Relationships between polymer additive molecular structure and intumescent flame retardant behaviour.

ANDERTON, Edwyn Christopher Morgan.

RELATIONSHIPS BETWEEN POLYMER-ADDITIVE
MOLECULAR STRUCTURE AND INTUMESCENT
FLAME RETARDANT BEHAVIOUR

by

EDWYN CHRISTOPHER MORGAN ANDERTON BSc(HONS) ALCM

A Thesis submitted to the Council for
National Academic Awards in partial fulfilment
of the requirements for the Degree of Doctor of Philosophy

Sponsoring Establishment : Department of Chemistry
Sheffield City Polytechnic

Collaborating Establishment : Alcan Chemicals Ltd

SEPTEMBER 1990

ABSTRACT

Relationships between Polymer-Additive Molecular Structure and Intumescent Flame Retardant Behaviour

by

Edwyn C. M. Anderton

This thesis describes studies of the relationship between the molecular structure of a range of organophosphorus-based polymer additives and their ability to confer intumescent flame retardant properties on the resulting polymers.

The development of intumescent fire retardants is discussed along with the principles of flame retardancy in general.

Much of the work centred around the chemistry of a key starting material, pentaerythritol phosphate (PEPA). This compound was found to be less reactive than expected, due to a combination of its neopentyl type structure and the electron withdrawing effect of the phosphoric ester functionality.

Various derivatives of PEPA were synthesised, most containing reactive functional groups which facilitated future development of the compound. The derivatives containing no reactive groups were investigated for their intumescent behaviour in their own right.

Derivatives of PEPA containing an acidic functionality were utilised in the production of intumescent salt systems using cations with a high nitrogen content in the form of s-triazines. The most promising was the trimethylolmelamine salt of a bis-PEPA derivative of phosphoric acid, which, on testing, proved to be more effective than the current "state of the art" intumescent additive. Metal salts of acidic PEPA-derivatives were also investigated.

Derivatives of PEPA containing a carbon-carbon double bond were investigated for their potential to polymerise and thus form more stable additives. Only one such polymer was successfully synthesised, that being poly(PEPA methacrylate). Despite being non-intumescent, due to its high thermal stability this polymer has potential as a flame retardant additive. The monomer was found to copolymerise with methyl methacrylate to form a polymer of high thermal stability.

When investigating the relationship between the molecular structure of the compounds developed and their intumescent behaviour, it was observed that only compounds containing an ionisable hydrogen atom exhibited intumescent decomposition on pyrolysis.

TO MY PARENTS

A never-ending source of encouragement and support

ACKNOWLEDGEMENTS

To Alcan Chemicals Ltd I express my gratitude for sponsoring this project. In particular I thank Dr. K. Evans for his decision to allocate company time and money to this research; L. Shiel for his enthusiasm and original ideas that initiated the project; and D. Chaplin for his practical assistance, particularly in testing some of the products.

Thanks are due to members of staff and fellow researchers of the Department of Chemistry for their assistance, also to Pat Rose for typing this thesis.

Many thanks also to my family and friends for their support and encouragement for the duration of the project.

Finally, a special thank you is reserved for my supervisor, Dr. D. W. Allen for his encouragement, guidance and contagious enthusiasm throughout the research programme.

CONTENTS

PAGE

CHAPTER 4 : POLYMERIC FLAME RETARDANTS 220

CHAPTER 1 : INTRODUCTION

1.1 THE DEVELOPMENT OF INTUMESCENT FLAME RETARDANTS

1.2 REFERENCES

1.1 THE DEVELOPMENT OF INTUMESCENT FLAME RETARDANTS

Ever since man harnessed fire for his own use, there has been a risk of that fire becoming out of control and endangering property along with life. In our present age of technology this risk has increased dramatically due to the many man-made polymers, present in everyday life, which are highly flammable. These objects, once alight, not only produce vast amounts of heat in a short space of time, but also generate huge quantities of thick smoke which can disable and kill people before they have chance to escape.[1-3]

There is, therefore, both a commercial and a humanitarian incentive for the production of chemicals which can stop, or at least slow down, the spread of fire.

The chemistry of fire retardants has centred around six elements: phosphorus, antimony, chlorine, bromine, boron and nitrogen.[4] Thousands of compounds of these elements have been synthesised for the purpose of conferring fire retardance on various substrates. Although other elements have been investigated (for example the other group Va elements, sodium silicate,[5] and zinc salts[6]) it has become clear that the above six elements hold the key to effective fire control. Of the six, phosphorus has the most complex and fully developed chemistry. In all its uses, phosphorus is the central element in the compound. Though antimony, in theory, could enter into the same multiplicity of reactions, the chemistry of this element has been little developed by comparison. Nitrogen, again in group V, has a much simpler chemistry due to its electronic structure (there is no possibility of _spd_ hybridisation), and for fire retardance, the number of nitrogen compounds of interest is limited. Boron has a well-developed chemistry, though very little of it has found its way into the field of fire retardancy and despite early uses in this area,[6] has received less and less attention in recent years. In contrast to phosphorus, antimony and nitrogen, the halogens are not found as central atoms in fire retardant compounds. Instead they are substituents primarily on organic compounds.

All organic compounds are potentially combustible and the fireproofing of a polymer does not mean that it will be incombustible. Even flame retardant materials can burn when certain conditions are attained and the basic role of flame retardant additives is to prevent, or at least slow down the onset of combustion by interfering with the combustion process of its substrate. Before the methods of flame retardation are discussed, it is important to understand the combustion process of polymers.[7] In the process of burning a polymer, three major steps may be identified, namely heating, degradation and inflammation.[8]

Heating

The application of a source of heat (flame) results first of all in an increase in the temperature of the polymeric material at a rate which depends on the temperature of the source, the heat flux and the heat capacity of the material. A thermoplastic polymer melts and flows under these conditions, whereas a thermosetting polymer is little changed. When a thermoplastic polymer melts it can flow and drip away from the region of flame before it starts to degrade.

Degradation

When the temperature of a polymer exceeds a certain critical value (peculiar to that polymer), decomposition occurs. This will depend on the chemical structure of the polymer; oxidation processes will often be involved, and monomers, oligomers and other low-molecular weight organic molecules, more or less oxidised, will be involved.

Inflammation

For a fire to occur, three elements must be present, namely fuel (gaseous hydrocarbons), oxygen and heat. This step depends essentially on the composition of the gaseous products of degradation generated by the preceding step, and their rate of formation. When the rate of evolution of volatile products attains a certain value, sufficient for its mixture with oxygen to be flammable, then flame appears. The combustion continues such that there is sufficient energy transferred to the surface, and also to the bulk of the product, to maintain the decomposition and production of the combustible gases. In this way the flame becomes self-fed and propagates itself.

This model of combustion of polymeric materials is valid for the majority of existing polymers.

The actual mechanism of burning hydrocarbon polymers is very complex and cannot be easily generalised. However, most studies carried out in this area have led to the formulation of a radical mechanism which envisages the formation of free radicals in the gaseous phase. Hydrogen and hydroxyl radicals are the most reactive propagating species. For instance, the highly exothermic oxidation of carbon monoxide to carbon dioxide is performed by hydroxyl radicals:[9, 10]

$$OH^{\cdot} + CO \rightarrow CO_2 + H^{\cdot}$$

Oxygen is consumed by radicals in the reaction:

$$H^{\cdot} + O_2 \rightarrow OH^{\cdot} + O^{\cdot}$$

. . .

Another possible mechanism suggested has been the involvement of ionic reactions:[11]

$$CH^{\cdot} + O^{\cdot} \rightarrow CHO^{+} + e^{-}$$

These ionic reactions are not considered to be as important as the radical reactions in the overall combustion process. It has been found that at atmospheric pressure, the molar fraction of positive ions in a flame is of the order of 10^{-7}. Under the same conditions, the molar proportion of radical species is of the order of 10^{-2} to 10^{-4}.

It is clear that to reduce the flammability of polymeric materials, one or more of the aforementioned burning steps must be interfered with. The four basic ways in which this can be achieved are:

<u>Endothermically</u>: components are added to the polymer which, during pyrolytic decomposition, consume sufficient heat to cool the substrate below its ignition point.

<u>Chemically</u>: components are added to the polymer which will react with the polymer during the degradation step and thus slow down the rate of pyrolytic fuel generation or inhibit the exothermic gas phase reactions.

Gas dilution: components are added to the polymer which, on pyrolytic decomposition, generate sufficient quantities of non-flammable gases which dilute the flammable gases produced by the burning polymer to a level below flammability limits.

Addition of protective coat: a non-flammable coating is either applied to the surface of the polymer, or is produced in the presence of a flame, which prevents the normal pyrolytic or combustion mechanisms. This is achieved by the coating insulating the substrate from the heat necessary for fuel production and/or by excluding the fuel gases generated from the inflammation step.

A very simple example of interfering with the combustion process, and thus extinguishing the flame, is that of blowing out a match. This involves cooling of both the substrate and the vapour space whilst simulataneously increasing the volume fraction of air in the combustion zone.

The major mechanism by which both halogens and metal oxides act as flame retardants is by absorbing the free radicals which provide the energy of the flame. As already mentioned, it has been known that various metals, their oxides and respective salts can function as flame retardants. The active radicals in the flame ($OH^\cdot$ and $H^\cdot$ etc) are absorbed at the surface of these particles with part of the collision energy being transferred to the metal oxides, forming radicals which are less reactive than the original radicals.[12, 13]

Halogenated fire retardants operate in a similar way. In the heat of the flame, the halogenated additives give off halogen acids (HX). These acids are well known flame inhibitors and are believed to react with the $H^\cdot$ and $OH^\cdot$ radicals, replacing them with less reactive halogen radicals. Thus the energy of the flame is diminished:

$$H^{\cdot} + HX \rightarrow H_2 + X^{\cdot}$$

$$OH^{\cdot} + HX \rightarrow H_2O + X^{\cdot}$$

The acid is usually regenerated by hydrogen transfer from gaseous hydrocarbons present in the flame:

$$X^{\cdot} + RH \rightarrow R^{\cdot} + HX$$

Again, the $R^{\cdot}$ produced is usually a less active radical than either $H^{\cdot}$ or $OH^{\cdot}$. In general, $H^{\cdot}$ and $OH^{\cdot}$ and the like are the most active species and their removal will be sufficient to snuff out the flame.[15] Evidence of this mechanism has been obtained from kinetic and spectroscopic studies of the concentration of $H^{\cdot}$ in the flame.[14] Of the halogens, only chlorine and bromine are of practical use in flame retardancy. Fluorine binds so tightly to carbon that it does not serve as a radical trap. Fluorinated organics are themselves flame resistant (eg Teflon) but due to their extreme stability they cannot confer this property on substances with which they may be mixed. Iodine compounds are too unstable to be of use as additives. Their instability creates difficulties with other important properties of the substrate such as resistance to UV light etc.

Halogenated fire retardants are most often used in conjunction with metal oxides, one of the most popular being antimony (III) oxide, Sb_2O_3.

Antimony oxide is not effective by itself, but when combined with a halogen compound it becomes a very good retardant. One of the main manufacturers of Sb_2O_3 provides a choice from a selection of halogen compounds to ensure that the one chosen will be stable at the compounding temperatures of the polymer.[16] For example, for use in low density polyethylene they recommend the addition of solid chlorinated paraffin (with a chlorine content of 70%), and for polypropylene, ethylenebisdibromo-norbornane di-carboximide is recommended.

On heating, volatile metal halides can be evolved (eg $SbCl_3$ or $SbBr_3$):

$$Sb_2O_3 + RX \rightarrow SbX_3$$

These antimony halides are then transformed into metal oxides in the flame:

$$SbX_3 + H^{\cdot} \rightarrow SbX_2 + HX$$

$$SbX_2 + H^{\cdot} \rightarrow SbX + HX$$

$$SbX + H^{\cdot} \rightarrow Sb + HX$$

$$Sb + O \rightarrow SbO$$

At these temperatures the oxide is produced as finely divided particles and can catalyse the recombination of radicals:

$$SbO + H^{\cdot} \rightarrow SbOH$$

$$SbOH + H^{\cdot} \rightarrow SbO + H_2$$

Therefore, as can be seen, the SbX_3 generated <u>in situ</u> in the flame acts as a very efficient flame retardant as it is not only a source of SbO, which catalyses the destruction of reactive radicals in the flame, but also generates quantities of HX which, as seen earlier, are also effective radical destroyers.

Despite their effectiveness, all halogenated flame retardants have serious drawbacks. The active compounds extinguish the flame by absorbing radicals whilst in the vapour phase, but it is this vapour phase that is dangerous. In a fire situation, not all the hydrogen halide gases produced have chance to react with radicals before escaping from the vicinity of the flame. Also, some reactions in the flame regenerate these gases, again liberating HX from the flame source. These hydrogen halide gases can damage expensive equipment in the vicinity of the treated products especially when sophisticated or strategically important systems such as computing or telecommunication centres are concerned. In the presence of metals (eg antimony), the metal halides produced increase the formation of obscuring toxic and corrosive smokes. Recently it has been suggested that, on burning, brominated aromatic fire retardants give rise to highly toxic brominated dibenzodioxin and dibenzofurans.[17-21] The final detrimental effect of including halogenated fire retardants in a product is that high loadings have to be used. Over 40% loadings of additives are needed in some cases (eg polypropylene) to achieve effective fire resistance, and this amount of foreign matter in a polymer can seriously affect its performance by drastically altering its physical properties.

Therefore, in recent years, attention has turned away from halogen systems. An area of present development is with alumina trihydrate (ATH), the largest tonnage of which is used in glass reinforced unsaturated polyester for applications including electrical switch boxes, building panels, machine housings and automotive parts. Other polymeric materials in which ATH has become established as a flame retardant additive include PVC, epoxy resins, polyurethanes, certain polyolefins and a wide range of elastomers. It also plays a significant role in the manufacture of flame retardant rugs and carpeting.[22]

ATH has the advantage of not only retarding the spread of fire, but also suppressing smoke evolution.[23] It is safe to handle and is non-toxic when thermally degraded. It acts during the heating and degradation steps of polymer combustion and thus helps to prevent the final step, inflammation. On heating, ATH decomposes to evolve water vapour in a strongly endothermic reaction (absorbing 1.97 kJg^{-1}), thus the heating of the polymer is slowed down and the onset of decomposition is delayed. The water vapour produced also dilutes the concentration of volatile gases produced and hinders access of oxygen to the surface of the polymer thus further suppressing ignition.[24]

Unfortunately, ATH has one major drawback: as found in the case of halogenated flame retardants, the loading needed to impart sufficient flame retardancy on a substrate in order to pass strict fire regulations is very high. In certain polymers, eg poly(methyl methacrylate) this loading can be as high as 65% which is sufficient to make the manufacturers turn towards alternative avenues of protection.

Over the past sixty years, the largest area of research into new flame retardants has centred round the development of intumescent materials.

An intumescent system is defined as a method of fire retardancy where a cohesive foam is formed on ignition which acts as an insulating barrier between the fire and the substrate.

At the present state of technology, there are two distinct techniques of intumescent protection. One is by applying an intumescent coating to the surface of the substrate, the other, a very recent development, is the use of intumescent additives during the preparation of the substrate. Obviously, for many substrates (eg wood, metals, etc) only the former method is possible, whereas the latter is gaining popularity in the field of polymers.

Due to the vast range of intumescent materials produced, a complete summary of the field is impractical. Therefore, the following discussion refers only to those formulations that can be regarded as a significant advance in the current state of technology at the time they were published.

The first recorded studies of intumescence as a fire retarding method were published in 1821.[25] Here, cellulosics were treated with ammonium phosphate and used to prevent the burning of theatre curtains.

The first patent to describe an intumescent coating was published in the 1930's, with diammonium phosphate as the active ingredient in a mixture with dicyandiamide and formaldehyde.[26] This coating was claimed to swell and form a layer of carbon on heating, though the actual word 'intumescent' was not used. It was not until 1948 that the term 'intumescent' appeared in the literature, where a phosphoric or sulphuric acid treated mixture of fatty acid esters and alcohols were admixed with asphaltic materials.[27]

From 1948 to 1950, Jones, Juda and Soll published three patents in which intumescent paint systems, as we know them today, were discussed.[28, 29, 30] These patents contained the first uses of the terms 'carbonifics' and 'spumifics'.

Carbonifics were defined as the compounds that act as a source of carbon for the char, and spumifics as compounds which induce foaming of the char by the evolution of gaseous products which bubble through and thus expand the carbon layer. Their carbonific was a mixture of an aldehyde and urea, the aldehyde being either formaldehyde or paraformaldehyde. They also experimented with non-resinous carbonifics for which they used starch, carbohydrates and proteins. The spumifics used were from a number of compounds which had previously been used as fire retardants, namely mono- and diammonium phosphate, phosphoric acid, etc. It was claimed that the spumific converted the urea/formaldehyde resin to a carbonaceous foam at a temperature of 140°C whilst the non-resinous carbonific yielded a carbon residue at 300°C or above. Additives (such as pigments, fungicides, etc) could be mixed in at low levels without seriously affecting the degree of foam formation. These 'coatings' were difficult to apply and possessed very little water resistance, but they proved to be the first commercial intumescent paints and this technology formed the basis of much future work.

An improvement on this work was claimed in 1951 by the addition of inert filler-pigments such as gypsum, silica, mica, etc. However, no performance data were quoted in the patent though these inert additives probably acted as foam nucleating agents.[31] A further extension of this work claimed the production of a latex paint with the aim of finding a latex that would not be coagulated by the high soluble salt content of the compound (in this case the salt was ammonium orthophosphate).[32]

By 1956, the formulations used for intumescent coatings were resembling those in use today. A typical example of the time used a copolymer of vinyl chloride - vinylidene chloride with pentaerythritol as the carbon source and dicyandiamide as the spumific agent.[33] A similar formula was developed around a new, compatible poly (vinylacetate) latex.[34] Techniques were found to improve plasticisation of the products[35] and to provide other polyols (sorbitol,[36, 37] dextrin[38]), other resins,[36, 37] and blowing agents.[38] Finally, an oil-based coating was built around the same intumescing ingredients with chlorinated rubber in naphtha to make a scrub-resistant system.[39]

It was now clear that one of the essential ingredients in an intumescent system was phosphorus. Most patents were claiming the utility of sulphates, sulphamates, borates, tungstates, etc, but phosphates were always listed as the preferred material. A recent paper has published work showing that the flame retardant properties of an intumescent foam covering a substrate are greatly improved if the foam itself shows a high phosphorus content as opposed to a purely carbonised layer.[40] There are only a few cases in the literature where phosphorus compounds are used in forms other than esters or nitrogen derivatives. In one such case, phosphoric acid itself was used in a two-part coating system.[41] One other has already been mentioned.[28, 29] The chemical reasons for the importance of phosphorus will be explained later.

Boron compounds were investigated, though never in any great depth. An early intumescent paint based on borax and boric acid used a linseed oil-phenolic resin with the boric acid present to reduce after-glow of the coating.[42] (This was the first patent to recommend a water-resistant binder.) By 1956, the art was more sophisticated with intumescence claimed in a patent using zinc borate.[43] Shortly afterwards, borax was claimed to be used as a glass-former[44] (to form a glass-like foam which would protect the substrate at higher temperatures). Later patents, (1965), look like the 'classical' intumescent systems of their time with a mixture of pentaerythritol, boric acid and zinc acetate being used as an intumescent agent.[45, 46]

As the technology had then reached the stage where the outlines of today's formulations were taking shape, the modern theory should now be explained. Recent papers have discussed the detailed mechanisms of thermal decomposition of intumescent ingredients in coatings,[47, 48] but only the basic ideas are summarised here.

As had already been determined, intumescent agents need the inclusion of several key ingredients which are all necessary for the intumescent phenomenon to occur. An intumescent catalyst is needed which will react with a carbonific compound to produce a carbon residue. A spumific compound is also included which will decompose to give large quantities of gas causing the carbonaceous char to expand and foam into a protective layer. In the case of intumescent coatings, a binder is needed which has the added benefit of forming a skin over the foam.

(a) Intumescent catalyst

The main function of an intumescent catalyst is the dehydration of the carbonific compound to a carbonaceous char. This is best achieved using an acid, of which by far the most commonly used is phosphoric acid. However, a free acid included into the product would add to the instability of the system. Therefore, the general method used is to incorporate a thermally unstable non-metallic salt of the acid which will decompose to produce the desired acid in situ when the appropriate temperature is reached under fire conditions. For example, in the case of dihydrogen ammonium phosphate used as the salt, the following reaction occurs:

$$NH_4H_2PO_4 \xrightarrow{heat} NH_3 + H_3PO_4$$

(b) Carbonific compound

This is a polyhydric organic compound which, when reacted with an acid as above, forms a carbonaceous char. It is this char that prevents or retards the flame spread in an intumescent coating. The carbonific compound can be either monomeric or polymeric. To be effective, it must have a high percentage of carbon to give a strong carbonaceous char, but it also needs a high hydroxyl content. The chemical reactions leading to the production of the char are still unclear and subject to debate, though they are obviously very complex. Basically, it is thought that the acid reacts with the carbonific compound to give a phosphorus ester,[49] eg in the case of pentaerythritol:

$$C_5H_8(OH)_4 + H_3PO_4 \rightarrow C_5H_8(OH)_4.H_3PO_4$$

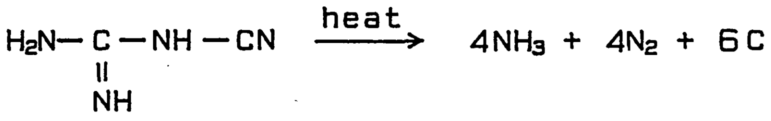
This product, on further heating gives the carbonaceous residue, along with water and regenerates the acid catalyst:

$$2C_5H_8(OH)_4.H_3PO_4 \xrightarrow{heat} 2H_3PO_4 + 8H_2O + 10C$$

(c) Spumific compound

These compounds decompose on heating to liberate large quantities of non-flammable gases such as ammonia, carbon dioxide and nitrogen.

For example, dicyandiamide decomposes on heating:



$$H_2N-\underset{\underset{NH}{\|}}{C}-NH-CN \xrightarrow{\text{heat}} 4NH_3 + 4N_2 + 6C$$

The remaining residue contributes to the carbonaceous char. Until fairly recently, the evolution of hydrogen halides at this stage was considered beneficial as they not only foamed the char, but also helped extinguish the flame itself by radical quenching. However, due to the environmental problems discussed earlier, this is now usually avoided.

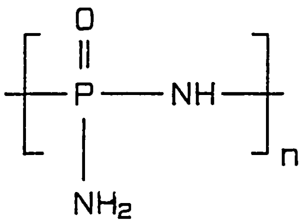
The presence of a compound of each of the above categories does not ensure by itself the intumescent behaviour of the mixture. Intumescence will occur only if the chemical reactions and physical processes involved take place in the necessary sequence as the temperature rises. For example, the carbonific compound must not decompose or volatilise at a lower temperature than that at which the inorganic acid is available for the dehydrating charring process. Also, it is important that the temperature of the spumific corresponds to that temperature at which the foaming carbonaceous char is still in a molten state. If released too late, the char will have been formed and the only effect would be to physically disrupt the char structure, affording no protection to the substrate. More than one spumific may be used so that gases are evolved over a broader temperature range.[48]

With the advances of this understanding, intumescent systems were becoming more effective as their formulations were improved. The main problem with intumescent coatings at this stage (ie the 1950's) was that despite acting as adequate fire retardants, their effectiveness as coatings was disappointing.[50] The intumescent paints were inferior to non fire-retardant paints in many ways which will be detailed later. The biggest problem was the water solubility of some of the coating ingredients. This resulted in their being leached from the coatings, especially in a moist environment, hence incurring a loss of the fire retardancy effect.

In an attempt to improve their fire retardant systems, companies started to move away from the use of the highly water soluble ammonium orthophosphates in favour of phosphorus compounds that possessed reduced water solubility whilst maintaining the other desirable characteristics (ie the ability to decompose on heating to an acidic residue, compatibility with other ingredients and a reasonable cost per unit of phosphorus).

An early patent to explore this field was from Japan in 1952. Here, the essential ingredients of the paint were $NH_2(CH_2)_6NH_2.H_3PO_4$ with sucrose and aminoplast resin.[51]

Also in 1952 appeared the first in a series of patents in which polyphosphorylamide was used[52-56] ie:

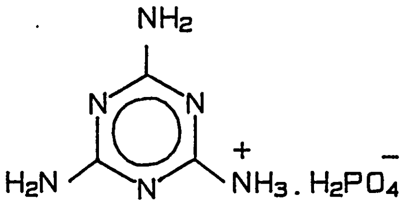


The monomer was developed in a reaction between ammonia and phosphoryl chloride. After polymerisation, this material was found to be relatively water insoluble. Various formulations were developed which were claimed to be tough, adherent and weather resistant. Unfortunately, despite the promising start and subsequent improvements,[57-59] formulations containing polyphosphorylamide were never commercialised because of process difficulties and economic problems.

