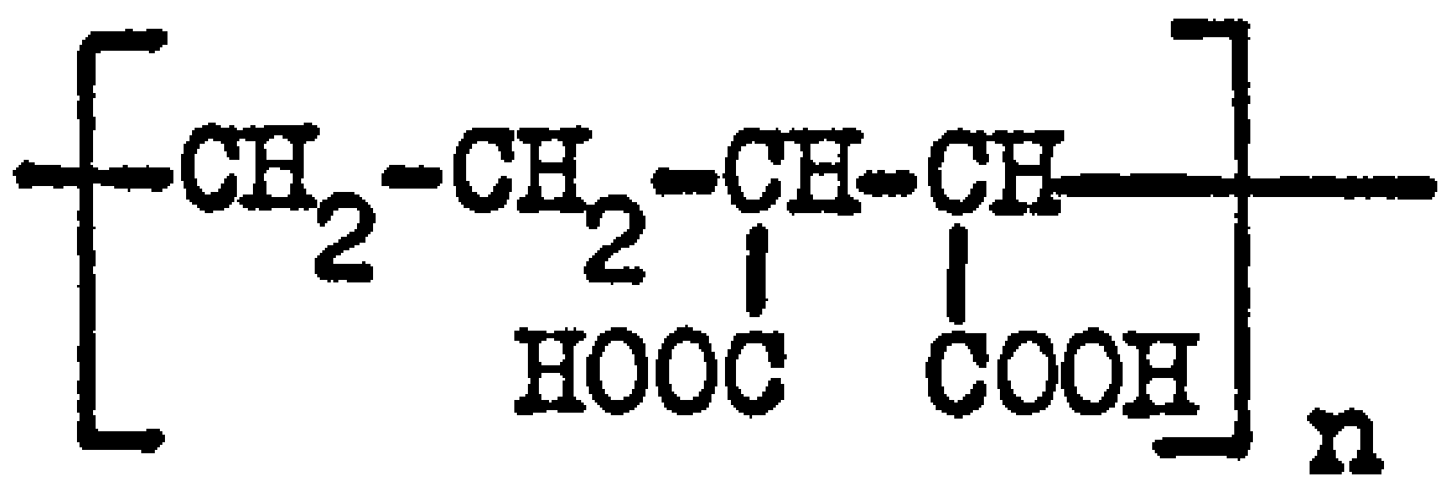
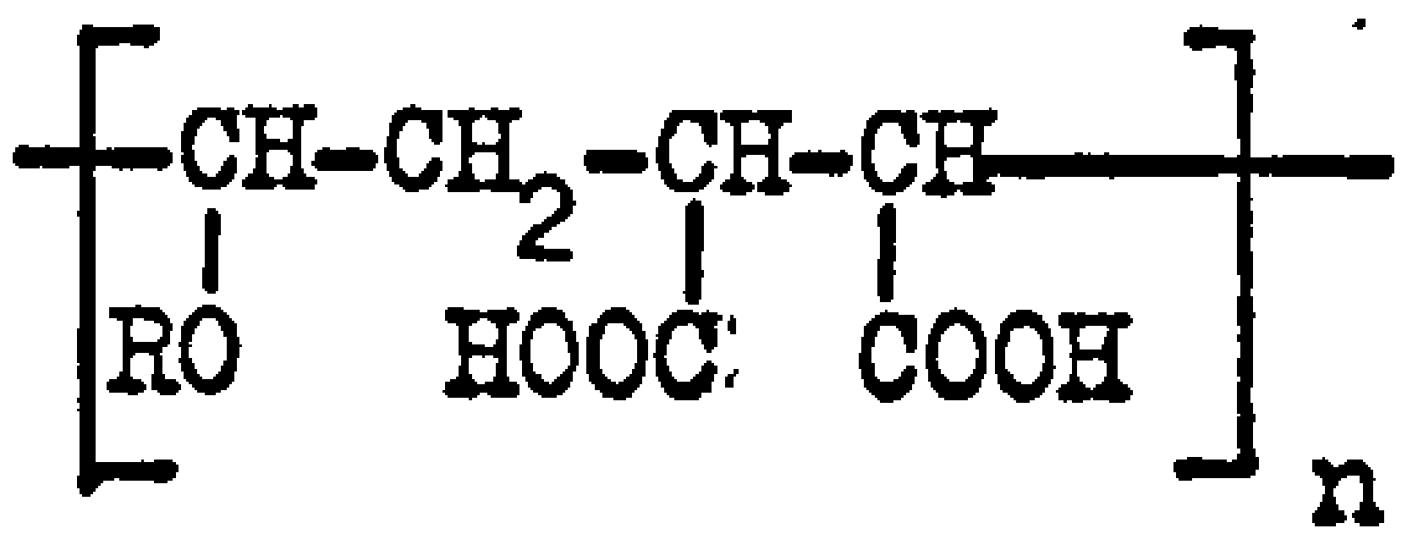
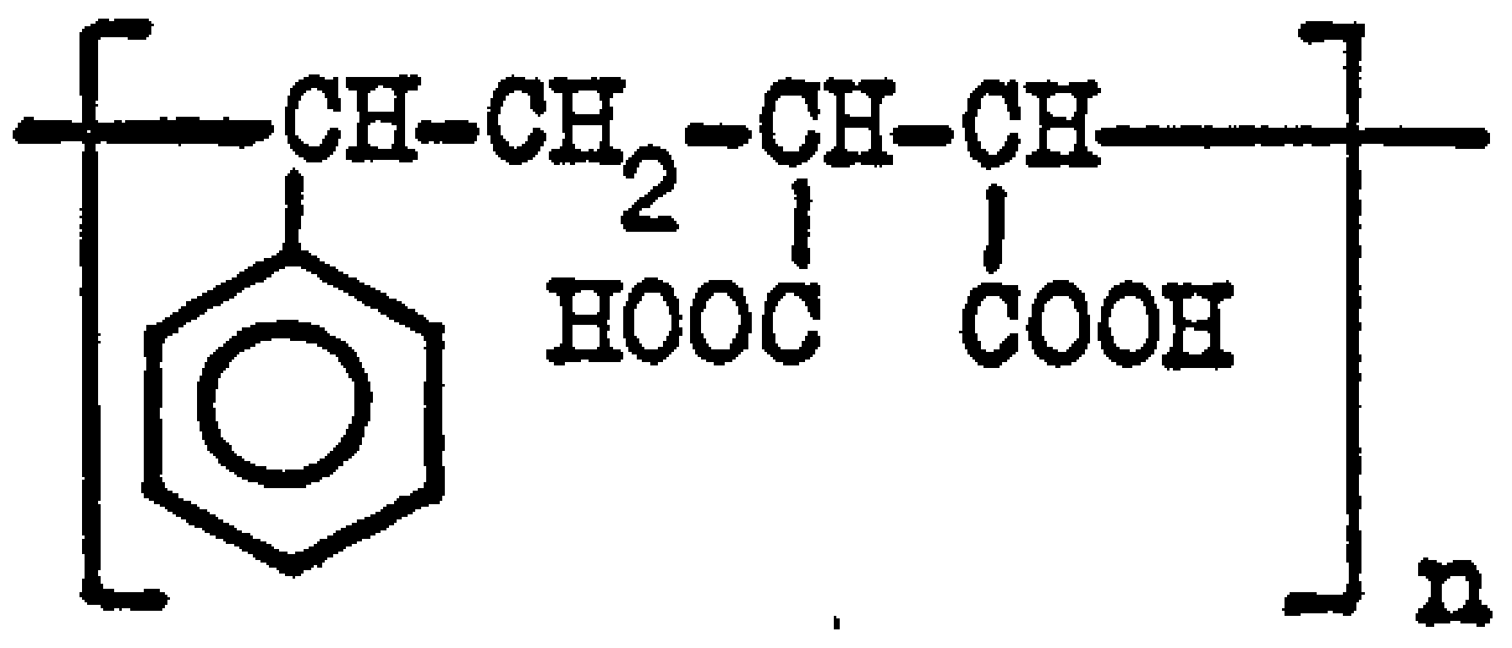
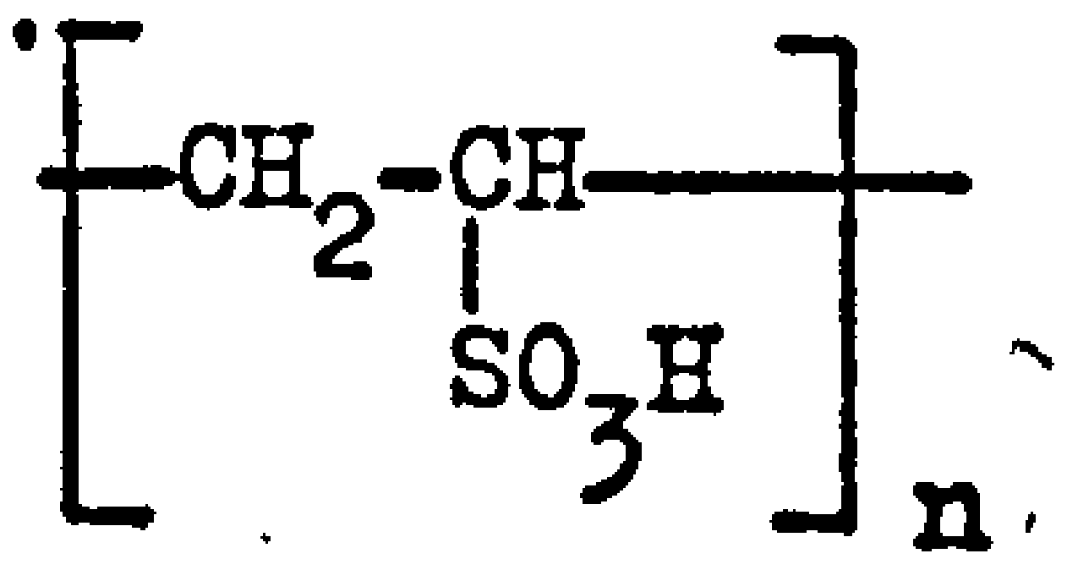
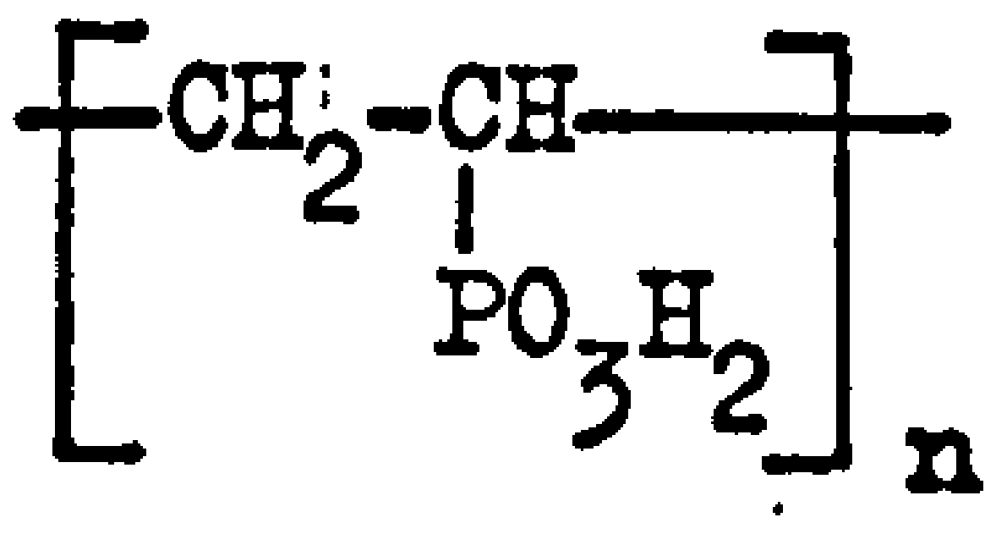
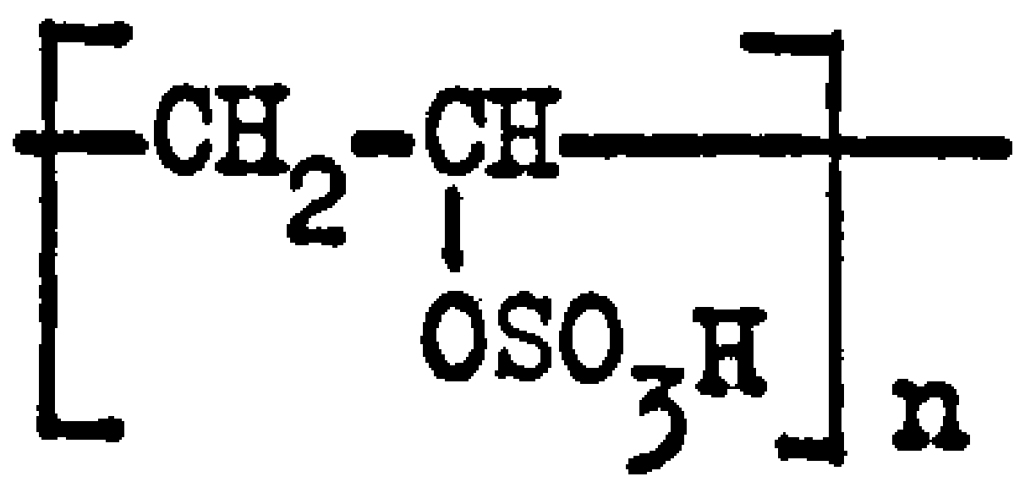
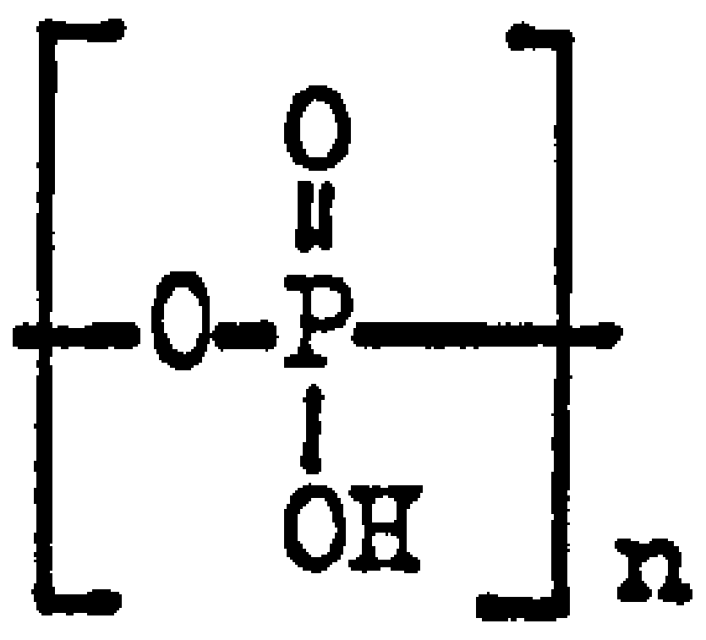
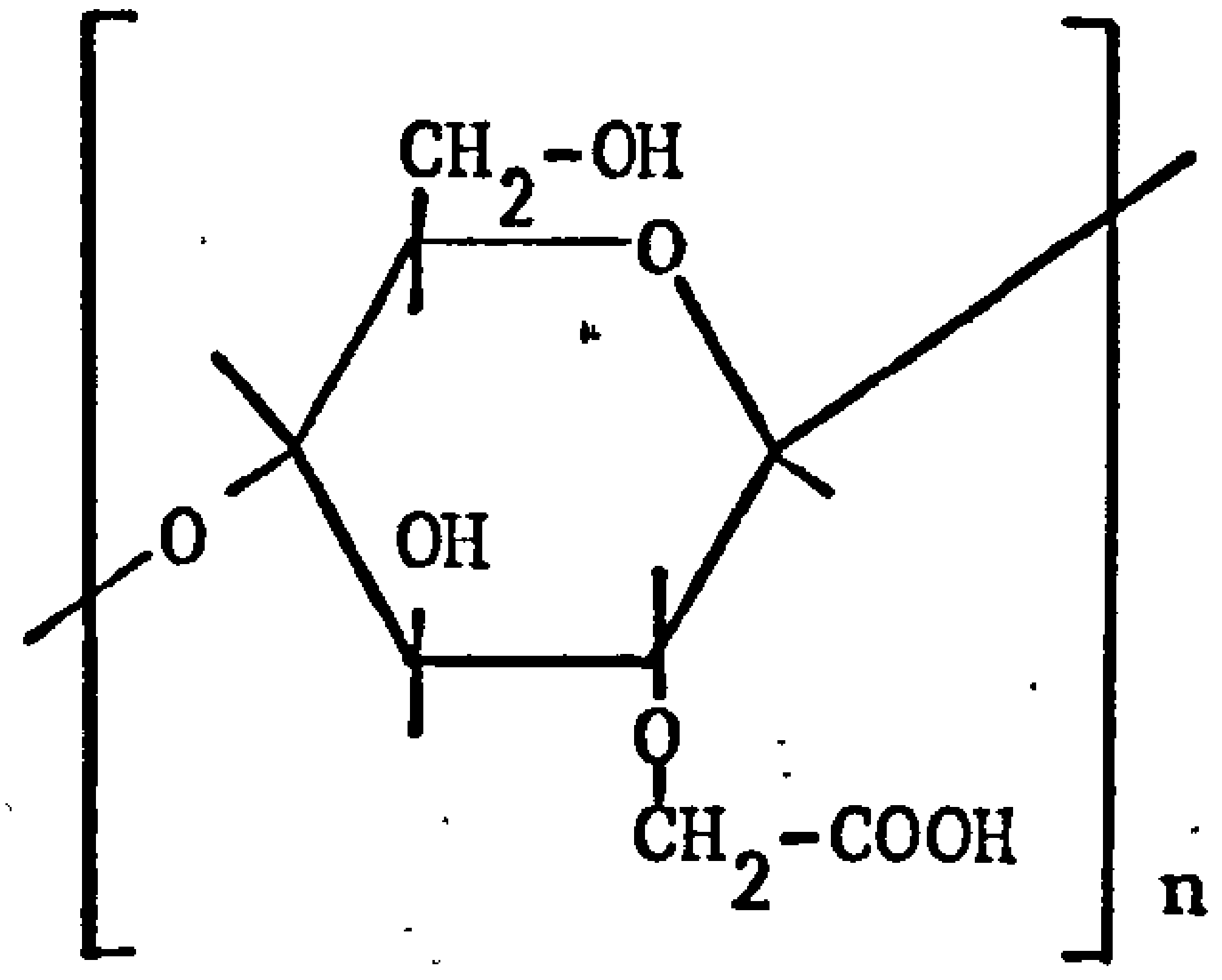
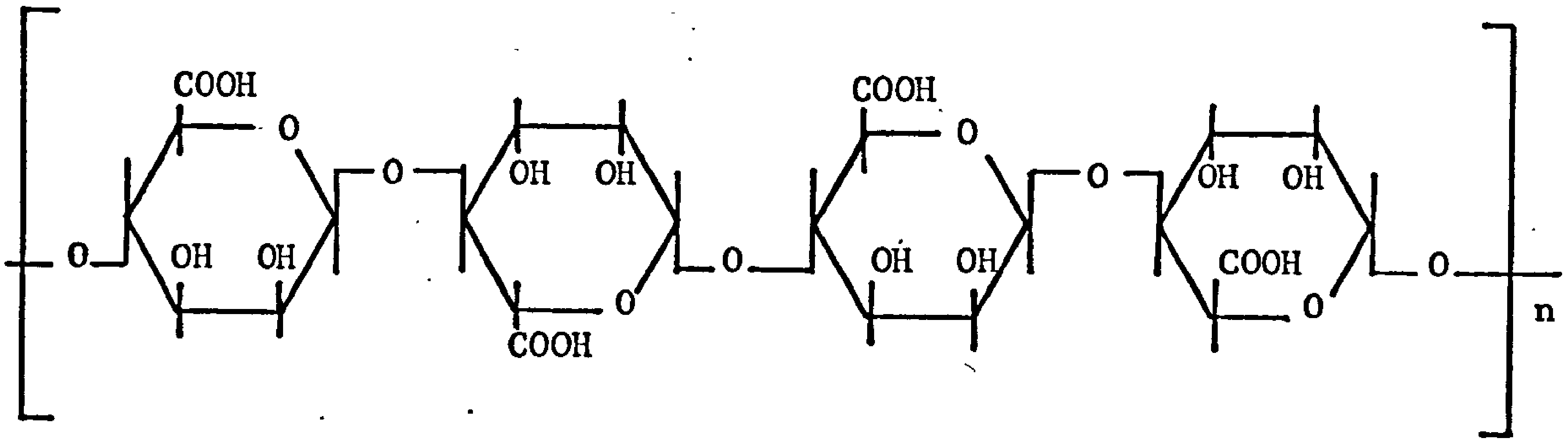
Name	Structure
Weak synthetic polyacids	
Poly(acrylic acid)	 $\left[-\mathrm{CH_2}-\underset{\mathrm{COOH}}{\mathrm{CH}}-\right]_n$
Poly(methacrylic acid)	 $\left[-\mathrm{CH_2}-\underset{\mathrm{COOH}}{\mathrm{C}}\mathrm{(CH_3)}-\right]_n$
Ethylene-maleic acid copolymer	 $\left[-\mathrm{CH_2}-\mathrm{CH_2}-\underset{\mathrm{HOOC}}{\mathrm{CH}}-\underset{\mathrm{COOH}}{\mathrm{CH}}-\right]_n$
Vinylalkyl ether-maleic acid copolymer	 $\left[-\underset{\mathrm{RO}}{\mathrm{CH}}-\mathrm{CH_2}-\underset{\mathrm{HOOC}}{\mathrm{CH}}-\underset{\mathrm{COOH}}{\mathrm{CH}}-\right]_n$ $\mathrm{R{=}CH_3, C_2H_5}$.
Styrene-maleic acid copolymer	
Strong synthetic polyacids	
Poly(ethylene sulphonic acid)	 $\left[-\mathrm{CH_2}-\underset{\mathrm{SO_3H}}{\mathrm{CH}}-\right]_n$
Poly(vinyl phosphonic acid)	 $\left[-\mathrm{CH_2}-\underset{\mathrm{PO_3H_2}}{\mathrm{CH}}-\right]_n$
Partially sulphated poly(vinyl alcohol)	 $\left[-\mathrm{CH_2}-\underset{\mathrm{OSO_3H}}{\mathrm{CH}}-\right]_n$
Poly(phosphoric acid)	 $\left[-\mathrm{O}-\underset{\mathrm{OH}}{\overset{\mathrm{O}}{\overset{\Vert}{\mathrm{P}}}}-\right]_n$

Table 1.6.1.1. (continued)

Name	Structure
Naturally occurring polyacids (weak acids).	
Carboxymethyl cellulose	
Alginic acid	

titrant salt and added neutral salt, since cations provided by these salts will also be attracted by the macroanion.[49] Bulky cations, such as tert-alkonium ions are only slightly bound by macroanions and tert-alkonium bases are often used in titrating polyacids.

With increasing neutralisation of a polyacid the coulombic charge on the macroions increases. Repulsion between the charged groups on the macroanion coil tends to unwind the coil to form an extended rod like configuration. Thus, neutralisation of polyacids is usually accompanied by an increase in the solution viscosity as the extending macroanion chains become increasingly disentangled (e.g. PAA and poly(methacrylic acid) (PMAA)).

Polyacids bind metal ions to a greater extent than their monomeric analogues. For example, Gregor et. al.[49] have found that PAA forms very strong complexes with Cu^{2+}, whereas glutaric acid only very weakly binds these ions, stability constant values differing by four orders of magnitude.

The strong counterion binding (especially polyvalent ions) by polyacids has been exploited in many applications, such as ion-exchange resins (e.g. cross-linked sulphonated polystyrene[44]) and chromatography gels (e.g. naturally occurring polymers[50]).

Over the last twenty years there has been much investigation of polyacid-metal ion systems. Most of the work has been carried out in dilute aqueous media, usually less than 0.1.M. Although much has been learnt about polyacid-metal ion interactions the subject is not fully understood.

A brief review of the literature on polyacid-metal ion interactions will be given, describing some of the features of the chemistry involved.

1.6.2. The solubility of polyacid-metal ion complexes:

Solubility studies have been carried out by precipitation titrations by many authors.

Costantino et. al.[51] have shown that the order of solubility for metal poly(methacrylates) increases in the order $Mg^{2+} < Cu^{2+} < Ni^{2+} < Co^{2+}$, when metal chloride solutions are added to 95% neutralised PMAA solutions.

Ikegami and Imai[52] have studied the precipitation of metal poly(acrylates) by a turbidiometric technique, supplemented by viscosity, conductivity and refractive index studies. Two types of precipitation can occur, depending upon the metal ions added and the degree of neutralisation of the PAA prior to adding metal salt solutions.

The first type of precipitation is where a high concentration of metal salt is required to induce precipitation of the PAA) ("H-type" precipitation). "H-type" precipitation occurs with metal ions that are not strongly bound to PAA (e.g. Na^{+}), or with metal ions that may be strongly bound but which do not render the polymer hydrophobic (e.g. Mg^{2+} with 25% neutralised PAA). "H-type" precipitation also occurs when metal salt solutions are added to undissociated PAA in, for example, dilute HCl solution, which supresses the dissociation of the polyacid. Under these conditions high concentration of salts of Na^{+}, K^{+}, Mg^{2+}, Ca^{2+} and Ba^{2+} are required to induce precipitation. The mechanism of "H-type" precipitation is a "salting out" effect i.e. the hydration spheres of the polymer macromolecules are disrupted, or dehydrated by the approach of a large number of charged metal ions and the polymer precipitates.

The second type of precipitation occurs with low metal salt concentrations and high degrees of neutralisation of PAA. Thus,

Ca^{2+}, Ba^{2+}, Mg^{2+}, Ag^{+} and La^{3+} cause "L-type" precipitation with 100% neutralised PAA. The mechanism of "L-type" precipitation involves the disruption of the hydration spheres stabilising the poly(acrylate) macromolecules in solution by the binding of metal ions. Ions which are strongly bound cause considerable dehydration of the carboxylate groups on the polymer, consequently only low concentrations of these ions will induce precipitation.

With 25% neutralised PAA Mg^{2+} gives "H-type" precipitation, whereas Ca^{2+} and Ba^{2+} give "L-type" precipitation. Here Ca^{2+} and Ba^{2+} are believed to be bound mainly as, -COO-M-OOC-, whereas Mg^{2+} is bound as, $-COO\text{-}M^{+}\ {}^{-}OOC-$. The latter form is more hydrophilic and hence the precipitation of Mg^{2+} with PAA at intermediate degrees of neutralisation is "H-type". Al^{3+} may be expected to behave similarly to Mg^{2+}.

Wall and Drenan[53] have studied the gelation of PAA with added Ca^{2+}, Sr^{2+} and Ba^{2+} salts, using a turbidiometric technique. Dilute solutions of PAA require proportionally less metal hydroxide to induce precipitation than stronger solutions, presumably due to the decreased likelihood of inter-chain interactions in dilute solution. Precipitation occurs much more readily with metal hydroxides than with metal chlorides, indicating that the production of carboxylate groups is important for ion-binding. Ba^{2+} is more efficient than Ca^{2+} or Sr^{2+} at precipitating PAA and Wall and Drenan consider this to indicate that the metal ion-polyacid bonding is not wholly ionic. However, since the ionic products $[COO^{-}]^{2} \times [M^{2+}]$ at the gel points for a series of Ba^{2+} concentrations gives a roughly constant value, the bonding is probably mainly ionic.