In a formulation similar to that mentioned above, a different water insoluble compound was used, namely the reaction product between ammonia and P_4O_{10}.[60] This was the first time that fibrous materials such as cotton, asbestos or wool flock were suggested to hold the intumescent mat together. Later, (in 1966), this principle was extended using rubber coated glass fibres.[61]

Nearly all the literature concerning intumescent materials at this time is confined to patents because the commercial reward for producing a successful flame retardant was sufficient to keep most original ideas out of the standard literature until they were well covered by patents. A good example is of a paper published on the use of urea-formaldehyde, starch and diammonium phosphate systems,[62] with all commercial aspects of the idea already covered by one of the patents mentioned previously.[51]

In 1953 a patent was published in which melamine was used for the first time in an intumescent formulation.[63] The claim was for the water insoluble reaction products of aminoplast resins and a non-oxidising acid such as melamine phosphate:



This type of material does not burn at temperatures as high as 750°C, but degrades to give carbon residues and phosphoric acid. Although melamine phosphate forms gel-like structures in water and is therefore useless in aqueous formulations, it found great use in solvent based systems and was still being used commercially in the 1970's.

Over the next few years no major breakthroughs were reported. The use of neoprene rubber binders was investigated,[64] the first mention of using less soluble guanylurea phosphate appeared,[65] and acidic zinc phosphates and borates were claimed to be useful.[66] The guanylurea phosphate provided a period of optimism as it was less soluble than the ammonium orthophosphates. However, it was still found to be sufficiently water soluble to be of no commercial use.

In 1954 it was recognised that the size of the pores or cells within the intumescent foams was important and claims were made of varying mixtures of china clay and zinc oxide (previously used as pigments for the paints) having a marked effect on the cell structure.[67] This area, despite being acknowledged as important, saw very little investigation and has only just reappeared in the literature over the past couple of years.

The year 1956 provided an interesting patent in which the basic ingredients of previous patents[28-30] were boosted with isano oil/polyamide resins as well as zinc borate as mentioned earlier.[43] The intumescent paints thus produced were resinous in character, did not deteriorate appreciably even on treatment with hot water and were satisfactory even at low loadings (it is the high loadings that are the major contributor to poor coating properties). This is another example of what initially appeared to be a major breakthrough ending without commercial use. The reason for this failure is not clear, though there is some evidence to doubt the insulative effectiveness of the char with large bubbles rather than micro-cellular foam being produced.[68]

Due to the lack of success in producing a highly intumescent water-insoluble formula, attention was turned, by one party, in patents already mentioned, to the lattices which bound the active ingredients.[32, 33] On examination of a range of chlorinated polymers, a vinylchloride/vinyldiene chloride copolymer was found to be best. Much later (in 1963) this area was re-opened with a patent claiming the use of a unique polyvinyl acetate emulsion.[69]

An attempt to rationalise the components of an intumescent paint and so define the percentage of the catalyst, spumific and carbonific needed for optimum intumescence was made.[70] However, the limits were found to be very broad. The study did show that the resinous binders used, despite being essential for good paint properties, were seriously affecting the degree of intumescence. This led to the suggestion of using halogenated resins with a claim that if the halogen content was high enough in the resin, the phosphorous source could be eliminated. However, the formulations quoted still contained over ten per cent phosphate.[71] Two more patents published around this time made revolutionary claims which turned out to be untrue. First was a claim that both acidic and basic metal phosphates were suitable for use in intumescent systems,[72] and the second was the use of non-acid releasing phosphates.[45]

Starting in 1964, a series of four papers were published by workers at the Southern Regional Research Laboratory of the US Department of Agriculture.[73-76] They described a series of oil-based intumescent coatings containing melamine phosphate and halogenated phosphate esters as the sources of acidic dehydrating agents. A large number of paint formulations were presented, each making use of pentaerythritol (as a urethane derivative) as the polyol and primary carbon source in the charring reaction with a chlorocarbon as the primary source of the blowing gas. All the formulations were comparable and none was outstanding. Their work achieved good coatings but fell just short of the mark in the ever stricter Government safety tests. There are commercial coatings on the market today, based on melamine phosphate, that are offsprings of these formulations.[77]

At about this time, a patent was published which although did not advance the technology of the art of intumescence, deserves a mention as it suggested a novel means of applying a uniform coating of predetermined thickness by using a tape of adhesive material.[61] The implications of this idea will be discussed later.

The last major field explored around the 1960's was that using ammonium polyphosphate. This material has reduced water solubility compared with ammonium orthophosphate and has been formulated into some very water resistant, water-based and oil-based paints. The ingredients of the paints were chosen in an attempt to reduce water solubility and therefore improve water and scrub resistance. Dicyandiamide was replaced by melamine, and pentaerythritol replaced by its dimer or trimer. Various other ingredients were used and their effect on performance compared, the basic conclusions being that as melamine phosphate formed a gel in water, it was not suitable for water-based paints and formulations containing monammonium phosphate did not generally resist water. Similar formulations were tried using oil-based paints but were found to be unsuitable.[68] However, ammonium polyphosphate formulations caught on, with another comparison study published[78], followed by a new concept which used latex formulations for coating both wood and steel.[79] Ammonium polyphosphate had a greater success than the other catalysts that had been developed, producing two patents that provided commercially successful products.[80, 81]

There was continued research into the area of intumescent coatings and indeed, is still going on today. The field, however, never achieved the promise it showed in the early stages. There have been some recent minor successes[82-85] but the field produced far too many new formulations, mostly commercially unsuccessful, to mention here. The main commercial uses of intumescent paints are not in the bulk protection of substrates by coating as was first envisaged, but in the prevention of the spread of fire by hindering air passage to the flame. For example, they are used as adhesive strips round fire doors whereby the intumescent action seals a gap between the door and the frame in the event of a fire.[50] In the same manner, a ventilation duct incorporating a grid coated with intumescent paint can be blocked in the event of a fire.[86] Honeycombs coated with an intumescent paint can also provide a solid barrier to combat the spread of fire.

Despite these uses and the vast amount of time and money spent on the development of intumescent coatings, they still suffer from several disadvantages. The principal commercial disadvantage is their high cost, but there are also technological disadvantages which fall into five basic categories.

1 The problem which has instigated the main area of research is that of weatherability. Most of the components traditionally used in intumescent formulations are somewhat soluble in water. This is the case with most polyhydric alcohols, amines and amides which have polar groups capable of forming hydrogen bonds to water.

2 The physical and mechanical properties of an intumescent paint are far inferior to those of a non fire resistant paint. Such properties include brushability, being aesthetically pleasing and being available in a wide range of colours. The cause of the problem lies with the fact that, inevitably, the paints contain very high loadings of intumescent components and, unfortunately, these compounds are not compatible with the properties needed for a well-formulated paint. The end result is often a relatively thick, rough, uneven and unattractive coating with a tendency to peel. Peeling is not only aesthetically unappealing, but also provides an unprotected area of substrate and hence a potentially flammable area.

3 Paints, by nature, provide only a very thin coating over the substrate. Therefore the amounts of intumescent materials over a specific area are limited so that on foaming, the density of the char is sufficient to protect the substrate only for a few minutes. Once the char layer is removed, unprotected substrate remains with no means of further fire resistance.

4 Following from point 3, the intumescent materials are consumed by the fire, are non-returnable and hence sacrificial. In the breakdown of the chemicals, noxious gases are often evolved including ammonia, hydrogen cyanide and until recently, hydrogen halides. As already discussed, these gases are obviously undesirable.

5 When applying a paint by brush, roller, etc, it is difficult to achieve a uniform specified thickness. When using a rough

intumescent paint with poor brushing qualities, this problem is compounded. Unfortunately, many insurance companies and fire regulations necessitate an accurate application of a coating to a standard thickness in order to comply with regulations.[87]

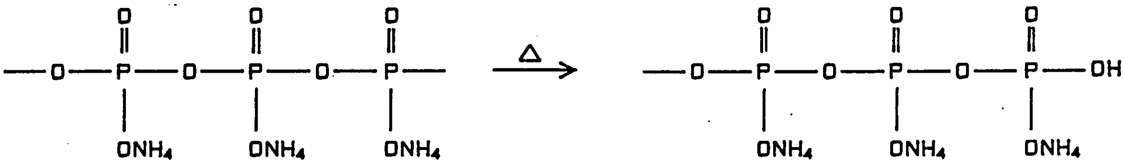
In 1972 came the first of two major breakthroughs which revolutionised the art of intumescent fire protection. A patent was published which claimed the possibility of an intumescent fire retardant additive, ie the intumescent formulation was added to the polymer mix before curing and was therefore incorporated inside the polymer matrix rather than merely being on the surface.[88] This and another patent that closely followed,[89] produced fire retarded polypropylene by the addition of typical intumescent mixtures of dipentaerythritol with either ammonium polyphosphate or melamine phosphate. This practice was never a success due to the unstability of the additives at polypropylene's processing temperature. It has been found, within the last couple of years, that this mixture actually affects the photo-oxidative behaviour of polypropylene as it protonates the photostabilizing additive and thus reduces its efficiency.[96]

However, it was not long before a suitable intumescent additive for polypropylene was available.[90-93] This involved heating P_2O_5 with dipentaerythritol and melamine to produce a light tan powder, the chemical structure of which was never properly characterised and was merely referred to as IFR (the initials of Intumescent Fire Retardant). This additive needed to be present in high loadings (30% by weight in the polymer mix), and reports showed that there were adverse interactions between the fire retardant additive and other additives present in polymeric materials.[94] For instance, the effectiveness of the intumescent reagent is significantly lowered in the presence of as little as one per cent of pigments such as carbon black or phthalocyanine green. Another drawback was the undesirable colour formation produced at the polymer's processing temperature. This was overcome to some extent by the addition of a colour stabilising compound such as a metal hypophosphite, but the problem was never satisfactorily solved.[95] The IFR was also much less effective when used in other polymers (such as polyethylene or polystyrene), probably due to improper matching of thermal behaviour of the additive with the temperature of degradation of the polymer.

A German patent of this time described metal salts (mainly zinc, magnesium and iron) of phosphonosuccinic acids.[97] These were used in conjunction with melamine and described as being both intumescent and active smoke suppressants. However, nothing more has been heard from this area.

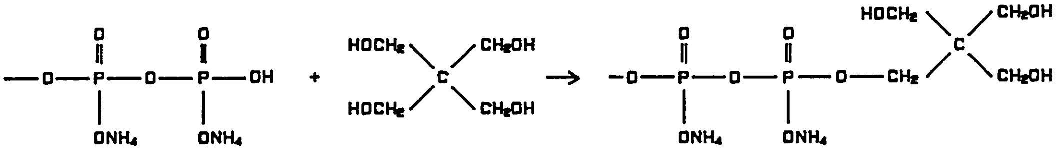
The next successful intumescent additives were again produced in Germany at the end of the 1970's.[98-100] Mixtures of ammonium polyphosphate and nitrogen containing compounds such as products of the condensation of formaldehyde with substituted ureas, or products of reaction between aromatic diisocyanate and pentaerythritol or melamine were used as intumescent additives for polymeric materials, in particular polyolefins and polystyrenes.

Following these and other publications, a study was undertaken of the chemical reactions that occur on heating typical intumescent mixtures of ammonium polyphosphate and pentaerythritol.[101-104] This showed that there were several steps of degradation. The first step (at about 210°C) involves the breakdown of the polyphosphate chain, Scheme 1:



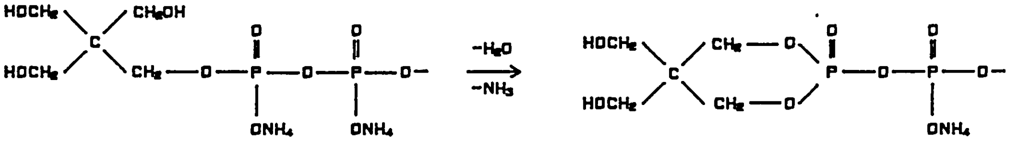
Scheme 1

This is followed by the formation of phosphate ester bonds with the pentaerythritol, Scheme 2:



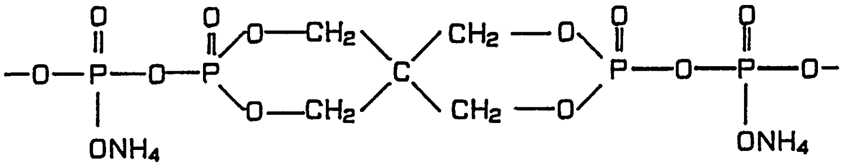
Scheme 2

This then forms a cyclic phosphate ester with the elimination of water and ammonia, Scheme 3:



Scheme 3

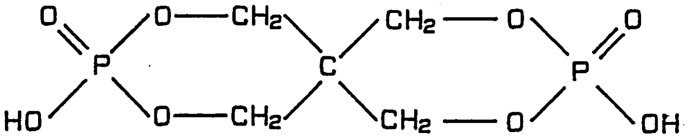
The regular occurrence of this sequence of reactions leads to pentaerythritol diphosphate structures identified in the product of the reaction:



The final structure of the product obtained on heating pentaerythritol and ammonium polyphosphate mixtures depends on the original molar ratio of $-CH_2-OH$ groups to phosphorus. For example, if this ratio is greater than two, then cross-linked structures and ether bonds can be formed.

When the product of the reaction between pentaerythritol and ammonium polyphosphate is heated above 300°C, it undergoes thermal degradation with charring accompanied by significant swelling.

In order to study this process, pentaerythritol diphosphate, compound (1), was used as a model compound.[48]



(1)

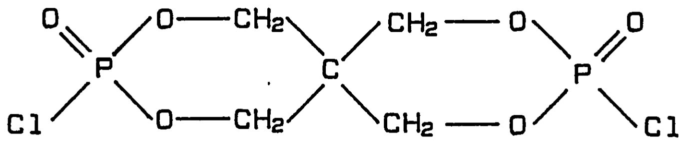
The basic findings of this study were that pentaerythritol phosphate undergoes several thermal degradation steps on heating above 280°C. Intumescence occurs between 300 and 350°C when the P-O-C ester bonds undergo thermal scission to produce a voluminous char which is impregnated by polyphosphoric acids.

Therefore it was concluded that the foaming must be occurring over a relatively narrow temperature range by the action of a limited fraction of the overall volatile products of degradation of pentaerythritol-ammonium polyphosphate mixtures. Any blowing agent added to such a mixture would need to supply gaseous products within the range 300-350°C if it were to increase foaming. It was discovered that urea, which was a common spumific agent used in intumescent coatings, actually decreased the intumescence and fire retardance of ammonium polyphosphate-pentaerythritol mixtures added to polypropylene.[105] This is because urea decomposes to release gaseous products between 150 and 300°C.

Work continued in the field of intumescent additives, but despite various patents being published, none produced a successful commercial product.[106-112] The main reason for failure was invariably the lack of thermal stability of the additive.

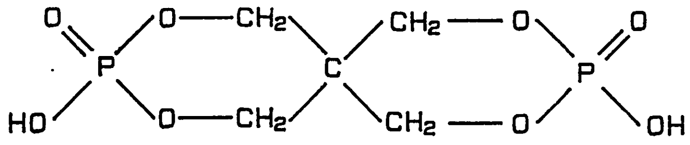
Most of the reported additives were either mixtures of, or undefined reaction products of, the three essential ingredients mentioned earlier, namely, an acid catalyst source, a carbonific and a spumific. The second major breakthrough came when Halpern et al synthesised a single molecule containing various functionalities which could act as all three vital ingredients simultaneously. When used separately, three independent ingredients have to react together to originate the intumescence phenomenon. When included in a polymer matrix, the compounds are effectively diluted and hence chemical interaction will be of low efficiency. When only one compound is involved, this problem is overcome. Halpern aimed to incorporate the three required structures in the form of phosphoric acid, pentaerythritol and melamine into one molecule. He took as his starting point the pentaerythritol diphosphate structure (1) used as a model in the thermal degradation studies discussed above. Derivatives of this diphosphate had previously been used as flame retardant additives in a range of polymers, but the active ingredients were halogens and the type of flame retardance described had no relevance in the field of intumescence.[113, 114]

Halpern studied the reaction of pentaerythritol with phosphorus oxychloride to produce the spiro compound: 3,9-bis(chloro)-2,4,8,10-tetraoxa-3,9-diphosphaspiro[5.5]-undecane-3,9-dioxide (2).[115]



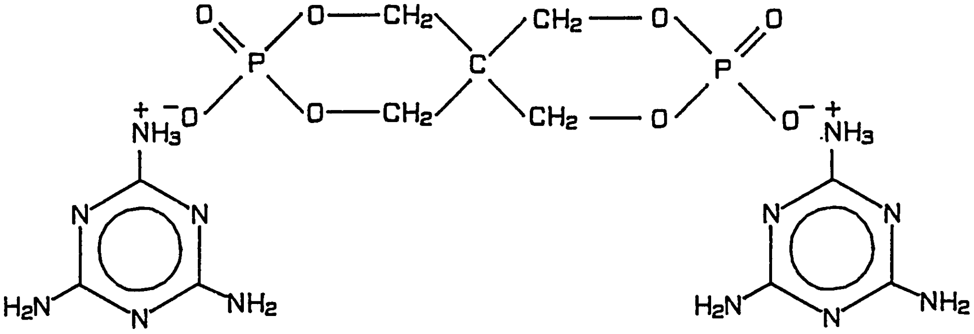
(2)

This undergoes simple hydrolysis to replace the two chlorine atoms with hydroxy groups to produce compound (1).



(1)

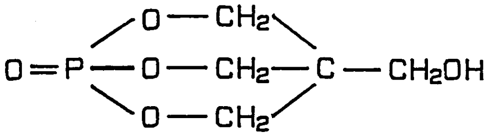
The pentaerythritol diphosphate (1) was then treated with two moles of melamine to produce the dimelamine salt (3).[116, 117]



(3)

Compound (3) was found to be an efficient fire retardant for polypropylene[118] and other polyolefins.[119] However, it was shown that for polypropylene, the efficiency of (3) was increased if it was used in conjunction with tripentaerythritol.[120] This showed that in compound (3), the optimum balance between carbonific, acid source and spumific units was not achieved with the compound needing more of the carbonific unit relative to the other two.

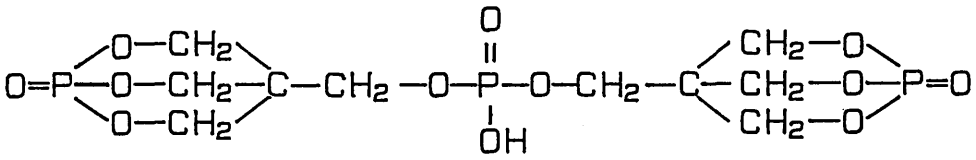
In an attempt to improve the char forming/blowing ratio, a new compound was synthesised. Again, pentaerythritol was treated with phosphorus oxychloride, but this time under different conditions with a different stoichiometry and produced pentaerythritol phosphate (4).[121]



(4)

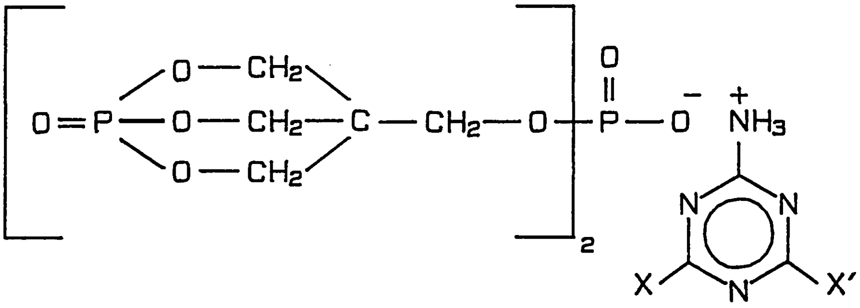
This compound had already been noted as a potential flame retardant additive, the history of which will be detailed in Chapter 2.

Pentaerythritol phosphate (PEPA) was then treated with more phosphorus oxychloride to produce a mixture of the acid, bis(4-hydroxymethyl-2,6,7-trioxa-1-phosphabicyclo[2.2.2]octane-1-oxide) phosphate, (5), and the corresponding acid chloride.



(5)

This in turn was reacted with various s-triazines, including melamine, to produce s-triazine salts:



In the patents covering this invention, X and X′ were described as the same or different hydroxy or amine groups.[122, 123] However, work was concentrated on the most promising system which used melamine ($X = X' = NH_2$). This salt provides ideal properties for use as a flame retardant. It is a white, free flowing powder which is only slightly soluble in water and insoluble in most organic solvents. It is highly thermally stable and processes into polypropylene without decomposition. When subjected to an open fire, it intumesces to form a voluminous, thermally insulating char.[124]

These compounds, despite being patented five and a half years ago, are still regarded as the state of the art in the field of intumescent additives for polymers and are the standards by which new materials are judged.

Despite the great potential of intumescent additives, their incorporation in polymeric materials poses specific problems, different from those of coatings. First of all, the degradation of the polymer must not interfere with the processes leading to the intumescence of the additives. Also, the additive must be thermally stable at the processing temperature of the polymer. And finally, the additive must be able to develop the protective char over the entire surface of the burning polymer, despite being diluted within the polymer instead of being concentrated at the surface as in coatings. As in the case with coatings, a low water solubility of the additives is necessary to avoid the additives leaching from the polymeric material.

Over the past couple of years, some efforts have concentrated on a new field of flame retardant additives. These additives are polymeric themselves which provides them with increased stability. Though they possess no intumescent properties, these polymeric additives are proving to be very efficient in retarding the burning of polymers. These systems will be discussed fully in Chapter 4.

Research into other areas of flame retardancy still persists, with halogenated systems still attracting attention despite their toxicity risks. For instance, the flammability of polypropylene is claimed to be greatly reduced on the addition of a twenty per cent loading of tertiary phosphine oxides containing halogenated phenoxy groups, whilst the mechanical properties of the polymer are not adversely affected.[125] Halogenated systems also seem to be of interest in China where current work is investigating the flame retardancy effect of brominated phenolphthalein on epoxy resins.[126]

As previously mentioned, the structures and properties of the chars formed during intumescent decomposition have received very little attention. Apart from the paper mentioned, published in 1954,[67] and a paper from the early 1970's describing the amount of heat energy various chars were capable of absorbing,[127] no work was published in this area until 1989 when two papers were published from Italy.[128, 129] The first of these investigated the possibility of examining char structures using electron-microscopy and microanalysis. The second related the effects of a range of inorganic fillers to the structure of the char. It was observed that the presence of inorganic fillers altered the appearance of the outer surface of the char. The smooth surface obtained in the absence of fillers became rugged due to the formation of agglomerates in the presence of fillers (eg CaO and TiO_2). Also, cracks were visible.

The aim of the work described in this thesis relates the molecular structure of a range of organophosphorus-based polymer additives to their ability to confer intumescent flame retardant properties on the resulting polymers. Both monomeric and polymeric additives have been investigated. The chemistry of the key starting material, pentaerythritol phosphate, (4), has been developed because a better understanding of its reactivity will facilitate the ability to use the compound in the manufacture of flame retardants.

1.2 REFERENCES

1 J. Kracklaur in 'Flame-Retardant Polymeric Materials', vol 2, Ed M. Lewin, S. M. Atlas and E. M. Pearce, Plenum Press, New York, 1978, p 285.

2 Benjamin/Clarke Associates, 'Fire Deaths', Technomic, Lancaster, 1984.

3 H. L. Kaplan, A. F. Grand and G. Hartzell in 'Combustion Toxicology', Technomic, Lancaster, 1983.

4 J. W. Lyons in 'The Chemistry and Uses of Fire Retardants', Chapter 2, Wiley Interscience, New York, 1970.

5 G. Black and H. Saunders, Product. Eng., 1948, 8, 140.

6 M. Westgate in 'Fire Retardant Paints, Advances in Chemistry', Series no 9, American Chemical Soc., Washington DC, 1954.