Millich and Calvin[54] have studied ion binding to the poly(ethylene sulphonate) ion by observing coacervate formation with the addition of metal salts to potassium poly(ethylene sulphonate) solution. Alkali metal salts induce coacervation at low temperature, whilst heavy metal salts give coacervates at room temperature. Staining techniques have shown the heavy metal ions to be localised within the coacervate phase. From experimentally determined phase diagrams the order of phase separating ability increases in the order $Fe^{3+} > Cu^{2+} > Ag^{+}$.

Ito and Suzuki[55] have shown the relative effectiveness of carboxylic and sulphonic acids as cation precipitating agents by studying a range of acrylic acid-ethylene sulphonic acid copolymers. With increase in the sulphonic acid content the viscosities of the aqueous copolymer solutions decrease and the amount of salts of Ca^{2+}, or Ba^{2+} required to induce precipitation increases.

1.6.3. Stability constants of metal ion- polyanion complexes:

The stability of a metal complex in solution is quantitatively described by an equilibrium or stability constant, which measures the tendency for the complex to remain in solution without dissociating into its constituent ions. Two types of stability constant are in common use.

1. Stepwise stability constants (k), which are used to express equilibria of the type:

$$M + A \rightleftharpoons MA \qquad k_1 = \frac{[MA]}{[M]\,[A]}$$

$$M + A \rightleftharpoons MA_2 \qquad k_2 = \frac{[MA_2]}{[MA]\,[A]}$$

$$\vdots$$

$$MA_{N-1} + A \rightleftharpoons MA_N \qquad k_N = \frac{[MA_N]}{[MA_{N-1}]\,[A]}$$

There will be N such equilibria, where N represents the maximum co-ordination number of the metal ion, M, for the ligand L.

2. Overall stability constants, (K) which describe equilibria of the type:

$$M + A \rightleftharpoons MA \qquad K_1 = \frac{[MA]}{[M][A]}$$

$$M + 2A \rightleftharpoons MA_2 \qquad K_2 = \frac{[MA_2]}{[M][A]^2}$$

$$\vdots$$

$$M + NA \rightleftharpoons MA_N \qquad K_N = \frac{[MA_N]}{[M][A]^N}$$

Stepwise and overall stability constants are related by the following general equation:

$$K_i = k._1.k_2.k_3 \text{ --- } .k_i = \prod_{j=1}^{j=i} k_j$$

Stability constant determinations have been carried out with a limited number of polyacids and metal ions. Potentiometric methods have featured predominantly in these stability constant determinations, but the conditions and theory applied differs from author to author. A direct comparison of results from different sources is impossible, although useful trends can be obtained.

Morawetz, Kotliar and Mark[56] have determined stability constants for styrene-maleic acid (SMA) and vinylethyl ether-maleic acid (VEEMA) copolymers with Mg^{2+}, Ca^{2+}, Sr^{2+} and Ba^{2+} ions. Table 1.6.3.1. shows the results obtained. The stability constants are taken at an arbitrary point, where the average charge per carboxylate pair (Z) = 1.3, because the values of stability constants vary with the degree of charging of the polyacid chains. The stability constant values apply to complexes in 1M KNO_3 at 298.15 ± 0.1.

As can be seen from table 1.6.3.1. the polyacids bind alkaline earth ions more strongly than their monomeric analogue, succinic acid.

Monobe[57] has illustrated the effect of the variation of a stability constant with degree of charging of a polymer chain.

Stability constants for SMA (K_{sma}) and vinylacetate-maleic acid copolymer (K_{vama}) vary markedly with Z. Thus, for Ca^{2+}, or Ba^{2+} at low Z $K_{sma} < K_{vama}$, whilst at high Z $K_{vama} < K_{sma}$.

Felber, Hodnett and Purdie[58] have recently determined stability constants for metal ions with ethylene-maleic acid copolymer (EMA) in very dilute solution free from added neutral salts. Table 1.6.3.2. shows the stability constants reported, which have been calculated with activity coefficient corrections. The values are mean stability constants (since no allowance has been made for the effect of the degree of charging of the polymer chains) and apply to complexes at 298.15± 0.05 under N_2.

Gregor, Luttinger and Loebl [49] have developed a method for calculating stability constants from pH titration data, which does not depend upon the degree of charging of a polyanion. Average constants, B_{av}, are determined by a method based on that of Bjerrum (see section 3.4.2.), where $B_{av}^2 = B_2$ = the second overall stability constant. Table 1.6.3.3. shows some stability constants determined with PAA in IM KCl solution at 298.15± 1 under N_2.

Mandel and Leyte[60] have modified Gregor's method and obtained values of stability constants with PMAA in salt free solutions. Their results are shown in table 1.6.3.3.

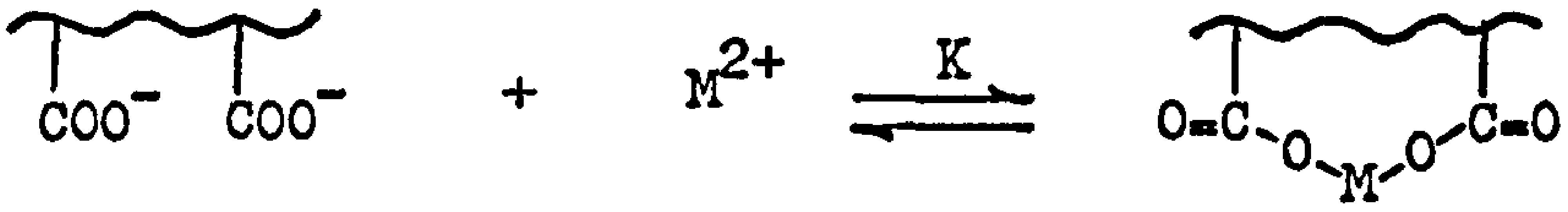
pH measurements have also been applied to ion-binding studies with carboxylic ion exchange resins[61,62] and with certain naturally occurring polymers, such as alginic acid and carboxymethyl cellulose.[63]

1.6.4. Volume changes with ion-binding to polyacids.

Strauss et. al.[64,65] have reported a dilatometric method of studying the degree of site binding of metal ions to polyacids. The method involves the measurement of volume changes occurring when metal ions are site bound to polyanions in aqueous solution. Volume changes occur because during site binding there is a

Table 1.6.3.1.

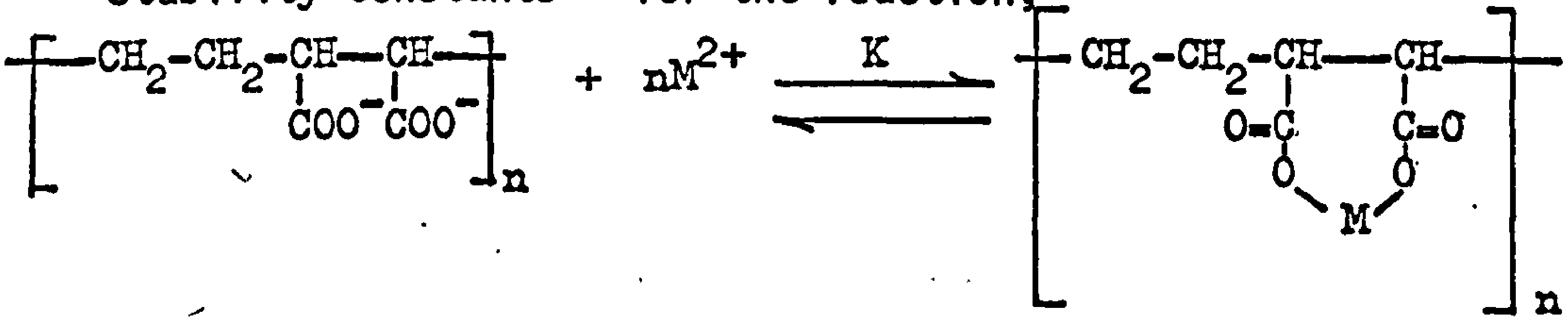
Stability constants[56] for the reaction,



Acid	Log K			
	Ca^{2+}	Mg^{2+}	Ba^{2+}	Sr^{2+}
VEEMA	2.45	2.30	2.00	1.96
SMA	2.11	1.74	1.36	1.46
Succinic acid	1.16	1.02	0.97	0.75

Table 1.6.3.2.

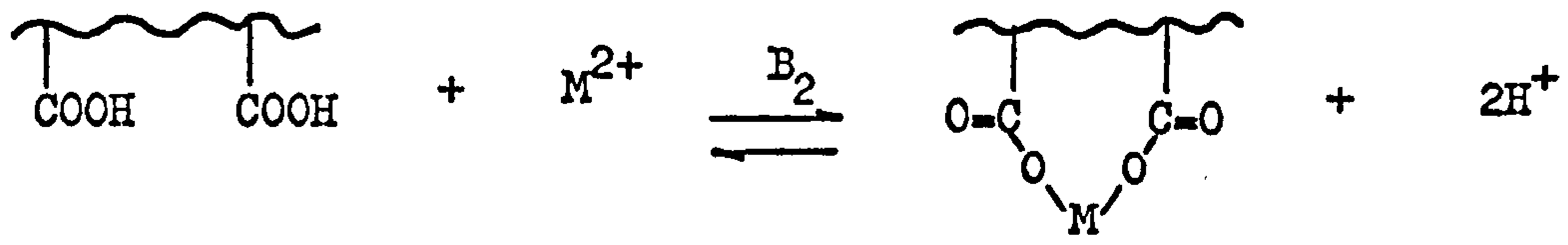
Stability constants[58] for the reaction,



Ion	Mean K	value
Mn^{2+}	6.41 ± 0.2	$X10^{8}$
Co^{2+}	4.29 ± 0.3	$X10^{8}$
Ni^{2+}	3.76 ± 0.2	$X10^{8}$
Cu^{2+}	4.45 ± 0.42	$X10^{10}$
Zn^{2+}	4.97 ± 0.3	$X10^{8}$
Cd^{2+}	2.13 ± 0.14	$X10^{9}$

Table 1.6.3.3.

Stability constants for the reaction,



Ion	$-\text{Log } B_{av} (= - \frac{1}{2} \log B_2)$	
	PAA[49,59]	PMAA[60]
Mg^{2+}	3.8	3.1
Ca^{2+}	3.7	-
Co^{2+}	3.4	2.8_5
Ni^{2+}	-	2.8
Mn^{2+}	3.0	-
Zn^{2+}	3.0	2.6
Cu^{2+}	1.82	1.8
Cd^{2+}	-	2.2

Table 1.6.4.1.

ΔV_t values (ml per equiv. total metal ion)[64]

Polyanion	Li^+	Na^+	K^+	Mg^{2+}	Ca^{2+}
Poly(styrene sulphonate)	0.9	1.2	1.5	2.1	2.9
Poly(vinyl sulphonate)	3.4	4.7	5.6	7.2	10.6
Poly(acrylate)	4.5	4.1	3.9	11.7	17.3
Poly(methacrylate)	2.9	3.1	3.0	9.2	13.7
Poly(vinyl phosphonate)	9.6	9.4	7.7	19.6	24.7
Poly(vinyl hydrogen phosphonate)	6.8	5.9	5.3	15.8	22.2
Poly(phosphate)	11.3	11.0	9.6	24.4	25.5
Poly(styrene sulphonate) cross-linked.	5.4	-	-	-	13.0

Table 1.6.4.2.

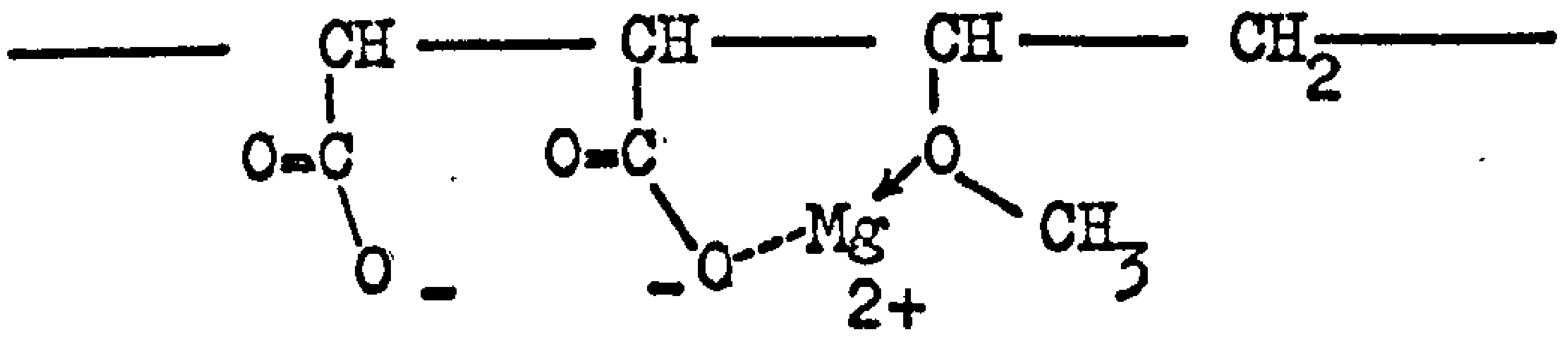
ΔV_t values (ml per equiv. total metal ion)[65]

Polyanion	Mg^{2+}	Ba^{2+}	Ag^{+}	Li^{+}	K^{+}
Poly(acrylate)	26.6	33.2	20.8	4.35	2.75
Ethylene-maleate copolymer	23.8	28.2	18.4	3.10	2.63
Vinylmethyl ether -maleate copolymer	40.8	44.6	18.6	9.87	5.44

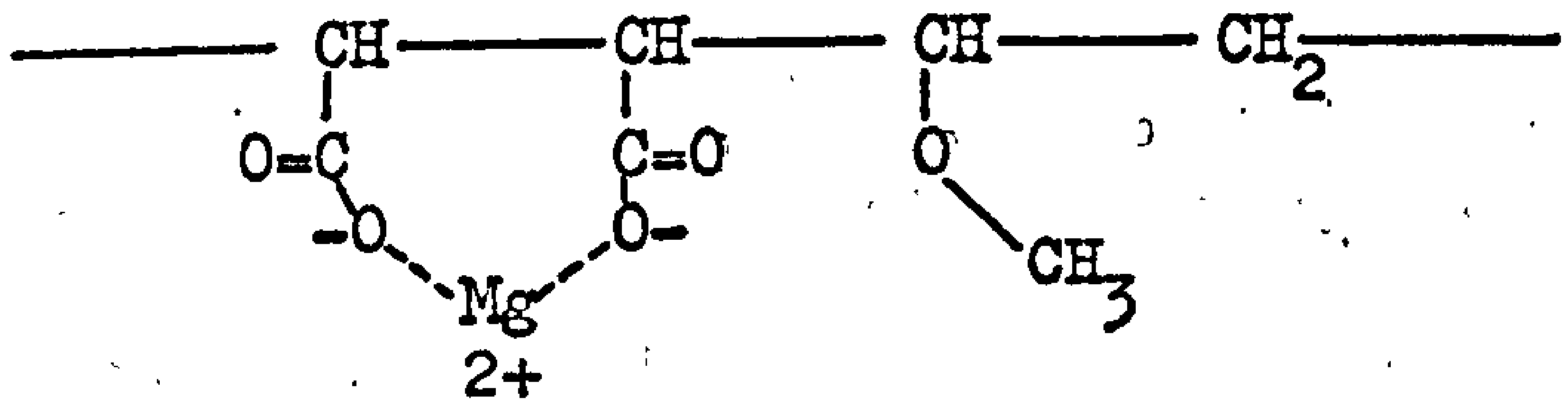
disruption of the hydration layers of the interacting species and the densities of water in bulk and hydration water are slightly different. The volume change with site binding (ΔV_t) has been reported to be a sensitive indicator of the degree of site binding among both different polyanions and different metal ions. The higher the ΔV_t value the higher the degree of ion site binding in solution. Tables 1.6.4.1. and 1.6.4.2. show ΔV_t values obtained with tetramethylammonium salts of various polyacids in tetramethylammonium chloride solution, containing various metal chlorides (or nitrates) at 303.15$\pm$ 0.001.

A detailed study of the binding of Mg^{2+} has shown that with poly(acrylate) and ethylene-maleate copolymer polyanions incomplete dehydration of the reacting species occurs, because the binding is electrostatic. For comparison, the covalent binding of H^+ ions leads to complete dehydration of the H^+ ion and polyanion. With vinylmethylether- maleate copolymer considerable dehydration of the polyanion and Mg^{2+} ion occurs at low degrees of neutralisation of the polyacid. This is believed to be a consequence of co-operative interaction of the ether groups on the polymer with the formation of a chelate ring (IV). At higher degrees of neutralisation the dehydration effect diminishes to a value close to that of ethylene-maleate copolymer and poly(acrylate) with Mg^{2+}, indicating a breakdown of the cheate rings (IV) to structures similar to those obtained with Mg^{2+} and ethylene-maleate copolymer (V).

No chelates of type (IV) are believed to occur with Ag^+ and vinylmethylether-maleate copolymer, because of the linear co-ordination geometry of this ion. This is reflected in the ΔV_t values in table 1.6.4.2., which are roughly equal for all three polyanions.



(IV)



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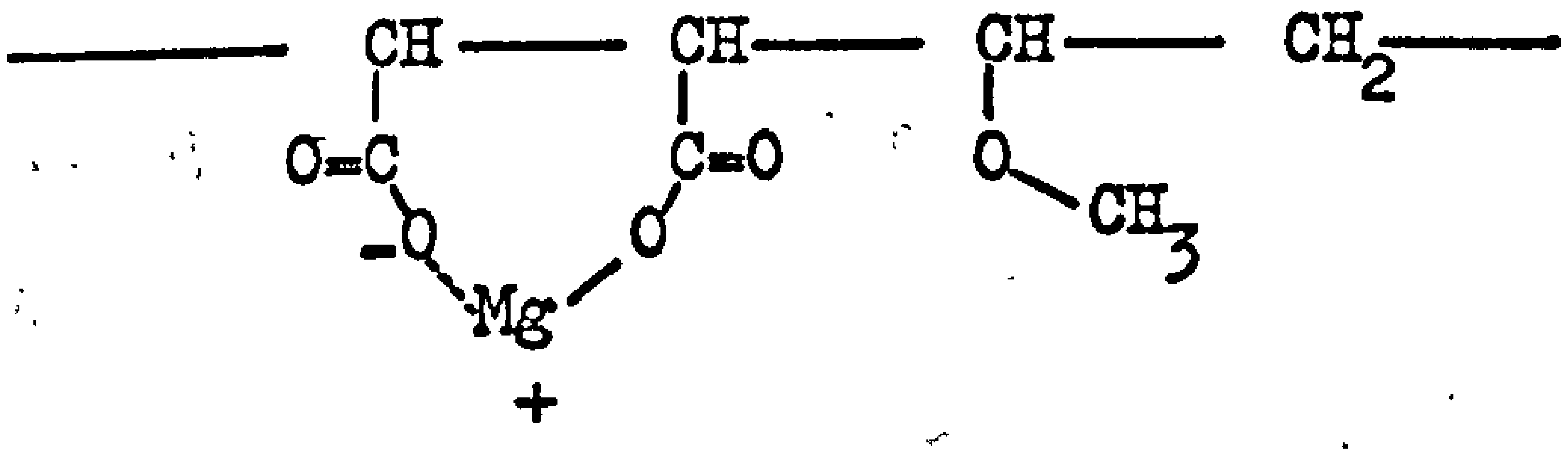


(V)

1.6.5. The effect of additives on ion-binding to polyacids.

The binding of Al^{3+} to polyacids has been found to be significantly enhanced by the addition of salts of organic acids, such as tartaric, citric, lactic and oxalic[66]. The effect has been demonstrated with SMA, PAA and carboxymethyl cellulose.

Commercial ASPA cements utilise a PAA solution modified with tartaric acid to improve the working and setting characteristics of the cement. It is likely that the setting characteristics of these cements are related to an enhancement of the binding of Al^{3+} to the PAA.

1.6.6. The effect of polyacid tacticity on ion-binding.

The literature on the effects of tacticity on ion-binding is limited.

Costantino et. al.[51] have examined PMAA and found that tacticity is important in determining complex solubility. Mg^{2+} shows a slight preference for the syndiotactic polymer. Cu^{2+} showed a strong preference for the syndiotactic polymer, whilst Co^{2+} a strong preference for the isotactic polymer.

Monjol[67] has reported that chelation of Cu^{2+} with PAA is independent of polymer stereoregularity and is greater than the chelation with PMAA where stereoregularity is important.

From spectroscopic kinetics studies Geuskin et. al.[68] have shown that the rate of formation of Cu^{2+} chelates with PAA is independent of tacticity. The isotactic polymer undergoes a conformational change during complexing.

1.6.7. The effect of polymer molecular weight on ion-binding.

Mc.Laren, Watts and Gilbert[69] have studied the effect of molecular weight on ion-binding to PAA. With PAA of molecular weight ($\bar{M}w$)$\approx 10^6$, prepared by u.v. polymerisation, ion-binding of Cu^{2+} and Ni^{2+} depends upon the PAA concentration. At low concentration (1.5 X 10^{-4}M) the stability constants for the complexing of Cu^{2+} and Ni^{2+} are slightly higher and the degree of co-ordination higher than values obtained at higher concentration (2.5 X 10^{-3}M). It is suggested that with high molecular weight PAA the polymer chains interact markedly in the higher concentration solution and that these interactions may be further enhanced by chain branching resulting from the method of preparation of the polymer. These strong chain interactions may hinder the binding of metal ions.

1.6.8. The nature of metal ion-polyacid binding:

Information on the nature of metal ion-polyacid binding is scanty and sometimes conflicting.

Alkali and alkaline earth metal ions are generally believed to be bound by essentially ionic bonding.[64,53] Wall and Gill have inferred from spectroscopic studies that Cu^{2+} binds to PAA in solution by a different kind of bonding to that of alkaline earth metal ions[70]. Nielsen[37] considers the bonding in metal oxide - PAA hot pressed solid composites to be ionic in character with CaO, ZnO or PbO. Whatever the exact nature of the bonding the alkaline earth metal ions are more weakly bound than other divalent ions, such as Zn^{2+}, Cu^{2+} and Cd^{2+}.

Very little is known about the co-ordination numbers of metal ions with polyanion ligands. Often the number of carboxylate groups bound is equated to the valency of the metal ion. Higher co-ordination numbers have been indicated in stability constant studies with divalent ions (e.g. Cu^{2+}), although here theory limits the meaningful calculation of co-ordination numbers greater than 2. The co-ordination geometry appears to be important in the stability of the complexes formed. For example, Cu^{2+} and Zn^{2+} are more strongly bound to EMA than Ni^{2+}, Co^{2+} or Mn^{2+} ions and thermodynamic data indicates that Zn^{2+} and probably Cu^{2+} have a 4 co-ordinate tetrahedral bonding geometry.[71]

The structure of metal ion-polyacid complexes is not known with certainty. Inter-chain cross-linking has been suggested for alkaline earth metal ions and Al^{3+} with concentrated PAA solution[21,53] and with Ca^{2+}, Zn^{2+} and Pb^{2+} in solid poly(acrylates).[37] However, most stability constant determinations assume chelate formation i.e. intra-chain binding. Cu^{2+} is usually assumed to form chelate structures with polyacids. With alginic acid and carboxymethyl cellulose both simple salt formation and inter-chain cross-linking have been postulated.[72] Conformational changes of a polyacid upon binding with metal ions tend to indicate the presence of intra-chain chelate formation with some metal ions.

Macromolecules of PAA are coiled in solution. Wojtczak[73] showed from viscosity measurements that at low degrees of neutralisation with Ca^{2+}, Ba^{2+} and Sr^{2+} hydroxides the PAA tends to uncoil slightly, but at higher degrees of neutralisation the macromolecules recoil until eventually they become even smaller than pure PAA macromolecule coils. These results indicate a constriction of the PAA macromolecules by intra-chain binding of the alkaline earth metal ions. However, Jacobson[74] considers PAA macromolecules to uncoil up to complete neutralisation, due to increasing electrostatic repulsion between charged carboxylate groups, even in the presence of bound Mg^{2+} ions.

PAA macromolecules have been reported to be constricted by bound Cu^{2+} [70,75] and Ag^{+} [76] ions, indicating chelation. Wall and Gill[70] have shown that the equilibrium constant for complex formation is proportional to $\frac{1}{c}$ and not $1/c^2$ (where c = concⁿ of carboxyl groups), indicating that two carboxylate groups on the same macromolecule bind each Cu^{2+} ion.

It is possible that both inter- and intra- chain complexing occurs between metal ions and polyacids in solution. Intra-chain complexing may be expected to be the most likely situation for entropic reasons, especially in dilute solution.

In concentrated solutions of polyacids, e.g. 20-50% w/w, the likelihood of inter-chain binding would be increased. Thus, the inter-chain cross-linking presumed to be present in ASPA cements would appear to be a reasonable hypothesis. Also, higher co-ordination numbers may be possible in highly concentrated polyacid solutions by virtue of the higher localised carboxyl group concentrations possible.

Thus information on ion-binding in dilute solution may be of limited applicability in predicting behaviour in highly concentrated solution. There is no literature discussing in depth the ion-binding in highly concentrated polyacid solutions.

1.7. The objectives of the research.

Three main aspects have been investigated in this thesis.

1. Experiments have been performed to establish some fundamental concepts for the reaction of polyacid solutions with ion-leachable aluminosilicate glass (G200 glass). Special emphasis has been directed towards establishing relationships between the polyacid structure and its reactivity with G200 glass, together with the water stability of the products obtained.

2. To avoid co-operative effects with the different ions leached from G200 glass, polyacid-metal oxide mixes have been studied and the results compared to G200 glass-polyacid products. Relationships have also been sought between the polyacid structure and its reactivity with metal oxides, together with the water stabilities of the products formed.

3. Ion-binding studies in dilute solution have been carried out to determine the usefulness of stability constant values in predicting the water stabilities of polyacid-metal oxide cement products.

The literature on ionomer cement products is very limited. This work is aimed at laying a broad foundation for future research and development of ionomer cements by covering preliminary ground work hitherto unreported in the literature. The work was considered necessary as ionomer cements, especially ASPA cement, have considerable promise in many applications.

2. EXPERIMENTAL DETAILS

2.1. The preparation of polyacids and their solutions.

2.1.1. The preparation of poly(acrylic acid) in water.[6]

Materials:

Solution A. 2500 ml acrylic acid, distilled in vacuo from stabilised reagent grade monomer. Purity (by titration against sodium hydroxide with phenolphthalein indicator) ≯98%.

2500 ml distilled water.

500 ml iso-propanol (A.R. grade).

Solution B. 62.5g ammonium persulphate (A.R. grade).

1500 ml distilled water.

Solution C. 62.5g ammonium persulphate (A.R. grade).

5000 ml distilled water.

The reagents were obtained from Hopkins and Williams Ltd.

Method:

Solution C was placed in a 201 reaction vessel fitted with a reflux condenser, a mechanical stirrer, a thermometer and a gas inlet tube. After flushing overnight with O_2 free N_2 the solution was heated to 353.

With constant stirring and flushing with O_2 free N_2 a mixture of 275 ml of solution A and 75 ml of solution B was slowly added over 5 minutes at 5 minute intervals. During the addition of the monomer the reaction temperature of 353-358 was maintained by the heat of the reaction.

When all of the monomer had been added the solution was maintained at 353-358 for a further 2 hours and was then cooled. The resulting solution was concentrated by distillation under reduced pressure for 18 hours, keeping the solution well stirred and the temperature of the distilling vapours below 323. 6.35 kg of distillate were collected.

Product:

The product was a water white, very viscous, colourless liquid. Analysis of the solution by titration against sodium hydroxide, using phenolphthalein indicator, yielded the following results:

Conversion of monomer to polymer ∿ 100%.

PAA content of the solution = 47.3% w/w.

The relative viscosity of the PAA (see section 2.1.3.) was found to be 1.37.

2.1.2. The preparation of poly(acrylic acid) in benzene.

Two batches of PAA were prepared by similar methods, but in one iso-propanol was added as a chain transfer agent.

Materials:

Table 2.1.2.1. shows the reagents employed in the two preparations.

The acrylic acid and iso-propanol were supplied by Hopkins and Williams Ltd. and the benzoyl peroxide by May and Baker Ltd.

Method:

Solution A was heated at 353, with stirring, until a polymer haze developed. Solution B was then slowly added, keeping the reaction temperature at about 353 and the reactants thoroughly stirred. The heating and stirring was continued for a period after all the solution B had been added.

Table 2.1.2.2. shows the conditions employed for the two preparations.

The resulting white PAA slurry was filtered off, washed with benzene and dichloromethane, and dried at 323-343 for 3-5 hours at

Table 2.1.2.1.

Materials for the preparation of PAA in benzene.

Reagent	Batch 5, table 3.1.1.1.		Batch 6, table 3.1.1.1.	
	Solution A	Solution B	Solution A	Solution B
Acrylic acid, distilled in vacuo from stabilised reagent grade monomer (g) (Purity - as in section 2.1.1.).	15.0	75.0	10.0	50.0
Benzene (solvent grade) (ml)	250	210	200	150
Iso-propanol (A.R. grade) (ml)	0	0	2	10
Benzoyl peroxide (reagent grade) (g)	0.15	0.625	0.10	0.417

Table 2.1.2.2.

Heating times employed in the preparation of PAA in benzene

Conditions	Batch 5, table 3.1.1.1.	Batch 6, table 3.1.1.1.
Addition time for solution B (hr)	3	3.5
Heating time after the complete addition of solution B (hr)	17	3

Table 2.1.2.3.

Analysis results for the PAA batches prepared in benzene.

Property	Batch 5, table 3.1.1.1.	Batch 6, table 3.1.1.1.	Analysis method.
% conversion of monomer to polymer.	∿97	∿97	Titration against sodium hydroxide with phenolphthalein indicator.
% PAA content of product.	91.9	93.4	
% water content in product, assuming no other impurities.	8.1	6.6	
Relative viscosity.	2.27	1.72	See section 2.1.3.
Molecular weight, $\bar{M}_v$.	-	9.1×10^5	

$8.5- 9 \times 10^4$ $Nm.^{-2}$

Products:

Both preparations gave white, free flowing, very fine powders, which were very soluble in water.

Analysis of the products gave the results shown in table 2.1.2.3.

2.1.3. The determination of the relative viscosities and molecular weights of the prepared poly(acrylic acid) samples.

The relative viscosities, $\eta_{rel.}$, of the PAA samples were determined with a constant level viscometer at 298.2, using solutions containing 1% w/v of PAA in 2.0M sodium hydroxide.

Viscosity average molecular weights, $\overline{M}_v$, were determined by the method of Sakamoto.[77]

2.1.4. The preparation of 2-hydroxyethyl methacrylate (HEMA)-acrylic acid copolymers in water.

Two copolymers, one containing 5 mole % and the other 10 mole % of HEMA, with acrylic acid were prepared.

Materials:

The materials used in the preparation of the copolymers are shown in table 2.1.4.1.

The reagents, except the HEMA, were supplied by Hopkins and Williams Ltd. The HEMA was supplied by Rohm and Haas Co. Ltd. Slight adjustments were made with the copolymer formulations to allow for the HEMA purity.

Method:

The copolymers were prepared by an analogous method to that used for the preparation of aqueous PAA (see section 2.1.1.). The solutions were concentrated by distillation under reduced pressure to about 44% w/w before use.

Table 2.1.4.1.

Reagents used in the preparation of HEMA-acrylic acid copolymers

Reagent	Batch 15, table 3.1.1.1.	Batch 14, table 3.1.1.1.
	5 mole % HEMA	10 mole % HEMA
Solution A		
Acrylic acid, distilled from reagent grade monomer. (Purity-as in section 2.1.1.) (g)	33.3	31.5
HEMA (95% pure) (g)	3.0	6.0
Distilled water (ml)	33.3	33.3
Iso-propanol (ml)	6.7	6.7
Solution B		
Ammonium persulphate (A.R. grade) (g)	0.83	0.83
Distilled water (ml)	20.0	20.0
Solution C		
Ammonium persulphate (A.R. grade) (g)	0.83	0.83
Distilled water (ml)	66.7	66.7

Products:

The prepared solutions were water white, clear, viscous liquids; the copolymer containing 10% HEMA giving the more viscous solution. The solution of copolymer containing 10% HEMA gelled in 14 days and that containing 5% HEMA gelled within 2 months.

The viscosities of HEMA- acrylic acid copolymer solutions were found to be very sensitive to the reaction conditions employed.

2.1.5. The preparation of aqueous poly(ethylenesulphonic acid) from sodium ethylenesulphonate.

2.1.5.1. The determination of the purity and the infra-red spectrum of the sodium ethylenesulphonate monomer.

Analysis of the monomer for purity.

Sodium ethylenesulphonate was obtained from Polysciences Inc. (U.S.A.) as an aqueous solution, which upon analysis was found to contain 34.33% w/w solids.

A dried, weighed sample of the sodium ethylenesulphonate was converted to ethylenesulphonic acid by dissolving it in water and passing the solution through an ion-exchange column containing Zeokarb 225 resin (H^+ form). After washing the column through with water the combined effluents were titrated against sodium hydroxide, using bromothymol blue indicator. From duplicate samples a molecular weight of 131.8 was obtained for the sodium ethylenesulphonate (theoretical value = 130.1).

The infra-red spectrum of the monomer.

Table 2.1.5.1. shows the infra-red absorption bands obtained for a sample of the sodium ethylenesulphonate dried at 420.

The spectrum shows bands consistent with the structure of sodium ethylenesulphonate and was found to agree with the infra-red spectrum of a sample of sodium ethylenesulphonate prepared by

Table 2.1.5.1.

The infra-red absorption bands for sodium ethylenesulphonate in a KBr disc.

$CH_2=CH-SO_3Na$

Band (cm^{-1})	Shape	Plausible assignment	Ref.
3550	Strong, wide	Probably -O-H stretch.	78,79
1670	Medium, wide	-C=C- (Probably overlapped by an absorption band due to water).	78,79
1408	Weak	(-O-H bending).	78
1210	Strong, wide	$-SO_3^-$ (-S-O stretch)	80,81
1060	Strong, sharp	$-SO_3^-$ (-S-O symm. stretch).	80,81
978	Weak	-C-H o.p. deformation	78
770	Medium, sharp	-C-S stretch	80

established methods.[83,84] The -O-H absorption bands in the spectrum were probably due to the presence of water in the sample, since sodium ethylenesulphonate is exceedingly hygroscopic.

2.1.5.2. The polymerisation of the sodium ethylenesulphonate.

Breslow and Kutner[84] found that the yield of sodium poly(ethylenesulphonate) obtained by the polymerisation of aqueous sodium ethylenesulphonate increased with increase in the concentration of the monomer solution and reached a maximum at a monomer concentration of about 62% w/w. Consequently, to ensure a satisfactory yield of polymer the 34.33% w/w sodium ethylenesulphonate solution employed here was concentrated before use by careful distillation in vacuo.

The polymerisation of the sodium ethylenesulphonate[84] was carried out with a redox initiator and also by photochemical initiation. Table 2.1.5.2.1. summarises the details of each method.

The products were purified by precipitation from aqueous methanol[84] and then dried at 348-358 under 7.5 - 7.8 Nm^{-2} reduced pressure to obtain the polymers shown in table 2.1.5.2.2.

2.1.5.3. The infra-red spectrum of sodium poly(ethylenesulphonate).

The absorption bands from the infra-red spectrum of the sodium poly(ethylenesulphonate) prepared by persulphate-bisulphite initiated polymerisation are shown in table 2.1.5.3.1.

The infra-red spectrum was considered to be consistent with the structure of sodium poly(ethylenesulphonate). The -O-H absorption bands were probably due to residual water as the polymer is exceedingly hygroscopic.

2.1.5.4. The determination of the specific viscosities and molecular weights of the prepared sodium poly(ethylenesulphonate) samples.

The specific viscosities, $\eta_{sp.}$, of the sodium poly(ethylenesulphonate)

Table 2.1.5.2.1.

The polymerisation of sodium ethylenesulphonate in aqueous solution.

Reactants and conditions.	Chemical initiation	Photochemical initiation
Initiator	0.30g sodium metabisulphite 0.64g ammonium persulphate	u.v. lamp
Charge weight (g)	150	280
Monomer concentration (% w/w)	∿50	61
Reaction temperature	273.2-273.7	Room temperature.
Reaction time (hr)	48	24
Inert gas blanket	O_2 free N_2	O_2 free N_2
Stirring method	Mechanical	N_2 agitation
Comments	Initiator solution added over 5.33hr. At the reaction temperature some undissolved monomer was present.	N_2 agitation became impossible after a few hours, owing to the increase in solution viscosity. No undissolved monomer was present at the reaction temperature.

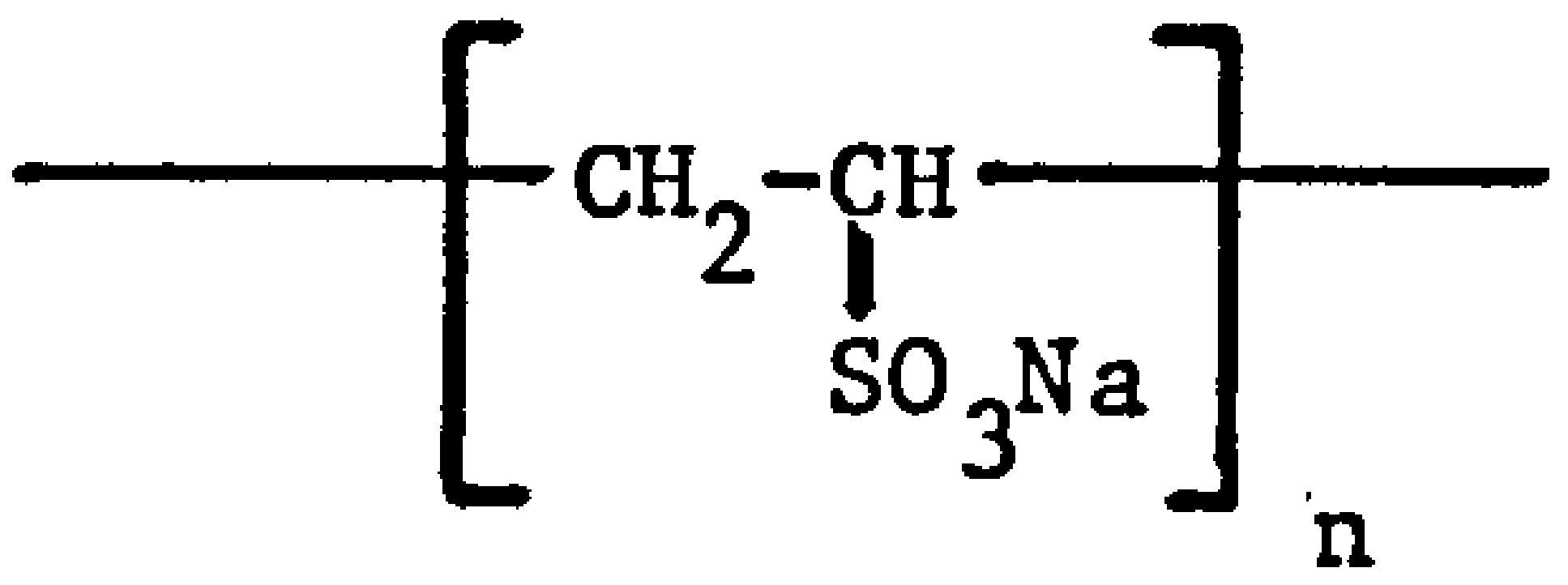
Table 2.1.5.2.2.

The properties of the prepared batches of sodium poly(ethylenesulphonate).

Method of preparation	Chemical initiation	Photochemical initiation
Nature of product.	Brittle, pale yellow hygroscopic solid.	Brittle, pale yellow hygroscopic solid, containing $\sim$2.5% residual water.
Yield (%)	25	80.7
Estimated residual monomer (by u.v. analysis). (%)	$\sim$1.5	$\sim$3
Specific viscosity (see section 2.1.5.4.).	0.46	0.89
Molecular weight, $\bar{M}_n$ (see section 2.1.5.4.).	1.3×10^4	2.6×10^4

Table 2.1.5.3.1.

The infra-red absorption bands for sodium poly(ethylenesulphonate) in a KBr disc.



$$\left[-CH_2-\underset{SO_3Na}{\underset{|}{CH}}-\right]_n$$

Band (cm^{-1})	Shape	Plausible assignment	Ref.
3550	Strong, wide.	-O-H stretch	78,79
2990	Weak, sharp.	-C-H stretch (alkane)	78,80
1660	Med. - strong, wide.	Probably due to water.	79
1460	Medium	-C-H deformation (alkane)	78,80
∿1200	Very strong, very wide*	$-SO_3^-$ (-S-O stretch) and possibly -O-H bending.	78,80, 81
1050	Very strong, wide.	$-SO_3^-$ (-S-O stretch)	80,81
720	Strong, wide	-C-H rocking (alkane)	78,80

* Possibly more than one band overlapping.

samples were determined with a constant level viscometer at 298.2, using solutions containing 1% w/v of the polymer in distilled water.

Number average molecular weights, $\overline{M}_n$, were estimated from the data of Breslow and Kutner.[84]

2.1.5.5. The conversion of the sodium poly(ethylenesulphonate) to poly(ethylenesulphonic acid).[85]

Aqueous solutions containing 28% w/w of sodium poly(ethylenesulphonate) were cooled in an ice bath and saturated with hydrogen chloride gas. Sodium chloride precipitated and was filtered off at the pump. After washing the precipitate with cold concentrated hydrochloric acid the combined filtrate and washings were carefully heated to drive off hydrogen chloride and water. The resulting concentrated solution was diluted with water and distilled under slightly reduced pressure to concentrate again. After several similar treatments with water a viscous, dark brown, odourless, chloride free solution was obtained. The test for the presence of chloride was by treatment with aqueous $AgNO_3$ and HNO_3, which gave no precipitate with the poly(ethylenesulphonic acid) (PESA) solution. A control test using sodium poly(ethylenesulphonate), alone and with added KCl, showed that the macroanion did not mask the test.

2.1.5.6. The analysis of the prepared poly(ethylenesulphonic acid) solutions.

The solids content of the prepared PESA solutions were estimated by drying at 413-418, allowing for slight decomposition of the polymer.

The % PESA content of the solutions were determined by titration against sodium hydroxide, using bromothymol blue indicator.

From the results of these two methods of analysis a value for the proportion of residual sodium ethylenesulphonate chain units in the polymer was estimated, allowing for the purity of the original monomer.

Table 2.1.5.6.1. shows the analysis results obtained.

The molecular weights of the prepared PESA samples were assumed to be identical to the samples of sodium poly(ethylenesulphonate) from which they were prepared (see table 2.1.5.2.2.).

2.1.5.7. The infra-red spectrum of poly(ethylenesulphonic acid).

A sample of the PESA solution, obtained from the sodium poly(ethylenesulphonate) made by persulphate-bisulphite initiated polymerisation, was dried at 405 for 1.75 hours. The infra-red spectrum of this sample is described in table 2.1.5.7.1.

The absorption band at 3500 cm^{-1} was probably due to -S-OH groups, although since PESA is highly hygroscopic an absorption band in this region due to water may also have been present.

2.1.6. The preparation of aqueous solutions of polyacids from their anhydrides.

2.1.6.1. The preparation of aqueous ethylene-maleic acid copolymer solution.

Materials:

33.4 g EMA-21 ethylene-maleic anhydride copolymer(ex. Monsanto Ltd.).

100g distilled water.

Method:

The EMA-21 copolymer powder was mixed with hot water to obtain a viscous, white paste. After heating the paste at upto about 365 with vigorous stirring, the viscosity decreased and a water white, clear solution containing 28% w/w of the polyacid was obtained. The solution was cooled before use.

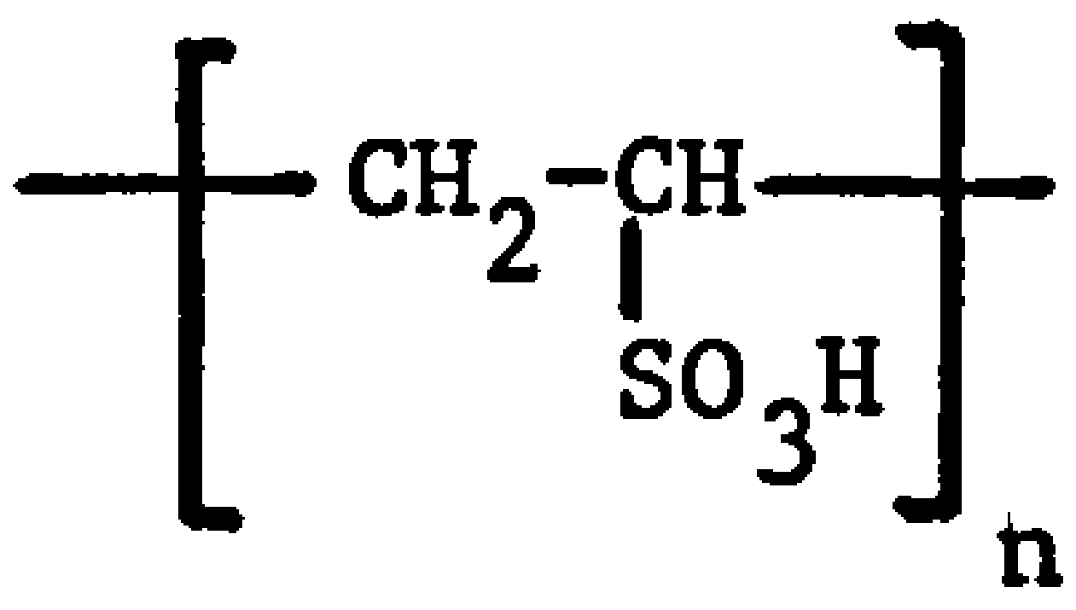
Table 2.1.5.6.1.

The analysis of the prepared PESA solutions.

Method of initiation of the polymerisation reaction.	Chemical initiation	Photochemical initiation
Approximate solids content (% w/w)	40.7	45.5
PESA content (% w/w)	36.9	43.3
Approximate content of residual sodium ethylenesulphonate chain units (mole %)	6.8	2.8

Table 2.1.5.7.1.

The infra-red absorption bands for PESA in a KBr disc.



$$\left[CH_2-\underset{SO_3H}{\underset{|}{C}H}- \right]_n$$

Band (cm^{-1})	Shape	Plausible assignment	Ref.
3500	Strong, wide	-O-H stretch (-S-OH or water)	78,79,86.
2690	Weak-med., sharp shoulder	-C-H stretch (alkane)	78,80
∿1650-1800	Medium, diffuse	Possibly due to water	79
1460	Weak, sharp	-C-H deformation (alkane)	78,80
∿1200	Very strong, very wide	$-SO_3^-$ (-S-O stretch)	80,81
1030	Very strong, wide	$-SO_3^-$ (-S-O symm. stretch)	80,81
∿820-840	Weak, doublet	Inconclusive	-
730	Weak, wide	-C-H rocking (alkane)	78,80

The composition of the EMA-21 copolymer:

A sample of the EMA-21 copolymer was dried for 4 days over P_2O_5, weighed and then dissolved in distilled water. Potentiometric titration of the solution gave an equivalent weight of 67 for the copolymer, indicating an ethylene: maleic anhydride ratio of approximately 1.25:1.

2.1.6.2. The preparation of styrene-maleic acid copolymer solution in aqueous acetone.

Materials:

10.0g	SMA 1000A styrene-maleic anhydride copolymer (ex. Arco Chemical Co., U.S.A.; supplied by Cornelius Chemicals Co. Ltd.
100 ml	distilled water.
100 ml	Acetone (solvent grade).

Method:

The materials were refluxed with stirring until a solution resulted together with a white syrup. After cooling, the upper layer was decanted to leave a viscous, white copolymer syrup.

The composition of the copolymer syrup:

Drying samples of the copolymer syrup to constant weight at 420 showed the solution to contain 50.2% w/w of copolymer (as the polyacid).

2.1.6.3. The preparation of other polyacid solutions in water.

Where commercial polyacids were not supplied in solution powdered samples were dissolved, with stirring, in hot water. The solutions were cooled before use.

2.1.7. <u>The preparation of solutions of polyacids in non-aqueous solvents.</u>

2.1.7.1. The preparation of styrene-maleic acid copolymer solution in dimethylformamide.

Materials:

10.0g SMA 1000A copolymer (ex. Arco Chemical Co., U.S.A.; supplied by Cornelius Chemicals Co. Ltd.).
1.0g distilled water.
10.00ml dimethylformamide

Method:

The materials were mixed together and there was a slight evolution of heat. With continuous stirring the mixture was heated to about 373 until a viscous, clear, brown solution resulted.

The theoretical quantity of water required to convert the anhydride to the acid was calculated to be 0.89g. Assuming complete hydrolysis to the polyacid the solution was estimated to contain 53% w/w of copolymer. The solution stood overnight before use.

2.1.7.2. The preparation of ethylene-maleic acid copolymer solution in dimethylformamide.

Materials:

7.44g EMA-21 copolymer (ex. Monsanto Ltd.)
1.1g distilled water
16 ml dimethylformamide.

Method:

The preparation of this solution was identical to that of SMA copolymer in dimethylformamide (section 2.1.7.1.). The solution was a viscous, clear, yellow-brown liquid.

The theoretical quantity of water required to hydrolyse the anhydride copolymer was calculated to be 1.0g. Assuming complete conversion to the polyacid the solution was estimated to contain 35.6% w/w of copolymer. The solution stood for 5 days before use.

2.1.7.3. The preparation of poly(acrylic acid) solution in dimethylformamide.

Materials:

10.0g PAA powder (batch 5, table 3.1.1.1.).

28.5 ml dimethylformamide.

Method:

The materials were stirred and heated until a viscous, clear, yellow-brown solution resulted, containing approximately 27% w/w PAA. The solution stood for 5 days before use.

2.1.7.4. The preparation of ethylene-maleic acid copolymer solution in 1,4-dioxan.

Materials:

10.0g EMA-21 copolymer (ex. Monsanto Ltd.).

1.5g distilled water

33 ml 1,4-dioxan.

Method :

The materials were mixed in a 3 necked flask, fitted with a stirrer and a reflux condenser. After heating and stirring for 1hr in a boiling water bath a viscous, clear and almost colourless solution resulted.

EMA-21 copolymer is insoluble in 1,4-dioxan, but the hydrolysed copolymer is soluble. Consequently the formation of a clear solution indicated that hydrolysis of the copolymer had taken place. The quantity of water required to hydrolyse the EMA-21 copolymer was calculated to be 1.35g. Assuming complete conversion to the polyacid the solution was estimated to contain 25% w/w of the copolymer.

The solution stood overnight before use.

2.2. The preparation of polyacid-metal oxide, or G200 glass mixes.

Samples of metal oxides, or G200 glass powders were spatulated on a glass block with aliquots of the various polyacid solutions. The metal oxides were either A.R. or reagent grade materials and the G200 glass was obtained from The Amalgamated Dental Co. Ltd.

The mixes were placed on poly(ethylene) film and allowed to age at room temperature and relative humidity.

Where specific P:L ratios have not been quoted in section 3 the mixes have been formulated to give putty like pastes with as much added oxide, or G200 glass powder as possible.

For studies on the organic solvent and aqueous acid and alkali resistance of PAA-G200 glass cement, mixes were prepared at a P:L = 3:1 and hardened for 18 hours at 310 before immersion.

Compressive strength tests on polyacid-G200 glass cements were performed by a method similar to that in BS 3365: part 1, 1969. Samples were hardened at 310 for 21 hours at room relative humidity before testing.

2.3. The infra-red spectroscopic analysis of polymer and cement samples.

Infra-red spectra were recorded on samples pressed into discs with KBr (B.D.H. Ltd., spectroscopic grade), using a Hilger and Watts Model H 1200 Infra-Red Spectrophotometer.

Cement samples were powdered with sand paper before mixing and grinding with KBr.

2.4. The determination of stability constants of metal ion-polyacid complexes by potentiometric titration.

2.4.1. The preparation of stock solutions:

All solutions were prepared using boiled out deionised water, unless otherwise stated. Solutions, except for buffers, were always stored under N_2 in poly(ethylene) bottles tightly stoppered with rubber bungs.

The sodium nitrate used was supplied by Hopkins and Williams Ltd. (A.R. grade) and was oven dried before use. Calcium and cadmium nitrates were obtained as hydrated A.R. grades from B.D.H. Ltd. The polyacids employed in this work are described in table 3.1.1.1. ; for the PAA see batch 1, for the EMA copolymer see batch 8 and for the PESA see batch 17.

PAA and EMA samples were dissolved in water and the solutions were dialysed for 10-12 days, using Visking dialysis tubing (pore size 2.4 nm) immersed in deionised water. The water was changed periodically. The dialysed polyacid solutions were diluted to 1l with sodium nitrate solution to obtain stock solutions containing approximately 0.02M polyacid (i.e. moles of carboxyl groups per litre) in 2.0 M sodium nitrate.

PESA stock solution was prepared by diluting an undialysed sample in 1l water. A 3.53M stock solution of sodium nitrate was prepared for use with the PESA solution.

Calcium and cadmium nitrate stock solutions were made by dissolving samples of the hydrated salts in water. 0.20M sodium hydroxide titrant solutions were prepared from standard ampoules supplied by B.D.H. Ltd.

Buffer solutions were prepared from dried A.R. grade reagents.

Two buffer solutions were used:

0.05M potassium hydrogen phthalate in deionised water.
pH at 293.2 = 4.00.[87]

0.01M borax in boiled out deionised water.
pH at 293.2 = 9.22.[87]

The potassium hydrogen phthalate was obtained from Hopkins and Williams Ltd. and the borax was supplied by B.D.H. Ltd.

The buffer solutions were stored in stoppered dark glass bottles and were replaced every 4-6 weeks.

2.4.2. The determination of the concentrations of the polyacid and metal nitrate stock solutions.

The stock polyacid solutions were titrated potentiometrically and their concentrations were found to be (in moles acid groups per litre):

PAA	1.85×10^{-2}M
EMA	1.79×10^{-2}M
PESA	2.07×10^{-2}M

The stock metal nitrate solutions were analysed by atomic absorption spectroscopy and their concentrations were found to be:

Ca^{2+}	6.01×10^{-3}M	) used with PAA and
Cd^{2+}	6.07×10^{-3}M	) EMA solutions.
Cd^{2+}	8.0×10^{-3}M	) used with PESA solution.

Sodium hydroxide titrant solutions were checked against standard hydrochloric acid, using bromothymol blue indicator.

2.4.3. The preparation of polyacid solutions for titration in the presence and absence of Ca^{2+} and Cd^{2+} ions.

PAA and EMA solutions were prepared by mixing 50 ml of their stock polyacid solutions with either 50 ml of water, or a volume of stock metal nitrate solution and a volume of water to bring the total volume of the solution to 100 ml.

PESA solutions were prepared by mixing 50 ml of the stock polyacid solution with 25 ml of stock sodium nitrate solution and adding either 25 ml of water, or 25 ml of stock cadmium nitrate solution. All solutions were mixed in covered poly(propylene) vessels, which had been previously flushed through with N_2.