7 S. J. Burge and C. F. H. Tipper, Combustion and Flame, 1969, 13, 495.

8 J. Brossas, Polymer Deg. and Stab., 1989, 23, 313.

9 C. P. Fenimore and G. W. Jones, Combustion and Flame, 1966,10, 295.

10 C. P. Fenimore and G. W. Jones, J. Phys. Chem., 1959, 63, 1834.

11 W. C. Kuryla and A. J. Papa, Flame Retardancy of Polymeric Materials, 1978, 4, 12.

12 J. E. Dolan in '6th International Symposium on Combustion', Academic Press, London, 1957, p 787.

13 H. Wise and W. A. Rosser in '9th International Symposium on Combustion', Academic Press, London, 1963, p 733.

14 J. Hastie, J. Res. Nat. Bureau of Standards, 1973, 77A, 733.

15 G. Camio and L. Costa, Polymer Deg. and Stab., 1988, 20, 271.

16 Cookson Ceramics and Antimony Ltd, Technical Memorandum no 4.

17 P. W. O'Keefe, Environmental Health Perspectives, 1978, 23, 347.

18 H. R. Buser, Environmental Science Technology, 1986, 20, 404.

19 H. R. Buser, H. P. Bosshardt and C. Ruppe, Chemosphere, 1978, 7, 109.

20 H. Thoma, S. Rist and O. Hutziner, Chemosphere, 1986, 15, 649.

21 H. Thoma, S. Rist and O. Hutziner, Chemosphere, 1987, 16, 277.

22 B. A. Chemicals Ltd, advertising brochure, publication no M300, 3K, August 1989.

23 E. M. Pearce, Pure and Applied Chemistry, 1986, 58, 925.

24 W. C. Kuryla and A. J. Papa, Flame Retardancy of Polymeric Materials, 1978, 4, 42.

25 J. Gay-Lussac, Ann. Chim (Paris), 1821, 18, 211.

26 H. Tramm, C. Clar, P. Kühnel and W. Schuff, US Patent 2,106,938.

27 J. Olsen and C. Bechle, US Patent 2,442,706.

28 G. Jones, W. Juda and S. Soll, US Patent 2,452,054.

29 G. Jones, W. Juda and S. Soll, US Patent 2,452,055.

30 G. Jones, W. Juda and S. Soll, US Patent 2,523,626.

31 H. A. Scholz and E. E. Saville, US Patent 2,566,964.

32 E. K. Stilbert, I. J. Cummings and W. Guerrant, US Patent 2,684,953.

33 E. K. Stilbert, I. J. Cummings and W. Guerrant, US Patent 2,755,260.

34 A. G. Hoechst, British Patent 874,762.

35 N. K. Peterson and I. J. Cummings, US Patent 2,917,476.

36 H. Sano, Japanese Patent 5278.

37 R. Fenner and R. Thompson, British Patent 978,623.

38 H. Gollbert and H. Kleinert, East German Patent 40,957.

39 P. Simon, US Patent 3,021,293.

40 K. M. Gibov, L. N. Shapovalova and B. A. Zhubanov, Fire and Materials, 1986, 10, 133.

41 L. Bercovici, Belgian Patent 669,341.

42 E. A. Lauring, US Patent 2,594,937.

43 A. O. Allen, T. Murray and F. P. Liberti, US Patent 2,754,217.

44 D. G. Stevenson and P. Walker, British Patent 968,336.

45 J. H. Basto, M. M. Capp, C. R. Davison and G. H. Garbaden, US Patent 3,037,951.

46 R. P. Silver, US Patent 3,221,035.

47 G. Camino and L. Costa, Polymer Deg. and Stab., 1988, 20, 271.

48 G. Camino and L. Costa, Rev. Inorg. Chem., 1986, 8, 69.

49 W. C. Kuryla and A. J. Papa, Flame Retardancy of Polymeric Materials, 1978, 4, 93.

50 M. Kay, A. Price and I. Lavery, J. Fire Retard. Chem., 1979, 6, 69.

51 T. Sakuri and T. Izumi, Japanese Patent 1,786.

52 M. L. Nielson, US Patent 2,596,937.

53 M. L. Nielson, R. W. Arnold and E. C. Chapin, US Patent 2,596,938.

54 M. L. Nielson and P. E. Marling, US Patent 2,596,939.

55 M. L. Nielson, US Patent 2,642,405.

56 M. L. Nielson and R. W. Arnold, US Patent 2,680,077.

57 R. Marotta, US Patent 2,676,162.

58 N. K. Peterson and I. J. Cummings, US Patent 2,917,476.

59 J. M. Venable, US Patent 2,956,037.

60 I. V. Wilson and R. Marotta, US Patent 2,600,455.

61 B. B. Kaplan, US Patent 3,284,216.

62 T. Sakurai and T. Izumi, J. Chem. Soc. Japan Indust. Section, 1953, 56, 156.

63 W. Juda and G. Jones, US Patent 2,628,946.

64 R. P. Stock, US Patent 2,650,206.

65 A. E. Gilchirst, US Patent 2,722,523.

66 G. L. Cunningham, US Patent 2,679,489.

67 A. J. Christianson, US Patent 2,681,326.

68 H. L. Vandersall, J. Fire and Flammability, 1971, 2, 97.

69 J. Schwartz and R. Pierrehumbert, American Paint J., 1963, July.

70 I. J. Cummings, Ind. and Eng. Chem., 1954, 46, 1985.

71 B. B. Kaplan, US Patent 2,984,640.

72 Lucius and Bruning, British Patent 874,762.

73 G. B. Verburg, E. T. Rayner, D. A. Yeadon, L. L. Hopper, L. A. Goldblatt, F. G. Dollear and H. P. Dupuy, J. Am. Oil Chem. Soc., 1964, 41, 670.

74 D. A. Yeadon, E. T. Rayner, G. B. Verburg, L. L. Hopper, H. P. Dupuy and H. Miller, Official Digest, 1965, 37, 1095.

75 G. B. Verburg, D. A. Yeadon, E. T. Rayner, F. G. Dollear, H. P. Dupuy, L. L. Hopper and E. York, J. Paint Technol., 1966, 38, 407.

76 E. T. Rayner, D. A. Yeadon, G. B. Verburg, F. G. Dollear, H. P. Dupuy, L. L. Hopper and H. Miller, J. Paint Technol., 1966, 38, 105.

77 D. A. Yeadon and E. T. Rayner, US Patent 3,396,129.

78 C. A. Meyer, Am. Paint J., 1968, September.

79 F. Liberti and R. Pierrehumbert, Am. Paint J., 1968, September.

80 P. G. Sears and H. L. Vandersall, Canadian Patent 822,594.

81 F. J. Hahn and H. L. Vandersall, US Patent 3,513,114.

82 G. Hamori, Hungarian Patent 176,775.

83 R. P. Mathis and J. S. Dix, US Patent 3,810,862.

84 R. D. Pratt, P. F. Proffitt and G. Webb, German Patent 2,606,139.

85 Y. Koida, Japanese Patent 76,106,152.

86 Anon., Heat Vent. Engrs. J. Air Condit., 1971, 44, 361.

87 A. Hall, Mod. Plastic Internat., 1972, 2, 30.

88 H. K. Wren, US Patent 3,633,463.

89 R. D. Mathis and J. S. Dix, US Patent 3,810,862.

90 D. G. Brady, US Patent 3,936,416.

91 D. G. Brady, US Patent 4,010,137.

92 R. A. Gray, US Patent 3,936,420.

93 H. C. Walters, US Patent 4,155,900.

94 D. G. Brady, J. Fire Retard. Chem., 1977, 4, 150.

95 C. W. Moberly, US Patent 4,328,132.

96 G. Camino, R. Arnaud, L. Costa and J. Lemaire, Die Ang. Mak. Chem., 1988, 160, 203.

97 H. Heine, German Patent 1,601,884.

98 G. Bertelli, P. Roma and R. Locatelli, German Patent 2,723,877.

99 G. Bertelli, P. Roma and R. Locatelli, German Patent 2,800,891.

100 F. Maruanoli, German Patent 2,839,710.

101 G. Camino, L. Costa and L. Trossarelli, Polymer Deg. and Stab., 1984, 6, 243.

102 G. Camino, L. Costa and L. Trossarelli, Polymer Deg. and Stab., 1984, 8, 13.

103 G. Camino, L. Costa and L. Trossarelli, Polymer Deg. and Stab., 1985, 12, 203.

104 G. Camino, L. Costa and L. Trossarelli, Polymer Deg. and Stab., 1985, 12, 213.

105 G. Camino, L. Costa and L. Trossarelli, Polymer Deg. and Stab., 1984, 7, 221.

106 T. Goulding, US Patent 4,195,139.

107 H. W. Bost and T. A. Yokley, US Patent 4,216,138.

108 H. W. Bost and E. A. Zeuch, US Patent 4,140,856.

109 H. W. Bost, US Patent 4,026,810.

110 H. W. Bost, US Patent 4,072,643.

111 H. W. Bost, US Patent 4,115,349.

112 H. W. Bost, US Patent 4,043,975.

113 J. A. Albright, US Patent 3,997,505.

114 J. A. Albright, US Patent 3,978,167.

115 R. Ratz and O. J. Sweeting, J. Org. Chem., 1963, 28, 1608.

116 Y. Halpern and I. Stokie, US Patent 4,154,930.

117 Y. Halpern, D. M. Mott and R. H. Niswander, Ind. Eng. Chem. Prod. Res. Rev., 1983, 23, 232.

118 Y. Halpern, German Patent 2,910,746.

119 C. T. Fleenor, US Patent 4,253,972.

120 Y. Halpern, US Patent 4,201,705.

121 Y. Halpern, US Patent 4,454,064.

122 Y. Halpern, D. M. Mott and D. Plaines, US Patent 4,478,998.

123 Y. Halpern, D. M. Mott and D. Plaines, US Patent 4,480,093.

124 Y. Halpern, D. M. Mott and R. Niswander, Eur Patent 01,26,491.

125 S. Varbanov, N. Peeva, S. Stoeva, E. Nedkov and G. Borisov, Eur. Polymer J., 1988, 24, 151.

126 C. P. Yang and T. M. Lee, J. of App. Polymer Science, 1987, 34, 2733.

127 J. A. Ellard, Am. Chem. Soc. Div. Org. Coatings and Plastics, 1973, 33, 531.

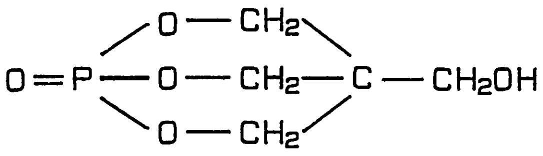
128 G. Bertelli, E. Marchetti, G. Camino, L. Costa and R. Locatelli, Die Ang. Mak. Chem., 1989, 169, 137.

129 G. Bertelli, E. Marchetti, G. Camino, L. Costa and R. Locatelli, Die Ang. Mak. Chem., 1989, 172, 153.

CHAPTER 2 : DEVELOPMENT OF THE CHEMISTRY OF PENTAERYTHRITOL PHOSPHATE (PEPA)

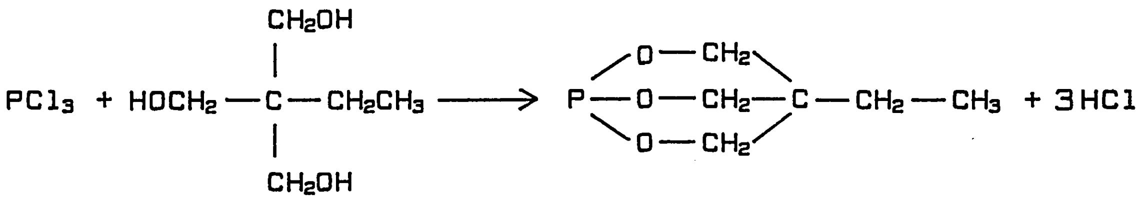
2.1 INTRODUCTION

The main intermediate in the majority of the flame retardant additives synthesised in the work described in this thesis has been pentaerythritol phosphate, (PEPA). PEPA is a white solid melting at approximately 207°C. It is characterised by the structure (1):



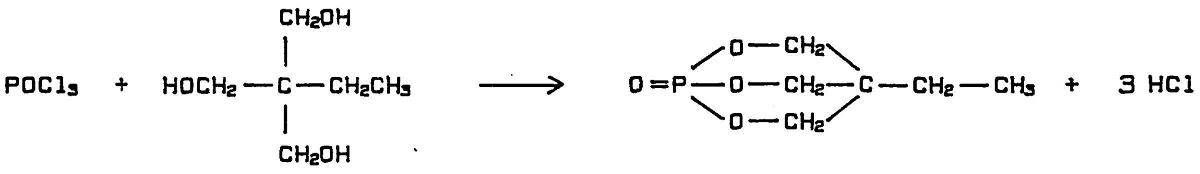
(1)

Until 1964, the standard method for preparing bicyclic phosphates was by oxidation of the corresponding phosphite. A patent published in 1964 described the synthesis of the 4-ethyl-substituted bicyclic phosphate (3).[1] This was prepared by oxidation of the related ethyl-substituted bicyclic phosphite, (2), using hydrogen peroxide. The bicyclic phosphite was prepared by the reaction between trimethylolpropane and phosphorus trichloride:



(2)

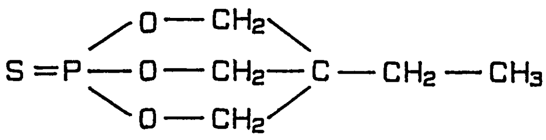
This method was accompanied by another route in which the bicyclic phosphate was prepared directly from trimethylolpropane by using phosphorus oxychloride:



(3)

A year later another patent was published which described the same reactions but with an increased yield by the use of a substantial quantity of pyridine as a hydrogen chloride acceptor.[2]

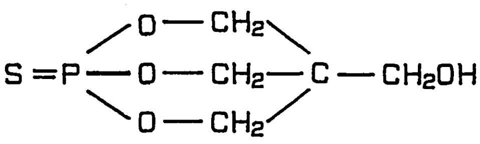
That year saw the publication of another patent which described the reaction of trimethylol propane with thiophosphoryl chloride to produce the trimethylolpropane thiophosphate (4):[3]



(4)

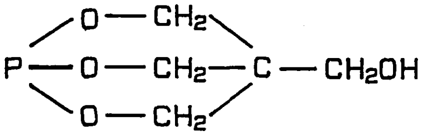
This, and compounds where the ethyl group was replaced by methyl and propyl groups, were prepared and claimed as effective herbicides.

The sulphur derivative of PEPA, ie compound (5), was described in a patent in 1966,[4] being prepared by the reaction of thiophosphoryl chloride on pentaerythritol.



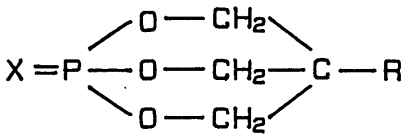
(5)

This was used as an intermediate in the preparation of novel herbicides. PEPA itself was first prepared in 1966 by the oxidation of pentaerythritol phosphite, (6), to its corresponding phosphate using hydrogen peroxide in isopropanol.[5]



(6)

The patent covered compounds of the general formula (7) where X was oxygen, sulphur or selenium, and R was CH_2OH or an alkyl chain.



(7)

It was not until 1984 that a patent was published in which a simple and relatively cheap method for the production of PEPA was claimed.[6] This followed logically from the work described so far and involved the reaction of pentaerythritol with phosphorus oxychloride in an inert solvent at about 90°C to give a high yield of PEPA. This method was a vast improvement on the methods previously mentioned as it did not need the expensive pentaerythritol phosphite, (6), as a starting material, nor did it require a hydrogen chloride acceptor. It also avoided the use of sulphur-containing compounds.

As early as the 1960's, bicyclic phosphites were recognised as important additives for polymers. For example, a patent from 1961 described the addition of pentaerythritol phosphite, (6), to polyvinyl halide resins where it acted as a heat stabiliser.[7]

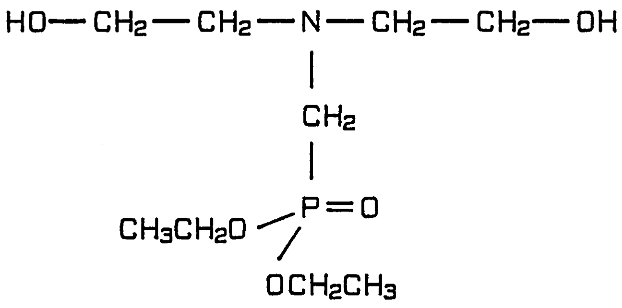
PEPA has been used as a flame retardant additive in its own right,[8] though it was found to be less effective for this purpose than when in derivatised forms.

Many patents have claimed the use of derivatives of PEPA as effective fire retardant additives in a variety of polymers. Probably the most important are the series of patents published by Halpern <u>et al</u> describing the use of salt systems developed from acidic derivatives of

PEPA.[9-16] These helped form the basis from which the work described in Chapter 3 of this thesis was developed.

Another important area has been in the synthesis of ester derivatives of PEPA and this work is described in the introduction to section 2.4 of this chapter.

It has been known for some time that some bicyclic phosphates are potent convulsants in mammals.[17] The convulsant activity has been attributed to the interference of a neurotransmitter. It was observed that rats suffered from adverse neurological effects when exposed to the combustion products of a polyurethane foam.[18] The foam had been treated with a fire retardant additive, namely *O*,*O*-diethyl-N,N-bis-(2-hydroxyethyl)aminomethyl phosphonate, (8):

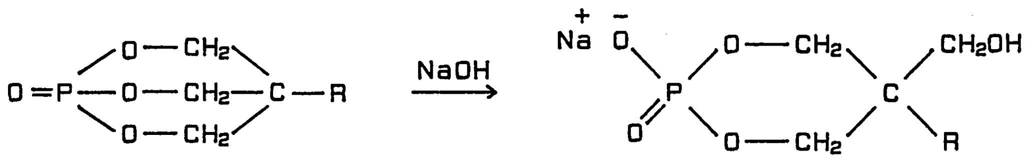


(8)

Because of the unusual nature of the toxic symptoms observed in the exposed rats, an extensive analytical study was initiated to identify the toxicant.[19] The results of this work revealed the offending compound to be the 4-ethyl-substituted bicyclic phosphate, (3), mentioned earlier. This was found to have a toxicity level six times greater than diisopropylfluorophosphate, a chemical warfare agent.

The compounds prepared and used in the work described in this thesis were virtually all ester derivatives of PEPA which, on pyrolysis, decomposed to give phosphoric acid and a carbonaceous char. Therefore these toxic properties did not apply, but great care was taken none the less whenever handling new compounds synthesised from PEPA.

An extra consideration necessary when working with systems based on PEPA was the avoidance of alkaline conditions. Bicyclic phosphates are known to be resistant to acid, but unstable in the presence of alkali:[20-22]



All the work described in this chapter is based on the development of the chemistry of PEPA. This was initiated with four basic objectives:

i) to develop acidic derivatives of PEPA which could be used in the synthesis of intumescent salts;

ii) to develop ester derivatives of PEPA which could be used as flame retardant additives in their own right;

iii) to develop derivatives of PEPA containing unsaturated carbon atoms, which could act as monomers in the production of polymeric flame retardant additives;

iv) to develop a better understanding of the chemistry of PEPA, knowledge of which could facilitate future reactions of this system.

2.2 SYNTHESIS OF STARTING MATERIALS

PEPA was prepared according to the method patented by Halpern _et al_[6] to yield a white powder, melting point 205-209°C. The product was soluble in water enabling nmr spectra to be obtained in D_2O. Unfortunately, the alcoholic proton was sufficiently acidic to exchange with a deuterium atom from the solvent, resulting in no signal in the ^{1}Hnmr spectrum for the OH proton. The spectrum showed a singlet at $\delta = 3.6$ ppm and a doublet at 4.8 ppm. The former was due to the CH_2-OH methylene protons while the doublet was a result of the P-O-CH_2 protons. The doublet was due to a spin-spin coupling between the endocyclic methylene protons and the phosphorus nucleus, indicating that the six endocyclic methylene protons were magnetically equivalent. The doublet peaks were not of equal intensity as might have been expected. This suggested that one of the peaks was masked by the signal for HOD. The spectrum was re-run in deuterated dimethyl sulphoxide (D_6-DMSO) to reveal three signals: a singlet at $\delta = 3.3$ ppm (C-$\underline{H}_2$-OH), a doublet at $\delta = 4.6$ ppm (P-O-C$\underline{H}_2$) and a singlet at $\delta = 5.1$ ppm (OH). ^{31}Pnmr showed a singlet at $\delta = -3.4$ ppm. ^{13}Cnmr showed two singlets at $\delta = 40$ and 60 ppm respectively, with a doublet, again caused by spin-spin coupling with phosphorus, at $\delta = 79$ ppm. Mass spectrometry showed the molecular ion at m/z = 180, the base peak being at m/z = 150 due to loss of CH_2O. The infrared spectrum (see Figure 2.1) gave a broad peak at 3400 cm^{-1} due to the OH stretching of the alcohol group, a strong peak at 1300 cm^{-1} due to the P=O vibration and four peaks between 950 and 1060 cm^{-1} for the P-O-CH_2R vibration.[23] All this evidence confirmed the structure as that of (1).

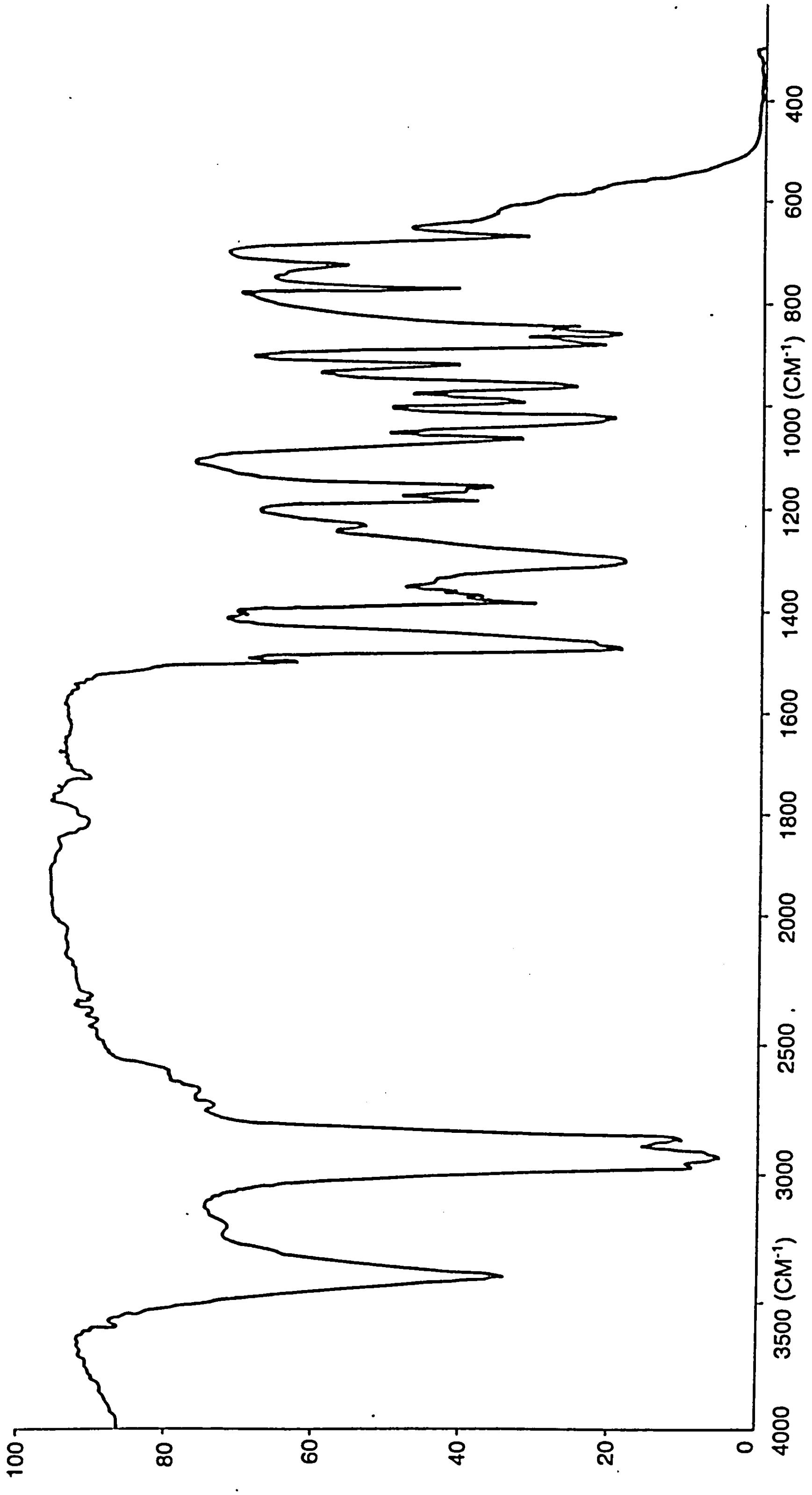
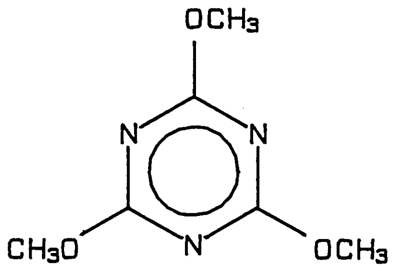


Figure 2.1

Infrared Spectrum of PEPA (1)

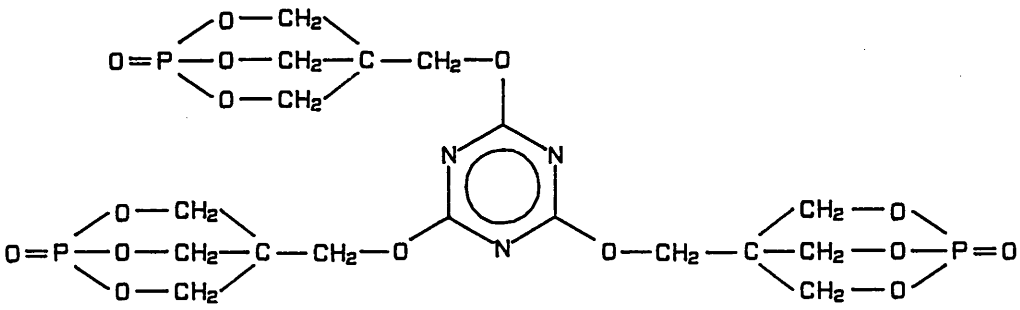
The only other non-commercially available starting material used in the work described in this chapter was trimethoxy-s-triazine. This was used in attempted transesterification reactions with PEPA described in section 2.3. The method was a standard literature procedure, treating cyanuric chloride with methanol in the presence of sodium hydroxide.[24] Analysis of the resulting crystalline solid concurred with the literature and confirmed the structure as that of (9).



(9)

2.3 ATTEMPTS TO INTRODUCE PEPA UNITS INTO THE s-TRIAZINE SYSTEM

A large proportion of the early work described in this chapter was spent in attempting to produce a target molecule of structure (10).



(10)

It was thought that such a compound would have great potential as an intumescent additive as it would contain an intumescent catalyst, a carbonific and a spumific source all within the same molecule.

Transesterification of trimethoxy-s-triazine (9)

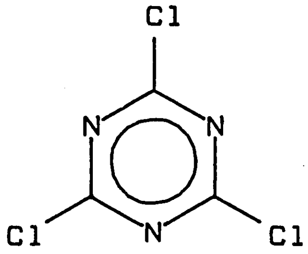
Initially, work concentrated on the attempted transesterification of compound (9). This compound is known to undergo such reactions, but all the reactions described needed the reacting alcohol to be a liquid and to be present as a mixture with its corresponding alkoxide ion (usually as a sodium salt).[25] As this was not possible with

PEPA, a different approach was used. PEPA was heated with (9) in dioxan with the addition of a catalytic amount of sodium hydroxide. The starting materials went into solution during the reaction and on cooling, a white precipitate formed. This was investigated by melting point, infrared spectroscopy and TLC, and found to be unreacted PEPA. TLC of the supernatant liquid showed it to contain the unreacted s-triazine. The experiment was repeated with a longer reaction time, but still afforded the unreacted starting materials. The reaction was then repeated using an acidic catalyst, namely toluene-4-sulphonic acid, ($CH_3C_6H_4SO_3H$). This time, after the solution had been heated under reflux for two hours, the mixture was distilled in an endeavour to remove any methanol produced, thus displacing the equilibrium in favour of the desired products. The only distillate collected came over at 100°C, the boiling point of dioxan, suggesting that no methanol had been formed and, ipso facto, no reaction had taken place. This was indeed the case as on cooling, a white precipitate formed which was found to be unchanged PEPA, the solvent still containing the unreacted s-triazine.

These two experiments were then repeated using a different solvent with a higher boiling point, the aim being that a reaction might be induced at the higher temperature. The solvent chosen was 2-methoxyethyl ether, $(CH_3OCH_2CH_2)_2O$, known as diglyme. This has a boiling point of 150°C and showed significant solubility of both starting materials. Again, after boiling for two hours the mixtures were distilled to remove any methanol produced, but the distillate in both cases was collected at 150°C. On cooling the solutions, no precipitate formed but TLC of the solutions revealed, in each case, both starting materials to be present with no trace of another compound.

As a final attempt, the two starting materials were heated together in the absence of a solvent. The s-triazine melted and dissolved the PEPA but the mixture soon turned black and on cooling became glass-like. TLC and infrared spectroscopy of this product were very complex and mass spectrometry showed no peaks higher than m/z = 140. This all suggested that the mixture had thermally decomposed. Due to these results, further attempts at producing compound (10) concentrated on reactions involving the use of cyanuric chloride.

Reactions between PEPA and cyanuric chloride (11)



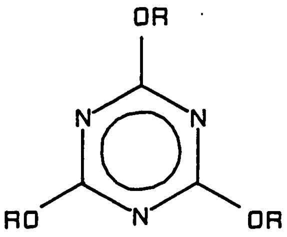
(11)

PEPA and cyanuric chloride were heated in a 3:1 molar ratio in dimethylformamide (DMF) under reflux conditions. TLC of the reaction mixture showed a complex set of spots indicating at least five different compounds. As one of these corresponded to unchanged PEPA, yet none corresponded to cyanuric chloride, it was considered possible that the s-triazine was not stable in boiling DMF. A control was carried out in which cyanuric chloride was heated under reflux in DMF on its own. TLC of this reaction mixture showed the same pattern as before and it was therefore concluded that cyanuric chloride decomposes to give a complex mixture of products on boiling in DMF.

The reaction was repeated in dioxan only to yield unrecovered PEPA (identified by infrared spectroscopy and melting point). TLC of the solution showed it to contain a large amount of cyanuric chloride.

An attempt was made to form the sodium salt of PEPA which would be more likely to react with the cyanuric chloride. PEPA was treated with sodium hydride in dioxan before the addition of cyanuric chloride. After heating under reflux, the solution was evaporated to yield a grey solid which showed evidence of both starting materials by TLC. Mass spectrometry of the solid showed the molecular ions of both starting materials, but no peaks of any greater m/z values.

According to the literature, cyanuric chloride will react with an aliphatic alcohol to produce cyanuric acid, (12, R = H), and the corresponding alkyl chloride.[26, 27]



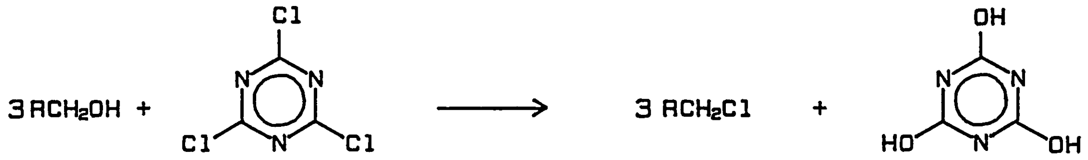
(12)

However, it is stated that with sodium hydroxide present, the trialkylcyanurate, (12, R = alkyl), is formed along with sodium chloride and water. All the alcohols quoted in the papers were liquids at room temperature and therefore acted as the solvent as well as being a reactant. Obviously this was not the case for PEPA, but, for the purposes of the present study, the method was still thought worthwhile attempting on PEPA with the use of a solvent. Both dioxan and dimethyl sulphoxide (DMSO) were used, but in each case a white precipitate formed on cooling which was investigated by infrared spectroscopy, melting point and proton nmr and found to be unreacted PEPA.

1,2-Dichlorobenzene, with a boiling point of 179-180°C, was employed to discover if a higher temperature would induce a reaction. No catalyst was added, but on heating under reflux conditions, neither starting material dissolved or reacted as the solid recovered by filtration proved to be a mixture of the two by TLC and infrared spectroscopy.

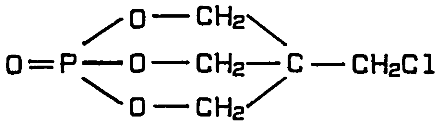
A different solvent was investigated that still had a high boiling point yet showed good solubility of the starting materials. Diglyme was used and a series of reactions were studied in this solvent. The reaction was attempted at three different ratios of PEPA:cyanuric chloride, namely 1:1, 2:1 and 3:1. The 1:1 experiment was repeated in the presence of triethylamine to act as a base and promote reaction by absorbing any hydrogen chloride produced. All four experiments yielded only unchanged starting materials. Finally, the 3:1 experiment was repeated using a longer reaction time, but even after twenty-eight hours the mixture yielded only the starting materials.

Continuing with the notion of using a longer reaction time, the heating of PEPA and cyanuric chloride in dioxan under reflux conditions was repeated, this time the experiment being kept at 100°C for twenty-eight hours. On cooling, a precipitate formed which appeared to consist of a white powder. However, on closer examination, this was found to contain a few white, crystalline needles. The powder proved to be mainly PEPA by infrared spectroscopy and melting point. The crystals however melted above 300°C and further analysis showed their structure to be that of (12, R=H), ie cyanuric acid. The reaction liquid still showed the presence of a large amount of cyanuric chloride, so obviously only a small proportion was being converted to the acid. The original cyanuric chloride used was checked to ensure it contained no cyanuric acid impurities, which it did not, and the dioxan had been dried so the cyanuric chloride had not been hydrolysed by water in the solvent. This suggested that the reaction fitted with the principles already mentioned from the literature,[26, 27] ie that in the absence of a base catalyst, aliphatic alcohols and cyanuric chloride react as in Scheme 1:



Scheme 1

This would have been satisfactory except for the recovery of the PEPA, which, according to the equation above, should have been the corresponding chloride, ie compound (13).



(13)

However, closer examination of the product by TLC showed it to contain slight traces of a less polar compound. The product was then examined by mass spectrometry which showed a doublet (ratio 3:1) at m/z = 199/201. This suggested the presence of at least some PEPA-chloride. In order to verify this, further reactions were investigated in which PEPA-chloride was synthesised by alternative methods and used for comparison. Details of these reactions are given later.

Returning to the PEPA/cyanuric chloride system, two more solvents were investigated. These were both basic solvents, the point being that such solvents might promote reaction. First acetonitrile and then pyridine were used, but both solvents yielded only unreacted starting materials, even after prolonged heating under reflux conditions.

It was becoming increasingly obvious that these two materials were not going to react together, in the absence of other reagents, to form the desired product. Therefore they were heated together, under reflux conditions, in dioxan for twenty-four hours in the presence of anhydrous sodium carbonate. The white solid eventually isolated was in poor yield (less than 10%) but showed reasonable intumescent properties. TLC of the solid showed no cyanuric chloride present, but traces of PEPA did remain. Microanalysis of the carbon, hydrogen and nitrogen content showed a fairly close match to the values calculated for the tri-substituted-s-triazine, (10). Unfortunately these hopes proved unfounded by further analysis. A sodium fusion test on the solid showed a large amount of chloride ions present. Initial mass spectrometry analysis was unhelpful as the spectrum obtained, using electron impact, was heavily lined with peaks at nearly every m/z value below 200. The ionising mode was therefore changed to the less vigorous technique of chemical ionisation. This revealed a fragmentation pattern similar to that of PEPA with the highest peak being at m/z = 180, the molecular ion for PEPA. The product was insoluble in virtually all common solvents, making nmr spectra too difficult to obtain. However, a very weak solution was obtained in DMF, which, on being spiked with D_2O for reference, afforded a sufficiently readable ^{31}Pnmr spectrum. This showed four main peaks, all of which corresponded to minor peaks obtained in a ^{31}P spectrum of crude PEPA. The infrared spectrum of the product was fairly similar to that of PEPA, the most significant peak being at 3400 cm^{-1} which showed the presence of an OH functionality. In conclusion it was decided that the solid produced was mainly untreated PEPA mixed with some breakdown products of both PEPA and cyanuric chloride. The cyanuric chloride was concluded to have been completely decomposed as no analytical method showed any presence of an s-triazine ring system.

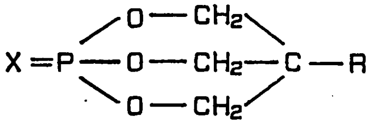
The final attempt at a reaction to produce (10) was by using more powerful conditions to generate the alkoxide ion of PEPA. Butyl lithium was treated with PEPA and cyanuric chloride added to the mixture. The end product was an orange oil which showed a complex composition by TLC and infrared spectroscopy. The oil was not intumescent and this fact, along with its strong colour, its viscosity and the relatively expensive starting material (especially on an industrial scale) made the product unsuitable for further development in the area of intumescent flame retardant additives.

At this stage it was decided that the reaction of PEPA with cyanuric chloride was unlikely to produce (10), so further work concentrated on the development of other intumescent systems.

Synthesis of PEPA-chloride (13)

As stated earlier, under certain conditions PEPA and cyanuric chloride reacted together to produce cyanuric acid (12, R = H) and PEPA-chloride (13). These products were obtained in very low yield and the chloride in particular was difficult to detect. The only evidence for the existence of PEPA-chloride was an extra spot on TLC and a doublet (split in a 3:1 ratio), corresponding to the molecular ion, observed by mass spectrometry. It was therefore decided to synthesise the PEPA-chloride by an alternative route, thus having a material for comparison by mass spectrometry and TLC.

The systematic name for (13) is 4-chloromethyl-2,6,7-trioxa-1-phosphabicyclo[2.2.2]octane-1-oxide. This compound is known in the literature, although its only reference is a passing comment in a paper that discusses the toxicity of a range of bicyclic phosphate derivatives.[28] The paper quotes a melting point of 170-171.5°C and claims that microanalysis gave accurate results, but no other data was given. The product was synthesised by the oxidation of the corresponding bicyclic phosphorothionate (7, X = S, R = CH_2Cl).



(7)

For the purposes of the work described here, a different method for the generation of (13) was used, the reaction involving treatment with triphenylphosphine and carbon tetrachloride, Scheme 2:

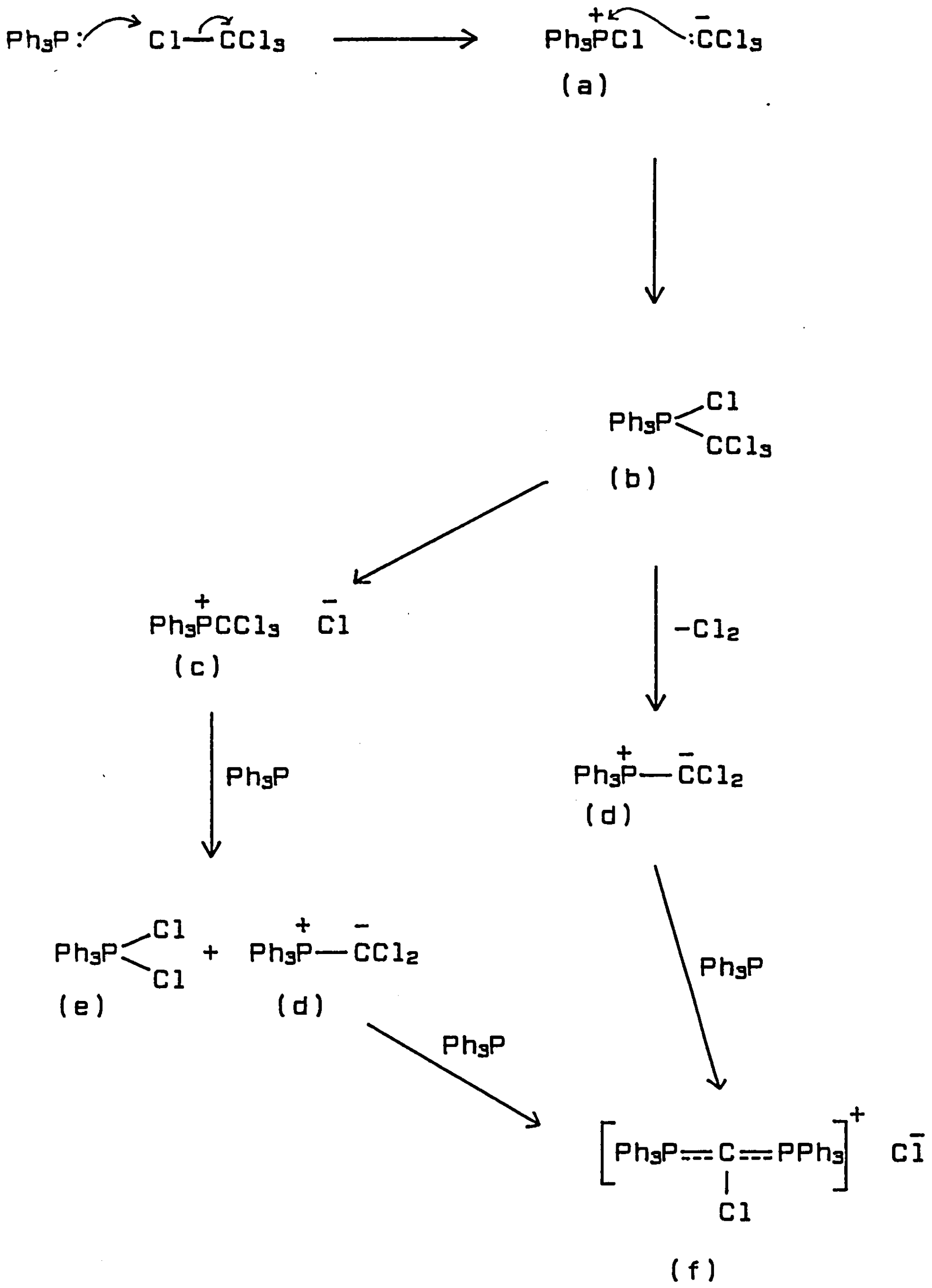
$$Ph_3P + CCl_4 + R{-}OH \longrightarrow Ph_3P{=}O + CHCl_3 + R{-}Cl$$

Scheme 2

This reaction was performed to give a white powder which was washed with toluene in an endeavour to remove the triphenylphosphine oxide. Despite this, TLC of the powder showed it to contain two components. One had an R_f value identical to that for triphenylphosphine oxide, ($Ph_3P{=}O$), the other had an R_f value equal to the spot assumed to be (13) from the PEPA/cyanuric chloride reaction. On heating, the product had two distinct melting points. Some melted at around 155°C, leaving some solid sticking to the sides of the melting point tube. This remaining solid melted at 170-173°C. These two values are consistent with the literature quoted melting points of triphenylphosphine oxide[29] and PEPA-chloride[28] respectively. Mass spectrometry of the product showed the two molecular ions, $Ph_3P{=}O$ at m/z = 278 and PEPA-chloride at m/z = 199/201. The latter peak corresponded to that from the PEPA/cyanuric chloride reaction.

These results were considered sufficient to conclude the presence of PEPA-chloride in the previous reaction between PEPA and cyanuric chloride, especially when taken with the fact that cyanuric acid was found in that reaction product. The mixture obtained in the triphenylphosphine reaction was undoubtedly PEPA-chloride and triphenylphosphine oxide, despite repeated trituration and washing with toluene in which triphenylphosphine oxide is soluble.

In order to understand the mechanisms involved in Scheme 2, the reaction was studied by ^{31}Pnmr. The mechanism proposed for the addition of carbon tetrachloride to triphenylphosphine is shown in Scheme 3:[30]


Ph3P: Cl—CCl3
Ph3PCl :CCl3
(a)
Ph3P Cl CCl3
(b)
Ph3PCCl3 Cl
(c)
-Cl2
Ph3P
Ph3P—CCl2
(d)
Ph3P Cl Cl
(e)
+
Ph3P—CCl2
(d)
Ph3P
Ph3P
[Ph3P=C=PPh3]+ Cl
Cl
(f)

Scheme 3

The intermediate (b) is formed so quickly that the ion pair (a) has not yet been detected in a Ph_3P/CCl_4 system. However, the phosphonium salt (c) is much more stable and subsequently is observable by ^{31}Pnmr. This salt was first detected for certain in the system $[(CH_3)_2N]_3P/CCl_4$[31] and has actually been isolated from the Ph_3P/CCl_4 system.[32] This salt has also been shown to react with more Ph_3P to yield a mixture of (d) and (e).[32] (d) is also formed directly from (b) by the elimination of chlorine. In both cases, the ylide (d) is a very reactive intermediate and cannot be detected by ^{31}Pnmr. It reacts very rapidly with Ph_3P to form the [chloro(triphenylphosphoranediyl)methyl]triphenylphosphonium chloride, (f).

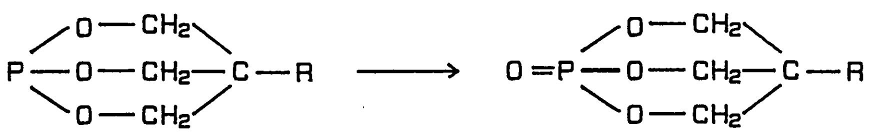
In order to study the effects of Ph_3P/CCl_4 on PEPA, Ph_3P was dissolved in deuterated acetonitrile and its ^{31}Pnmr spectrum recorded. This gave a singlet at $\delta = -5.7$ ppm. Carbon tetrachloride was added to the system and the spectrum recorded. The Ph_3P peak had totally disappeared, to be replaced by four peaks, at $\delta = 48.7$, 47.5, 32.9 and 25.2 ppm. This was expected due to the four stable intermediates, (b), (c), (e) and (f). It is known that in the R_3P/CCl_4 2-component system, this formation of intermediates shows great solvent-dependence. The fastest reactions recorded have been those in acetonitrile.[33] A solution of PEPA in deuterated acetonitrile was prepared and the ^{31}Pnmr spectrum of this solution recorded before adding the solution to the Ph_3P/CCl_4 system. This new mixture showed six peaks on the ^{31}Pnmr spectrum. One peak, $\delta = -7.5$ ppm, corresponded to the peak observed in the pure PEPA solution. Although this peak would appear to be due to PEPA, it could also correspond to the PEPA-chloride as most PEPA derivatives show a chemical shift very close, if not equal, to that of PEPA. Three of the peaks, δ = 25, 32 and 47 ppm, corresponded to intermediates previously observed in the Ph_3P/CCl_4 system. This left two new peaks at δ = 65 and 29 ppm. The final product, along with R-Cl and $CHCl_3$ is triphenylphosphine oxide which has a chemical shift (in D_3-acetonitrile) of δ = 28 ppm and hence accounts for one of the additional peaks. The other can be accounted for by the intermediate from which R-Cl is formed,[34] ie $(Ph_3P\text{-}O\text{-}R)^+\ Cl^-$.

This mixture was kept in the spectrometer probe and spectra recorded over the subsequent twenty-four hours, but the spectra never altered to any great extent, there always being six peaks at δ = -7.5, 25, 28, 32, 47 and 65 ppm.

The reaction therefore appears to proceed by the mechanism proposed by Appel,[30] the products obtained being a mixture of PEPA-chloride (13) and triphenylphosphine oxide. This in turn was considered to be sufficient evidence for the existence of PEPA-chloride in the product from the PEPA/cyanuric chloride reaction.

2.4 SYNTHESIS OF ESTER DERIVATIVES OF PEPA

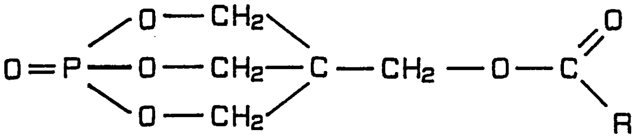
Many derivatives of PEPA are cited in the literature. However, they are never prepared by simple derivatisation methods on PEPA itself. Initially, the process involved conversion of the phosphite (14) to the corresponding phosphate (15):[35]



(14) (15)

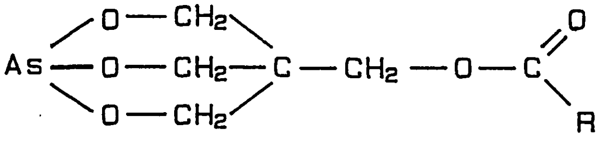
Such examples include oxidation by hydrogen peroxide or oxygen,[36-38] by MnO_2 and mercuric oxide,[39, 40] even using N_2O_4 in methylene chloride.[41, 42]

More recently other methods have been described. For instance, a Polish patent from 1977 describes the synthesis of "various fatty acid monoesters of pentaerythritol phosphate", the products being of the general formula (16):[43]



(16)

This method used the conversion of the corresponding bicyclic arsenite, (17), by treatment with phosphorus oxychloride in benzene with the presence of pyridine as a catalyst.