2.4.4. The titration of the prepared polyacid solutions.

All titrations were carried out in covered poly(propylene) vessels under a constantly flowing N_2 blanket. Before titrations were started the polyacid solutions were equilibrated in an oil bath at 298.2± 0.2.

pH measurements were made using a Pye-Unicam Model 290 Mark 2 pH meter with Pye-Ingold Model 401 (E07) or Model 405.88 (E07) combination electrodes. The pH meter was calibrated with the stock buffer solutions, making appropriate temperature corrections.

To determine the equilibrium conditions during the titrations the pH meter output was also connected to a Smith's Servoscribe RE 511.20 millivolt chart recorder. Stable pH readings were shown by stable vertical traces from the chart recorder. About 10-30 minutes was usually sufficient to attain a stable pH reading.

The pH electrode was checked twice daily against the stock buffers. For the PAA and EMA titrations the maximum drifts experienced were about 0.01 pH unit, whilst for PESA titrations it was about 0.02 pH unit.

Titrant solutions were added to the polyacid solutions from a microburette, or from a micrometer pipette (a 200-1000μl Finnpipette, ex. Jencons Ltd.). The micrometer pipette delivery was checked twice before each addition of titrant and once after each addition.

After each addition of titrant solution the polyacid solutions were stirred for a few minutes. pH readings were taken in stationary solutions.

During the titration of the PAA and EMA with added cadmium nitrate a precipitate was formed. No precipitate formed in the other titrations.

3. RESULTS AND DISCUSSION

3.1. The reactivity of ion leachable aluminosilicate glass with various aqueous polymer solutions.

3.1.1. Introduction.

There is very little literature on polyacid-aluminosilicate glass cements containing polyacids other than PAA. Copolymers of acrylic acid with acrylonitrile, or acrylamide, have been briefly reported as being suitable for ASPA type cements[8] and an acrylic acid-itaconic acid copolymer is at present being evaluated at The Laboratory of The Government Chemist.

To expand the literature on the types of polymer suitable for preparing ionomer cements with G200 glass ten previously unreported polymers have been studied, with special emphasis on commercially available types (table 3.1.1.1.).

Further preliminary studies on PAA-G200 glass cement have also been carried out. A 'one-pack' powdered PAA and G200 glass system has been developed and the solvent resistance of PAA-G200 glass cement has been examined.

3.1.2. General summary of the products formed between G200 glass and the polymer solutions studied.

Table 3.1.2.1. summarises the products obtained by mixing G200 glass powder with the polymer solutions described in table 3.1.1.1. The water stabilities of the products have been determined in water at room temperature.

3.1.3. The properties of poly(acrylic acid) - G200 glass cements.

3.1.3.1. The properties of the polyacid component.

Aqueous solutions of PAA tend to gel on ageing if their concentrations are high, for example at 47.3% w/w (batch 1 table 3.1.1.1.)

Table 3.1.1.1.

Types and properties of polyacids and their aqueous solutions.

POLYMER	POLYMER PROPERTIES	SOURCE (and trade name)	BATCH NO.	SOLUTION CONCENT-RATION USED	SOLUTION PROPERTIES	COMMENTS
Poly(acrylic acid) (PAA)	ηrel.= 1.37	Prepared in aqueous solution	1	47.3% w/w	Viscous, clear colourless liquid. pH ~0.5	Prepared from dental formulation[6] (see section 2.1.1.)
	M.Wt.[88] ~ 3.5×10^3	Allied Colloids Ltd. (Versicol E5)	2	25% w/w[88]	η= 16 cp.[88] pH~1.5	Used as supplied solution
	M.Wt.[88] ~ 7.6×10^4	Allied Colloids Ltd. (Versicol E9)	3	25% w/w[88]	η = 200 cp[88] pH ~1.6	"
	M.Wt.[88] ~ 2.6×10^6	Allied Colloids Ltd. (Versicol E15)	4	15% w/w[88]	η= 3.7×10^4 cp[88] pH~1-2	"
	$\eta_{rel.}$ = 2.27	Prepared in benzene.	5	-	-	Fine, white, dusty powder. Very soluble in water. Contained~ 8% water.
	$\eta_{rel.}$ = 1.72 $\bar{M}_v$ ~ 9×10^4	"	6	-	-	Fine, white, dusty powder. Very soluble in water. Contained~ 6.6% water.

Table 3.1.1.1. (continued)

POLYMER	POLYMER PROPERTIES	SOURCE (and trade name)	BATCH NO.	SOLUTION CONCENTRATION USED	SOLUTION PROPERTIES	COMMENTS
Poly(methacrylic acid) (PMAA)	M.Wt.[88] ~2.6x10^{4}	Allied Colloids Ltd. (Versicol K13)	7	20% w/w[88]	η=5.4x10^{3}cp.[88] pH~1.8	Used as supplied solution.
Ethylene-maleic acid copolymer. (EMA)	Equiv. Wt. = 67 Mole ratio 1.25:1	Monsanto Ltd (EMA-21)	8	28% w/w	Clear, colourless, viscous liquid. pH ~1.3	Supplied as powdered anhydride. Hydrolysed before use.
Vinylmethyl ether-maleic acid copolymer (VEMA)	Mole ratio ~1:1[89]	General aniline and Film Corp. (Gantrez S95)	9	40% w/w	Pale brown, clear, viscous liquid. pH ~1.2	Supplied as powdered acid.
Styrene-maleic acid copolymer (SMA)	M.Wt.~1600) Mole ratio= 1:1)[90]	Cornelius Chemicals Co. Ltd.(ex. Arco Chemical Co., U.S.A.) (SMA 1000 A)	10	50.4% w/w (in acetone-water)	White viscous syrup	Supplied as powdered anhydride. Hydrolysed before use.
Sodium acrylate-acrylic acid copolymer	M.Wt.[91] ~5x10^{6} Mole ratio[92] ~ 1:1	Allied Colloids Ltd. (Versicol S19)	11	21% w/w	Very viscous, white solution. pH ~4.8	Supplied in powder form.
Styrene-mono-sodium maleate copolymer	Mole ratio~13:9	Yorkshire Chemicals Ltd. (Resin SMC)	12	25% w/w[93]	Pale brown liquid pH~5.8.	Used as supplied solution.

Table 3.1.1.1. (continued)

POLYMER	POLYMER PROPERTIES	SOURCE (and trade name)	BATCH NO.	SOLUTION CONCENT-RATION USED	SOLUTION PROPERTIES	COMMENTS
Methylacrylate-methyl methacrylate-sodium acrylate copolymer.	-	Allied Colloids Ltd. (Glascol HN2)	13	30% w/w[94]	Cloudy white liquid pH$\approx$7	Used as supplied solution.
Acrylic acid-2-hydroxyethyl methacrylate (HEMA) copolymer.	Mole ratio$\approx$9:1	Prepared in aqueous solution	14	$\approx$ 44% w/w	Clear, colourless, viscous liquid. Gelled in <14 days.	Gelling limited practical applications
	Mole ratio $\approx$ 9.5:0.5	"	15	$\approx$ 44% w/w	Clear, colourless, viscous liquid, Gelled in <2 months.	"
Poly(ethylene-sulphonic acid)	$\eta_{sp.}$=0.61 $\bar{M}n \approx 13x10^3$	Prepared in aqueous solution using a redox initiator	16	36.85% w/w	Brown, viscous clear liquid.	-
(PESA)	$\eta_{sp.}$=1.11 $\bar{M}n \approx 26x10^3$	Prepared in aqueous solution using u.v. light.	17	43.3% w/w	Brown, viscous clear liquid. pH<0.	-
Ethylacrylate-acrylic acid copolymer	Emulsified. Particle size $\approx$ 0.2μ.[95]	Scott Bader Ltd. (Texicryl 13-300)	18	$\approx$ 40% w/w[95] Emulsion in water.	White liquid. Low viscosity. pH $\approx$ 2.2	Used as supplied emulsion.

Table 3.1.2.1.

Products formed between various polyacids (and polyacid salts) and G200 glass.

POLYMER			PRODUCT WITH G200 GLASS POWDER				WATER STABILITY OF SET PRODUCT.		
Polyacid	Solution concentration	Batch Number	P:L ratio	Mix characteristics	Condition of product after 2 days at room temp.	Comments	Age before immersion	Immersion time	Effect on product.
Poly(acrylic acid)	47.3% w/w	1	3:1	Stiff, putty like paste	Hard, coherent	Set in ∿25 min	∿1 day	Many days	Uneffected
			2:1	Putty like paste	"	Set in ∿40 min	"	"	"
			1:1	Thin, putty like paste	"	Set in ∿2½ hr	"	"	"
	25 % w/w	2	3:1	Thin paste	"	Set in ∿15 min	"	"	"
	25 % w/w	3	-	Putty like paste	"	-	"	"	"
	15% w/w	4	2:1	Putty like paste	"	Set in ∿1½ hr	"	"	"
			1:1	Very stiff putty like paste	"	Set in ∿25 min			

Table 3.1.2.1. (continued)

POLYMER			PRODUCT WITH G200 GLASS POWDER				WATER STABILITY OF SET PRODUCT.		
Polyacid	Solution concentration	Batch Number	P:L ratio	Mix characteristics	Condition of product after 2 days at room temp.	Comments	Age before immersion	Immersion time	Effect on product.
Poly(methacrylic acid)	20% w/w	7	-	Putty like paste	Hard, coherent	Set in 1-2hr	3 days	21 days	Uneffected
Ethylene-maleic acid copolymer	28% w/w	8	-	"	"	Set in ∿1hr	18 hr	19 days	"
Vinylmethyl ether-maleic acid copolymer	40% w/w	9	-	"	"	-	"	3 days	Surface markedly softened
Styrene-maleic acid copolymer	∿50.4% w/w (in acetone-water)	10	-	"	"	Set in ∿18 hr. Little strength	"	3½ days	Uneffected*
Sodium acrylate-acrylic acid copolymer	∿21% w/w	11	∿1:1	Putty like paste	Hard, coherent	Hardened in <20 hr	20 hr	24 hr	Soft, coherent, weak, much swollen.

Table 3.1.2.1. (continued)

POLYMER			PRODUCT WITH G200 GLASS POWDER				WATER STABILITY OF SET PRODUCT.		
Polyacid	Solution concentration	Batch Number	P:L ratio	Mix characteristics	Condition of product after 2 days at room temp.	Comments	Age before immersion	Immersion time	Effect on product
Styrene-mono-sodium maleate copolymer	25% w/w	12	-	Putty like paste	-	Hard, coherent after setting at 310.	-	-	Rapidly disintegrated
Methylacrylate-methyl methacrylate-sodium acrylate copolymer.	30% w/w	13	3:1	Crumbly paste	Hard, coherent	Crumbly mass after 40 min. Hardened overnight.	∿18 hr	<20 min	"
Acrylic acid-2-hydroxyethyl methacrylate (HEMA) copolymer	∿44% w/w	14	2:1	Putty like paste	Hard, coherent	Set in ∿40 min	2 days	2 days	Cement surface softened
			1:1	Thin putty like paste	"	Set in >2½ hr	"	"	"
	∿44% w/w	15	3:1	Putty like paste	"	Set in ∿25 min	"	"	Uneffected
			2:1	"	"	Set in ∿40 min	"	"	Very slight surface softening

Table 3.1.2.1. (continued)

POLYMER			PRODUCT WITH G200 GLASS POWDER				WATER STABILITY OF SET PRODUCT.		
Polyacid	Solution concentration	Batch Number	P:L ratio	Mix characteristics	Condition of product after 2 days at room temp.	Comments	Age before immersion	Immersion time	Effect on product
Poly(ethylenesulphonic acid)	36.85% w/w	16	-	Putty like paste	-	Not set ater 20hr	4 days	-	Rapidly disintegrated
	43.3% w/w	17	3:1	Stiff putty like paste. Heat evolved during mixing.	Partially set.	Hard after 5 days	5 days	<½ hr	"
			2:1	Putty like paste.	"	"			
Ethylacrylate-acrylic acid copolymer	40% w/w	18	3:1	Very thin slurry	Set, but weak	Brittle solid after 5 days	5 days	8 days	Uneffected
	Emulsion		2:1	Very thin slurry	"	"	"	"	"

* Also stable after soaking 5 days in ~1:1 acetone-water mixture.

the solution slowly thickens, but remains workable, over 9-12 months. The gelling is, however, reversible and the solution is restored by warming.

The polymerisation of acrylic acid in benzene gives a bulky, extremely fine powdered form of PAA, which by virtue of the high surface area afforded by the small polymer particles rapidly dissolves in water.

The tacticities of the PAA batches prepared in water (table 3.1.1.1., batch 1) and benzene (table 3.1.1.1., batches 5 and 6) are probably 100% atactic. Monomer concentrations are kept low in their preparations by the slow continuous monomer addition processes used. At concentrations of monomer below 20-25% atactic polymers are reported formed in water and in aromatic hydrocarbon media.[96] No information is available on the tacticities of the commercial PAA samples used.

3.1.3.2. The properties of the poly(acrylic acid)-G200 glass mixes and set cements.

The reaction of PAA with G200 glass proceeds through four overlapping phases for all molecular weights and solution concentrations studied.

1. A viscous, sticky phase.
2. A "stringy" soft rubbery phase.
3. A coherent rubbery gel phase.
4. A coherent, hard inflexible state.

During phase 1 Ca^{2+} and Al^{3+} ions are leached into solution by acid attack on the G200 glass. Partial cross-linking of the polymer chains by Ca^{2+} and Al^{3+} ions probably occurs in phase 2 and in stages 3 and 4 this cross-linking develops to form an extensive network structure. It is only during the first stage that the cement may be worked and further mixing of the paste during stages 2 or 3 can lead to a product, which although hard is structurally weak. The surfaces of hardened cements (at stage 4) are still reactive and can be firmly bonded together with fresh cement paste.

Mix workability, setting time and the mechanical strength of the hardened cement can depend upon the molecular weight of the PAA, the concentration of the PAA solution and the P:L ratio employed. Table 3.1.3.1.1. shows some generally applicable rules.

A disadvantage encountered with aqueous PAA solutions is their inherent stickiness and high viscosity, which makes them inconvenient to handle. To overcome these difficulties a "one-pack" cement system has been developed in which the G200 glass is mixed with powdered PAA. Water is added to the powdered components and the cement paste prepared by spatulating the mix on a glass block i.e. in the same way as a mix is prepared from aqueous PAA.

The powdered PAA and G200 glass mixture can be stored at 32% relative humidity for at least 7 days without any visible signs of reaction by the absorption of atmospheric moisture. At higher relative humidities (e.g. 66-80%) the powdered mix shows signs of clumping after a few days. Powdered mixes aged at 66% relative humidity over 25 days still form satisfactory cements with water. Samples aged at 80% humidity for 25 days, however, give granular mixes which do not pass through a "stringy" phase when spatulated with water, although hard cements are still obtained.

The workability of the powdered mix depends upon the molecular weight of the PAA. If the molecular weight is too high a low P:L ratio is required to give a workable paste. Low P:L ratios can have a detrimental effect on the properties of the set cement (see table 3.1.3.1.1.).

Table 3.1.3.1.1.

Some parameters in PAA-G200 glass cement mixes.

Property Changes.	Effects.
Increase P:L ratio (constant polymer conc.^{n} & MWt).	Mix viscosity increases. Workability becomes more difficult. Setting time decreases. Compressive strength increases (see also ref. 4.). Resistance to cracking and crazing increases.
Increase polymer concentration (constant P:L ratio and polymer MWt).	Polymer solution viscosity increases. Mix viscosity increases (see also ref. 2). Workability becomes more difficult. Increases compressive strength (see also ref. 2.). Resistance to cracking and crazing increases.
Increase polymer MWt. (constant P:L ratio and polymer concentration)	Polymer solution concentration often limited by increase in viscosity. Mix viscosity increases. Workability becomes more difficult. Little or no effect on compressive strength.[20]

3.1.3.3. The stability of poly(acrylic acid)-G200 glass cements towards water, aqueous acids and alkalis and organic solvents.

Table 3.1.3.3.1. shows that PAA-G200 glass cement has excellent resistance towards water and many organic solvents. Strong acid and alkali rapidly destroy the cement and may attack the glass and also dissociate the polyacid-metal complex in the matrix.

These preliminary results indicate that PAA-G200 glass cement has considerable potential in non-dental applications where resistance to solvents may be required. The dehydrating effect of hydrophilic solvents and the effect of solvents on the compressive strength of the cement have not, however, been studied.

3.1.4. The properties of the products formed between G200 glass and polymers other than poly(acrylic acid).

3.1.4.1. The properties of the polymer solutions.

The ethyl acrylate - acrylic acid emulsion and the polymer solutions, except for the HEMA-acrylic acid copolymer solutions, remain stable over a period of at least several months.

The HEMA-acrylic acid copolymer solutions gel on ageing at room temperature. The gel is thermally irreversible (even at ~365) and swells, but remains coherent, in boiling water. Inter-(and perhaps intra-) molecular esterification is probably responsible for the gelation of these solutions, since experiments on mixtures of the copolymer solutions with PAA solutions have shown that the gelling time increases with increase in the hydroxyl:carboxyl group ratio present. Similar gels result with mixtures of glycerol and PAA solution.

The tacticities of none of the polymers studied is known. Consequently any possible effects of differences in polymer tacticity on the formation of cements with G200 glass cannot be considered here.

Table 3.1.3.3.1.

The resistance of PAA-G200 glass cement to aqueous acid and alkali and to various solvents.

Solvent	Cement stability
Water	Stable indefinitely
Ethanol	Stable*
Dimethylformamide	Stable*
Methylethyl ketone	Stable*
Tetrahydrofuran	Stable*
Glacial acetic acid	Stable*
Chloroform	Stable*
Ethyl acetate	Stable*
1N aqu. NaOH.	Rapidly disintegrates
1N aqu. HCl	Rapidly disintegrates

* Over at least 9 months.

3.1.4.2. The properties of the polymer solution - G200 glass mixes and set products.

Pastes formed by mixing G200 glass with the polymer solutions shown in table 3.1.1.1. often have different properties to the mixes prepared with PAA. Thus, although PMAA, HEMA-acrylic acid copolymer, VEMA and EMA solutions give mixes that set rapidly in four distinct phases (see section 3.1.3.2.), the other polymer solutions behave differently.

SMA copolymer solution in aqueous acetone gives a workable paste, which tends to lose acetone on mixing. The use of the mixed acetone-water solvent is necessary as the copolymer is only sparingly soluble in pure water. When fully set the cement is weak and brittle, possibly because of the very low molecular weight ($\sim$1600) of the copolymer.

Sodium acrylate-acrylic acid copolymer, styrene-monosodium maleate copolymer, methyl acrylate-methyl methacrylate- sodium acrylate copolymer and PESA solutions give mixes with G200 glass that set slowly on standing without showing the rapid formation of a "stringy" rubbery phase. With these products the lower surface of the mix, which is in contact with poly(ethylene) film, usually remains soft after the upper layer has hardened, indicating that setting is due to a simple drying our process.

Ethyl acrylate - acrylic acid copolymer emulsion does not form a rapidly setting paste with G200 glass powder. As a consequence of the low viscosity of the emulsion the cement pastes are thin slurries, even at a P:L ratio as high as 3:1. When the P:L ratio is increased to values much higher than 3:1 the mix becomes an incoherent, crumbly paste, bearing no resemblence to a G200 glass - PAA solution mix.

Table 3.1.2.1. summarises the stability in water of each of the cements in the range studied. Like PAA; EMA, PMAA, SMA and ethyl acrylate - acrylic acid copolymer give cements that are stable in water. HEMA-acrylic acid copolymer, containing 5 mole % of HEMA, will also form a water stable cement with G200 glass, but only at a high P:L ratio. Three manifestations of instability in water are apparent for the remaining cement products.

1. Surface softening and weakening, as typified by VEMA-G200 glass cement.

2. Bulk softening and swelling, as is shown by the acrylic acid - sodium acrylate cement.

3. Total disintegration, which is typified by PESA-G200 glass cement.

The mechanical properties of the set cements have not been studied in detail. Preliminary experiments on PAA and EMA cements with G200 glass have been carried out, since these two polyacids are structural isomers. Table 3.1.4.2.1. shows the compressive strengths and moduli of cements prepared from PAA and EMA solutions and G200 glass under identical conditions. The compressive strength of the cement prepared from G200 glass and EMA is nearly twice that obtained with the PAA-G200 glass cement. A modulus difference is also observed between the two cements. The very slight difference between the concentrations of the polyacid solutions ($\sim$3%) is considered insignificant compared to the strength properties observed. The EMA used in these tests is not an exactly 1:1 copolymer, but has a mole ratio of 1 maleic acid: 1.25 ethylene residues. Thus the EMA has a slightly higher proportion of unsubstituted $-CH_2-$ groups in its structure, compared to the PAA, which may possibly explain the lower modulus (i.e. greater flexibility) of the EMA-G200 glass cement.

Table 3.1.4.2.1.

Mechanical properties of PAA-G200 glass and EMA-G200 glass cements (P:L=3:1)

Property	PAA (∿25% w/w soln., batch 3, table 3.1.1.1. (Mean of 4 values)	EMA (∿28% w/w soln., batch 8, table 3.1.1.1.). (Mean of 5 values)
Compressive strength (MNm^{-2})	45.0	98.7
Young's Modulus (MNm^{-2})		
at 1% strain	300	200
at 1.5% strain	500	300
at 2% strain	700	500

Another important consideration with cements prepared from polyacids and G200 glass is the evaporation of water from the hardened cements. Water loss from cements prepared from G200 glass and PAA has been shown to cause cracking and crazing of the surface of the cement, shrinkage and a loss of compressive strength.[97] EMA-G200 glass cements also show a tendancy to shrink, crack and craze by loss of water, more especially if the samples are large and are made at a low P:L ratio. The incorporation of an inert filler, such as fine sand, into an EMA-G200 glass (or PAA-G200 glass) cement mix can considerably reduce, or even eliminate, shrinkage and cracking due to water loss, thus enabling the satisfactory preparation of large specimens. Inert fillers also have a pronounced effect on the mixing characteristics of the cement paste in that they tend to reduce the stickiness of the mix and improve the handling characteristics.

3.1.5. Chemical features of the products formed between G200 glass and aqueous polymer solutions.

Although a detailed investigation of the chemical composition and structure of the cements prepared from G200 glass and aqueous polyacid solutions has not been carried out, much information can be obtained from the mixing and setting characteristics of the cement pastes and the stabilities of the hardened products in water.

From the range of polymers studied (table 3.1.1.1.) four types of polymer structures are identifiable.

1. Polyacids with hydrophobic side groups or no side groups.
2. Polyacids with hydrophilic side groups.
3. Polyacids partially neutralised to their sodium salts.
4. Polyacids completely neutralised to their sodium salts.

3.1.5.1. Cements prepared from G200 glass and polyacids with hydrophobic side groups or no side groups.

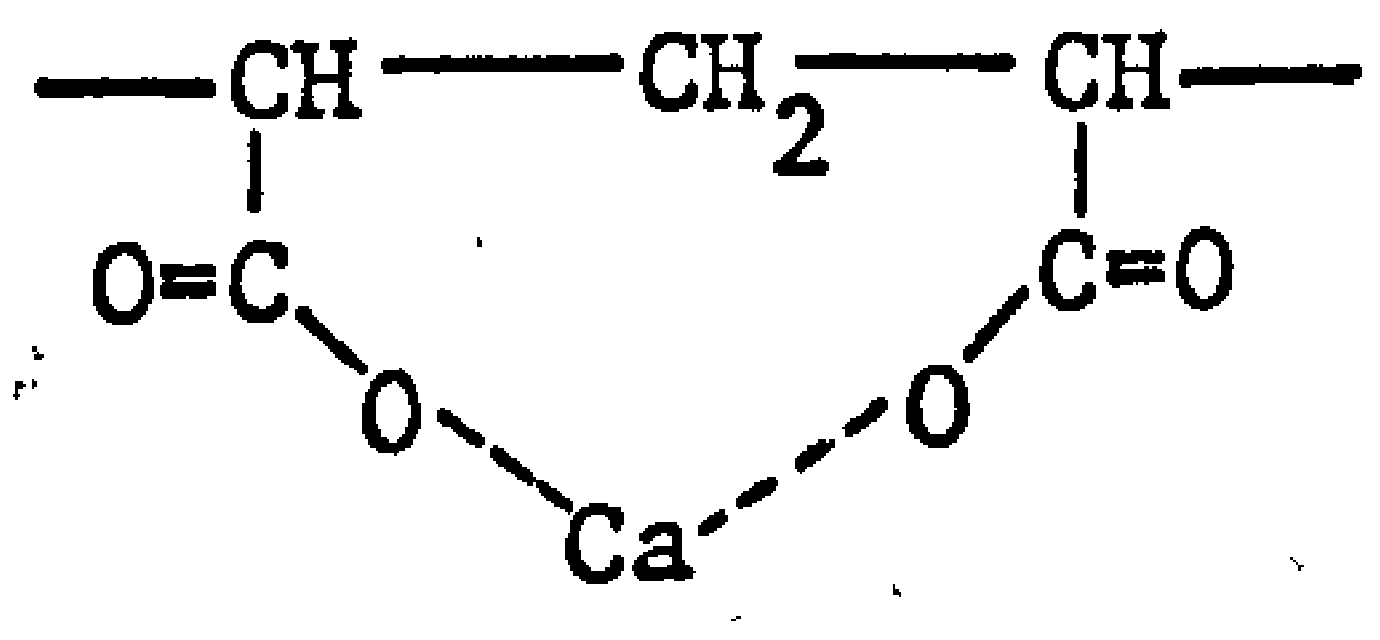
This group of cements includes the products made from G200 glass and PAA, PMAA, EMA, SMA, PESA and ethyl acrylate - acrylic acid copolymer.

With PAA, PMAA and EMA solutions chemical reactions can be seen to occur with G200 glass, because the pastes become rubbery on mixing and set quickly to cements that are stable in water. Wilson et. al.[21] have postulated the existence of ionic structures (III) in ASPA cement. Other species may also be possible, for example (VI - VIII), in the cement matrix. Similar structures may also be present in cements made from G200 glass and aqueous PMAA and EMA. Structures of type (VI) would not be expected to contribute towards the formation of the matrix cross-linked network.