(17)

Arsenic trichloride was removed and the reaction mixture filtered, the filtrate being neutralised with sodium hydroxide. The patent[43] claimed the preparation of the monolaurate, the monostearate and the acetate.

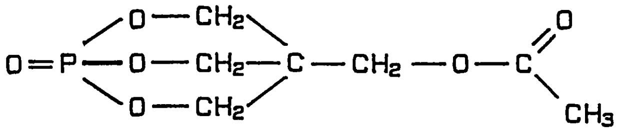
In 1981, a Japanese study investigated the fact that bicyclic phosphates are potent convulsants in mammals.[28] Various bicyclic phosphates were synthesised and characterised, their studies concentrating on structure (15) above where R was an alkyl chain, a simple ether or a halo-alkane. Their method involved the reaction of corresponding triols with phosphorus oxychloride, again in the presence of pyridine. The complex triols needed for such reactions were not readily available, hence the methods were complicated by the difficult reactions needed to obtain such triols as intermediates.

A European patent published in 1984 claimed the use of many ester derivatives of PEPA as novel flame retardant additives for polyphenylene ether.[44] The esters quoted in the patent were not characterised, nor were details of their synthesis given. The patent referred merely to such esters as "being described in the literature", their source being that of reference 35 above.

The aim of the work described in this section of the present study was to synthesise derivatives of PEPA for fire retardant applications by methods as simple and cheap as possible in order to render any useful products feasible for commercial production.

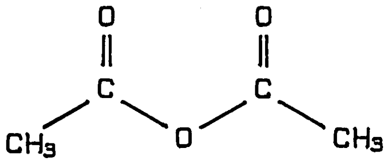
Synthesis of 4-acetoxymethyl-2,6,7-trioxa-1-phosphabicyclo[2.2.2] octane-1-oxide (18)

The simplest ester of PEPA is of structure (16) where R = CH_3, ie compound (18).



(18)

This compound is known, being described in the Polish patent[43] and mentioned in the European patent,[44] both quoted above. A novel but simpler method of preparation was sought for the purposes of this study. PEPA was heated in dioxan with an equimolar amount of acetic anhydride (19).



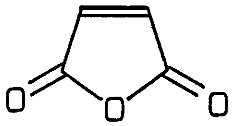
(19)

On cooling, a solid precipitated which was filtered and found to be unreacted PEPA. However, TLC of the reaction solution showed evidence of another compound, more polar than PEPA. This solution was therefore poured into petrol to produce a white solid, which, although found to consist of mainly untreated PEPA, did show some evidence (by infrared spectroscopy) of a carbonyl group. The reaction was repeated using an excess of acetic anhydride but again produced a reaction mixture similar to the previous experiment.

PEPA was then dissolved in hot acetic anhydride (with no solvent present), and, on cooling, produced a white precipitate. TLC analysis of this solid showed it to consist of only one component, the R_f value of which was greater than that of PEPA. The product had a new melting point, 40°C lower than that of PEPA. The infrared spectrum of the product showed no OH peak, but did reveal a large carbonyl absorption peak at 1740 cm^{-1}. The spectrum also showed a peak at 1380 cm^{-1}, characteristic of CH_3 absorption when adjacent to an ester bond. Apart from these points, the infrared spectrum was identical to that of PEPA. Mass spectrometry showed a molecular ion at m/z = 223, along with the usual fragmentation pattern observed with pure PEPA. ^{13}Cnmr showed the usual PEPA skeleton with two extra peaks at δ = 206 ppm (carbonyl) and 20 ppm (methyl). ^{31}Pnmr showed a singlet at δ = -9.0 ppm. The ^{1}Hnmr spectrum showed the usual PEPA doublet at δ = 4.7 ppm and singlet at 4.0 ppm. These were accompanied by a singlet at δ = 2.0 ppm which is the correct chemical shift for methyl protons in an O-C(O)-CH_3 environment. This singlet also had the correct integral to confirm this (see Figure 2.2). Finally, microanalysis data closely matched the theoretical values and the product was confirmed as being of structure (18).

Synthesis of mono[1-oxo-2,6,7-trioxa-1-phosphabicyclo[2.2.2]oct-4-ylmethyl]maleate (21)

In an attempt to synthesise an ester of PEPA which contained a double bond (hence having potential for subsequent polymerisation), and also contained a carboxylic acid group (therefore having salt formation potential), the reaction between PEPA and maleic anhydride, (20), was investigated.



(20)

Maleic anhydride is a solid, melting at 55°C. PEPA was dissolved in excess molten maleic anhydride to form a solution which, on cooling, completely solidified into a very hard, white solid. This solid was

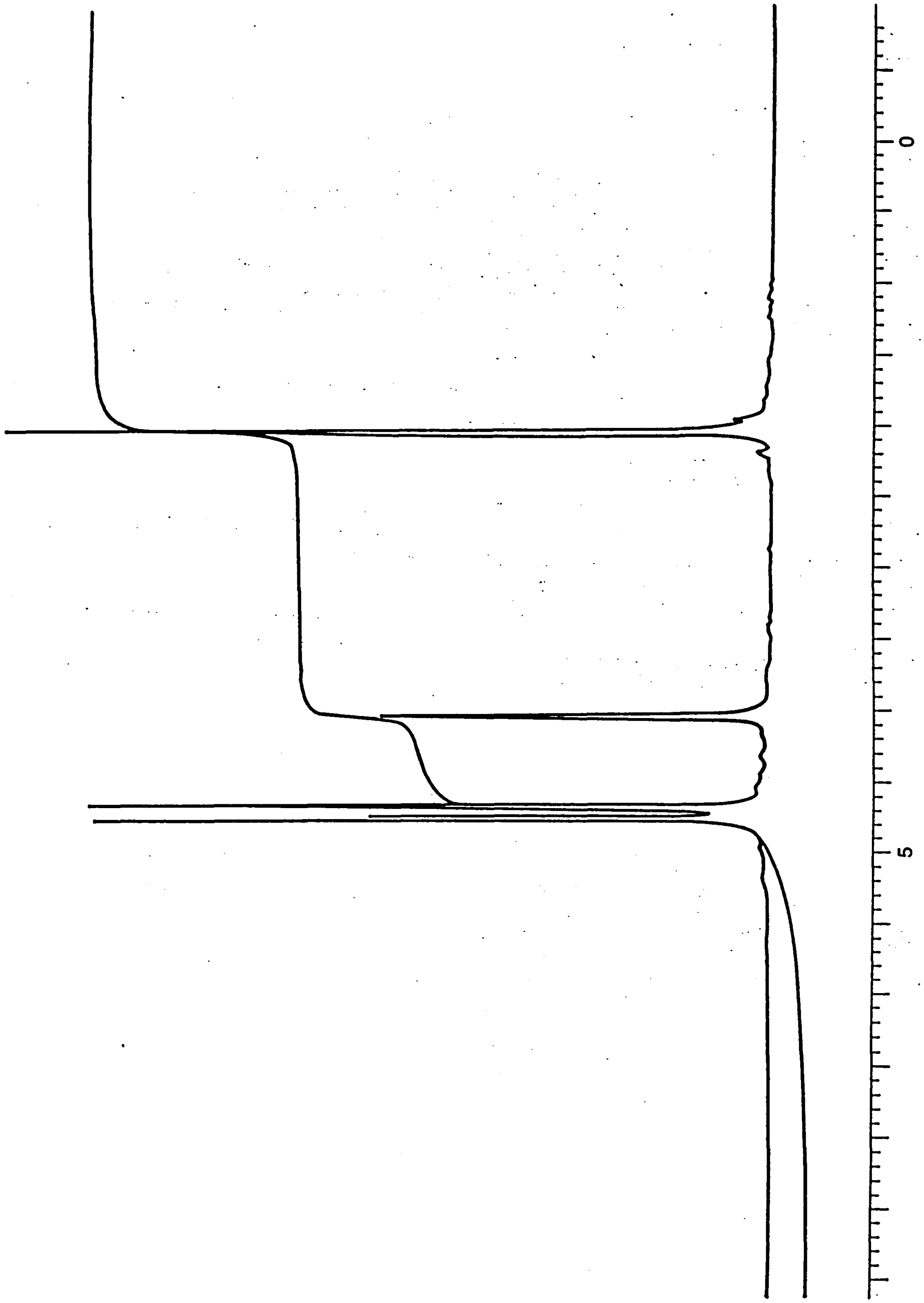
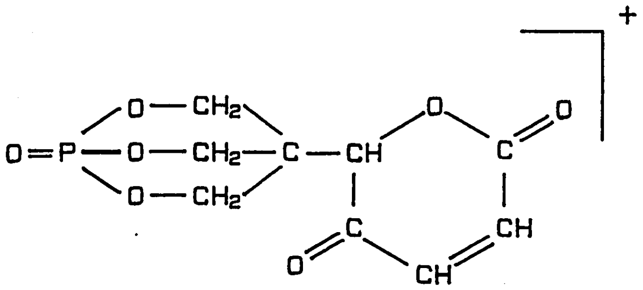


Figure 2.2

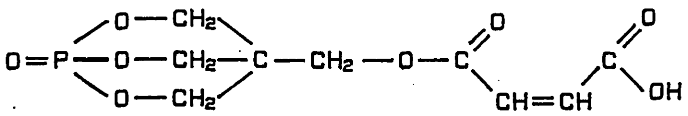
^{1}Hnmr Spectrum of 4-acetoxymethyl-2,6,7-trioxa-1-phosphabicyclo[2.2.2]octane-1-oxide (18) soxhlet-extracted with ether over twenty-four hours which removed all the unreacted maleic anhydride leaving behind the product, a fine white powder. This solid was less polar than PEPA on TLC and had a different melting point. When added to a saturated solution of sodium bicarbonate, the product caused effervescence, showing it to contain some form of acidic functionality.

Infrared spectroscopy of the product showed a broad peak at 2700-3100 cm^{-1}, typical of the OH stretching in a carboxylic acid. The spectrum also showed peaks at 1725 cm^{-1}, indicating carbonyl absorption, and 1650 cm^{-1} indicating C=C absorption. The rest of the spectrum was very similar to that of PEPA. Mass spectrometry did not show a molecular ion, a fact not too surprising as carboxylic acids are known to readily decompose before reaching the detector in a mass spectrometer. The highest peak observed was at m/z = 261, corresponding to the loss of OH. A strong peak at 260 indicated the loss of H_2O which could be due to the formation of a stable six-membered ring:



A peak at m/z = 233 corresponded to the loss of HCO_2^- and one at m/z = 219 to the loss of $^+CH_2COOH$. The rest of the spectrum showed the usual PEPA fragmentation pattern.

The ^{1}Hnmr spectrum provided two broad singlets, each with an integral of one, at δ = 6.4 and 6.8 ppm. These showed the presence of the -CH=CH- moiety. As both of these carbons contain COOR groups, the protons are effectively equivalent and therefore no splitting was observed. This makes it impossible to ascertain whether the bond is cis or trans. However, the original bond, in maleic anhydride, has to be cis and therefore it can be assumed to retain this structure in the product. Also observed in the ^{1}Hnmr spectrum was that the usual singlet at δ = 4.2 ppm, due to the C-$C\underline{H}_2$-O protons of PEPA, appeared as a doublet with an integral of 3 instead of 2. This suggested that the signal for the acidic proton coincided with that for the methylene group. The ^{31}Pnmr spectrum showed a very clean singlet at δ = -8.9 ppm (see Figure 2.3) and the ^{13}Cnmr spectrum showed the usual PEPA skeleton with four extra carbon atoms, two of which were carbonyls, the other two being C=C. The microanalysis results, being very close to the theoretical values, were the final confirmation of the product being of structure (21).



(21)

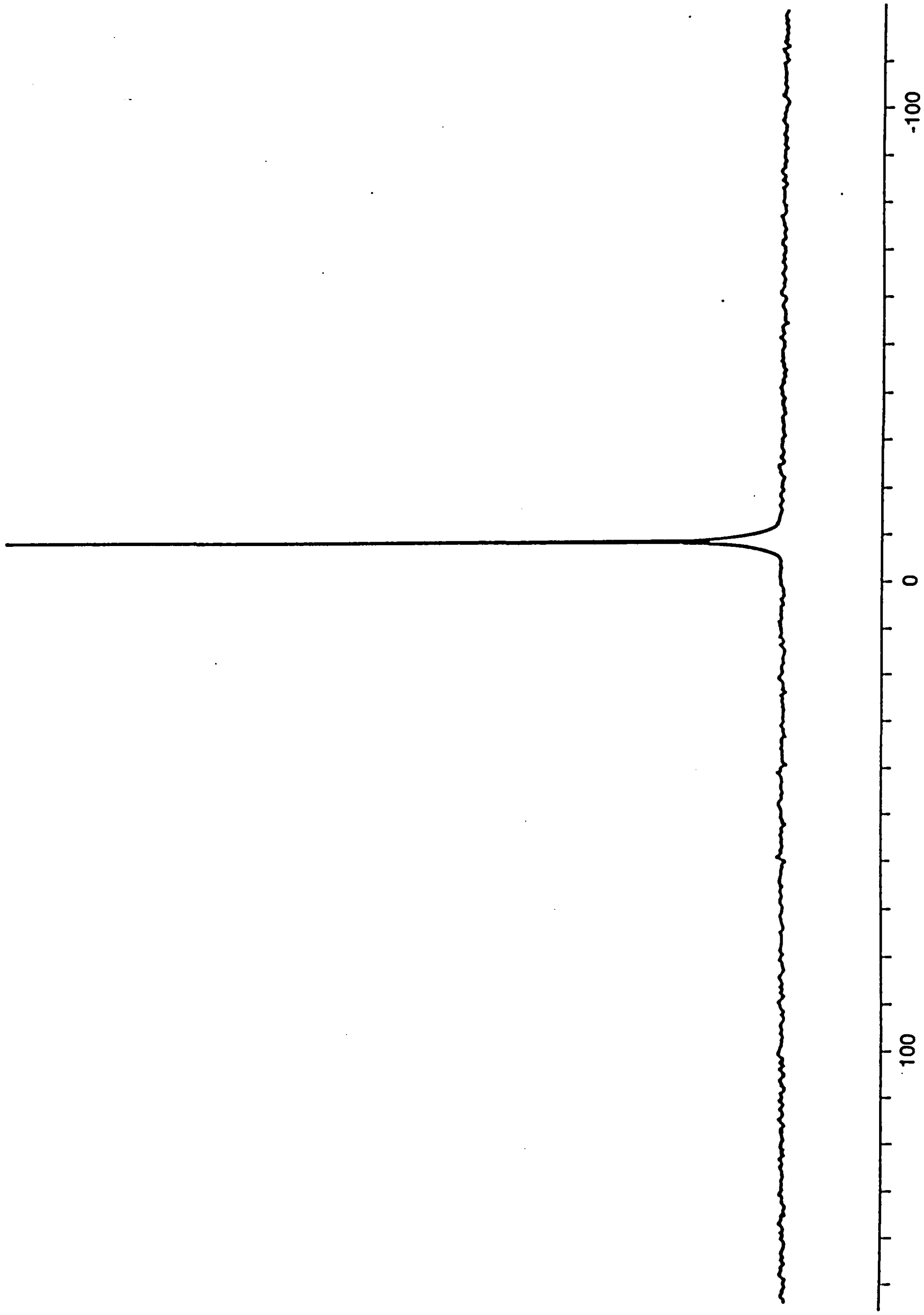


Figure 2.3

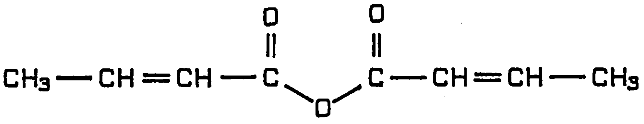
^{31}Pnmr Spectrum of mono[1-oxo-2,6,7-trioxa-1-phosphabicyclo [2.2.2]oct-4-ylmethyl]maleate (21)

The above reaction involved a molar ratio of maleic anhydride to PEPA of 5:1. This would be expensive on a large scale, not only for the cost of the excess anhydride, but also for the extraction process needed to remove the excess anhydride from the product. The reaction conditions were therefore investigated in an attempt to render them more economically viable. The reaction was repeated using an equimolar ratio of the starting materials. This afforded a very sticky product which was washed and even boiled in ether but remained a sticky solid. The reaction was again repeated with a 10% excess of the anhydride, yet this still produced a sticky mass. The starting materials (in a 2:1 molar ratio) were heated in dioxan under reflux but did not produce a significant amount of product. Finally, equimolar amounts of the starting materials were again heated together, with ether being poured over the hot melt after completion of the reaction, and the solid produced crushed under ether. This produced a white powder which, when left for about an hour, turned into the same sticky mass as before. Crushing this under liquid nitrogen produced a fine, free flowing powder but this reverted to its original sticky state on returning to room temperature. Even dissolving the product in a minimum of acetone and precipitating from ether did not improve the properties so it was concluded that in order for (21) to be synthesised, the anhydride needed to be present in at least a five-fold molar excess.

Following the production of (21), three more ester derivatives of PEPA were synthesised, all containing carbon-carbon double bonds which, it was hoped, would enable the products to undergo subsequent polymerisation reactions to produce polymers containing repeated PEPA units. The three anhydrides used for the reactions were crotonic anhydride, (22), methacrylic anhydride, (24), and endo-5-norbornene-2,3-dicarboxylic anhydride, (26).

Synthesis of 1-oxo-2,6,7-trioxa-1-phosphabicyclo[2.2.2]oct-4-ylmethyl crotonate (23)

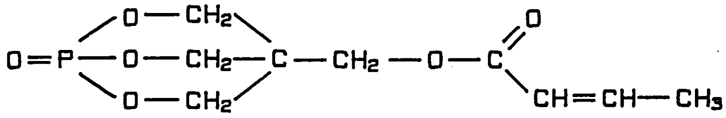
PEPA was heated in an excess of crotonic anhydride, (22), (a liquid at room temperature) and on cooling the resulting solution, a solid crystallised.



$$CH_3-CH=CH-\overset{\overset{O}{\|}}{C}-O-\overset{\overset{O}{\|}}{C}-CH=CH-CH_3$$

(22)

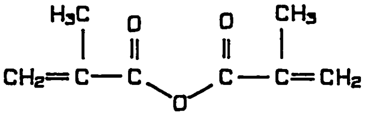
The product showed evidence of unsaturation. Infrared spectroscopy revealed absorption at 1650 cm^{-1} which is typical of alkenes. ^{1}Hnmr showed two broad singlets at $\delta = 5.7$ and 6.0 ppm, typical of protons in a R-CH=CH-R environment. ^{13}Cnmr showed two peaks corresponding to the two carbon atoms joined by a double bond. The remainder of these spectra also confirmed the structure, as did a clean single peak in the ^{31}Pnmr spectrum, a sharp melting point (163-165°C) along with evidence of the molecular ion at m/z = 248 by mass spectrometry. Finally, a very close matching of the microanalysis results to the theoretical values confirmed the structure of the product to be that of (23).



(23)

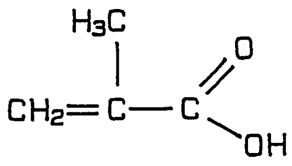
Attempted synthesis of 1-oxo-2,6,7-trioxa-1-phosphabicyclo[2.2.2]oct-4-ylmethyl methacrylate

Methacrylic anhydride, (24), being of similar structure to crotonic anhydride, (22), was expected to react with PEPA in a similar way.



(24)

Unfortunately, this was not the case. In all the reactions of PEPA with an anhydride, when the anhydride is a linear compound, a by-product of the corresponding carboxylic acid is produced. In this case, methacrylic acid, (25), is formed:

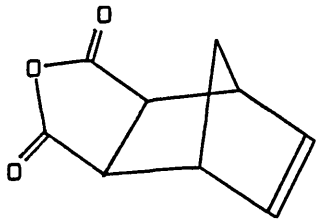


(25)

This acid is known for its self polymerisation properties on heating[45] to form a glass-like polymer. On treating PEPA with methacrylic anhydride at 150°C, the solution soon turned into a yellow solid. It was assumed that the reaction was occurring, but at the reaction temperature the by-product was forming a polymer. The reaction was repeated at 125°C with the same result. On repeating at 120°C however, the mixture did not solidify. On cooling, no precipitate appeared so the solution was poured into ether to yield a white solid. This solid was found to be unchanged PEPA. Thus it would appear that the reaction will not proceed below 125°C, yet above this temperature the by-product solidifies rendering the desired product inaccessible. As the expected structure of the product would have contained a sterically unhindered double bond, and thus been very useful in the synthesis of polymeric flame retardants, an alternative route was sought by treating PEPA with the corresponding acid chloride. This reaction was successful and details are given later in this section.

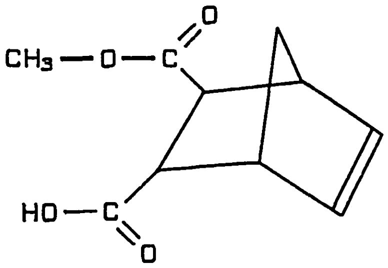
Synthesis of mono[1-oxo-2,6,7-trioxa-1-phosphabicyclo[2.2.2]oct-4-ylmethyl]endo-5-norbornene-2,3-dicarboxylate (28)

Endo-5-norbornene-2,3-dicarboxylic anhydride is a white solid of structure (26):



(26)

The corresponding PEPA ester was expected to show complex spectral patterns. Therefore, in order to facilitate the interpretation of such spectra, a simple ester of endo-5-norbornene-2,3-dicarboxylic anhydride was prepared by heating the anhydride in methanol to produce the corresponding methyl ester of structure (27):



(27)

This was characterised by the usual techniques, all of which confirmed the structure as (27), including a molecular ion observed by mass spectrometry and appropriate matching to the theoretical values by microanalysis.

The anhydride (26) was then heated with PEPA at 165°C for three hours, the product obtained being extracted with ether to remove the excess anhydride. Even after forty-eight hours of extraction, the product still showed evidence of a small amount of the anhydride by TLC. However, after recrystallisation from glacial acetic acid, TLC showed only one component to be present. As expected, the spectra obtained were complex. The product was not soluble in any of the common solvents except acetone, but then only sparingly on heating. Due to this poor solubility, ^{13}Cnmr was not possible and both ^{31}P and ^{1}Hnmr spectra had very noisy base lines. Despite this, one main peak was visible in the ^{31}Pnmr spectrum and ^{1}Hnmr showed identifiable peaks although reliable integration was not possible. The peaks observed were consistent with the proposed structure. More evidence was provided by mass spectrometry (Figure 2.4) which showed the molecular ion at $m/z = 344$ with an expected peak at $m/z = 300$ for the loss of carbon dioxide. The remainder of the spectrum showed a mixture of the fragmentation patterns typical of both starting materials. Microanalysis revealed a close match to the theoretical values and the product was confirmed as being of structure (28).