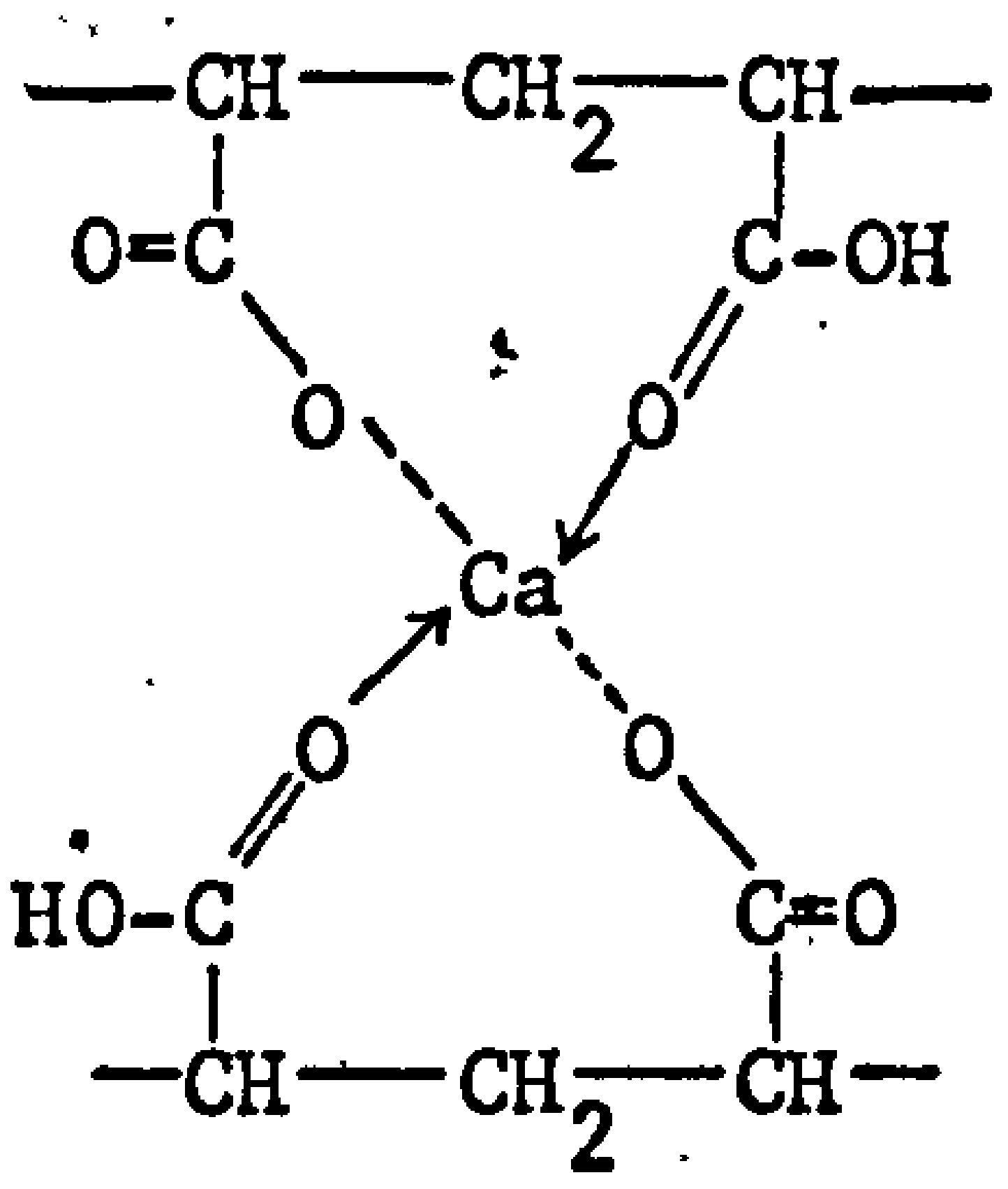
In the G200 - SMA cement the formation of a network structure is not easily seen, because the loss of acetone from the cement paste during mixing causes the viscosity of the mix to increase. However, the insolubility of the product cement in aqueous acetone, even after 6 hours' immersion at 355, indicates that a reaction has taken place, possibly to form structures similar to those in PAA-G200 glass cement.

PESA solution behaves very differently with G200 glass. When the two components are mixed there is an evolution of heat, which suggests that the polyacid vigorously attacks the glass. Indeed from a consideration of the very low pH (<0) of the PESA solution substantial acid attack on the glass would be expected. However, despite the presence of Ca^{2+} and Al^{3+} leached into the polyacid solution, the rapid formation of a network structure is not observed as is apparent from the long setting time of the mix. The setting process appears to be due to a simple drying out of the mix (see section 3.1.4.2.). These observations suggest that the poly(ethylenesulphonate) complexes in the matrix are readily dissociated in water and are thus unable to form a network structure until most of the water in the mix has evaporated away. When placed in water the hardened cement would be expected to disintegrate by dissociation of the matrix into its constituent ions. This view is supported by the fact that G200-PESA cement does in fact rapidly disintegrate in water.

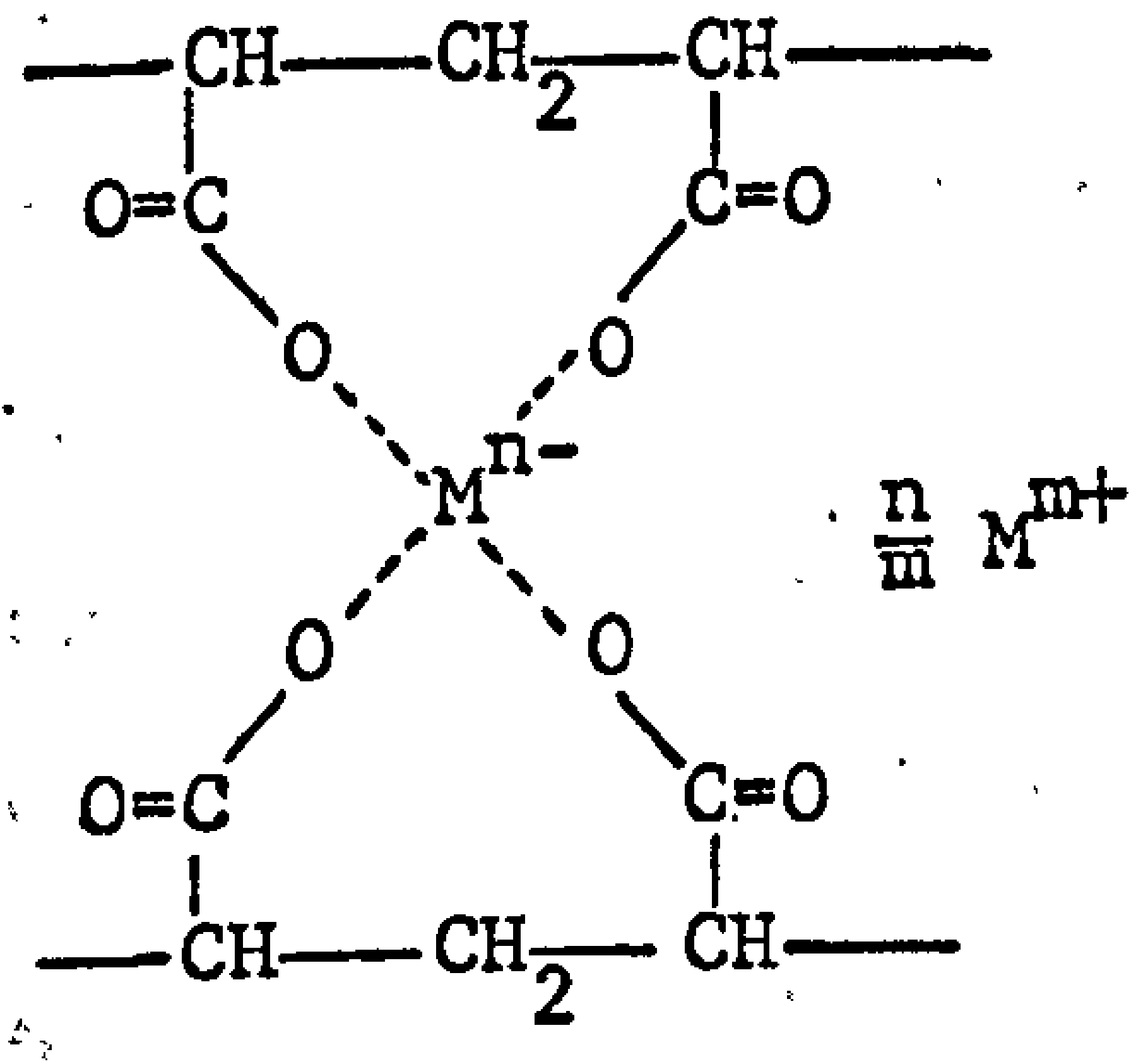
The difference in behaviour between PAA-G200 glass mixes and PESA-G200 glass mixes may be tentatively explained as follows: although both cements probably contain ionic complexes in their matrices, the degree of ionic character of the metal-polyanion bonding may differ considerably between the two types of polyanion. The PESA-metal ion complexes would be expected to have M-O bonding with a higher degree of ionic character than exists in the PAA-metal ion complexes. A comparison of the acid strengths of PESA ($pK_a \sim 2.9$[98]) and PAA ($pK_a = 6.17$[49]) in aqueous solution illustrates this point. The pK_a's of aqueous acids tend to increase with increase in the number of equivalent oxygen atoms in their anions.[99] There are three equivalent oxygen atoms in the sulphonate group (IX), but only two in the carboxylate group (X) and accordingly PESA is a stronger acid than PAA, i.e. in water PESA is dissociated to a greater extent than PAA. Thus, although PAA may form Ca^{2+} and Al^{3+} complexes with sufficient covalent character to form a network structure during the mixing of the cement paste, the PESA complexes are too highly dissociated to give a cross-linked structure until the mix has lost a sufficient amount of water to the atmosphere to allow the complex to precipitate. Fluoride ions, which are also leached from G200 glass by acids, probably have an effect on the water stability of G200 glass-PAA cement and these tentative explanations are made with the assumption



(VI)

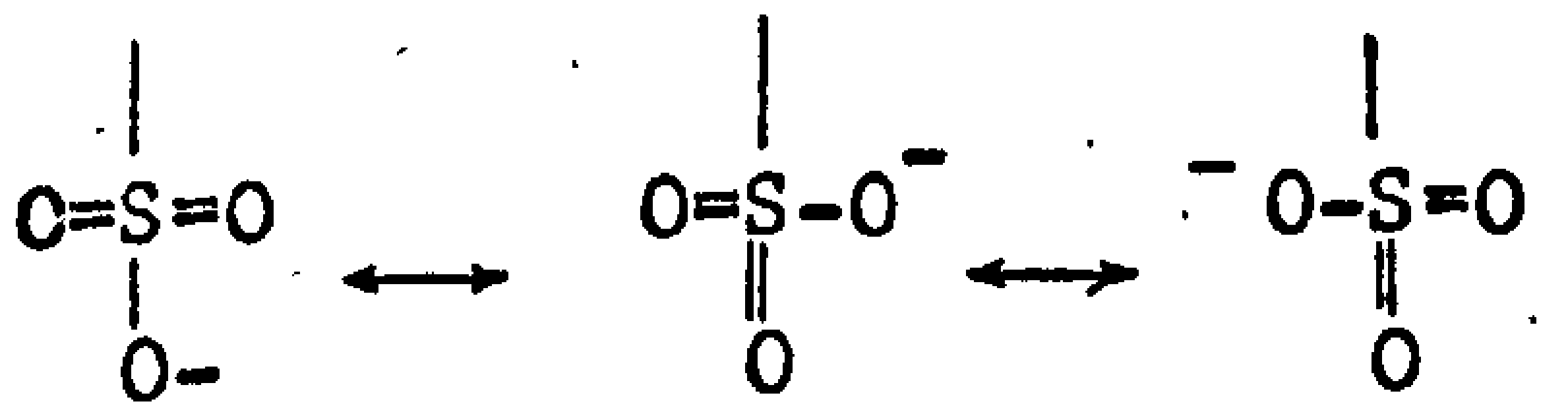


(VII)

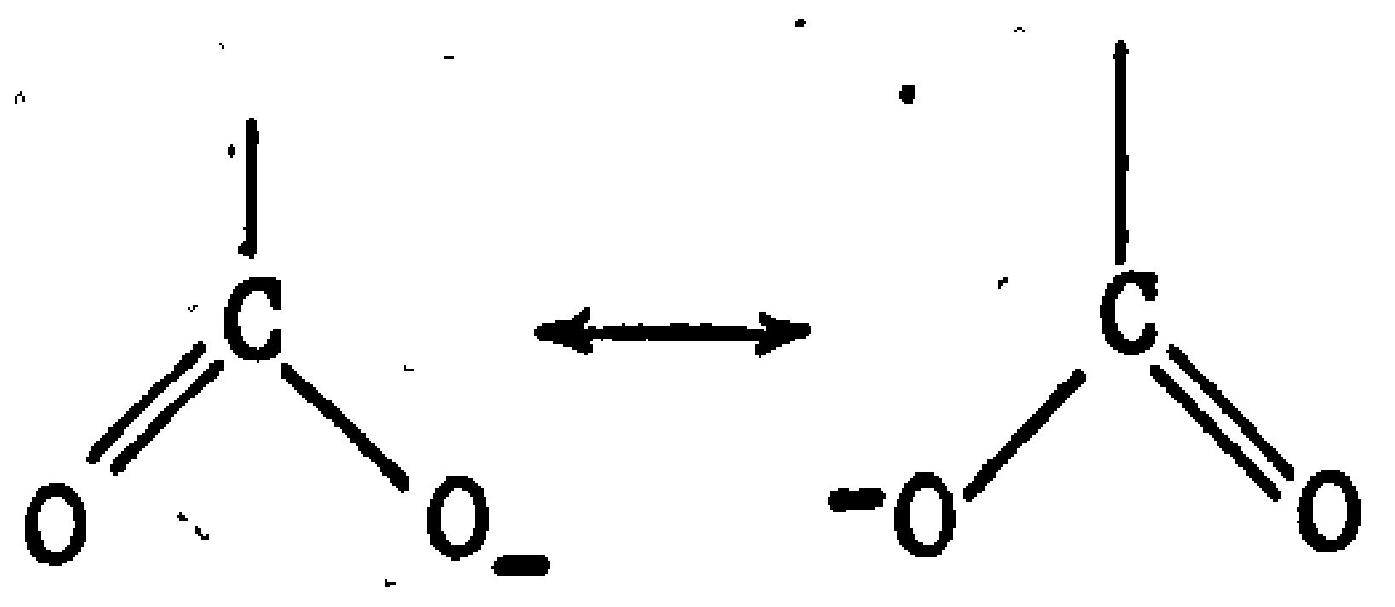


(VIII)

$M = Ca^{2+}$, or Al^{3+}



(IX)



(X)

that with PESA the intervention of the fluoride ions is retained.

Ethyl acrylate - acrylic acid copolymer emulsion also forms water stable cements with G200 glass, although the slow setting of the mixes suggests that setting occurs by a drying out process to leave an insoluble mixture of the copolymer and G200 glass. Although the pH of the emulsion is certainly low enough to expect an acid leaching reaction with the glass to occur, it is possible that the carboxylate groups on the copolymer are not accessible for a cross-linking reaction to take place, since they are localised in the tiny copolymer droplets dispersed in the emulsion. The infra-red spectrum of G200 glass - ethyl acrylate - acrylic acid copolymer cement aged for 17 hours shows a strong band at about $1700cm^{-1}$ with a strong shoulder at about $1725cm^{-1}$, which are probably the carbonyl absorption bands for the ester and carboxyl groups present. The band at $1700cm^{-1}$ is probably due to the carboxyl group, since similar bands have been observed in ASPA cements.[19] The spectrum shows the absence of a band in the region of $1500\text{-}1600cm^{-1}$, suggesting that very little, or no, carboxylate groups are present in the cement, i.e. that the cement does not contain metal poly(acrylate) complexes.

3.1.5.2. Cements prepared from G200 glass and polyacids with hydrophilic side groups.

This group of cements includes the products made from G200 glass with VEMA, or HEMA-acrylic acid copolymer solutions. Both of these products set fairly rapidly, indicating that the polyacids are capable of forming a cross-linked gel with Ca^{2+} and Al^{3+} ions, but neither cement is stable in water. The cements do not, however, disintegrate in water, but instead they show swelling and softening of their surfaces. With the HEMA-acrylic acid copolymer cements with G200 glass their stability in water decreases with increase in the HEMA content of the copolymer, i.e. with increase in the content of hydroxyl groups, which are hydrophilic. These results suggest that the presence of hydrophilic side groups (in these cases hydroxyl and methoxy groups) on the polyacids have a detrimental effect upon the stability of the corresponding G200 glass-polyacid cements in water. The presence of many hydrophilic groups in the polyacid complexes of these cements may render their matrices susceptible to the absorption of water, with consequent swelling, softening and weakening of the cements' surfaces.

3.1.5.3. Cements prepared from G200 glass and polyacids partially neutralised to their sodium salts.

This group of cements includes the products made from G200 glass with acrylic acid-sodium acrylate copolymer and styrene-monosodium maleate copolymer solutions. The pH's of these copolymer solutions are ∿4.8 and ∿5.8, respectively, much higher than the pH's of all of the other poly(carboxylic acid) solutions investigated. With these copolymer solutions a slower and much less complete attack would be expected, compared to the parent polyacids. With styrene-monosodium maleate copolymer the reaction with G200 glass must be negligible, because the product does not appear to rapidly form a network structure, sets by a drying out process and when hard is quickly disintegrated by water. The acrylic acid-sodium acrylate copolymer behaves in a similar way as styrene-monosodium maleate copolymer with G200 glass, except the hardened product is not disintegrated by water. Instead the cement is swollen to about twice its original size when placed in water. Since acrylic acid-sodium acrylate copolymer is completely soluble in water it appears that some reaction does take place with G200 glass and a cross-linked structure is formed. The probable low degree of cross-linking and the presence of an abundance of hydrophilic sodium acrylate groups in the cement matrix are likely to be responsible for the swelling effect observed when the cement is immersed in water.

3.1.5.4. Cements prepared from G200 glass and polyacids completely neutralised to their sodium salts.

This group of cements includes products made from G200 glass with methyl acrylate-methyl methacrylate-sodium acrylate copolymer and sodium poly(acrylate)[97] solutions.

Since the pH's of these copolymer solutions are close to 7 they cannot be expected to form cements with G200 glass. Indeed mixes made from G200 glass with these copolymers harden very slowly and disintegrate in water. Ion exchange of Na^+ for Ca^{2+} or Al^{3+} ions in the G200 glass does not appear to occur to any significant degree and the cement products obtained are probably no more than G200 glass particles bound by partially air dried polymer.

3.1.6. Concluding Comments.

The results of these preliminary studies on cements prepared from G200 glass with aqueous polymer solutions have demonstrated clearly the need to consider the structure of the polymer and the nature of its solution if coherent water stable cements are to be prepared. Cements which set rapidly to a coherent product which is stable in water have been shown to be best prepared from poly(carboxylic acids) with hydrophobic groups, or no substituents on their polymer chains.

3.2. The reactivity of metal oxides with various aqueous polyacid solutions.

3.2.1. Introduction.

Ion leachable aluminosilicate glasses, such as G200 glass, are mixtures of many inorganic components and in aqueous acid media release not only Ca^{2+} and Al^{3+} ions, but also ions such as Na^+, $PO_4{}^{3-}$ and F^-.

In order to gain some understanding of the requirements for cement formation and to eliminate the problems of competitive and co-operative effects between the ions provided by G200 glass a range of metal oxide - polyacid products have been studied.

The range of oxides which have been chosen for this work is wide and includes basic oxides, such as CaO, Y_2O_3 and NiO and amphoteric oxides, such as PbO and ZnO, which would be expected to dissolve in strong aqueous polyacid solutions, and acidic oxides, for example MoO_3, B_2O_3 and CrO_3, which give rise to anions in solution and would not be expected to form cements with aqueous polyacids. Relatively inert oxides, as exemplified by BeO, TiO_2 and ZrO_2 have also been studied; such oxides would not be expected to dissolve in aqueous polyacids. Some potentially acid soluble oxides may exhibit low solubility as a result of morphological modification, or dehydration, especially if heated to high temperatures. Notable examples are MgO, ZnO and Al_2O_3. Complications may also arise with oxides that are slightly soluble in water, such as V_2O_5 and CaO, in that the stability in water of the metal oxide-polyacid cement products may be effected by the hydrophilic nature of the excess oxide present.

Pourbaix[100] has reported phase diagrams for the solubilities of many oxides at various pH values, together with the types and relative predominance of the dissolved ions produced in solution. Generally, in acid solution the solubility of many oxides decreases as the pH rises, reaching a minimum, and then rises as the pH is further increased. The type of ion dissolved in solution varies with pH, e.g. the regions of relative predominance for ions of bismuth are $Bi^{3+}/BiOH^{2+}$, pH=2.00 and $BiOH^{2+}/BiO^{+}$; pH=3.37, but hydroxo and oxo cations are only really important with M^{3+} or M^{4+} ions.

Bearing in mind these limitations suitable oxides were selected and reacted with a carefully chosen range of polyacid solutions (table 3.2.1.1.).

3.2.2. The cement forming properties of metal oxides with various aqueous polyacids.

The nature of the products formed between the various oxides and aqueous polyacids are summarised in tables 3.2.2.1. to 3.2.2.6. Also shown in these tables are the water stabilities of the products obtained and G200 glass-polyacid products have been included for comparison. The oxides in the tables are arranged in the descending order of their periodic groups across the periodic table: transition metal oxides are placed in similar orders towards the end of each table.

A summary of all of the cements found to be stable in water is given in table 3.2.2.7. for comparison purposes.

The mixing characteristics of the metal oxide-polyacid cements vary considerably with the nature of the oxide and to some extent on the type of polyacid used. Oxides that react very rapidly with the polyacid solutions often form pastes that become "stringy" and rubbery on mixing, for example MgO, CaO and ZnO with PAA, PMAA, VEMA and EMA. Sometimes an oxide may react so quickly that a crumbly mix is produced, which although rather difficult to mould often sets to a hard coherent mass. Crumbly mixes of this type are produced by PbO and CdO with PESA solution. PMAA and Ag_2O give a very reactive mix that can absorb relatively large quantities of the polyacid solution and remain a coherent gel. The gel expands considerably as the aqueous polyacid is absorbed but shrinks to a much smaller

Table 3.2.1.1.

Polyacid solutions in water for polyacid-oxide mixes.

Batch No.*	Polymer	Concn. % w/w
1	Poly(acrylic acid)	47.3
7	Poly(methacrylic acid)	20
8	Ethylene-maleic acid copolymer	28
9	Vinylmethyl ether-maleic acid copolymer.	40
10	Styrene-maleic acid copolymer.	50.4[a]
16	Poly(ethylenesulphonic acid)	36.85

* See table 3.1.1.1.

a = in cold acetone-water.

Table 3.2.2.1.

The reaction of aqueous PAA solution with various oxides and G200 glass and the stability of the products in cold water.[97]

INORGANIC PHASE	PRODUCT WITH PAA			WATER STABILITY OF PRODUCTS		
	Nature of the product	Age of product	Comments	Age before immersion	Immersion time	Effect on product
BeO	Soft, flexible, coherent	24 hr	-	24 hr	-	Rapidly disintegrated
MgO (deactivated)	Hard, coherent	"	-	"	2 weeks	Softened markedly, remained coherent.
CaO	"	"	Oxide slaked on mixing	"	"	"
SrO_2	"	"	-	"	"	"
BaO	"	"	Oxide slaked on mixing	"	"	"
Y_2O_3	"	"	Set in ∿3 hr	"	"	Uneffected

Table 3.2.2.1.(continued)

INORGANIC PHASE	PRODUCT WITH PAA			WATER STABILITY OF PRODUCTS		
	Nature of the product	Age of product	Comments	Age before immersion	Immersion time	Effect on product
ZnO	Hard, coherent	24 hr	Set in $\sim$2 min	24 hr	2 weeks	Uneffected
CdO	"	"	Set in $\sim$30 min	"	"	"
HgO	"	"	Set in $\sim$40 min	"	"	"
B_2O_3	"	"	Set in 20-30 min	"	-	Rapidly disintegrated
γ-Al_2O_3	"	"	Set in $\sim$12 hr	"	-	"
Chromatographic grade Al_2O_3	"	"	Set in $\sim$2½ hr	"	-	"
In_2O_3	Soft, flexible coherent	24 hr	-	24 hr	-	Rapidly disintegrated

Table 3.2.2.1. (continued)

INORGANIC PHASE	PRODUCT WITH PAA			WATER STABILITY OF PRODUCTS		
	Nature of the product	Age of product	Comments	Age before immersion	Immersion time	Effect on product
SiO_2	Soft, flexible coherent	24 hr	-	24 hr	-	Rapidly disintegrated
SnO_2	"	"	-	"	-	"
PbO	Hard, coherent	"	Set in ∿20 min	"	2 weeks	Uneffected
Pb_3O_4	"	"	Set in ∿14 hr	"	"	"
Bi_2O_3	"	"	Set in ∿40-60 min	"	"	"
TiO_2	Soft, flexible, coherent	"	-	"	-	Rapidly disintegrated
ZrO_2	"	"	-	"	-	"
V_2O_5	"	"	-	"	-	"
Nb_2O_5	"	"	-	"	-	"

Table 3.2.2.1. (continued)

INORGANIC PHASE	PRODUCT WITH PAA			WATER STABILITY OF PRODUCTS		
	Nature of the product	Age of product	Comments	Age before immersion	Immersion time	Effect on product
CrO_3	Soft, flexible coherent	24 hr	-	24 hr	-	Rapidly disintegrated
MoO_3	"	"	-	"	-	"
MnO_2	"	"	-	"	-	"
Fe_2O_3	"	"	Set in ∿9 hr	"	-	"
CoO	Hard, coherent	"	Set in ∿9 hr	"	-	Rapidly disintegrated
NiO	"	"	Set in ∿14 hr	"	-	"
CuO	"	"	Set in ∿4-9 hr	"	2 weeks	Uneffected
Ag_2O	"	"	-	"	"	No softening. Very slight disintegration.

Table 3.2.2.1. (continued)

INORGANIC PHASE	PRODUCT WITH PAA			WATER STABILITY OF PRODUCTS		
	Nature of the product	Age of product	Comments	Age before immersion	Immersion time	Effect on product
G200 glass	Hard, coherent	24 hr	Set in ∿½ hr	24 hr	Indefinite	Uneffected

N.B. $Al(OH)_3$ also gives a setting cement with aqueous PAA. The cement hardens in about 2-3 hr. Even after 17 hours' ageing the cement slowly softens and disintegrates when immersed in water.

Table 3.2.2.2.

The reaction of aqueous PMAA solution with various oxides and G200 glass and the stability of the products in hot and cold water†.

INORGANIC PHASE	PRODUCT WITH PMAA			WATER STABILITY OF PRODUCTS				
				Cold Water			Hot Water*	
	Nature of product	Age of product	Comments	Age before immersion	Immersion time	Effect on product	Age before immersion	Effect of 6hr immersion at 353
BeO	Hard, coherent	2 days	-	3 days	-	Rapidly disintegrated	-	-
MgO (deactivated)	"	"	Smooth mix	"	2 hr	Softened and broke into small pieces	-	-
CaO	"	"	Very smooth mix	"	2 days	"	-	-
Y_2O_3	"	"	Set in <2hr, smooth mix	"	21 days	Uneffected	65 hr	Uneffected

Table 3.2.2.2. (continued)

INORGANIC PHASE	PRODUCT WITH PMAA			WATER STABILITY OF PRODUCTS				
				Cold Water			Hot Water*	
	Nature of product	Age of product	Comments	Age before immersion	Immersion time	Effect on product	Age before immersion	Effect of 6hr immersion at 353
ZnO	Hard, coherent weak	2 days	Set in <2hr, crumbly mix	3 days	21 days	Uneffected	65 hr	Uneffected
CdO	Hard, coherent	"	Set rapidly, crumbly mix	"	"	"	"	"
HgO	"	"	Set in <2hr, crumbly mix	"	"	"	"	"
Al_2O_3 (chromato-graphic grade)	"	"	-	"	-	Rapidly disinte-grated	-	-

Table 3.2.2.2. (continued)

INORGANIC PHASE	PRODUCT WITH PMAA			WATER STABILITY OF PRODUCTS				
				Cold Water			Hot Water*	
	Nature of product	Age of product	Comments	Age before immersion	Immersion time	Effect on product	Age before immersion	Effect of 6hr immersion at 353
In_2O_3	Hard, coherent	2 days	-	3 days	-	Rapidly disintegrated	-	-
SnO_2	"	"	-	"	-	"	-	-
PbO	"	"	Set in <2hr, crumbly mix	"	21 days	Uneffected	65 hr	Uneffected
Pb_3O_4	Hard, coherent	"	Set in <2hr. Smooth mix. Less reactive than PbO	"	"	"	"	"
Bi_2O_3	"	"	Set in 1-2hr Very smooth mix	"	"	"	"	"

Table 3.2.2.2. (continued)

INORGANIC PHASE	PRODUCT WITH PMAA			WATER STABILITY OF PRODUCT				
				Cold Water			Hot Water*	
	Nature of product	Age of product	Comments	Age before immersion	Immersion time	Effect on product	Age before immersion	Effect of 6hr immersion at 353
TiO_2	Hard, coherent	2 days	-	3 days	-	Rapidly disintegrated	-	-
ZrO_2	"	"	-	"	-	"	-	-
V_2O_5	"	"	-	"	-	"	-	-
MoO_3	"	"	-	"	-	"	-	-
MnO_2	"	"	-	"	-	"	-	-
Fe_2O_3	"	"	-	"	-	"	-	-
CoO	"	"	-	"	-	"	-	-
NiO	"	"	-	"	-	"	-	-

Table 3.2.2.2. (continued)

INORGANIC PHASE	PRODUCT WITH PMAA			WATER STABILITY OF PRODUCTS				
				Cold Water			Hot Water *	
	Nature of product	Age of product	Comments	Age before immersion	Immersion time	Effect on product	Age before immersion	Effect of 6hr immersion at 353
CuO	Hard, coherent	2 days	Set in <2hr Smooth mix	3 days	21 days	Uneffected	65 hr	Uneffected
Ag_2O	"	"	Very reactive. Crumbly mix	"	"	"	"	"
G200 glass	"	"	Set in 1-2hr Very smooth mix	"	"	"	"	"

* Samples heated at once in water with no prior cold water soaking.

Table 3.2.2.3.

The reaction of aqueous EMA solution with various oxides and G200 glass and the stability of the products in hot and cold water.

INORGANIC PHASE	PRODUCT WITH EMA			WATER STABILITY OF PRODUCTS				
				Cold water			Hot water*	
	Nature of product	Age of product	Comments	Age before immersion	Immersion time	Effect on product	Age before immersion	Effect of 6 hr immersion at 353
BeO	Hard, coherent	2 days	-	2 days	-	Disintegrated	-	-
MgO (deactivated)	"	"	-	"	18 days	Softened markedly. Remained coherent.	-	-
CaO	"	16 hr	-	18 hr	19 days	Softened very slightly. Very slight decomposition	14 days	Hardened. Very slight decomposition
Y_2O_3	"	"	Smooth mix	"	"	Uneffected	"	Uneffected
ZnO	"	"	Set in <5 min	"	"	"	"	"
CdO	"	"	Set in <5 min Crumbly mix	"	"	"	"	"

Table 3.2.2.3. (continued)

INORGANIC PHASE	PRODUCT WITH EMA			WATER STABILITY OF PRODUCTS				
				Cold water			Hot water*	
	Nature of product	Age of product	Comments	Age before immersion	Immersion time	Effect on product	Age before immersion	Effect of 6 hr immersion at 353
HgO	Hard, coherent	16hr	Set in <25 min. Smooth mix	18 hr	19 days	Uneffected	14 days	Uneffected
Al_2O_3 (chromatographic grade)	"	2 days	-	2 days	-	Rapidly disintegrated	-	-
In_2O_3	"	"	-	"	-	"	-	-
SnO_2	"	16 hr	-	18 hr	-	"	-	-
PbO	"	"	Set in <10 min. Crumbly mix	"	19 days	Uneffected	14 days	Uneffected
Pb_3O_4	"	"	Set in <30 min. Fairly smooth mix, becoming rubbery.	"	"	"	"	"

Table 3.2.2.3. (continued)

INORGANIC PHASE	PRODUCT WITH EMA			WATER STABILITY OF PRODUCTS				
				Cold water			Hot water*	
	Nature of product	Age of product	Comments	Age before immersion	Immersion time	Effect on product	Age before immersion	Effect of 6 hr immersion at 353
Bi_2O_3	Hard, coherent	2 days	-	2 days	-	Disintegrated	-	-
TiO_2	"	"	-	"	-	Rapidly disintegrated	-	-
ZrO_2	"	"	-	"	-	"	-	-
V_2O_5	"	"	-	"	-	"	-	-
Nb_2O_5	"	16 hr	-	"	-	"	-	-
MoO_3	"	2 days	-	18 hr	-	"	-	-
MnO_2	"	16 hr	-	"	-	"	-	-
Fe_2O_3	"	2 days	-	2 days	-	"	-	-

Table 3.2.2.3. (continued)

INORGANIC PHASE	PRODUCT WITH EMA			WATER STABILITY OF PRODUCTS				
				Cold water			Hot water*	
	Nature of product	Age of product	Comments	Age before immersion	Immersion time	Effect on product	Age before immersion	Effect of 6 hr immersion at 353
CoO	Hard, coherent	16 hr	-	2 days	-	Rapidly disintegrated	-	-
NiO	"	16 hr	-	18 hr	-	"	-	-
CuO	"	"	Set in <15 min. Smooth mix	"	19 days	Uneffected	14 days	Uneffected
Ag_2O	"	"	Set in <15 min. Crumbly mix.	"	"	"	"	"
G200 glass	"	"	Set in ∿1hr Smooth mix	"	"	"	"	"

* Samples heated at once in water with no prior cold water soaking.

Table 3.2.2.4.

The reaction of SMA (in aqueous acetone) with various oxides and G200 glass and the stability of the products in hot and cold water and cold aqueous acetone.

INORGANIC PHASE	PRODUCT WITH SMA			STABILITY OF PRODUCTS IN WATER AND AQUEOUS ACETONE					
				Cold solvents				Hot water*	
	Nature of product	Age of product	Comments	Age before immersion	Solvent	Immersion time	Effect on product	Age before immersion	Effect of 6 hr immersion at 353
MgO (deactivated)	Hard, coherent, little strength	18 hr	-	18 hr	W	3½ hr	Uneffected	28 days	Uneffected
				+	WA	5 days	"		
CaO	Incoherent	-	Crumbly mix, even after first slaking the oxide in acetone-water mixture.	-	W	-	-	-	-
				-	WA	-	-		
ZnO	Hard, coherent, very little strength	18 hr	Expanded slightly	18 hr	W	3½ hr	Uneffected	28 days	Uneffected
				+	WA	5 days	"		
HgO	Hard, coherent, little strength	"	-	18 hr	W	3½ hr	"	"	"
				+	WA	5 days	"		

Table 3.2.2.4. (continued)

INORGANIC PHASE	PRODUCT WITH SMA			STABILITY OF PRODUCTS IN WATER AND AQUEOUS ACETONE					
				Cold solvents				Hot water*	
	Nature of product	Age of product	Comments	Age before immersion	Solvent	Immersion time	Effect on product	Age before immersion	Effect of 6 hr immersion at 353
Al_2O_3 (chromatographic grade)	Hard, coherent little strength	18 hr	-	18 hr	W	3½ hr	Uneffected	-	-
				+	WA	1 hr	Disintegrated		
PbO	"	"	-	18 hr	W	3½ hr	Uneffected	28 days	Uneffected
				+	WA	5 days	"		
Bi_2O_3	"	"	-	18 hr	W	3½ hr	"	-	-
				+	WA	-	Rapidly disintegrated		

Table 3.2.2.4. (continued)

INORGANIC PHASE	PRODUCT WITH SMA			STABILITY OF PRODUCTS IN WATER AND AQUEOUS ACETONE					
				Cold solvents				Hot water*	
	Nature of product	Age of product	Comments	Age before immersion	Solvent	Immersion time	Effect on product	Age before immersion	Effect of 6 hr immersion at 353
CoO	Hard, coherent, little strength	18 hr	-	18 hr	W	3½ hr	Uneffected	-	-
				+	WA	24 hr	Disintegrated		
NiO	"	"	-	18 hr	W	3½ hr	Uneffected	-	-
				+	WA	-	Rapidly disintegrated		
CuO	"	"	-	18 hr	W	3½ hr	Uneffected	28 days	Uneffected
				+	WA	5 days	Very slight surface softening		

Table 3.2.2.4. (continued)

INORGANIC PHASE	PRODUCT WITH SMA			STABILITY OF PRODUCTS IN WATER AND AQUEOUS ACETONE					
				Cold solvents				Hot water*	
	Nature of product	Age of product	Comments	Age before immersion	Solvent	Immersion time	Effect on product	Age before immersion	Effect of 6 hr immersion at 353
G200 glass	Hard, coherent, little strength	18 hr	-	18 hr	W	3½ hr	Uneffected	28 days	Uneffected
				+	WA	5 days	"		

W = water   WA = Approximately equal volumes of acetone and water.

* Samples heated at once in water with no prior cold solvent soaking.

\+ Immersed in water-acetone mixture after first soaking in cold water for 3½ hr.

Table 3.2.2.5.

The reaction of aqueous VEMA with various oxides and G200 glass and the stability of the products in hot and cold water.

INORGANIC PHASE	PRODUCT WITH VEMA			WATER STABILITY OF PRODUCTS				
				Cold water			Hot water	
	Nature of product	Age of product	Comments	Age before immersion	Immersion time	Effect on product	Age before immersion	Effect of 6hr immersion at 353
MgO (deactivated	Hard, coherent	4 days	Became rubbery during mixing	6 days	2 days	Softened slightly, but coherent	*	Hardened
CaO	"	18 hr	Reacted rapidly. Oxide slaked	18 hr	3 days	Uneffected	*	Uneffected
Y_2O_3	"	"	-	"	"	Slightly weakened, no disintegration	*	"
ZnO	"	"	Reacted rapidly	"	"	Uneffected	*	"
CdO	"	"	"	"	"	"	*	"
HgO	"	"	"	"	"	"	*	"
PbO	"	"	"	"	"	"	*	"

Table 3.2.2.5. (continued)

INORGANIC PHASE	PRODUCT WITH VEMA			WATER STABILITY OF PRODUCTS				
				Cold water			Hot water	
	Nature of product	Age of product	Comments	Age before immersion	Immersion time	Effect on product	Age before immersion	Effect of 6hr immersion at 353
Pb_3O_4	Hard, coherent	18 hr	Became rubbery on mixing	18 hr	3 days	Very slight disintegration	*	Uneffected
Bi_2O_3	"	"	-	"	10 min	Disintegrated	-	-
CuO	"	"	-	"	3 days	Uneffected	*	Uneffected
Ag_2O	"	"	Reacted rapidly	"	"	Weakened and softened. Fern like growths.	*	-
G200 glass	"	"	-	"	"	Surface markedly softened.	*	Surface a little weak.

* Immersed in hot water after the cold water soaking.

Table 3.2.2.6.

The reaction of aqueous PESA with various oxides and G200 glass and the stability of the products in hot and cold water.

INORGANIC PHASE	PRODUCT WITH PESA			WATER STABILITY OF PRODUCTS				
				Cold water			Hot water	
	Nature of product	Age of product	Comments	Age before immersion	Immersion time	Effect on product	Age before immersion	Effect of 6hr immersion at 348
LiOH	Soft	13 days	-	-	-	-	-	-
BeO	"	6 days	-	-	-	-	-	-
MgO (deactivated	Hard, coherent	18 hr	-	18 hr	-	Rapidly disintegrated	-	-
CaO	"	16 hr	-	16½ hr	-	"	-	-
BaO	"	Few seconds	Oxide slaked.	Few minutes	-	"	-	-
Y_2O_3	"	16 hr	-	16 hr	24 days	Uneffected	*	Uneffected
ZnO	"	24 hr	-	24 hr	-	Rapidly disintegrated	-	-

Table 3.2.2.6. (continued)

INORGANIC PHASE	PRODUCT WITH PESA			WATER STABILITY OF PRODUCTS				
				Cold water			Hot water	
	Nature of product	Age of product	Comments	Age before immersion	Immersion time	Effect on product	Age before immersion	Effect of 6hr immersion at 348
CdO	Fairly hard, coherent	17 hr	Set in ∿ 45min	17 hr	24 days	Uneffected	*	Uneffected
HgO	Hard, coherent	"	Set in ∿ 30min	"	"	"	*	"
B_2O_3	Incoherent, crumbly	41 hr	-	-	-	-	-	-
Al_2O_3 (chromatographic grade)	Soft, coherent	13 days	-	-	-	-	-	-
$Al(OH)_3$	Very hard, coherent	16 hr	-	16½ hr	-	Softened and disintegrated	-	-
In_2O_3	Hard, coherent	6 days	-	6 days	-	Softened rapidly	-	-
SnO_2	Soft, coherent	13 days	-	-	-	-	-	-

Table 3.2.2.6. (continued)

INORGANIC PHASE	PRODUCT WITH PESA			WATER STABILITY PRODUCTS				
				Cold water			Hot water	
	Nature of product	Age of product	Comments	Age before immersion	Immersion time	Effect on product	Age before immersion	Effect of 6hr immersion at 348
PbO	Hard, coherent	1 hr	Effervesced on mixing. Set in 15 sec.	17½ hr	24 days	Uneffected	*	Uneffected
Pb_3O_4	"	17 hr	-	"	"	Softened, but remained coherent	-	-
Bi_2O_3	Hard, coherent very brittle	"	Set in <30 sec	"	"	Uneffected	*	Uneffected
TiO_2	Soft, coherent	13 days	-	-	-	-	-	-
ZrO_2	"	12 days	-	-	-	-	-	-
V_2O_5	"	13 days	-	-	-	-	-	-
MoO_3	"	"	Turned blue on mixing	-	-	-	-	-

Table 3.2.2.6. (continued)

INORGANIC PHASE	PRODUCT WITH PESA			WATER STABILITY PRODUCTS				
				Cold water			Hot water	
	Nature of product	Age of product	Comments	Age before immersion	Immersion time	Effect on product	Age before immersion	Effect of 6hr immersion at 348
MnO_2	Hard, coherent. Softer core.	15½ hr	-	16 hr	-	Very rapidly disintegrated	-	-
Fe_2O_3	Soft, coherent	6 days	-	-	-	-	-	-
NiO	Hard, coherent	17 hr	-	17½hr	-	Rapidly disintegrated	-	-
CuO	"	41 hr	-	6 days	-	"	-	-
Ag_2O	"	17½ hr	Set in ∿1hr	17½hr	-	"	-	-
G200 glass	"	4 days	-	4 days	-	"	-	-

* Immersed in hot water after the cold water soaking.

Table 3.2.2.7.

Comparison of the water stability of metal oxide (and G200 glass) - polyacid hardened cements

INORGANIC PHASE	AQUEOUS POLYACID PHASE					
	PAA	PMAA	EMA	VEMA	SMA*	PESA
MgO	3	3	3	2	1^{**}	4
CaO	3	3	2	1	-	4
Y_2O_3	1	1	1	1	-	1
ZnO	1	1	1	1	1^{**}	4
CdO	1	1	1	1	-	1
HgO	1	1	1	1	1^{**}	1
PbO	1	1	1	1	1^{**}	1
Pb_3O_4	1	1	1	1	-	3
Bi_2O_3	1	1	4	4	4^{**}	1

Table 3.2.2.7. continued

INORGANIC PHASE	AQUEOUS POLYACID PHASE					
	PAA	PMAA	EMA	VEMA	SMA*	PESA
CuO	1	1	1	1	1**	4
Ag_2O	1	1	1	3	-	4
G200 glass	1	1	1	3	1**	4

1 = Stable, no disintegration)
2 = Softened slightly) In water except for**
3 = Softened markedly)
4 = Unstable, disintegrated completely)

** Soaked in aqueous acetone.

hard mass on drying out with standing.

As a general rule, oxides that give slow setting or non-setting mixes give very smooth pastes with the polyacid solutions. Most slow setting mixes give hardened products that are unstable in water, although there are noteable exceptions, such as the cements made from CuO and the poly(carboxylic acid) solutions. SMA solution in aqueous acetone does not form very smooth easily workable pastes with metal oxides, probably because of the high viscosity of the copolymer syrup and loss of acetone from the mix during spatulation. CaO dehydrates the SMA syrup and prevents the formation of a coherent cement paste.

The stabilities of the hardened oxide-polyacid cements in water are very markedly dependent upon both the type of oxide and structure of the polyacid used. The cements either remain hard, soften or completely disintegrate when placed in water. MgO and CaO give cements with PAA that soften in cold water, but which harden again when the water is heated. When the water is cooled the CaO-PAA cement returns to a soft coherent state, whereas the MgO-PAA cement remains hard. Hopkins[101] has studied the behaviour of divalent metal salts of PAA and has reported that Mg^{2+} and Ca^{2+} salts of PAA exhibit a reversible, temperature dependent change in tensile strength and modulus when placed in water. The rigidity of the salts increases as the temperature of the water is increased. Thus, although the CaO-PAA cement behaves in a similar way to the Ca^{2+} salt of PAA, the MgO-PAA cement's properties differ from the Mg^{2+} salt of PAA in that the increase in rigidity observed when the cement is heated in water is not reversed upon cooling. MgO-EMA cement, which softens in cold water, also hardens when the water temperature is increased.

From table 3.2.2.7. it is evident that the poly(carboxylic acids) form a greater range of water stable cements than PESA, which only produces water stable cements with oxides of metals that lie towards the bottom of the groups in the periodic table.

3.2.3. The determination of the chemical reactivity of various oxides with aqueous polyacids.

Infra-red spectroscopy[97] has been employed in determining the reactivity of various oxides with PAA solution. Acidic and relatively inert oxides do not appear to react with PAA, for no carboxylate ion absorption bands at 1510-1660 cm^{-1} are observable in the infra-red spectra of their cements. Many basic or amphoteric oxides combine with aqueous PAA to give cements, whose infra-red spectra show a carboxylate ion absorption band at 1510-1660 cm^{-1}, alone, or together with a carboxyl group absorption band at 1700-1725 cm^{-1}. Table 3.2.3.1. summarises the oxides which react with, or are inert towards aqueous PAA. It is reasonable to assume that the oxides that react with aqueous PAA will also react with the other polyacid solutions.

Further infra-red studies on cements made from Al_2O_3 (chromatographic grade), or $Al(OH)_3$ and aqueous PAA have been carried out. Both products exhibit a carboxylate group infra-red absorption band at about 1700 cm^{-1} and a weaker carboxylate ion absorption band at about 1550 cm^{-1}, indicating that PAA reacts to some extent with Al_2O_3 and $Al(OH)_3$.

Information on the chemical reactivity of oxides with aqueous polyacids can also be obtained from an examination of the setting characteristics and water stabilities of the cements formed. Cements that set rapidly are obviously formed as a result of chemical reaction between the polyacid solution and the oxide. If a fast setting cement is found to be unstable in water then the complex formed in the matrix network is hydrolytically unstable. With slow setting cements two

Table 3.2.3.1.

The chemical reactivity of various oxides with aqueous PAA as determined by infra-red spectroscopy.[97]

Oxides which react with PAA	Oxides which do not react with PAA
MgO, CaO, SrO_2, BaO	BeO, In_2O_3,
Y_2O_3, ZnO, CdO,	SnO_2,TiO_2,
HgO, PbO, Pb_3O_4,	ZrO_2, V_2O_5, Nb_2O_5,
Bi_2O_3, CoO, NiO,	MoO_3, Fe_2O_3.
CuO, Ag_2O.	

possibilities arise,

(1) a slow chemical reaction takes place, which may be controlled by the solubility of the oxide in the aqueous polyacid, or

(2) no reaction takes place between the oxide and the aqueous polyacid, but the mix slowly dries out to a hard mass.

If a hardened slow setting cement disintegrates in water then either the product has formed as in (1) and the matrix is hydrolytically unstable, or (2) has occurred and the unchanged polyacid dissolves in water to liberate the oxide particles. Thus, simple water stability tests cannot distinguish between products formed as in (1) with those produced by (2), although infra-red evidence may indicate whether a reaction has in fact occurred. For example, infra-red spectra from metal oxide-PAA cements suggest that NiO and CoO cements probably fall into case (1) and TiO_2 and Fe_2O_3 cements are formed as in (2).

3.2.4. The chemistry of the formation of metal oxide-polyacid cements.

The chemistry of the formation of cements from metal oxides and aqueous polyacids is not simple to predict. Many factors may be involved in the formation of a complex network in the cementing matrix and in determining the hydrolytic stability of the matrix. The following paragraphs attempt to relate cement properties to the nature of the metal ions and polyacids in the cementing matrix, but the interpretations are only offered as tentative hypotheses.

Since the formation of a network structure in the complex matrix of an ionomer cement must involve the binding of metal ions to definite sites (i.e. ligands) on the polymer macromolecules a measure of the degree of site binding may be useful in predicting the properties of the cement. Strauss[64,65] has determined the degree of site binding of certain metal ions to various polyanions in dilute solution (see section 1.6.4.). For Mg^{2+} ion the degree of site binding to the polyanions of PAA, EMA and VEMA increases in the order EMA$\approx$PAA< VEMA (see table 1.6.4.2.), which parallels the order of increasing stability in water of the corresponding MgO- polyacid cements, i.e. MgO-PAA$\approx$ MgO-EMA<MgO-VEMA. The binding of Mg^{2+} to the anions of PAA, PMAA and EMA is probably predominantly ionic and may give rise to hydrophilic structures, which may be partly dissociated in water. These structures would explain the softening of MgO-PAA, MgO-PMAA and MgO-EMA cements in water (see table 3.2.2.7.). With the MgO-VEMA cement there may be an interaction of the $-O-CH_3$ groups on the polymer with the Mg^{2+} ions, since Strauss has observed such interactions between Mg^{2+} ion and the polyanion of VEMA in dilute aqueous media. Intra-molecular co-ordination afforded by the $-O-CH_3$ groups on VEMA may provide protection of the Mg^{2+} ion from inter-molecular co-ordination involving water molecules and may explain the observed differences in the water stabilities of MgO-VEMA and MgO-EMA, or MgO-PAA cements.

Mg^{2+} ions are less extensively site bound to the polyanion of PESA than the polyanions of PAA and PMAA (see table 1.6.4.2.), a fact which may contribute to the lower water stability of MgO-PESA cement compared to MgO-PAA and MgO-PMAA cements.

With Ca^{2+} ion Strauss has reported that the degree of site binding to the polyanions of PAA, PMAA and PESA increases in the order PESA<PMAA<PAA (table 1.6.4.1.), which roughly parallels the water stabilities of the corresponding CaO-polyacid products (table 3.2.2.7.).

When comparing the degrees of ion site binding of Mg^{2+} and Ca^{2+} to polyanions with MgO and CaO-polyacid cements, satisfactory correlations are not possible. For example, the difference between the degrees of ion site binding with Mg^{2+} and the polyanions of PAA and PESA is the same as the difference between the degrees of ion site binding of Mg^{2+} and Ca^{2+} with the polyanion of PMAA (table 1.6.4.1.);

yet the water stability of MgO-PAA cement is greater than the MgO-PESA product, whilst the water stability of CaO-PMAA cement is about the same as MgO-PMAA cement. Consequently, the ion binding data of Strauss is of limited value in predicting the stabilities of polyacid-metal oxide products in water.

No information is available in the literature on the degree of site binding of ions to the polyanion of SMA in aqueous solution. The observed higher water stabilities of cements prepared from SMA and CaO, or MgO, compared to similar cements made from, for example CaO, or MgO and PAA may possibly be explained by the presence of the pendant hydrophobic phenyl groups on the SMA macromolecules. These hydrophobic groups may exert a protecting influence on the polyacid-metal ion complex matrix from attack by water molecules.

The only monovalent metal oxide that has been studied is Ag_2O, which forms water stable cements with aqueous PAA, PMAA and EMA, but not with aqueous VEMA and PESA.

Strauss[65] considers that the bonding of Ag^+ to the polyanions of PAA and EMA in dilute aqueous solution occurs by covalent linear co-ordination (via two sp hybrid orbitals from Ag^+) between carboxylate ligands widely spaced along the polymer chain. With the polyanion of VEMA in dilute solution chelation of Ag^+ between adjacent carboxylate and methoxy groups probably does not occur, since the steric strain in the ring would be too great (see section 1.6.4.).

In Ag_2O-VEMA cement the high polyacid concentration may favour the formation of inter-chain bonding of Ag^+ as opposed to the intra-chain chelates postulated by Strauss in dilute solutions. It is likely that these inter-chain complexes do not involve the methoxyl groups on the polymer, since the cement is unstable in water. The only difference between the water stable Ag_2O-EMA cement and Ag_2O-VEMA cement is the presence of methoxy groups in the matrix of the latter cement. An abundance of uncomplexed hydrophilic methoxy groups in Ag_2O-VEMA cement may render the matrix susceptible to water absorption, swelling and softening, whereas their absence in Ag_2O-EMA cement gives a matrix that is stable towards water.

In the case of Ag_2O-PESA cement, the Ag^+ ions may be bound to the polyanion by bonds with a high degree of ionic character. Such bonding would localise the Ag^+ ions at individual sulphonate groups on the polymer chains, since the metal ion is monovalent. No cross-linked network would be expected in the matrix of Ag_2O-PESA cement and this may be the reason for the lack of cohesion within the cement (i.e. disintegration of the cement) when placed in water. This situation contrasts the more covalent binding between carboxylate ligands on the polyanions of PAA, or EMA, and the Ag^+ ion, as suggested by Strauss.

The insolubility in water of the metal ion-polyanion complex matrix in metal oxide-polyacid cements may be expected to play a role in the setting process and water stability of the cement. Costantino et. al.[51] have reported the following order of increasing solubility in water for metal complexes of PMAA:
$Co^{2+} < Ni^{2+} < Cu^{2+} < Mg^{2+}$, which is not the order found for the water stabilities of the corresponding metal oxide-PMAA cements (see table 3.2.2.7.). This suggests that factors other than the insolubility of the matrix complexes are important when considering the water stabilities of metal oxide-polyacid cements.

The degree of ionic or covalent character in the bonds formed between the metal ions and polyanions in a metal oxide-polyacid cement may be an important factor in the formation of a water stable network structure in the cement matrix.

Zn^{2+} and Cd^{2+} ions have ionic radii of about the same size as those of Mg^{2+} and Ca^{2+} ions, respectively, (table 3.2.4.1.) and hence have similar ionic potentials. However, by virtue of the greater polarising powers of Zn^{2+} and Cd^{2+} ions, compared to Mg^{2+} and Ca^{2+} ions, the bonding in zinc and cadmium compounds often has a higher degree of covalent character than that in similar compounds of magnesium and calcium. The water stabilities of cements prepared from MgO (or CaO) and, for example, aqueous PAA or PMAA, are lower than the water stabilities of the corresponding cements containing ZnO (or CdO). This difference in the stability of these cements in water may be a consequence of a higher degree of covalent character in the Zn^{2+} (or Cd^{2+})-polyanion matrix network bonding. Similar situations may exist in cements prepared with PbO and HgO.

PESA only forms water stable cements with the oxides of the heavier metals, such as PbO, HgO and CdO. Again this may reflect a higher contribution of covalent character in the bonding between the metal ions and polyanions in the matrices of these cements, compared to a greater degree of ionic character in the matrix bonding in cements made from the oxides of lighter elements, such as CaO, ZnO or CuO, and PESA.

Another possible factor influencing the properties of metal oxide-polyacid cements is the size of the metal ion produced in solution. Bi_2O_3 forms water stable cements with acrylic polyacids and PESA, but not with maleic acid copolymers. Bi^{3+} is a large ion (table 3.2.4.1.) and can form $BiOH^{2+}$ and BiO^+ ions at relatively low pH's in solution. The size of the $BiOH^{2+}$, or BiO^+, ions may be too large to form stable complexes with maleic acid copolymers, where the acid groups are adjacent, but not too large to complex with acrylic polyacids and PESA, where the acid groups are separated by methylene groups. The Y^{3+} ion is smaller than the Bi^{3+} ion (see table 3.2.4.1.) and whilst hydroxo-cations, such as YOH^{2+}, may be formed in solution[103]

Table 3.2.4.1.