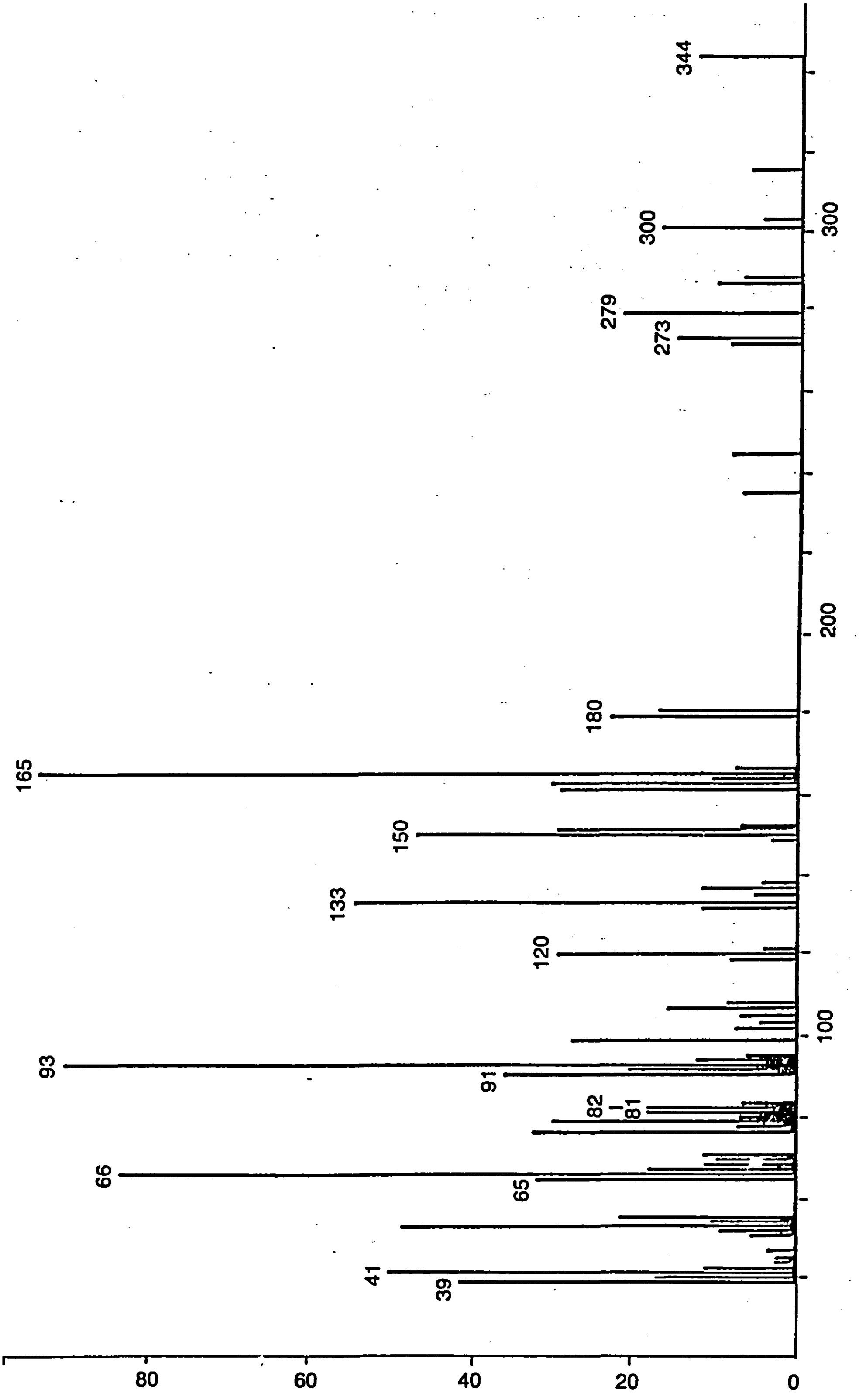
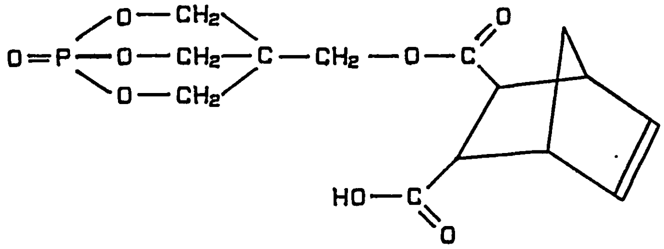


Figure 2.4

Mass Spectrum of mono[1-oxo-2,6,7-trioxa-1-phosphabicyclo [2.2.2]oct-4-ylmethyl]endo-5-norbornene-2,3-dicarboxylate (28)



(28)

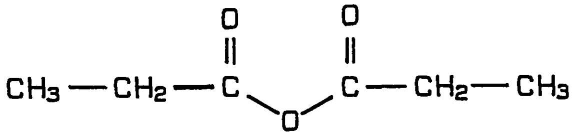
Once successfully synthesised and characterised, products (21), (23), (28) and later, (50) were investigated for their potential to polymerise, both individually and as various co-polymers, to form potentially flame retardant polymers to be used as additives. The results of this work are described in Chapter 4.

Another group of ester derivatives of PEPA synthesised from corresponding anhydrides were prepared. These consisted of saturated carbon chains or rings and as such had no potential for further reactions. They were of interest, however, as the addition of such a substituent increased the carbon content, thereby increasing the carbonific potential of the product. Such compounds could be physically mixed with a high nitrogen containing compound (such as melamine) which would provide a spumific source, and could therefore be sources of relatively inexpensive flame retardants.

The first such compound was the acetate, (18), which has already been discussed earlier in this section. The second was the propanoate ester.

Synthesis of 1-oxo-2,6,7-trioxa-1-phosphabicyclo[2.2.2]oct-4-ylmethyl propanoate (30)

This was prepared in the usual manner by dissolving PEPA in an excess of hot propionic anhydride, (29), the solution being kept at 150°C for three hours.



(29)

On cooling the solution no solid formed, so the solution was poured into cold ether to precipitate the product as a white solid. Infrared spectroscopy of this product showed the disappearance of the OH group from PEPA and the appearance of a carbonyl group at 1740 cm^{-1}. ^{1}Hnmr showed the usual PEPA peaks plus the typical quartet-triplet peaks of an ethyl group (see Figure 2.5). ^{31}Pnmr gave a clean singlet and ^{13}Cnmr showed the usual PEPA carbon skeleton with two additional peaks. Three additional peaks would be expected, but, as previously, the alkyl carbons appeared at a chemical shift which was dominated by a multiplet due to the solvent, so the 'missing' carbon peak was probably obscured. Mass spectrometry showed the molecular ion (m/z = 236) and together with a new, distinct melting point and accurate microanalysis, the product was confirmed as being of structure (30).

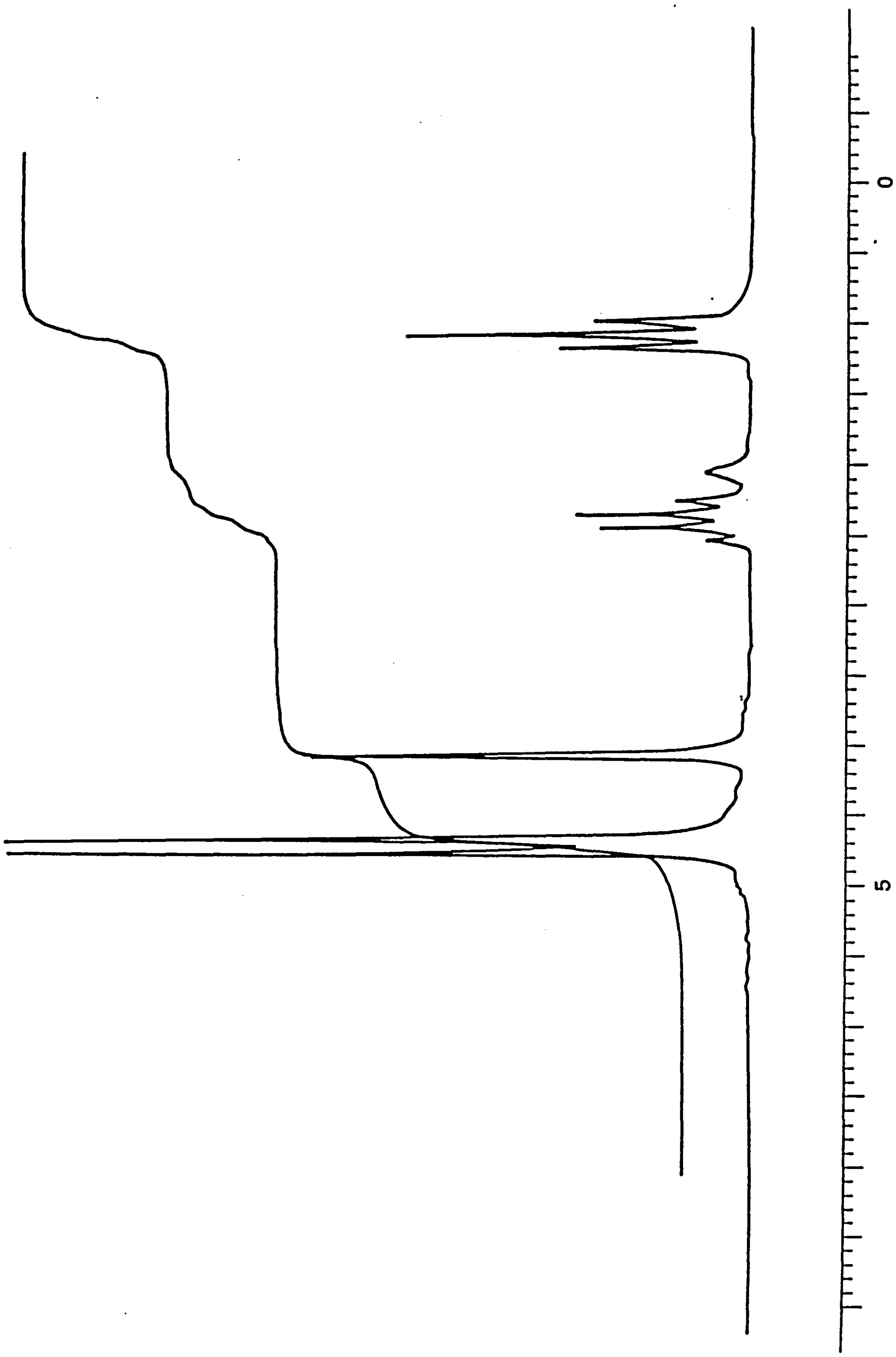
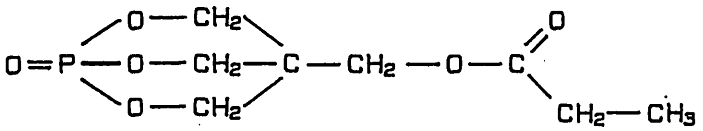


Figure 2.5

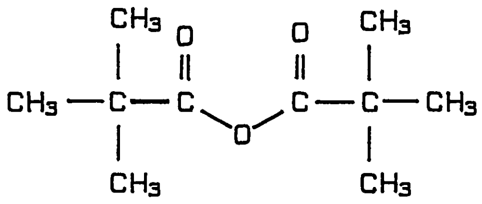
^{1}Hnmr Spectrum of 1-oxo-2,6,7-trioxa-1-phosphabicyclo [2.2.2]oct-4-ylmethyl propanoate (30)



(30)

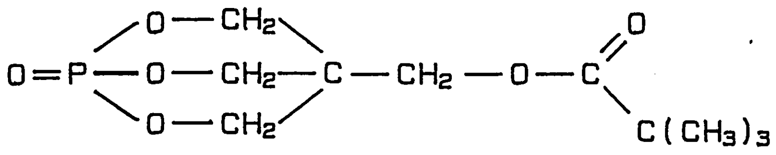
Synthesis of 4-trimethylacetoxymethyl-2,6,7-trioxa-1-phosphabicyclo [2.2.2]octane-1-oxide (32)

Treatment of PEPA with trimethylacetic anhydride, (31), similarly afforded a white powder of the desired structure.



(31)

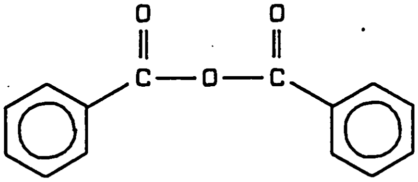
Initial concern that unreacted PEPA had been recovered, due to the melting point of the product being very close to that of PEPA, was soon dismissed on examination of the spectral analysis. All spectra confirmed the product as being of structure (32), including a molecular ion observed by mass spectrometry, a singlet in the ^{1}Hnmr spectrum of integral nine and satisfactory microanalytical results. The only spectrum not showing all the expected peaks was that of ^{13}Cnmr. This gave the PEPA skeleton with only two extra peaks instead of the three anticipated. The third peak, as above, owing to an alkyl carbon was most likely obscured by the multiplet due to the solvent.



(32)

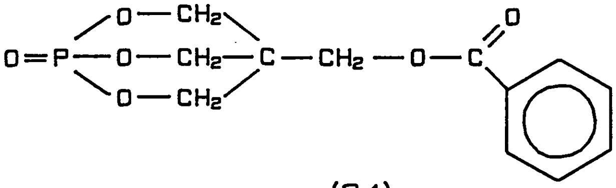
Synthesis of 1-oxo-2,6,7-trioxa-1-phosphabicyclo[2.2.2]oct-4-ylmethyl benzoate (34)

The benzoate ester derivative of PEPA has been quoted in a patent, but no characterisation or method of synthesis were given[44] (see introduction to section 2.4). For the purposes of the work described in this thesis it was prepared using the usual anhydride method, employing benzoic anhydride, (33):



(33)

A grey powder was recovered which recrystallised to provide a fine white powder. The product showed the usual PEPA structure by infrared spectroscopy, ^{1}Hnmr, ^{13}Cnmr and mass spectrometry. These techniques also revealed the presence of an ester link along with a mono-substituted benzene ring. Mass spectrometry showed the molecular ion (m/z = 284) and microanalysis showed the composition to be very close to the theoretical values. The structure was therefore confirmed as being (34):



(34)

These last four compounds, (18), (30), (32) and (34) were investigated for their intumescent properties, both separately and when mixed with melamine. The results are discussed in Chapter 3.

The final area covered in the production of ester derivatives of PEPA from the respective anhydrides was the synthesis of derivatives that contained a free carboxylic acid group. The reason for producing such compounds was that they could be treated with a suitable base (such as melamine or a derivative of melamine) to produce a salt that might exhibit intumescent decomposition.

As previously explained, PEPA reacts with an anhydride to produce the ester along with the corresponding carboxylic acid, Scheme 4:

$$\text{PEPA—OH} + \text{R—}\overset{\text{O}}{\overset{\|}{\text{C}}}\text{—O—}\overset{\text{O}}{\overset{\|}{\text{C}}}\text{—R} \longrightarrow \text{PEPA—O—}\overset{\text{O}}{\overset{\|}{\text{C}}}\text{—R} + \text{RCOOH}$$

Scheme 4

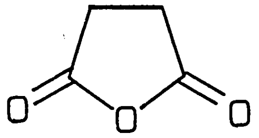
In the case of a cyclic anhydride, the resulting ester derivative will be connected to the acid group, Scheme 5:

Scheme 5

Two such esters, (21) and (28), which have already been described earlier in this section, were prepared from maleic anhydride, (20), and endo-5-norbornene-2,3-dicarboxylic anhydride, (26), respectively.

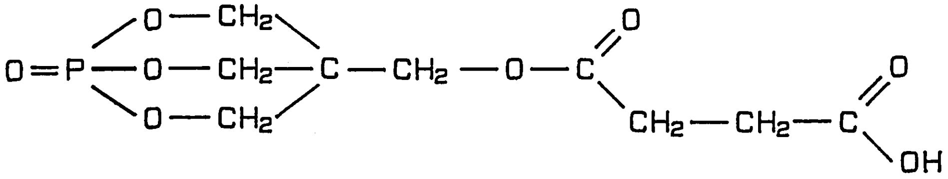
Synthesis of mono[1-oxo-2,6,7-trioxa-1-phosphabicyclo[2.2.2]oct-4-ylmethyl]succinate (36)

The structure of succinic anhydride, (35), is similar to that of maleic anhydride, (20).



(35)

Treatment of PEPA with (35) yielded the reduced form of the maleate ester, ie the succinate ester, (36):

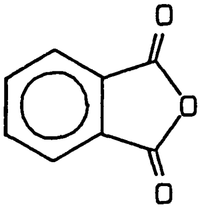


(36)

This was characterised by the usual methods. Mass spectrometry showed the molecular ion at m/z = 280 with a strong peak at m/z = 236 arising from the loss of CO_2. ^{1}Hnmr produced the usual PEPA spectrum with two additional peaks; a broad singlet at $\delta = 8.8$ ppm, typical of an OH proton and a multiplet at $\delta = 2.6$ ppm of integral four. This multiplet is probably due to the CH_2 protons in the substituent chain which are in similar environments, $-O-C(O)-CH_2-CH_2-C(O)-O-$, and hence will show similar chemical shifts, the resulting peaks being superimposed. ^{31}Pnmr and ^{13}Cnmr both verified structure (36) with final confirmation coming from the accurate microanalysis results.

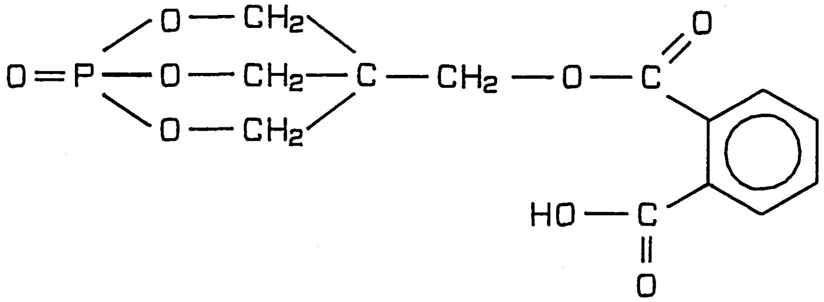
Synthesis of mono[1-oxo-2,6,7-trioxa-1-phosphabicyclo[2.2.2]oct-4-ylmethyl]phthalate (38)

Excess phthalic anhydride, (37), was treated with PEPA under the usual conditions to produce a white solid.



(37)

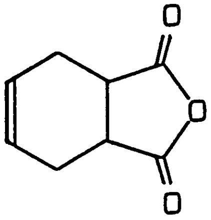
The mass spectrum of this product did not show any peaks above m/z = 180, (180 = rmm of PEPA). However, it was found to effervesce when added to sodium bicarbonate solution, indicating the presence of an acidic group. Infrared spectroscopy showed absorption for both carbonyl and aromatic systems as well as the typical PEPA bands with the notable absence of the PEPA OH. The ^{1}Hnmr spectrum showed a peak corresponding to four protons at a shift of δ = 7.6 ppm, typical for an ortho-substituted benzene ring, as well as a broad OH peak and the usual PEPA peaks. Final confirmation of the carbonyl and aromatic entities came from the ^{13}Cnmr spectrum. The microanalysis results were very close to the theoretical values for structure (38) which was therefore concluded to have been produced.



(38)

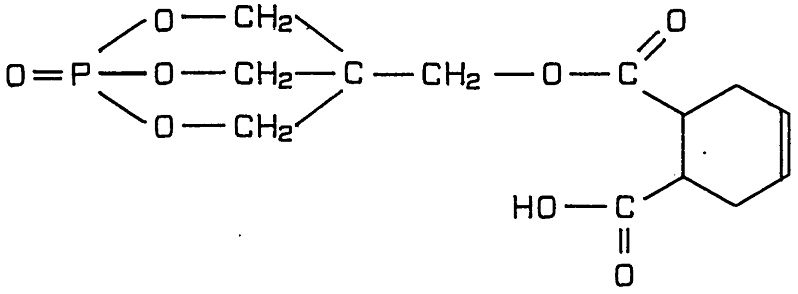
Synthesis of mono[1-oxo-2,6,7-trioxa-1-phosphabicyclo[2.2.2]oct-4-ylmethyl]1,2,3,6-tetrahydrophthalate (40)

Cis-1,2,3,6-tetrahydrophthalic anhydride, (39), being structurally very similar to phthalic anhydride, (37), produced no surprises in its reaction with PEPA in producing a compound similar to (38).



(39)

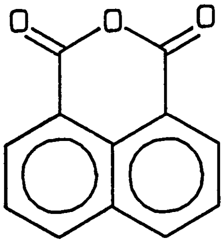
The product showed similar spectral characteristics to (38). A molecular ion was observed by mass spectrometry, as was a peak showing the loss of CO_2. The two carbon atoms in the ring that were unsaturated were masked in the ^{13}Cnmr spectrum by the peak caused by the solvent, but the remainder of the spectrum, along with ^{1}Hnmr, ^{31}Pnmr, infrared spectroscopy and microanalysis results, confirmed the product as being (40).



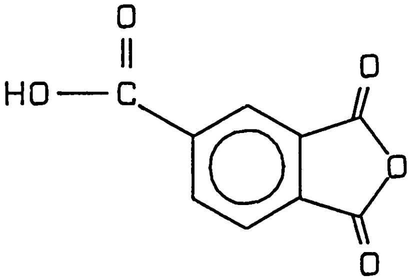
(40)

Unsuccessful reactions

Two anhydrides, when treated with PEPA, did not produce the desired products. These were 1,8-naphthalic anhydride, (41), and 1,2,3-benzenetricarboxylic anhydride, (42):



(41)

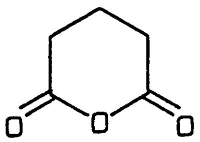


(42)

Both these compounds have high melting points so when PEPA was added to the molten compound, in each case the mixture soon became black and viscous, chromatographic analysis showing both to be complex mixtures. It was concluded that when the temperature is taken too high, PEPA thermally decomposes, thus these two reactions were not pursued further.

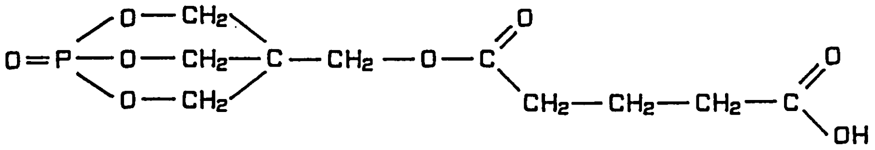
Synthesis of mono[1-oxo-2,6,7-trioxa-1-phosphabicyclo[2.2.2]oct-4-ylmethyl]glutarate (44)

Glutaric anhydride, (43), was treated with PEPA to give the expected product, (44).



(43)

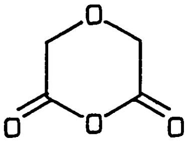
The product's structure was confirmed by the usual techniques. Mass spectrometry showed the molecular ion at m/z = 294. ^{1}Hnmr gave a multiplet at $\delta = 2.1$ ppm, probably due to the 3 x CH_2 protons being superimposed as the integral was six. ^{31}Pnmr gave a clear singlet and ^{13}Cnmr provided the expected spectrum with the absence of one CH_2 carbon peak, presumably being masked by the solvent peak as in many previous examples. Microanalysis results were almost identical to the calculated values and the structure was confirmed as (44).



(44)

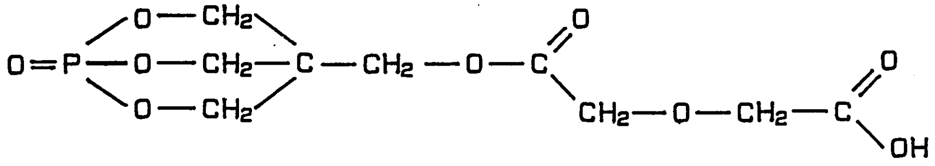
Synthesis of mono[1-oxo-2,6,7-trioxa-1-phosphabicyclo[2.2.2]oct-4-ylmethyl]2,2'-oxydiacetate (46)

The final anhydride used in this series of experiments was diglycolic anhydride, (45):



(45)

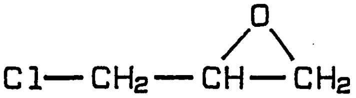
No molecular ion was observed by mass spectrometry, but peaks showing the target molecule with the loss of CO_2 and $CH_3CO_2^-$ were noted. On the ^{1}Hnmr spectrum the -CH_2-O-CH_2 protons appeared to be of the same chemical shift as the O-CH_2-C protons of PEPA, as the three peaks appeared very close to this value, too close to determine individual integrals, but the total integral was six. The rest of the spectra and microanalysis confirmed the structure as (46):



(46)

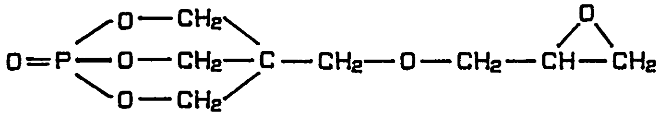
Reactions with epichlorohydrin (47)

In the search for compounds that would form potentially reactive derivatives when treated with PEPA, attention settled on epichlorohydrin, (47):



(47)

The aim was to produce a target molecule of structure (48). Such a molecule would be very reactive due to the presence of the epoxide ring and therefore have considerable potential for further elaboration.



(48)

After experience gained from the work with anhydrides described earlier in this section, PEPA was treated with neat epichlorohydrin, the solution obtained being heated under reflux conditions first for two and a half, then eight and finally twenty-four hours. In each case, only unreacted PEPA was recovered.

The experiment was repeated with a base (triethylamine) present to promote reaction, but on pouring the reaction mixture into ether, an orange oil was recovered. The reaction solution had shown the presence of PEPA by TLC before being poured in ether and the oil itself showed evidence of the alcohol group of PEPA being intact.

A final attempt was made at producing (48), this time using a solvent. The solvent chosen was acetonitrile, both for its solubility of the starting materials, and for its basicity. After heating under reflux the solution showed unreacted PEPA to be present by TLC, with no other compounds of the PEPA moiety present. The attempted synthesis of (48) was therefore given low priority in order to concentrate on more promising systems.

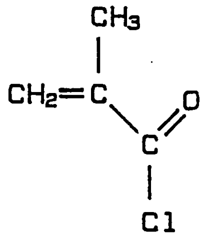
Reaction of PEPA with acid chlorides

Work in the area of reactions between PEPA and acid chlorides was initiated by the lack of success in the reaction between PEPA and methacrylic anhydride, (24), as discussed earlier. It was considered that the target molecule could be prepared via the acid chloride, in this case methacryloyl chloride. In order to obtain suitable conditions for such a reaction, a model reaction between PEPA and acetyl chloride, CH_3COCl, was attempted. The target molecule was the PEPA acetate, (18), previously synthesised from the treatment of PEPA with acetic anhydride (see earlier).

The two starting materials were heated in dioxan under reflux conditions in the presence of triethylamine. On cooling, a white solid precipitated, which was found to be neither PEPA nor acetyl chloride by TLC. ^{1}Hnmr of this solid showed the expected PEPA peaks plus a singlet of integral three, presumably for the methyl protons. Unfortunately the spectrum also showed, at a lower chemical shift, a triplet and a quartet, typical of an ethyl group. It was apparent that the product was contaminated with triethylammonium chloride, a by-product of the reaction. Attempts to wash away this impurity proved unsuccessful as the product became sticky when treated with water. The product also had no distinct melting point.

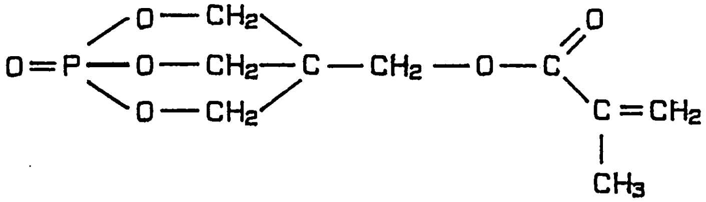
The conditions were therefore altered slightly and the reaction repeated. The solvent was changed to acetonitrile and an excess of the acetyl chloride was used. After cooling, the reaction mixture was poured into a saturated solution of sodium bicarbonate to destroy any remaining excess acylating agent. A pink solid remained after vigorous stirring which was filtered and dried to give a light pink solid. This recrystallised from glacial acetic acid to provide a white solid. All spectra of this product were identical to those of compound (18), therefore this method was deemed a success.

With conditions having been established, the reaction between PEPA and methacryloyl chloride, (49), was attempted.



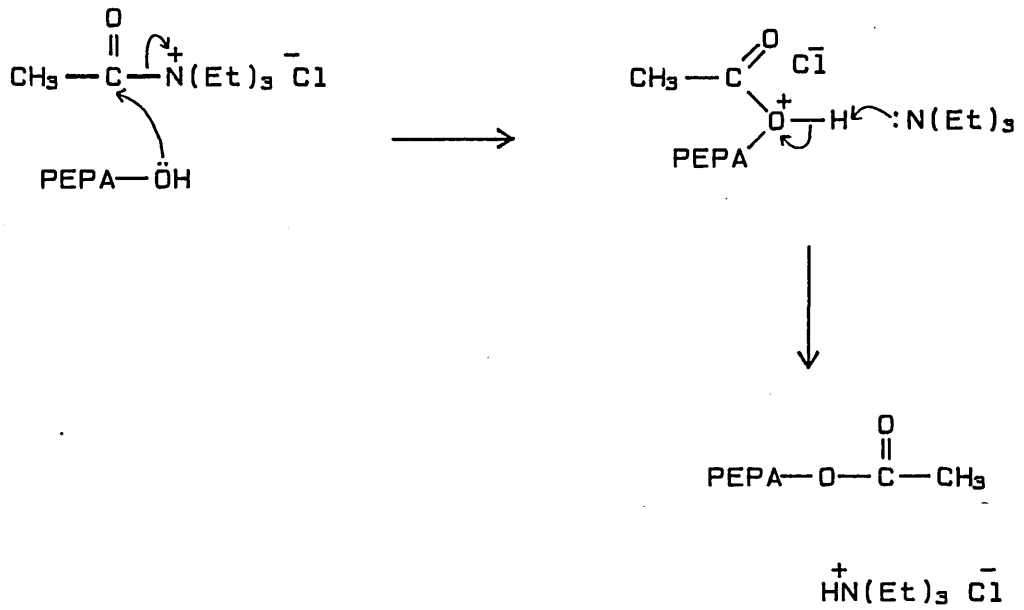
(49)

Again, a pink solid was recovered which recrystallised to give a white powder. This proved by analysis to be of structure (50). Infrared spectroscopy showed the OH of PEPA to have gone and the spectrum showed the peaks corresponding to a carbonyl and C=C absorption. ^{1}Hnmr gave the expected spectrum, as did ^{13}Cnmr and ^{31}Pnmr. Mass spectrometry showed a molecular ion at m/z = 248 (see Figure 2.6) and finally, the microanalysis results were in close agreement with the theoretical values.



(50)

In the above two reactions, triethylamine was added to the acid chloride before the addition of PEPA. This generated the acyl triethylammonium ion; in the case of the acetyl chloride reaction, this was the acetyltriethylammonium ion. This in turn reacted with PEPA to give the product, Scheme 6:



Scheme 6

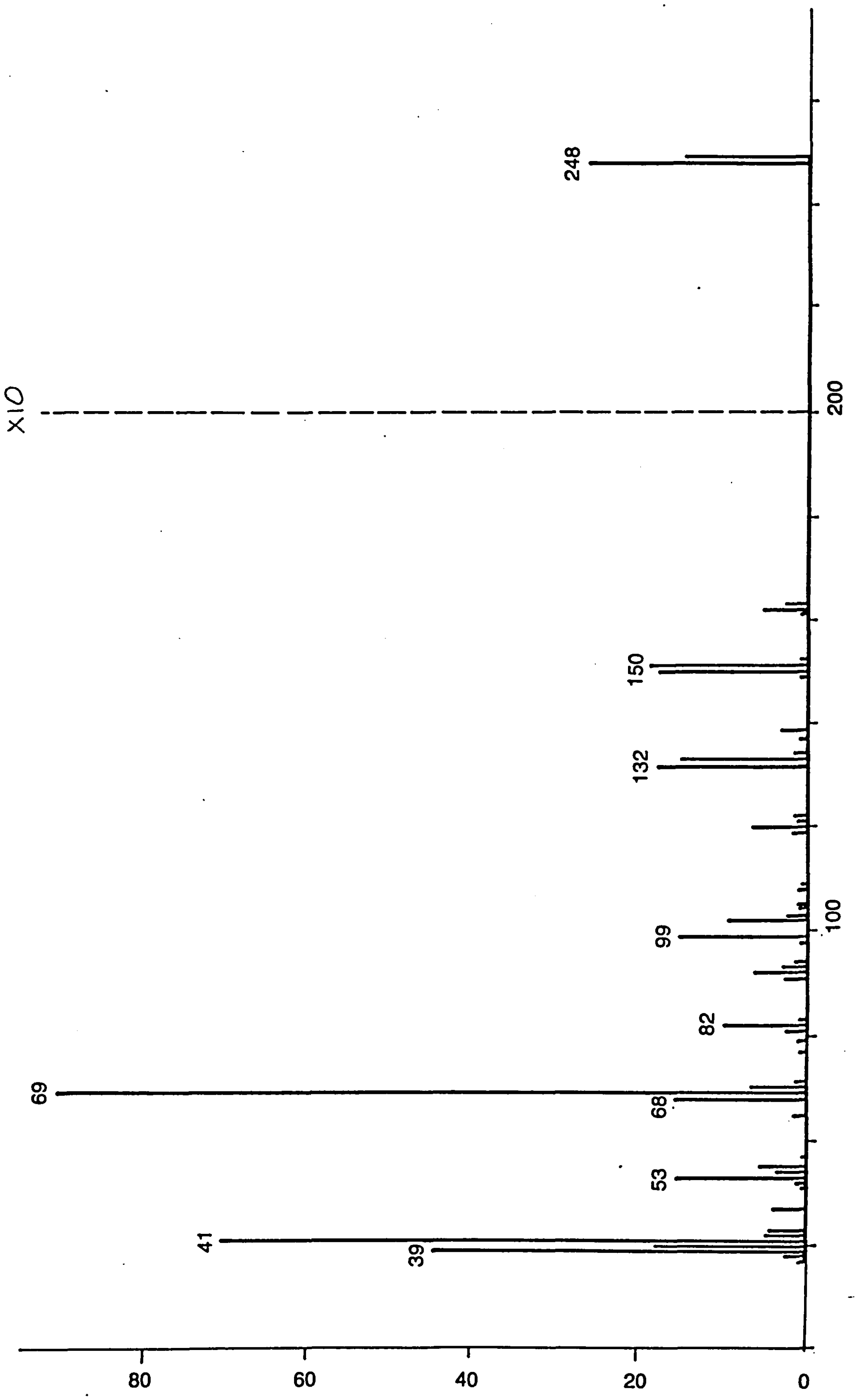
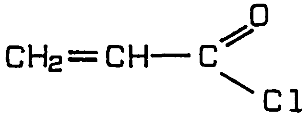


Figure 2.6

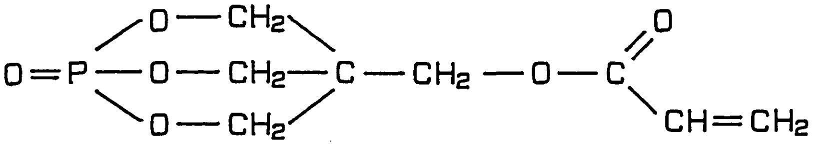
Mass Spectrum of 1-oxo-2,6,7-trioxa-1-phosphabicyclo[2.2.2] oct-4-ylmethyl methacrylate (50)

The methacrylate ester, (50), was subsequently used in the synthesis of polymeric flame retardants (see Chapter 4).

A similar reaction with acryloyl chloride, (51), was considered possible, to give the product (52), again having strong potential as a monomer in polymer formation.



(51)

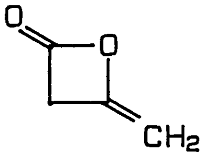


(52)

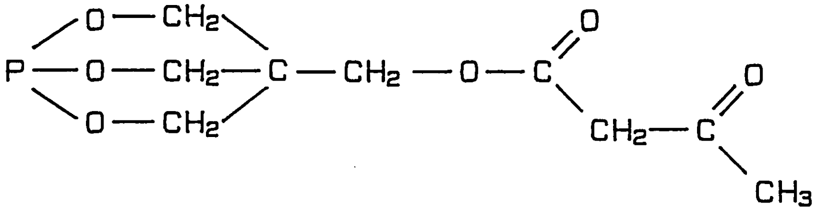
However, this never proved successful, the only product obtained being a dark brown oil. This was triturated with ether but to no avail. TLC showed the oil to consist of a mixture of compounds and the infrared spectrum was very complex. The reaction was repeated using various conditions, including a change of solvent and a shorter reaction time. In all cases the product recovered was a dark brown oil, so the work in this area was given low priority in order to concentrate on the chemistry of the accessible methacrylate ester, (50).

Reaction between PEPA and diketene

A German patent from 1976 claimed the production of a ß-keto ester of pentaerythritol phosphite.[46] Pentaerythritol phosphite, (6), was treated with diketene, (53), to give a product of structure (54).



(53)



(54)

This idea was attempted on PEPA, the target molecule being the corresponding ß-keto ester of PEPA. Following knowledge gained in acylation reactions of PEPA, the latter was treated with neat diketene, the resulting solution being heated at 130°C for four hours. An orange solution initially formed and quickly turned a deep red. No precipitate formed on cooling so the solution was poured into ether to form a deep red oil. Infrared spectroscopy of this oil gave a complex spectrum and TLC showed it to be a mixture of many components. Therefore less harsh conditions were examined.

Equimolar amounts of PEPA and diketene were dissolved in acetonitrile and heated under reflux for three hours. On cooling, the mixture was poured into ether to afford a white solid. Although this solid was identical to PEPA by melting point and on TLC, the infrared spectrum revealed slight traces of a carbonyl peak at 1750 cm^{-1}, the rest of the spectrum being identical to that of PEPA (including a strong OH absorption). The reaction was therefore repeated with twice the amount of diketene and heated for five hours. This time the infrared spectrum of the product showed two pronounced peaks at 1710 and 1750 cm^{-1}, though an OH peak at 3400 cm^{-1} was still present. TLC of the product showed it to consist of two components (one of which was PEPA), but whereas most of the product melted at 204°C, it also showed signs of slight melting at around 150°C.

The diketene concentration was increased again and the reaction mixture maintained at reflux temperature overnight. This time, TLC of the system showed only one spot, more polar than PEPA. The infrared spectrum showed a pattern similar to that of PEPA but with two differences: the alcohol peak at 3400 cm^{-1} had disappeared and there were two strong peaks in the carbonyl region at 1710 and 1750 cm^{-1}. The ^{1}Hnmr spectrum showed four peaks: a doublet at $\delta = 4.8$ ppm and a singlet at $\delta = 3.7$ ppm, ratio 6:2 corresponding to the usual PEPA structure; a singlet at $\delta = 4.2$ ppm (ratio 2) and a singlet at $\delta = 2.2$ ppm (ratio 3). This was consistent with the expected structure. ^{31}Pnmr identified a clear singlet at $\delta = -9.0$ ppm (Figure 2.7). ^{13}Cnmr showed the expected PEPA carbon skeleton with three extra peaks: one at $\delta = 206$ ppm corresponding to a ketone, one at

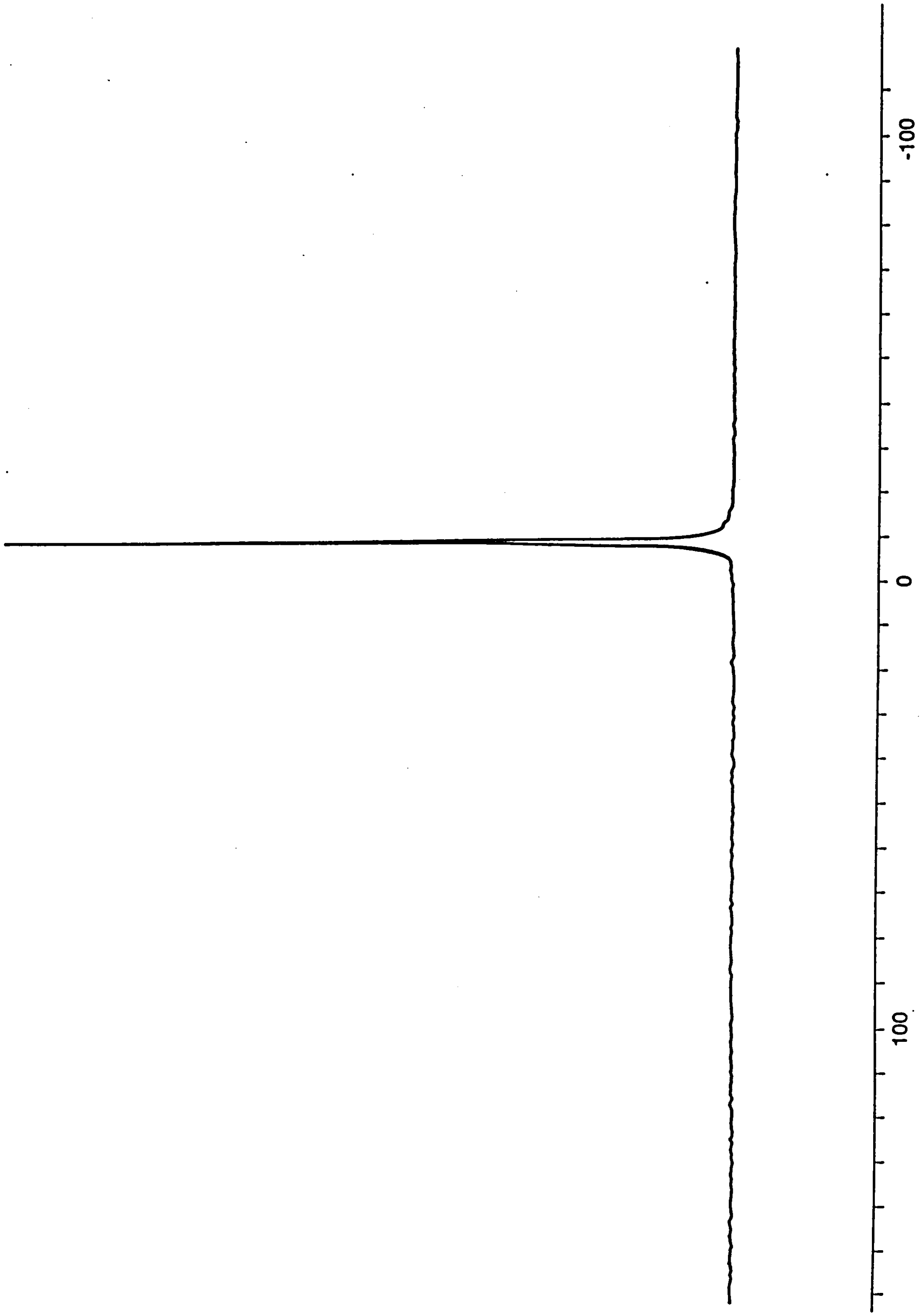
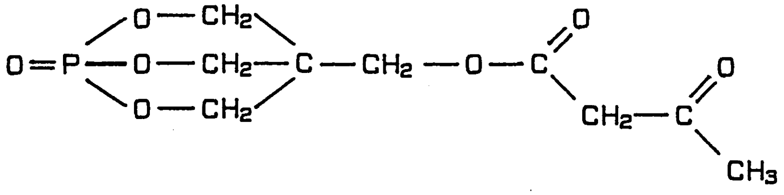


Figure 2.7

^{31}Pnmr Spectrum of 1-oxo-2,6,7-trioxa-1-phosphabicyclo [2.2.2]oct-4-ylmethyl acetoacetate (55)

δ = 167 ppm consistent with an ester and one at δ = 49 ppm which could be due to either the CH_2 or CH_3 carbon atom. The fourth peak expected but not seen (due to the remaining CH_2 or CH_3) as noted on previous occasions, was most likely masked by the multiplet signal due to the solvent, (deuterated acetone). The mass spectrum showed a molecular ion at m/z = 265 with a peak at m/z = 222 (M - $^+COCH_3$), together with peaks at m/z = 180 and below corresponding to the usual fragmentation pattern of PEPA. Microanalysis results were extremely close to the theoretical values, so the product was concluded as being of structure (55):



(55)

Reactions with chlorophosphoryl reagents

PEPA was treated with a series of chlorophosphoryl compounds in the hope that any resulting products might either prove to be promising intumescent additives themselves, or at least offer scope for further development. The reagents studied were diphenyl chlorophosphate, $(PhO)_2P(O)Cl$, phenyl dichlorophosphate, $PhOP(O)Cl_2$, and phenylphosphonic dichloride, $PhP(O)Cl_2$.

The initial method used heated the starting materials under reflux conditions in acetonitrile. These reactions proved unfruitful with unchanged PEPA being isolated. Conditions were altered with dioxan used as the solvent in order to raise the reaction temperature and a base, triethylamine, present to absorb any hydrogen chloride produced and thus help pull the equilibrium over. On cooling the reaction mixtures, in each of the three cases, a white solid precipitated which was found to be unreacted PEPA by TLC, melting point and infrared spectroscopy. TLC of the reaction solutions showed all three to contain large quantities of the respective phosphates. The reaction conditions were again altered, this time concentrating on only one system, that of diphenyl chlorophosphate. The previous reaction was repeated but without the base present and nitrogen was continuously bubbled through in an attempt to drive off any hydrogen chloride produced. Once again a white solid precipitated on cooling which was found to be PEPA, the supernatant liquid containing unreacted diphenyl chlorophosphate. An inorganic base, anhydrous sodium carbonate, was used in the reaction mixture but failed to promote any reaction as once again unreacted PEPA was recovered. This last reaction was repeated in acetonitrile to discover whether or not a basic solvent would have any effect. This was obviously not the case as yet again unreacted PEPA was isolated.

Finally, in the light of the conditions found to give optimum results with anhydride systems, PEPA was heated in a large excess of the chlorophosphate in the absence of a solvent. This method was used on all three original starting materials, but in all cases, although a white crystalline material precipitated, it was found to be unreacted PEPA, so this approach was abandoned.

Hydrogenation of ester derivatives of PEPA

Of the ester derivatives of PEPA described earlier in this section, four contain a carbon-carbon double bond that is not part of a ring system. These are compounds (21), (23), (28) and (50). A useful confirmatory test for such unsaturation is hydrogenation followed by analysis of the product. Another reason for the hydrogenation of these compounds was that if they did successfully polymerise, then the infrared spectrum of the polymer would be very similar to that of the hydrogenated monomer, thereby providing supportive evidence of the structure of the polymers.

The norbornene ester, (28), was never successfully hydrogenated as the compound was not soluble in any solvent under the conditions needed for the reaction.

The maleate ester, (21), did undergo successful hydrogenation by stirring a solution (in acetone) under hydrogen in the presence of a palladium catalyst. The product obtained was identical to compound (36), the ester produced on treatment of PEPA with succinic anhydride. This was confirmed by all the usual spectral techniques and microanalysis.

The crotonate ester, (23), was also successfully hydrogenated. The absorption peak due to the double bond disappeared from the infrared spectrum, accompanied by a shift in the carbonyl wavenumber from 1725 cm^{-1} to 1740 cm^{-1}. The $-CH_2-CH_2-CH_3$ chain was observed in the ^{1}Hnmr spectrum (see Figure 2.8) and both ^{13}Cnmr and ^{31}Pnmr supported the structure, as did mass spectrometry (showing a molecular ion at $m/z = 250$) and accurate microanalysis. The product was therefore of structure (56), ie 1-oxo-2,6,7-trioxa-1-phosphabicyclo[2.2.2]oct-4-ylmethyl n-butanoate.

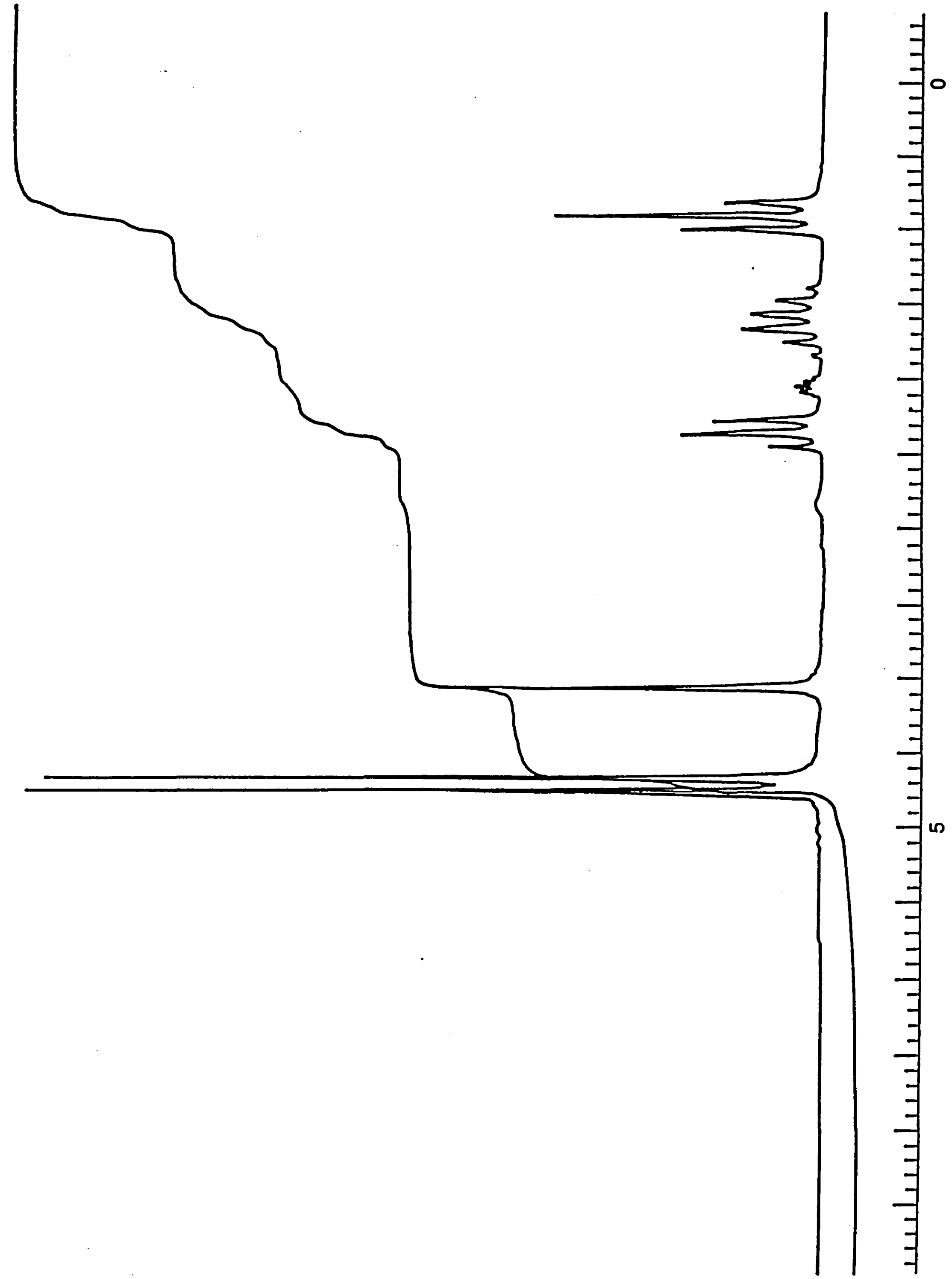
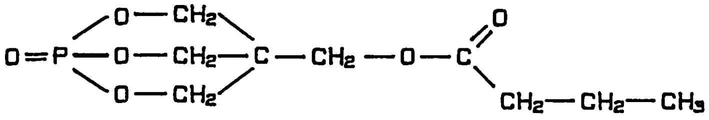


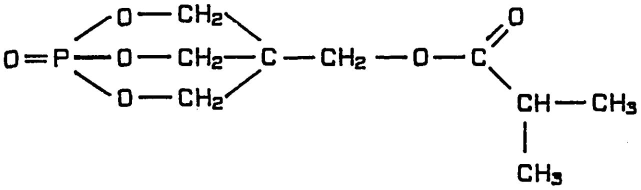
Figure 2.8

^{1}Hnmr Spectrum of 1-oxo-2,6,7-trioxa-1-phosphabicyclo [2.2.2]oct-4-ylmethyl n-butanoate (56)



(56)

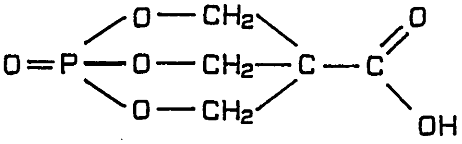
The final ester to be hydrogenated was the methacrylate ester, (50). Again, infrared spectroscopy of the product showed the C=C absorption peak to have gone and the carbonyl peak to have moved slightly. The product exhibited a new melting point, (120°C), and all nmr spectra confirmed the product as being (57), ie 1-oxo-2,6,7-trioxa-1-phosphabicyclo[2.2.2]oct-4-ylmethyl t-butanoate, a fact verified by the observation of a molecular ion by mass spectrometry and accurate microanalysis results.