Ionic Radii (nm)[102]

Mg^{2+}	0.065
Ca^{2+}	0.099
Zn^{2+}	0.074
Cd^{2+}	0.097
Bi^{3+}	0.120
Y^{3+}	0.093

they may not be too large to complex with maleic acid copolymers. All of the polyacids which have been tested with Y_2O_3 give water stable cements (table 3.2.2.7.).

The water stability of a polyacid-metal oxide cement may depend upon the water stability of the metal ion-polyanion complexes in the cement matrix. Stability constants (see section 1.6.3.) provide a quantitative measure of the tendency of complexes to dissociate in water and consequently may provide a useful guide in interpreting the stability of polyacid-metal oxide cements in water. The water stabilities of metal oxide-PAA cements roughly parallel the order of increasing stability constants for the corresponding metal poly(acrylate) complexes, i.e.

for the water stabilities of the cements, CuO=ZnO>CaO=MgO>NiO (see table 3.2.2.7.).

for the stabilities of the complexes, CuO>ZnO>NiO>CaO>MgO (see table 1.6.3.3.).

Metal ions giving complexes with the highest stability constants (Cu^{2+} and Zn^{2+}) are also present in the complex matrices of the water stable cements (PAA-CuO and PAA-ZnO). Complexes with lower stability constants are found in cements that are unstable when placed in water. But the parallel is not rigorous, since although Co^{2+} forms a complex with a higher stability constant than Mg^{2+} or Ca^{2+} ions with PAA, the PAA-CoO cement disintegrates in water, whilst the PAA-MgO and PAA-CaO cements remain coherent and become extremely soft. It is possible that Co^{2+} ions show little tendency for inter-chain bonding (i.e. network formation) and give mainly intra-chain chelate complexes, whilst with Cu^{2+}, Zn^{2+}, Mg^{2+} and Ca^{2+} ions inter-chain bonding predominates. This view is supported by an examination of the setting characteristics of the metal oxide-polyacid cements. PAA-CoO mixes set very slowly compared to the MgO, CaO, ZnO and CuO-PAA products, which may indicate that the setting of the cement containing CoO is by a drying out process as opposed to the formation of a network structure. If this is the case then CoO-PAA cement may be expected to disintegrate in water, irrespective of the resistance to dissociation of the metal ion-polyanion bonding, due to a lack of inter-chain binding in the matrix. The formation of inter- or intra-chain complexes may depend upon the ionic radii, the electronegativities and co-ordination geometry of the metal ions, but a meaningful exploration of these aspects of binding in metal oxide-polyacid cements is made impossible by the lack of detailed literature on complex formation in very viscous, highly concentrated polyacid solutions.

Similar arguments may apply to metal oxide-PMAA cements (see tables 1.6.3.3. and 3.2.2.7.), where both CoO and NiO may form products with PMAA by a process similar to that postulated for CoO with PAA.

3.2.5. Comparison of G200 glass-poly(acrylic acid) cement with CaO-poly(acrylic acid) and Al_2O_3 (or $Al(OH)_3$)-poly(acrylic acid) cements.

G200 glass reacts rapidly with aqueous PAA to form a cement containing a mixed Ca^{2+} and Al^{3+} poly(acrylate) matrix, in which Ca^{2+} predominates.[21] Thus the water stability of G200 glass-PAA cement must depend upon the stabilities of the Ca^{2+} and Al^{3+}-polyanion complexes in the matrix.

Al_2O_3-PAA cement is unstable in water. Even the cement made from $Al(OH)_3$, which would be expected to be more soluble in acids than Al_2O_3 and which gives a fairly rapidly setting product with aqueous PAA, softens and eventually disintegrates when immersed in water. This behaviour is not reflected by G200 glass-PAA cement in water.

CaO-PAA cement softens markedly in water, but remains coherent. In G200 glass-PAA cement the Ca^{2+} poly(acrylate) component of the matrix must play a major role in determining the stability of the cement in water, since it is the predominant species present; yet the cement, unlike CaO-PAA cement, is very stable in water.

It is possible that the F^- and PO_4^{3-} ions, which are also leached from G200 glass by aqueous PAA, have an influence on the water stability of the Ca^{2+} and Al^{3+} poly(acrylate) species in the complex matrix of G200 glass-PAA cement. The F^- and PO_4^{3-} ions may also complex with the Ca^{2+} and Al^{3+} ions bound to the PAA in the matrix and thereby reduce the susceptibility of the matrix complexes to attack, or hydration, by water molecules. This view is supported by the fact that a mixture of CaO and CaF_2 (fused at 1475) will form a water stable cement with PAA, whereas CaO-PAA and CaF_2-PAA products alone are not stable in water.[97]

An anomaly arises with CaO-VEMA and G200 glass-VEMA products, for whereas CaO-VEMA cement is stable in water, G200 glass-VEMA cement is softened by immersion in water. In G200 glass-VEMA cement a co-operative metal ion binding effect with the $-O-CH_3$ groups on the polymer may not occur, possibly as a result of preferential complexing by F^- or PO_4^{3-} ions. The presence of uncomplexed $-O-CH_3$ groups in the matrix of G200 glass-VEMA cement may render the matrix susceptible to water absorption, softening and swelling. In the CaO-VEMA cement the $-O-CH_3$ groups on the copolymer may be complexed to the Ca^{2+} ions in the matrix to give a water stable cement.

3.2.6. Concluding comments.

The study of metal oxide-polyacid cements has shown that cement formation and properties are dependent upon the type of oxide and polyacid employed in their preparation. Although some indication of the chemistry involved in the formation of water stable cements can be obtained from these preliminary studies, detailed interpretations can only be speculative. Arising from this work, however, is evidence that the chemistry of G200 glass-PAA cement is probably more complex than has been presupposed and probably involves complexation of leached F^- and PO_4^{3-} to the Ca^{2+} and Al^{3+} ions in the matrix of the cement.

3.3. The reactivity of polyacids with metal oxides and G200 glass in non-aqueous solvents.

Setting cements have been prepared by reacting polyacids with metal oxides, or G200 glass, in non-aqueous solvents. Table 3.3.1. lists the polyacid solutions studied and table 3.3.2. summarises the stability in water and solvents of some of the products obtained.

Many oxides, such as TiO_2, SnO_2, Fe_2O_3 and ZrO_2 give non-setting mixes with the polyacid solutions in table 3.3.1., even after ageing for 9-14 days. Some oxides, such as NiO and CoO give flexible or slow setting products that are unstable in both water and the solvents employed in the polyacid solutions. A practical point arising from this work is that generally the non-aqueous solutions of polyacid give smooth mixes, even with the most reactive oxides, which is often an advantage over the aqueous polyacid solutions.

From table 3.3.2. it is apparent that a wide variety of water or solvent stable products can be made from non-aqueous polyacid solutions. It is surprising, however, that 1,4-dioxan can behave as a solvent for what is essentially an ionic acid-base type of reaction, for the dielectric constant of 1,4-dioxan (table 3.3.3.) is very low. However, these non-aqueous systems are likely to contain small amounts of water (approximately <3%) and this may be sufficient to allow some reaction to occur by an ionic mechanism. Also, in commercial ionomer resins, ionic cross-linking is believed to occur in a viscous, aliphatic hydrocarbon medium.

The results obtained with mixes in non-aqueous solvents differ slightly from those obtained with aqueous polyacids (c.f. tables 3.3.2

Table 3.3.1.

Polyacid solutions in non-aqueous solvents.

POLYACID		SOLUTION PROPERTIES	
Type	Batch No. (see table 3.1.1.1.).	Solvent	Concentration (% w/w)
SMA	10	Dimethylformamide	53
EMA	8	Dimethylformamide	35.6
PAA	5	Dimethylformamide	27
EMA	8	1,4-dioxan	25

Table 3.3.3.

Dielectric constants of solvents.[104]

Solvent	Dielectric constant
Water	78.5
Dimethylformamide	36.7
1,4-dioxan	2.2

Table 3.3.2.

Solvent stability of cements prepared in non-aqueous media.

Inorganic phase	SMA in dimethyl-formamide	PAA in dimethyl-formamide	EMA in dimethyl-formamide	EMA in 1,4-dioxan
MgO	1	3	3	3
CaO	1^a	1	2	1
Y_2O_3	4^*	1	4^*	1
ZnO	1	1	1	1
CdO	1	1	1	1
HgO	1	1	1	1
PbO	1	1	1	1
Pb_3O_4	4^*	1	4^*	1
Bi_2O_3	4^*	4^{**}	4^{**}	-
CuO	4	1	1	1
Ag_2O	1	1	1	1
G200 glass	4^*	1	3^b	3^b

1. Stable, no disintegration in water or solvent for the polyacid.
2. Coherent, but softened very slightly in water. Stable in solvent for the polyacid.
3. Coherent but softened markedly in water. Stable in solvent for the polyacid.
4. Unstable, disintegrated.

* = In dimethylformamide

** = In water, or in dimethylformamide.

a = Weakened markedly

b = Surface effect.

and 3.2.2.7.), although this may simply be a result of a difference in the solvating effects of the non-aqueous solvents compared with water.

3.4. The binding of selected cations to various polyacids in aqueous solution.

3.4.1. Introduction

The most outstanding feature of cements made from metal oxides and aqueous polyacids is their variable stability in water. Even oxides that are soluble in aqueous polyacids may give cements that are unstable in water and this leads to the assumption that, providing the oxides react with aqueous polyacids, the water stability of the cements formed must be determined by the stability of the matrix salts or complexes towards water. As long as the matrix does not contain uncomplexed, hydrophilic polymer substituents, the water stability of the matrix salts or complexes must be dependent upon the effect of water molecules on the M-O bonds present. The stability of M-O bonds in complexes can be assessed quantitatively in aqueous solution by stability constants (see section 1.6.3.) and some interpretations of the water stability of metal oxide-polyacid cements in terms of the stability constants of the matrix complexes has been briefly mentioned in section 3.2.4.

The stability constants of metal ion-polyanion complexes for a variety of ions with particular polyacids can be found in the literature (see section 1.6.3.), but a precise comparison of the stability constants for a given ion with a number of polyacids cannot be made as each author chooses different experimental conditions to determine them.

In order to assess the usefulness of stability constant data in predicting the water stability of cements made with a metal oxide and different polyacids ion binding studies have been carried out on two polyacids with two different metal ions, using identical experimental conditions.

For this study PAA and EMA have been investigated, since they are structurally isomeric and possess only carboxyl groups and no other potential ligands. The cations which have been chosen for reaction with these polyacids are Ca^{2+} and Cd^{2+}. They have been selected for the following reasons: CaO forms cements with aqueous PAA and EMA with distinctly different softening properties in water (table 3.2.2.7.) and CdO forms cements with these polyacids with greater water stabilities than the CaO based cements, even though Ca^{2+} and Cd^{2+} have about the same ionic radius (table 3.2.4.1.).

The binding of Cd^{2+} to PESA has also been studied, since the CdO-PESA cement is water stable and there are no reported stability constants for PESA-Cd^{2+} complexes in the literature.

The experimental technique which has been employed in these studies is based on a potentiometric method developed by Gregor[49] and modified by Mandel and Leyte.[60]

3.4.2. Gregor's method (modified by Mandel and Leyte) for determining the stability constants of metal ion-polyanion complexes.

Gregor's method for determining the stability constants of metal ion-polyanion complexes is based on the method of Bjerrum for complexes of monomeric ligands.[49]

Consider a series of complexes in solution,

$$MA_1 + MA_2 \text{ ---- } + MA_i \text{ ---- } + MA_n$$

For the equilibrium $M + iA \rightleftharpoons MA_i$ the following relationship can be derived (according to Bjerrum),[105,106]

$$\bar{n} = \frac{\sum_{1}^{n} i\, K_i \left[A\right]^{i}}{1 + \sum_{1}^{n} K_i \left[A\right]^{i}} \quad \text{-------} \quad (1)$$

where, $\bar{n}$ = average number of ligands, A, bound to the central metal ion, M.

n = the maximum value i can take = the co-ordination number of M with ligand A.

K_i = the overall stability constant, defined as in (2)

$$K_i = \frac{[MA_i]}{[M][A]^i} \quad \text{-----} \ (2)$$

$\bar{n}$ is therefore dependent upon $[A]$ and a plot of $\bar{n}$ against - log $[A]$ is called the formation curve for the system of complexes.

It can be shown that at half integral values of $\bar{n}$, $-\log [A]$ (at $\bar{n} = j - \frac{1}{2}$) = $-\log k_j$, where k_j is a step wise stability constant for the equilibrium,

$$MA_{j-1} + A \rightleftharpoons MA_j$$

k_j is defined as, $k_j = \dfrac{[MA_j]}{[MA_{j-1}]\ [A]}$ ---- (3)

At integral values of $\bar{n}$ average stability constants are obtained. For example at $\bar{n} = 1$ the value of $-\log [A] = -\log K_{av}$, where $K_{av}^2 = k_1k_2 = K_2$. K_2 is the overall stability constant for the formation of the second complex and is defined by equation (2). k_1 and k_2 are defined by the general equation (3).

For a polyacid, such as PAA, with a divalent metal ion, such as Cu^{2+}, the constant K_2 would relate to the equilibrium (4) and k_1 and k_2 would correspond to (5) and (6).

$$Cu^{2+} + 2\ \text{-COO}^- \rightleftharpoons (\text{-COO})_2\ Cu \quad \text{----} \ (4)$$

$$Cu^{2+} + \text{-COO}^- \rightleftharpoons \text{-COO}\ Cu^+ \quad \text{-----} \ (5)$$

$$\text{-COO}\ Cu^+ + \text{-COO}^- \rightleftharpoons (\text{-COO})_2\ Cu \quad \text{----} \ (6)$$

However, for polyacids, equilibria such as (4), (5) and (6) involve a net change of charge on the macromolecular chains. The configuration and binding properties of a polyacid chain depend markedly upon its charge. Thus, although equilibria (4), (5) and (6) are valid for monomeric acids, they are not valid for polyacids.

Gregor considers equilibria of the type

$$2\ \text{-COOH} + \text{Cu}^{2+} \overset{B_2}{\rightleftharpoons} \text{-(COO)}_2\text{Cu} + 2\text{H}^+ \text{ ----- (7)}$$

to be more satisfactory for polyacids, because they involve no change of charge on the polymer chains. B_2 is an overall stability constant, which is defined by equation (8)

$$B_2 = \frac{[MA_2]\,[H^+]^2}{[M]\,[HA]^2} \text{ -------- (8)}$$

B_2 is a valid constant for both monomeric and polymeric acids.

It is assumed that the binding of metal ions to the carboxylate ligands does not influence the dissociation equilibrium of the remaining carboxyl groups, i.e. that remaining carboxyl groups attain a dissociation equilibrium identical to the uncomplexed polyacid. This can only be true if the number of carboxylate groups bound is less than or equal to the charge on the participating metal ion.

Equation (1) can be modified in terms of B_i values to obtain equation (9).

$$\bar{n} = \frac{\sum_1^n i\, B_i \left(\frac{[HA]}{[H^+]}\right)^i}{1 + \sum_1^n B_i \left(\frac{[HA]}{[H^+]}\right)^i} \text{ ---- (9)}$$

where B_i is the overall stability constant for the formation of the

i^{th} complex, MA_i.

A formation curve can therefore be drawn by plotting $\bar{n}$ against $-\log\left(\frac{[HA]}{[H^+]}\right)$ and from the curve obtained, at

$$\bar{n} = \tfrac{1}{2},\ -\log\left(\frac{[HA]}{[H^+]}\right) = -\log b_1$$

$$\text{at}\quad \bar{n} = 1,\ -\log\left(\frac{[HA]}{[H^+]}\right) = -\log B_{av}$$

$$\text{and at}\quad \bar{n} = 1\tfrac{1}{2},\ -\log\left(\frac{[HA]}{[H^+]}\right) = -\log b_2$$

b_1 and b_2 are stepwise stability constants describing equilibria (10) and (11) respectively.

$$HA + M^{2+} \rightleftharpoons MA^+ + H^+ \quad \text{--- (10)}$$

$$HA + MA^+ \rightleftharpoons MA_2 + H^+ \quad \text{--- (11)}$$

B_{av} is an average stability constant and

$B_{av}^2 = b_1 b_2 = B_2$.

B_2 is defined by equation (8).

Gregor calculates stability constants from the results obtained by titrating PAA alone and in the presence of varying concentrations of added divalent metal salt. Titration plots of pH against $\log\left(\frac{\alpha}{1-\alpha}\right)$, where α = the degree of neutralisation, have shown that the curve is depressed by the addition of the divalent metal salt. However, neutral salts of non-complexing metals (such as Na^+ salts) also depress the titration curves, since the presence of neutral salt increases the dissociation of the carboxyl groups and thus decreases the apparent pK_a of the acid (see section 1.6.1.). But even in the presence of a swamping concentration of a neutral sodium salt the titration curves are still lowered by the presence of divalent metal ions, such as Cu^{2+}, indicating that these ions are strongly complexed to the PAA and displace hydrogen ions from the polyacid into solution.

By comparing the titration behaviour of PAA alone and with added divalent metal salts, in the presence of high concentrations of neutral Na^+ or K^+ salts, Gregor has obtained a set of stability constants for a number of divalent metal ions (see table 1.6.3.3.).

In order to construct the formation curve of metal-polyacid complexes, $-\log [A]$ and $-\log \left(\frac{[HA]}{[H^+]}\right)$ values must be calculated from titration results at different stages during the titration of the polyacid in the presence of the complexing ions. Although calculation of $-\log \left(\frac{[HA]}{[H^+]}\right)$ values is relatively simple, the determination of $-\log [A]$ values is tedious (see reference 49).

Mandel and Leyte[60] have proposed a more convenient way of determining $-\log [A]$ values. A calibration plot of $-\log \left(\frac{[HA]}{[H^+]}\right)$ against $-\log [A]$ is constructed from the titration results obtained for the polyacid in the absence of complexing metal ions, where calculation of $-\log [A]$ values is simple. Assuming that the chelation of divalent ions does not change the dissociation equilibrium of the polyacid, the required values can be obtained for the polyacid-divalent ion solutions by calculating $-\log \left(\frac{[HA]}{[H^+]}\right)$ and obtaining the value of $-\log [A]$ by interpolation from the calibration plot.

$[A]$, $\bar{n}$, $[HA]$ and $[H^+]$ can be determined from the titration results as follows:[49,107]

$[H^+]$ is calculated from the solution pH at any point in the titration, since $pH \simeq -\log [H^+]$.

The total concentration of ligand $[A_t]$ in solution is given by

$$[A_t] = [HA] + \alpha [A_t] + [H^+]_1 + [H^+]_2$$

where, $[H^+]_1$ = protons displaced by the complexing metal ion

$[H^+]_2$ = protons dissociated from HA.

$[H^+]_1 + [H^+]_2$ = the total concentration of protons in solution, which is measured by the solution pH.

$$\therefore \; [HA] = 1-\alpha \; [A_t] \; - \; [H^+]$$

$[A_t]$ is known and can be adjusted for dilution throughout the titration. α is known from the amount of titrant solution added.

$-\log \left(\frac{[HA]}{[H^+]}\right)$ can therefore be calculated and $-\log [A]$ determined from the calibration plot.

$\bar{n}$ can then be calculated, since,

$$\bar{n} = \frac{[A_t] - [HA] - [A]}{[M_t]}$$

where $[M_t]$ is the total concentration of metal ions initially present. $[M_t]$ can be corrected for volume changes due to dilution of the solution during titration.

For the calibration plot $[A]$ is obtained from a reference titration of an equal volume of the polyacid solution alone, from which, $[A] = \alpha [A_t] + [H^+]$

The formation curve of the metal ion-polyacid complexes can then be obtained by plotting $\bar{n}$ against the corresponding values of $-\log \left(\frac{[HA]}{[H^+]}\right)$.

3.4.3. The binding of Ca^{2+} and Cd^{2+} ions to poly(acrylic acid) and ethylene-maleic acid copolymer in aqueous solution.

3.4.3.1. The construction of the formation curves from potentiometric titration results.

Tables 3.4.3.1.1. and 3.4.3.1.2. show the results obtained from the titration of PAA (9.25×10^{-3} M) and EMA (8.95×10^{-3}M) in 1.0M $NaNO_3$ solution. The $-\log [A]$ and $-\log \left(\frac{[HA]}{[H^+]}\right)$ values are calculated from the values of α and pH measured experimentally and are plotted in graphs 3.4.3.1.1. and 3.4.3.1.2. to obtain the calibration curves for the titration of these polyacids.

Tables 3.4.3.1.3. to 3.4.3.1.6. show the titration results and calculated $\bar{n}$ and $-\log\left(\frac{[HA]}{[H^+]}\right)$ values for PAA (9.25×10^{-3}M) and EMA (8.95×10^{-3}M) in 1.0M $NaNO_3$ solution with various concentrations of added $Ca(NO_3)_2$ and $Cd(NO_3)_2$. The formation curves, obtained by plotting $\bar{n}$ against $-\log\left(\frac{[HA]}{[H^+]}\right)$, for the Ca^{2+} and Cd^{2+} complexes of PAA and EMA are illustrated in graphs 3.4.3.1.3. and 3.4.3.1.4.

The calculations employed with the titrations of the polyacids alone and with added Ca^{2+} and Cd^{2+} salts have been adjusted to allow for the dilution of the polyacid solutions by the titrant solution.

Table 3.4.3.1.1.

The results from the titration of PAA in 1.0M $Na\ NO_3$.

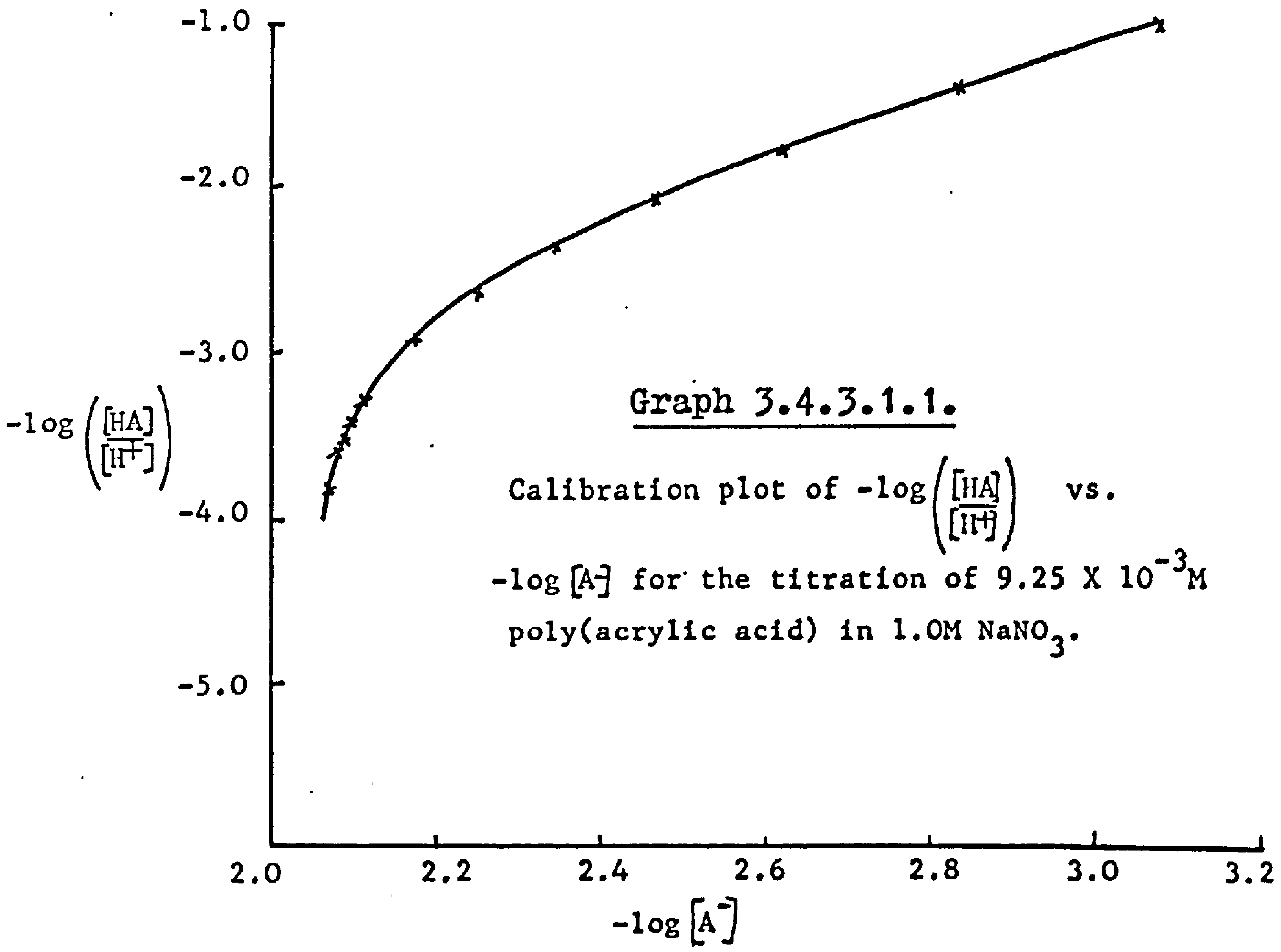
α	pH	$-\log [HA]$	$-\log [A]$	$-\log \left(\frac{[HA]}{[H^+]}\right)$
0.00	3.08	2.08	3.08	-1.00
0.13	3.51	2.11	2.84	-1.40
0.25	3.95	2.17	2.62	-1.78
0.38	4.35	2.25	2.46	-2.10
0.50	4.73	2.35	2.34	-2.38
0.68	5.13	2.47	2.25	-2.66
0.75	5.61	2.65	2.17	-2.95
0.88	6.25	2.95	2.11	-3.29
0.90	6.44	3.05	2.10	-3.39
0.92	6.63	3.15	2.09	-3.48
0.94	6.88	3.27	2.08	-3.60
0.96	7.29	3.45	2.07	-3.83
0.98	∿8.40	3.75	2.06	-6.34

Table 3.4.3.1.2.

The results from the titration of EMA in

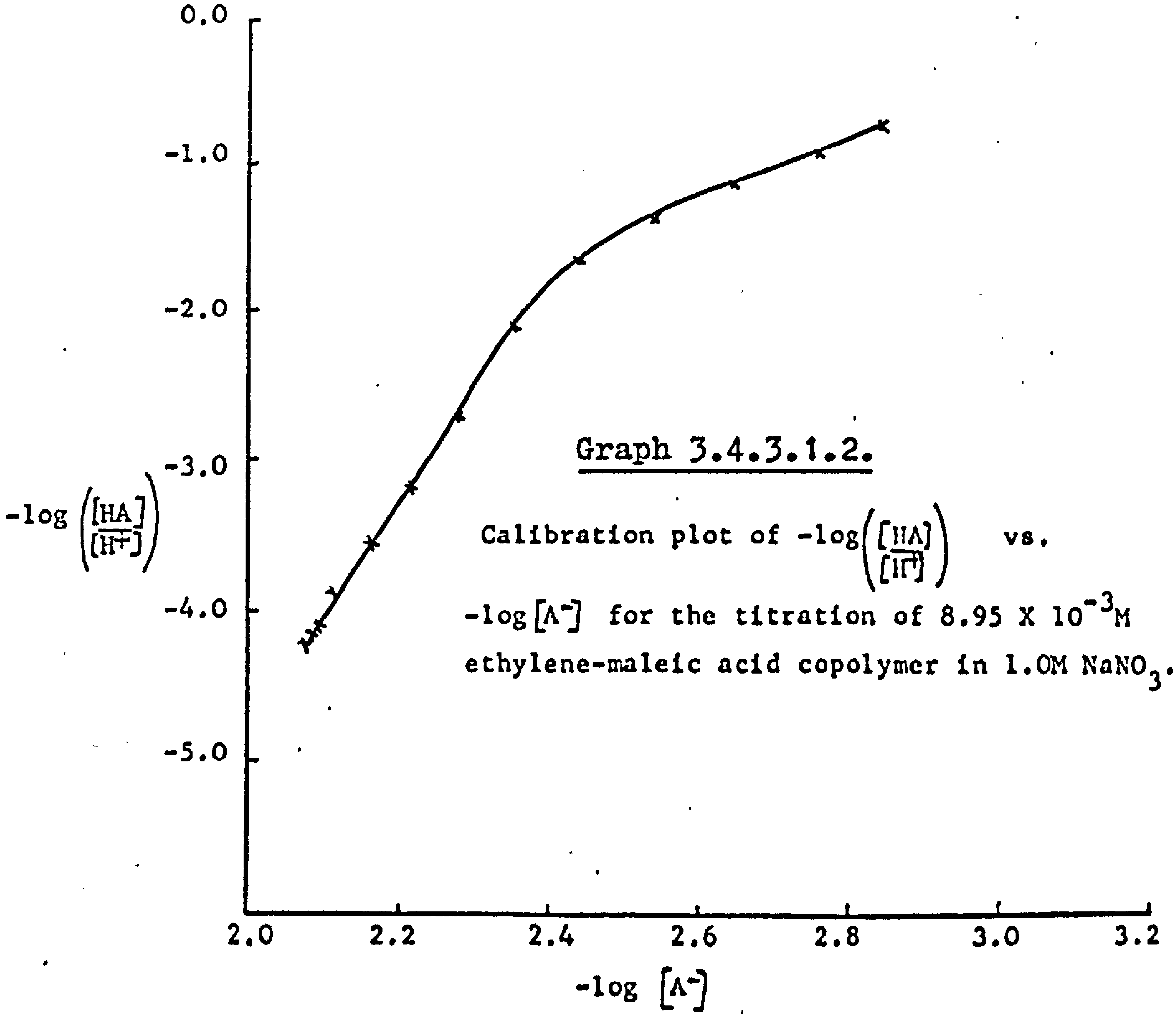
1.0M Na NO_3

α	pH	$-\log [HA]$	$-\log [A]$	$-\log \left(\frac{[HA]}{[H^+]}\right)$
0.00	2.85	2.12	2.85	-0.72
0.10	3.08	2.14	2.76	-0.93
0.20	3.33	2.18	2.65	-1.15
0.30	3.61	2.23	2.54	-1.38
0.40	3.95	2.29	2.44	-1.66
0.50	4.47	2.36	2.36	-2.11
0.60	5.19	2.46	2.28	-2.73
0.70	5.79	2.58	2.22	-3.20
0.80	6.32	2.76	2.16	-3.56
0.90	6.97	3.07	2.11	-3.90
0.94	7.43	3.30	2.09	-4.12
0.96	7.63	3.47	2.08	-4.16
0.98	8.00	3.77	2.08	-4.23
1.00	∿8.40	-	2.07	-8.40



Graph 3.4.3.1.1.

Calibration plot of $-\log\left(\frac{[HA]}{[H^+]}\right)$ vs. $-\log[A^-]$ for the titration of 9.25×10^{-3}M poly(acrylic acid) in 1.0M $NaNO_3$.



Graph 3.4.3.1.2.

Calibration plot of $-\log\left(\frac{[HA]}{[H^+]}\right)$ vs. $-\log[A^-]$ for the titration of 8.95×10^{-3}M ethylene-maleic acid copolymer in 1.0M $NaNO_3$.

Table 3.4.3.1.3.

The results from the titration of PAA in 1.0M Na NO_3 in the presence of various concentrations of $Ca(NO_3)_2$.

α	pH	$-\log [HA]$	$-\log \left(\frac{[HA]}{[H^+]}\right)$	$-\log [A]$ *	$\bar{n}$
		6.01×10^{-4} M Ca^{2+}			
0.63	5.12	2.47	-2.65	2.26	0.16
0.75	5.58	2.65	-2.93	2.18	0.17
0.88	6.19	2.95	-3.24	2.12	0.33
0.90	6.37	3.05	-3.32	2.11	0.30
		1.50×10^{-3} M Ca^{2+}			
0.75	5.52	2.65	-2.86	2.20	0.23
0.90	6.22	3.05	-3.17	2.13	0.44
0.95	6.71	3.36	-3.35	2.10	0.35
0.97	7.08	3.87	-3.21	2.12	0.73
		3.00×10^{-3} M Ca^{2+}			
0.75	5.47	2.65	-2.81	2.21	0.17
0.90	6.15	3.05	-3.10	2.15	0.29
0.95	6.62	3.36	-3.26	2.12	0.27
0.97	7.03	3.87	-3.16	2.13	0.43

* Estimated from the calibration curve (graph 3.4.3.1.1.).

Table 3.4.3.1.4.

The results from the titration of EMA in 1.0 M $NaNO_3$ in the presence of various concentrations of $Ca(NO_3)_2$.

α	pH	$-\log[HA]$	$-\log\left(\frac{[HA]}{[H^+]}\right)$	$-\log[A]$ *	$\bar{n}$
		1.50×10^{-3} M Ca^{2+}			
0.75	6.04	2.67	-3.38	2.19	0.03
0.90	6.93	3.07	-3.87	2.12	0.11
0.95	7.53	3.37	-4.16	2.08	0.12
		2.40×10^{-3} M Ca^{2+}			
0.80	6.21	2.76	-3.45	2.18	0.10
0.90	6.79	3.07	-3.73	2.14	0.19
0.94	7.17	3.31	-3.86	2.12	0.20
0.96	7.36	3.47	-3.89	2.11	0.22
0.98	7.68	3.77	-3.91	2.11	0.28
0.99	7.88	4.07	-3.81	2.13	0.43
		3.00×10^{-3} M Ca^{2+}			
0.75	5.91	2.67	-3.25	2.21	0.11
0.90	6.86	3.07	-3.80	2.13	0.08
0.95	7.44	3.37	-4.07	2.09	0.01
0.97	7.70	3.59	-4.11	2.09	0.07

* Estimated from the calibration curve (graph 3.4.3.1.2.).

Table 3.4.3.1.5.

The results from the titration of PAA in 1.0M $NaNO_3$ in the presence of various concentrations of $Cd(NO_3)_2$.

α	pH	-log $[HA]$	-log $\left(\frac{[HA]}{[H^+]}\right)$	-log $[A]$ *	$\bar{n}$
		1.52×10^{-3}M Cd^{2+}			
0.13	3.46	2.11	-1.35	2.87	0.09
0.25	3.80	2.17	-1.62	2.71	0.32
0.38	4.07	2.25	-1.82	2.60	0.66
0.50	4.38	2.34	-2.03	2.49	0.89
0.63	4.66	2.48	-2.19	2.42	1.25
		3.04×10^{-3}M Cd^{2+}			
0.13	3.42	2.11	-1.31	2.90	0.05
0.25	3.68	2.18	-1.50	2.78	0.27
0.38	3.89	2.26	-1.64	2.70	0.51
0.50	4.14	2.35	-1.79	2.61	0.72
0.63	4.35	2.48	-1.87	2.57	1.02

* Estimated from the calibration curve (graph 3.4.3.1.1.).

Table 3.4.3.1.6.

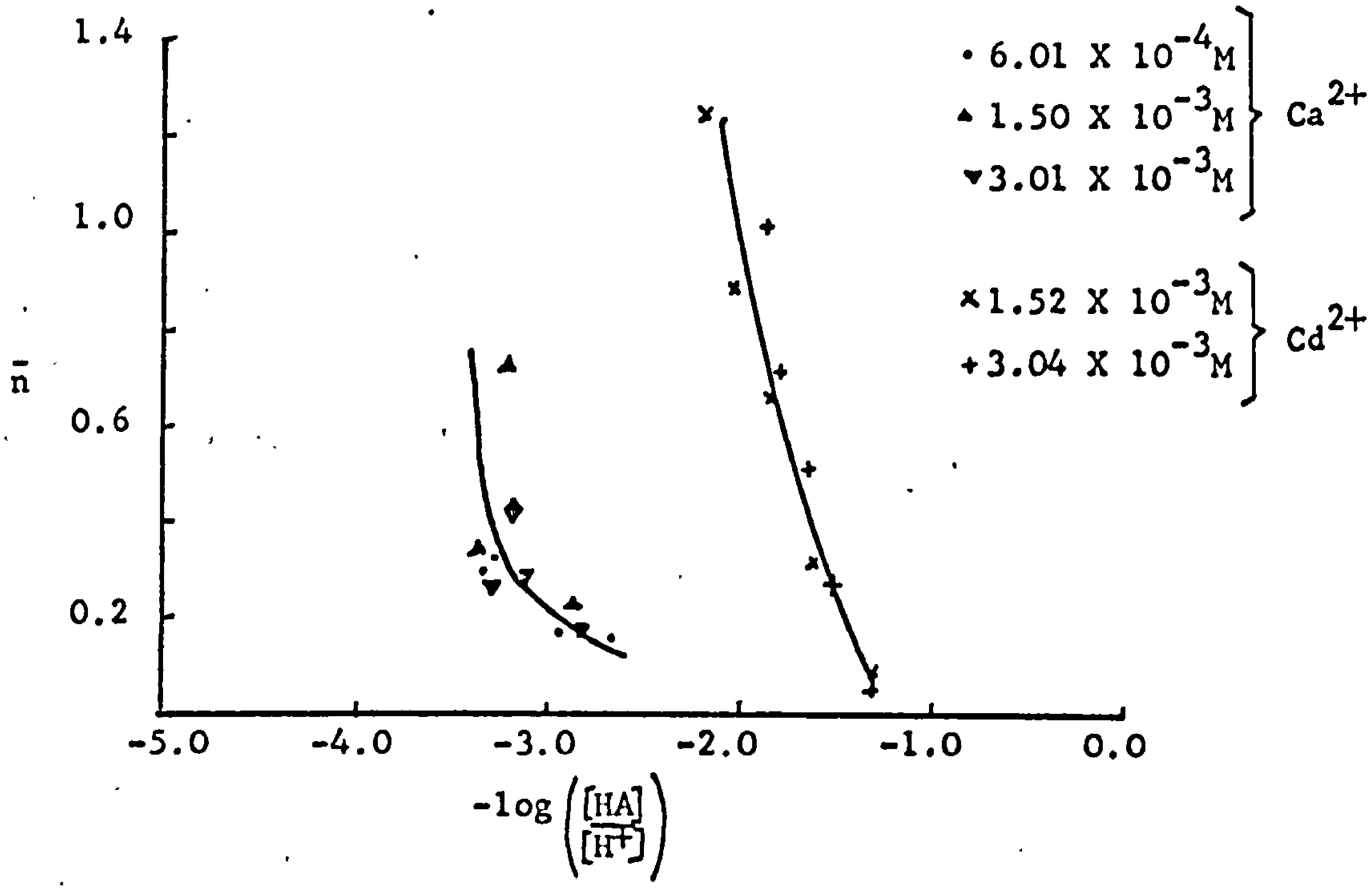
The results from the titration of EMA in 1.0M $NaNO_3$ in the presence of various concentrations of $Cd(NO_3)_2$.

α	pH	$-\log [HA]$	$-\log \left(\frac{[HA]}{[H^+]}\right)$	$-\log [A]$ *	$\bar{n}$
		$1.15 \times 10^{-3} M\ Cd^{2+}$			
0.30	3.58	2.23	-1.35	2.56	0.08
0.45	4.12	2.32	-1.80	2.41	0.09
0.60	4.72	2.46	-2.26	2.34	0.44
0.70	4.95	2.59	-2.36	2.33	0.92
0.80	5.41	2.76	-2.65	2.29	1.24
0.85	5.72	2.89	-2.83	2.27	1.31
0.90	6.11	3.07	-3.05	2.24	1.36
		$3.04 \times 10^{-3} M\ Cd^{2+}$			
0.15	3.17	2.16	-1.00	2.73	0.05
0.30	3.56	2.23	-1.33	2.57	0.08
0.45	4.04	2.33	-1.72	2.43	0.10
0.60	4.40	2.46	-1.94	2.38	0.38
0.70	4.54	2.59	-1.95	2.38	0.66
0.80	4.85	2.77	-2.08	2.36	0.87
0.85	5.05	2.89	-2.16	2.35	0.98
0.90	5.42	3.07	-2.35	2.33	1.03
0.95	6.14	3.37	-2.77	2.28	0.98

* Estimated from the calibration curve (graph 3.4.3.1.2.).

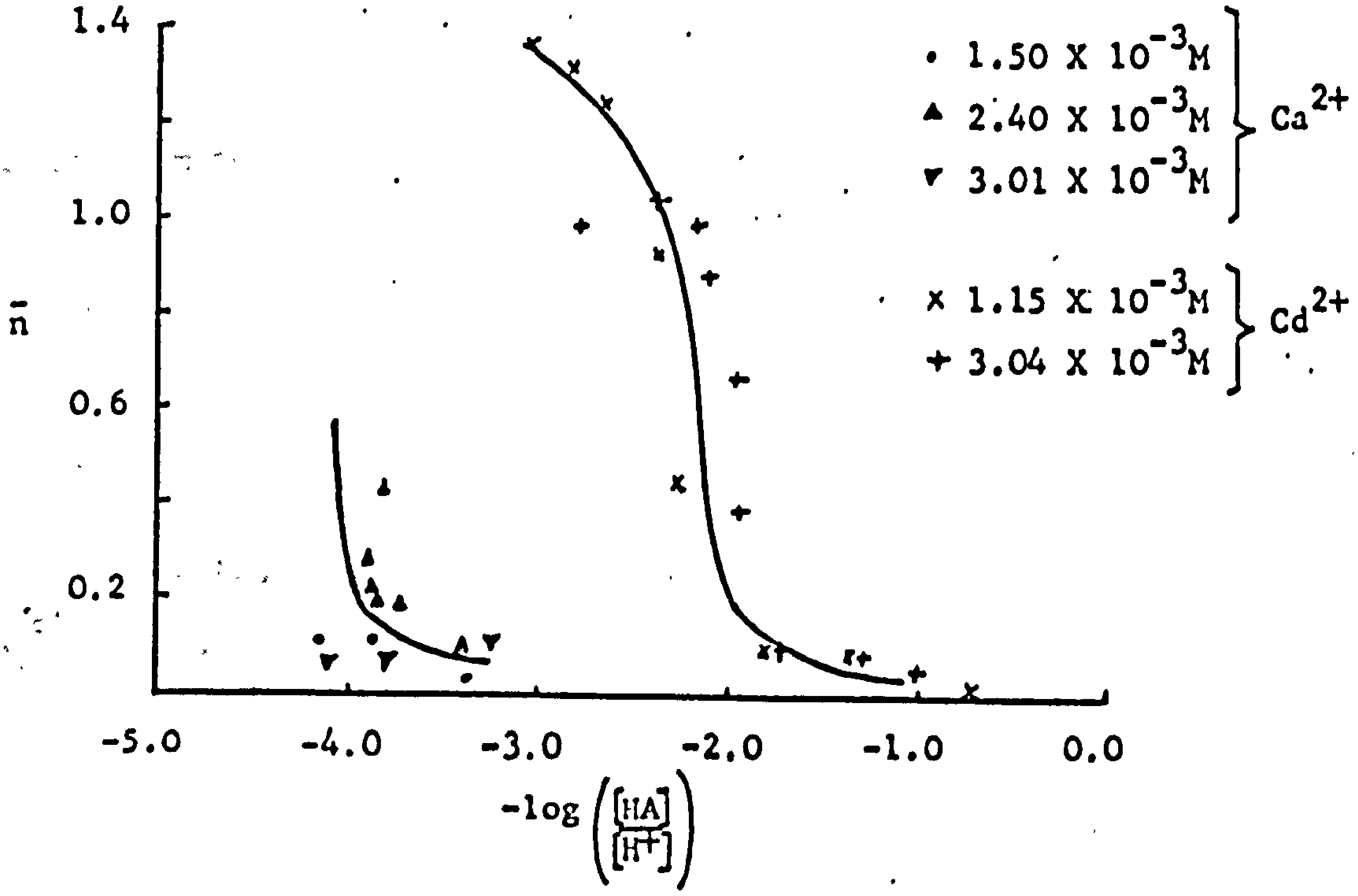
Graph 3.4.3.1.3.

Formation curves for poly(acrylic acid) (9.25×10^{-3}M) with Ca^{2+} and Cd^{2+} ions in 1.0M $NaNO_3$.



Graph 3.4.3.1.4.

Formation curves for ethylene-maleic acid copolymer (8.95×10^{-3}M) with Ca^{2+} and Cd^{2+} ions in 1.0M $NaNO_3$.



3.4.3.2. The binding of Ca^{2+} ions to poly(acrylic acid) and ethylene-maleic acid copolymer.

The titration results for PAA and EMA solutions with added $Ca(NO_3)_2$ follow very closely the titration results of the polyacids in the absence of $Ca(NO_3)_2$, until at very high degrees of neutralisation (α) a distinct deviation occurs. Consequently, $\bar{n}$ values can only be calculated at very high values of α and only a small part of the formation curve can be uncovered. At very high values of α, a slight error in the volume of added titrant solution can give rise to a large error in the pH of the polyacid solution, for the solution pH rises sharply at values of α approaching 1. The scatter of the points on the formation curves for Ca^{2+} complexes of PAA, or EMA, is most probably due to slight errors in measuring small aliquots of the 0.20M NaOH titrant solution. To avoid large changes in the ionic strength of the polyacid solution, only about 5ml of titrant solution have been used to completely neutralise 100ml of the polyacid solution.

Values of log B_{av} cannot be obtained from the formation curves. However, by a short extrapolation, log b_1 values may be estimated, but these values have little precise meaning since it is likely that complexation occurs in overlapping steps with these polyacids.[49] Log b_1 values from the formation curves are:

for PAA $\quad \log b_{1\,PAA}^{Ca^{2+}} \approx -3.35$

for EMA $\quad \log b_{1\,EMA}^{Ca^{2+}} \approx -4.05$

The value of $\log b_{1\,PAA}^{Ca^{2+}}$ is of the same order as that obtained by Gregor,[59] from whose data with 0.06M PAA in 1M KCl a value of

$\log b_{1\,PAA}^{Ca^{2+}} \approx -3.55$ to -3.60 can be estimated. The small discrepancy between the experimentally determined value of $\log b_{1\,PAA}^{Ca^{2+}}$ and the literature value is most probably due to the different neutral salts employed in the PAA solutions. From a detailed study of the effects of neutral salts on the formation of Cu^{2+}-PAA complexes, Gregor[49] has shown that a change of neutral salt from $NaNO_3$ to KCl in the polyacid solution can lead to large differences in the observed stability constant.

The $\log b_1$ values obtained for Ca^{2+} are so widely separated that to a first approximation,

$$\log b_{1\,EMA}^{Ca^{2+}} < \log b_{1\,PAA}^{Ca^{2+}}$$

From the positions and shapes of the formation curves it is probable that,

$$\log B_{av\,EMA}^{Ca^{2+}} < \log B_{av\,PAA}^{Ca^{2+}},$$

although the curves cannot be safely extrapolated to $\bar{n} = 1$ to obtain numerical $\log B_{av}$ values.

3.4.3.3. The binding of Cd^{2+} ions to poly(acrylic acid) and ethylene-maleic acid copolymer.

The binding of Cd^{2+} to PAA and EMA is very strong, much stronger than for Ca^{2+}. Log B_{av} values are readily obtained from the formation curves and are,

for PAA, $\log B_{av\,PAA}^{Cd^{2+}} = -1.95$

for EMA, $\log B_{av\,EMA}^{Cd^{2+}} = -2.30$

With PAA the formation curve of the Cd^{2+} complexes can be drawn up to $\bar{n} = 1$ from titration results at values of α less than 0.63. Consequently the scatter of the points on the graph is small. The points on the formation curve for EMA-Cd^{2+} complexes lie close to a common curve when calculated from titration results at values of α up to 0.90. The point at $-\log \left(\frac{[HA]}{[H^+]}\right) = 2.77$; $\bar{n} = 0.98$, which has been calculated from a titration result at α=0.95, shows the widest deviation from the formation curve, probably as a result of small experimental errors in measuring the titrant solution.

The stability constants obtained show that Cd^{2+} is more strongly bound to PAA than to EMA, which is similar to the trend observed for the binding of Ca^{2+} to these polyacids (see section 3.4.3.2.).

There are no reported log B_{av} values for Cd^{2+}- complexes with PAA and EMA in the literature. However, from preliminary ion binding studies on Cu^{2+}, which also forms strong complexes with PAA, a value of log B_{av}= -1.2 has been obtained for PAA in 1.0M $NaNO_3$. This value agrees closely with a value of between -0.99 and -1.17 obtained by Gregor,[49] which attests the experimental technique used in this work. The slight discrepancy between the experimental and literature values may be due to sample differences or differences in the choice of titrant alkali (which Gregor does not disclose).

3.4.4. The binding of Cd^{2+} ions to poly(ethylenesulphonic acid) in aqueous solution.

With PESA (1.04×10^{-2}M) the titration results for the polyacid with and without added Cd^{2+} ion (2×10^{-3}M) in 0.88M $NaNO_3$ solution, are almost identical (table 3.4.4.1.), even up to α= 0.99. No formation curve can therefore be constructed for this system. It is possible that Gregor's method is unsuitable for PESA, since PESA is a very strong acid and in neutral salt solution is almost completely dissociated.[98] A marked depression in the titration curve of the polyacid in the presence of Cd^{2+} ions, compared to the polyacid alone, would seem unlikely, since pronounced proton displacement could not occur if most of the acid groups are already dissociated, especially if the metal ion is not extremely strongly complexed.

Table 3.4.4.1.

The results from the titration of PESA in $0.88M\ NaNO_3$, in the presence and absence of $2 \times 10^{-3}M\ Cd(NO_3)_2$.

α	pH of solution without added Cd^{2+} $(pH)_1$	pH of solution with added Cd^{2+} $(pH)_2$	$(pH)_1-(pH)_2$
0.00	1.89	1.87	0.02
0.10	1.94	1.91	0.03
0.19	2.00	1.96	0.04
0.29	2.05	2.02	0.03
0.39	2.12	2.09	0.03
0.48	2.20	2.17	0.03
0.58	2.29	2.26	0.03
0.68	2.41	2.38	0.03
0.77	2.57	2.54	0.03
0.87	2.81	2.79	0.02
0.96	3.42	3.42	0.00
0.98	3.82	3.81	0.01

3.4.5. Comparison of the experimentally determined stability constants with the water stability of metal oxide-polyacid cements.

The water stabilities of CaO-PAA and CaO-EMA cements(table 3.2.2.7.) do not parallel the order of magnitude of the stability constants determined for Ca^{2+}-PAA and Ca^{2+}-EMA complexes, i.e.

for water stability, CaO-PAA < CaO-EMA

for stability constants, $\log b_1{}^{Ca^{2+}}_{PAA} > \log b_1{}^{Ca^{2+}}_{EMA}$

The water stability of CaO-PAA cement is much less than CdO-PAA cement and similarly CdO-EMA cement is more stable in water than CaO-EMA cement. These trends for the stability of the cements in water are paralleled by the stability constant data.

Ca^{2+} and Cd^{2+} ions have approximately the same ionic radius (see table 3.2.4.1.) and form complexes free from the effects of ligand field stabilisation energy and Jahn-Teller stabilisation, which are often operative in transition metal complexes. The ionic potentials for Ca^{2+} and Cd^{2+} are roughly equal, consequently Ca^{2+} and Cd^{2+} may be expected to form ionic complexes with similar stability constants. However, $\log b_1^{Ca^{2+}} \ll \log b_1^{Cd^{2+}}$ for PAA and EMA complexes with Ca^{2+} and Cd^{2+} ions and also it is probable that $\log B_{av}^{Ca^{2+}} \ll \log B_{av}^{Cd^{2+}}$, indicating that the bonding in the Cd^{2+} complexes may have some covalent contribution, compared to that in the Ca^{2+} complexes. A higher degree of covalent character in the matrix bonding of the polyacid-CdO cements may explain the fact that the polyacid-CdO cements are more stable towards water than the polyacid-CaO cements.

Davies[108] has plotted stability constants of hydroxo metal complexes against the ionic potential of the metal ions and obtained a linear relationship for alkali and alkaline earth ions, where the

M-O bonding would be expected to be ionic. Transition metal ions, such as Co^{2+}, Ni^{2+}, Cu^{2+} and Zn^{2+} and ions such as Hg^{2+} and Pb^{2+} deviated from this linear relationship. Davies attributed the deviation to covalent character in the bonding and from the extent of the deviation calculated ionic and covalent contributions to the M-O bonds. Applying a similar method to PAA and PMAA, using the stability constants of Gregor[49,59] and Mandel and Leyte,[60] the following orders of increasing covalent character in M-OOC- bonds can be derived by assuming the Mg^{2+} and Ca^{2+} complexes are predominantly ionic:

$$Mg^{2+} = Ca^{2+} < Co^{2+} = Ni^{2+} < Zn^{2+} < Cd^{2+} < Cu^{2+}.$$

However, this order does not parallel precisely the order of the stabilities of the corresponding metal oxide-PAA, or PMAA, cements in water (see table 3.2.2.7.).

Thus, simple interpretation of the water stability of polyacid-metal oxide cements in terms of the degree of covalent contribution to the bonding between the metal ions and polyanions in their matrices, as determined from stability constant data, would appear to be insufficient for this series of ions.

3.4.6. Objections to the use of stability constants determined by Gregor's method.

There are objections to the use of the stability constants determined by Gregor's method for comparison with the properties of metal oxide-polyacid cements in water.

These are:

1. The optimum co-ordination number of the metal ion cannot be found, since complexes with more than two bound ligands cannot be considered.

2. The solutions used are dilute and may not adequately reflect the ion-binding behaviour of metal ions in viscous, highly concentrated polyacid solutions.

3. Neutral salt is added to the polyacid solution before titration, whereas in polyacid-metal oxide cements no neutral salt is added.

The most important objection is the solution concentration. In concentrated polyacid solutions the likelihood of inter-chain binding of metal ions is statistically greater than in dilute solution, where intra-chain chelates may be extensively formed. The extremely high density of ligand groups in highly concentrated polyacid solutions may favour higher co-ordination numbers than in dilute solutions and the co-ordination number may effect the nature and extent of inter-chain binding.

The failure of stability constant data to predict the water stabilities of certain metal oxide-polyacid cements may reflect a difference in the complexing of metal ions in dilute and in concentrated aqueous polyacid solutions.

4. SUGGESTIONS FOR FUTURE WORK.

Although some attempts have been made to elucidate the chemistry involved in the formation of ionomer cements, the subject is still largely speculative and requires further and more extensive studies to be carried out to gain a fuller understanding of these cements.

The usual techniques for studying ion binding are carried out in dilute solution and have limits as model systems. A better model would be the solid complexes of polyacids. The magnetochemistry of these solid complexes may give useful information on the stereochemistry of the metal ion-ligand bonding present in metal oxide-polyacid cements.

With G200 glass-polyacid cements the chemistry is further complicated by the presence of F^- and PO_4^{3-} ions. The influence of F^- and PO_4^{3-} ions on the formation of metal ion-polyanion complexes may be revealed by experiments to determine the stability constants of metal ions with polyacids in dilute solutions in the absence and presence of varying amounts of F^- and PO_4^{3-} ions. This study could be extended by an examination of the properties of metal oxide-polyacid cements containing acid soluble fluorides and phosphates, or salts of other complexing anions.

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