(57)

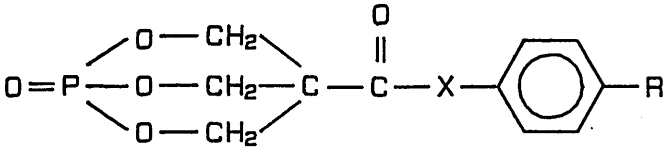
2.5 REACTIONS OF PEPA WITH NITRIC ACID

A Chinese paper has recently been quoted in Chemical Abstracts, claiming that PEPA could be converted to its corresponding acid, compound (58), by treatment with concentrated nitric acid.[47]



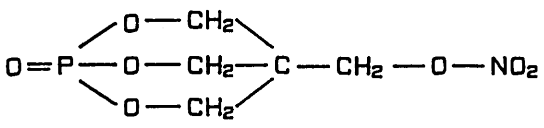
(58)

This acid was used as an intermediate in the preparation of a series of substituted bicyclophosphates of the general formula (59).



(59)

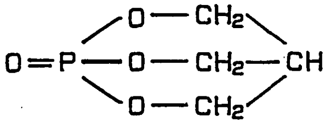
In the initial absence of the paper, and hence being devoid of a detailed method, PEPA was simply added to concentrated nitric acid and the resulting solution left for four hours. This solution was then diluted with water, extracted with dichloromethane and produced a yellow powder of low yield (30%). Initial analysis was encouraging, showing no traces of PEPA in the product. The product had a new, distinct melting point, 161-167°C, and was more polar than PEPA on TLC. The infrared spectrum showed the loss of the OH absorption peak from PEPA, but was inconclusive as to the existence of an OH from the acid functionality because this area was masked by the strong C-H vibrations from the nujol mull. A peak at 1630 cm^{-1} was observed and initially assigned as a carbonyl absorption peak from the acid group despite being of a lower value than might normally be expected. When added to a saturated solution of sodium bicarbonate, effervescence was observed, suggesting the presence of an acid group. However, spectral evidence rapidly began to point away from the expected simple PEPA-acid structure, ie (58). ^{13}Cnmr did not show a peak around $\delta = 170$ ppm as would have been expected for such an acid. In fact, ^{13}Cnmr revealed a spectrum of nothing more than the usual PEPA skeleton. This was confirmed by ^{1}Hnmr which again showed the usual PEPA spectrum, implying that the C-$\underline{CH}_2$-OH protons of PEPA were still present. The ^{1}Hnmr spectrum lacked a peak for an OH proton which would have been observed if either the acid had been synthesised or if the product was unreacted PEPA. Mass spectrometry showed the highest peak as being at m/z = 225, higher than the molecular ions for either PEPA (180) or the desired acid (194). The microanalysis results showed the composition to be greatly different from the structure of the acid, unexpectedly showing the presence of nitrogen. These results, when considered, showed an almost identical match to the theoretical values for the nitrate ester of PEPA, ie a compound of structure (60):



(60)

This structure is consistent with the nmr spectra obtained, the basic PEPA skeleton being maintained. R-O-NO_2 stretches occur in the infrared spectrum at 1630 cm^{-1}, explaining the results observed on the spectrum obtained. Structure (60) has a molecular mass of 225, explaining the peak observed by mass spectrometry which is, in fact, the molecular ion. A strong peak on the mass spectrum at m/z = 179 is explained by the loss of NO_2. The only unexplained observation was the reaction with sodium bicarbonate solution. However, it was noticed that after recrystallisation (from ethanol) the sample did not effervesce, so the initial reaction was probably due to some nitric acid trapped in the product. The product was therefore concluded as being of structure (60) ie 4-nitratomethyl-2,6,7-trioxa-1-phosphabicyclo[2.2.2]octane-1-oxide.

The Chinese paper[47] referred to above was eventually obtained and revealed that the nitric acid used in the claim was, in fact, a 60% solution. Also, the paper described the use of a catalyst, namely ammonium vanadate (NH_4VO_3). These conditions were copied and the reaction produced a white powder which recrystallised from water. However, analysis once more showed that the structure was not of the desired acid, (58). The infrared spectrum showed no evidence of either an OH or a carbonyl functionality, and mass spectrometry showed nothing of a higher m/z value than 150. This all suggested the structure as being that of (61), a fact which was verified by the nmr spectra and microanalysis.



(61)

It seemed likely that the acid, (58), had been formed, but on boiling in water during the recrystallisation stage it was decarboxylating, ie losing CO_2, to produce compound (61). This is a known compound, being reported in a European patent[44] discussed here in the introduction to section 2.4.

The reaction was therefore repeated to the recrystallisation stage. It was noticed that at this stage the product effervesced with sodium bicarbonate solution. Infrared spectroscopy and nmr data concurred with the literature[47] which, along with a molecular ion observed at m/z = 194 by mass spectrometry, confirmed the structure as (58).

This acid was used in attempts to synthesise intumescent salts for use as flame retardant additives (see Chapter 3).

2.6 CONCLUSIONS

Many derivatives of PEPA have been synthesised. Those containing a carboxylic acid functionality were used in the formation of intumescent salt systems, the resulting work being described in Chapter 3. The derivatives with a side chain containing a carbon-carbon double bond were investigated for their potential to polymerise, this work being discussed in Chapter 4.

The remaining compounds, ie PEPA derivatives containing no reactive functional groups, were investigated for their intumescent potential, both in their own right, and when mixed (physically) with melamine. Surprisingly, all these tests showed a lack of intumescence. On further study, a relationship between the molecular structure and the degree of intumescence of these and other derivatives of PEPA, was established. Details of these findings are given in the conclusions of Chapter 3 (section 3.6).

Throughout the course of the work described in this chapter, it became clear that PEPA did not show the reactivity normally associated with primary alcohols. For instance, the treatment of cyanuric chloride with an alcohol in the presence of a base is known to produce the corresponding trialkyloxy-*s*-triazine.[26, 27] This was found not to be the case with PEPA.

When cyanuric chloride and an alcohol are reacted in the absence of a base then cyanuric acid is formed along with the alkyl chloride. In the case of PEPA, the yield of cyanuric acid from such a reaction was less than 1%, the remainder of the cyanuric chloride being unaltered. In order to obtain the PEPA-chloride, ie compound (13), in any significant yield, far more powerful conditions were required (in this case treatment with Ph_3P/CCl_4).

The treatment of PEPA with an anhydride was found to afford no reaction if equimolar amounts were used and the mixture heated in a solvent. Even a large excess of anhydride produced a very low yield of product which would be contaminated with PEPA. In order for these systems to produce the desired products it was necessary to use a large excess of the anhydride in the absence of a solvent. Such a reaction would not proceed with less than a 3:1 molar ratio, and in some cases even more of the anhydride was needed.

Even these conditions were not sufficiently powerful to produce reactions with epichlorohydrin, diphenyl chlorophosphate, etc.

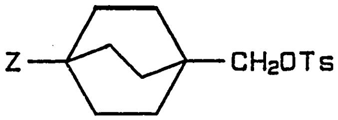
When PEPA was treated with diketene, a very reactive molecule, the diketene had to be present in just under a 7:1 molar ratio and the reaction took twenty-four hours.

It can therefore be concluded that for most reactions, PEPA must be in the presence of a very large molar excess of reactant, preferably in the absence of a solvent.

This surprising lack of reactivity of the alcohol function is the result of two factors, both due to the bicyclic structure of PEPA.

It is well established that nucleophilic substitution reactions occur less readily in molecules where the α or β carbons bear alkyl substituents. For instance, in the neopentyl system, $(CH_3)_3CCH_2$-X, the rate of substitution is about 10^{-5} times slower than in the respective ethyl system, CH_3CH_2-X.[48] Initially this was thought to be due to the electron donating polar effects of the substituents.[49, 50] However, it is now clear that the polar effects of alkyl groups are much too small to account for such a large retardation observed with the increased substitution.[51] The currently accepted explanation is that the rate decrease with increasing substitution is of steric origin, arising from nonbonded interactions in the transition state between the substituents and the entering and leaving groups.[52, 53] In the case of PEPA, the bicyclic structure in the ß position will provide sufficient steric hindrance to adversely affect nucleophilic substitution, ($\underline{S_N2}$), reactions on the carbon containing the alcohol group. This is demonstrated by the treatment of PEPA with cyanuric chloride. It is recognised that cyanuric chloride will react with an aliphatic alcohol to produce the corresponding alkyl chloride,[26, 27] yet with PEPA, despite being a primary alcohol, the yield of PEPA-chloride is negligible.

This steric effect does not influence the reactions of PEPA in which half esters are formed (eg reactions with anhydrides, acid chlorides, etc). These are still $\underline{S_N2}$ reactions, but this time PEPA is the nucleophile, attacking a carbonyl group (see Scheme 6). However, these reactions are also slow to proceed, a large excess of the electrophile being needed. The reason for this may be the poor nucleophilic behaviour of PEPA caused by the electron withdrawing effect of the phosphoric ester functionality of the bicyclic structure. It is known from studies on the 4-substituted bicyclo[2.2.2]octylmethyl tosylate system, (62), that electron withdrawing z groups do affect the reactivity of the tosylate functionality.[54]



(62)

2.7 EXPERIMENTAL

General Information

Infrared spectra were recorded on a Perkin Elmer 783 spectrophotometer. Samples were prepared as either potassium bromide (KBr) discs or nujol mulls. ^{1}Hnmr spectra were recorded on either a Joel PMX 60 SI or a Bruker WP 80 SY spectrometer. ^{13}Cnmr and ^{31}Pnmr spectra were recorded on a Bruker WP 80 SY spectrometer. Samples were prepared in the solvent stated in each method. Mass spectra were recorded on a Micromass 30 F mass spectrometer using electron impact at 70 eV, unless otherwise stated. Microanalyses were performed by the following: Butterworth Laboratories, Middlesex; Medac Ltd, Brunel University and Microanalysis Services, City University.

^{1}Hnmr and ^{13}Cnmr data is given on the δ scale using tetramethylsilane as an internal reference. ^{31}Pnmr data is given on the δ scale using 85% phosphoric acid as an internal reference with shifts to high field being negative in sign. Abbreviations used for the form of the signal are as follows: s = singlet, d = doublet, t = triplet, q = quartet and m = multiplet. Mass spectra (MS) data is given in units of m/z. Infrared data is given in units of cm^{-1}. For ^{13}Cnmr and infrared data, when the product is a derivative of PEPA, only the spectral peaks due to the substituents are quoted because the peaks resulting from the PEPA skeleton remain constant throughout.

Melting points are uncorrected. Thin-layer chromatography (TLC) was performed on Merck 5554 Alufolien Kieselgel $60F_{254}$ plates.

Dry dioxan was obtained by storage over sodium. Dry DMF was obtained by heating over calcium hydride followed by distillation under reduced pressure onto 4Å molecular sieves. Dry acetone was obtained by heating over calcium sulphate followed by distillation onto 4Å molecular sieves. Dry acetonitrile was obtained by shaking over 4Å molecular sieves. Dry isopropanol was obtained by heating under reflux with calcium oxide followed by distillation and storage over magnesium ribbon. Dry ethanol was obtained by warming over magnesium turnings/iodine followed by heating under reflux and subsequent distillation.

Hyflo super cell filter aid was obtained from BDH Chemicals. Aluminium isopropoxide was provided by Alcan Chemicals Ltd.

Synthesis of 4-hydroxymethyl-2,6,7-trioxa-1-phosphabicyclo[2.2.2] octane-1-oxide (PEPA) (1)

Pentaerythritol (42 g, 3.08×10^{-1} moles) was stirred with dioxan (210 mls) and the resulting slurry heated to 95°C. Phosphorus oxychloride (23.6 g, 1.54×10^{-1} moles) was added, with a further 23.6 g being added dropwise over the following two hours. The mixture was heated under reflux conditions for six hours during which a clear solution formed before a solid began to precipitate. On cooling, more solid precipitated which was filtered and washed respectively with cold dioxan (30 mls) and hexane (2 x 60 mls) before being dried under vacuum at 70°C. The crude product was recrystallised from dioxan to produce a white powder of yield 49 g (88%), melting point 205-209°C, (lit[6] 205-211°C).

IR (mull) 3400, 1300, 1060, 1020, 990 and 950. ^{1}Hnmr (D_6-DMSO) 3.3 (s, 2H), 4.1 (d, 6H), 5.1 (s, H). ^{31}Pnmr (D_2O) -3.4 (s). ^{13}Cnmr (D_2O) 79.8 (d), 60.4 (s), 41.8 (s). MS 180 (M^+), 150 ($M-H_2CO$).

Synthesis of trimethyl cyanurate (9)

Sodium hydroxide (20 g, 0.5 moles) was dissolved in methanol (166 mls). Cyanuric chloride (30.74 g, 1.66×10^{-1} moles) was added gradually over forty-five minutes whilst the reaction temperature was held at 29°C using a water bath. The subsequent mixture was stirred for two hours after which the precipitated sodium chloride was filtered off. The resulting solution was evaporated to leave a white powder which recrystallised from water to produce long needle-like, white crystals of yield 26.47 g (93%), melting point 129-134°C, (lit[24] 134-136°C).

^{1}Hnmr ($CDCl_3$) 4.0 (s). MS 171 (M^+).

ATTEMPTS TO SYNTHESISE TARGET MOLECULE (10)

Transesterification reactions

In all cases, unless otherwise stated, PEPA (1.58 g, 8.77×10^{-3} moles) and trimethoxy-s-triazine (0.5 g, 2.9×10^{-3} moles) were heated in a solvent (15 mls) under reflux conditions in the presence of a catalyst (c. 0.01 g).

1 In dioxan with sodium hydride

The solution was heated for one hour and on cooling yielded a white precipitate which analysed as PEPA, yield 1.20 g (76%), melting point 201-205°C.

The reaction was repeated with heating continued for six hours but with the same effect, PEPA being isolated. Yield 1.14 g (72%), melting point 203-206°C.

2 In dioxan with toluene-4-sulphonic acid

The solution was heated under reflux conditions for two hours after which it was distilled. Only one fraction of distillate was collected (99°C). On cooling, a white precipitate appeared which was characterised as unchanged PEPA of yield 1.28 g (81%), melting point 199-206°C.

3 In diglyme with sodium hydride

Initially a cloudy mixture formed, but after half an hour of reflux, the solution became a clear yellow. After three hours the solution was distilled but nothing came over with a boiling point below 150°C. TLC of the reaction liquid showed no reaction to have occurred, PEPA and trimethoxy-s-triazine being the only compounds present.

4 In diglyme with toluene-4-sulphonic acid

As above with identical results. No methanol was produced and TLC of the solution showed it to contain only the unreacted starting materials.

5 In the absence of a solvent

PEPA (1.58 g, 8.7×10^{-3} moles) and trimethoxy-s-triazine (0.5 g, 2.9×10^{-3} moles) were heated together on an oil bath at 160°C, the reaction flask being fitted with an air condenser. The triazine melted and the PEPA appeared to dissolve in it but after five minutes the mixture started to darken and after fifteen minutes was black and viscous. On cooling this formed a glass-like solid which had to be chipped out of the flask. Analysis revealed it to be a complex mixture of thermal breakdown components of the starting materials. Yield 1.92 g, melting point 64-79°C.

Reactions with cyanuric chloride (11)

In DMF

1 Cyanuric chloride (0.5 g, 2.7×10^{-3} moles) and PEPA (1.47 g, 8.1×10^{-3} moles) were heated in DMF (15 mls) under reflux conditions for one and a half hours during which the solution turned yellow. TLC of the reaction mixture showed a complex pattern.

2 Cyanuric chloride was heated, on its own, in DMF. TLC of the solution indicated a pattern very similar to the one observed above.

In dioxan

Cyanuric chloride (0.5 g, 2.7×10^{-3} moles) and PEPA (1.47 g, 8.1×10^{-3} moles) were heated in dioxan (15 mls) under reflux conditions. TLC of the solution showed unreacted cyanuric chloride and PEPA to be present. On cooling a white precipitate formed which was found to be PEPA. Yield 1.22 g (83%), melting point 201-205°C.

With sodium hydride

Sodium hydride (0.2 g, 8.1×10^{-3} moles) was washed with petrol under an inert atmosphere (nitrogen). The petrol was sucked off and dioxan (20 mls) added followed by PEPA (1.47 g, 8.1×10^{-3} moles) and the mixture heated under reflux conditions for two hours. Cyanuric chloride (0.5 g, 2.7×10^{-3} moles) was then added and heating continued for two and a half hours. The solvent was evaporated to afford a grey solid of yield 1.81 g.

MS 189/187/185/183 (M^+ for cyanuric chloride) and 180 (M^+ for PEPA).

With sodium hydroxide

PEPA (1.47 g, 8.1 x 10^{-3} moles) and cyanuric chloride (0.5 g, 2.7 x 10^{-3} moles) were added to sodium hydroxide (0.32 g, 8.1 x 10^{-3} moles) first in dioxan (20 mls) and then in DMSO (15 mls). After heating under reflux for three hours, both cases yielded a white precipitate which was found to be PEPA, melting point 203-206°C.

In 1,2-dichlorobenzene

PEPA (1.47 g, 8.1 x 10^{-3} moles) and cyanuric chloride (0.5 g, 2.7 x 10^{-3} moles) were heated in 1,2-dichlorobenzene under reflux conditions. Neither solid dissolved and on cooling were filtered off and found to be a simple physical mixture of the two.

In diglyme

Five reactions were attempted in diglyme, each using cyanuric chloride (0.5 g, 2.7 x 10^{-3} moles) with the addition of PEPA in the respective quantities: (1.47 g, 8.1 x 10^{-3} moles), (0.98 g, 5.4 x 10^{-3} moles), (0.49 g, 2.7 x 10^{-3} moles), (0.49 g, 2.7 x 10^{-3} moles) in the presence of triethylamine (0.27 g, 2.7 x 10^{-3} moles) and finally (0.49 g, 2.7 x 10^{-3} moles). In each case the mixtures were heated under reflux for four hours except for the final reaction which was heated for twenty-four hours. In all cases the reactants dissolved to give a yellow solution but none produced a precipitate on cooling. The solutions were all poured into separate amounts of petrol to give a yellow precipitate in each case, all of which were found to be mixtures of the starting materials.

In dioxan - twenty-four hour reflux

PEPA (1.47 g, 8.1 x 10^{-3} moles) and cyanuric chloride (0.5 g, 2.7 x 10^{-3} moles) were added to dioxan (20 mls) and the resulting solution heated under reflux conditions for twenty-four hours. On cooling, a white solid precipitated which was filtered, dried and found to consist of a white powder, melting point 204-207°C, containing a few white, crystalline needles, melting point > 300°C. The needles were found to be cyanuric acid, (12), by infrared and mass spectrometry. The white powder consisted mainly of PEPA but showed evidence of slight traces of PEPA-chloride, (13).

In acetonitrile

PEPA (0.49 g, 2.7 x 10^{-3} moles) and cyanuric chloride (0.17 g, 9.0 x 10^{-3} moles) were heated in acetonitrile (10 mls) under reflux conditions for four hours. On cooling, a precipitate formed which was found to be PEPA. Yield 0.33 g (67%), melting point 207-211°C.

In pyridine

PEPA and cyanuric chloride (quantities as above) were heated in pyridine under reflux conditions. The solvent turned yellow and then black over the course of three hours yet still contained some undissolved solvent. This solid was filtered off and found to be PEPA. Yield 0.45 g (92%), melting point 204-210°C.

With sodium carbonate

PEPA (1.47 g, 8.1×10^{-3} moles), cyanuric chloride (0.5 g, 2.7×10^{-3} moles) and sodium carbonate (0.86 g, 8.1×10^{-3} moles) were heated in dioxan (15 mls) under reflux conditions for twenty-four hours with mechanical stirring. A white solid gradually coagulated and remained in the flask for the duration of the reflux period. This solid was filtered and washed with water to remove any inorganics and unreacted PEPA. Yield 0.17 g (8.6%), melting point 150-250°C.

With butyl lithium

A two-necked flask was flame dried and PEPA (1.47 g, 8.1×10^{-3} moles) in dioxan (20 mls) added. A rubber septum was fitted to the flask and the system purged with nitrogen before butyl lithium (5 mls, 8.1×10^{-3} moles) was injected. This mixture (which turned yellow) was stirred for two hours before the addition of cyanuric chloride (0.5 g, 2.7×10^{-3} moles). The resulting mixture was heated under reflux, under nitrogen, for twenty-four hours. A yellow solid formed and the entire contents of the flask were poured into water in which everything dissolved. This solution was extracted by chloroform with the addition of sodium chloride to improve separation. The chloroform layer was dried (magnesium sulphate) and evaporated to leave an orange oil which proved to be a complex mixture of compounds.

Synthesis of 4-chloromethyl-2,6,7-trioxa-1-phosphabicyclo[2.2.2] octane-1-oxide (13)

Triphenylphosphine (2.6 g, 9.9×10^{-3} moles) was dissolved in acetonitrile (5 mls) then carbon tetrachloride (1 ml) injected. PEPA (0.45 g, 2.5 x 10^{-3} moles) was added and the mixture heated under reflux conditions to afford a clear, colourless solution. This was evaporated to leave a white powder which was triturated with toluene, filtered and washed with toluene (3 x 20 mls) to give a white powder of yield 0.44 g (88%), melting point 155 and 170-173°C, (lit[28] 171°C).

MS 278 (M^+ for $Ph_3P=O$) and 199/201 (M^+ for (13)).

SYNTHESIS OF ESTER DERIVATIVES OF PEPA

From reactions with anhydrides

In all cases, unless otherwise stated, PEPA (1.0 g, 5.5 x 10^{-3} moles) was heated in an excess of the anhydride on an oil bath at 150°C for three hours. All the reactions were carried out under nitrogen. If the anhydride was a liquid at room temperature and cooling the reaction solution produced no precipitate, then the solution was poured into ether. If the anhydride was a solid at room temperature then it was melted before the addition of PEPA and the solid obtained on cooling the reaction mixture was extracted with ether in a soxhlet funnel for twenty-four to thirty-two hours. The resulting products were all washed with ether and dried under vacuum from 30-50°C.

Synthesis of 4-acetoxymethyl-2,6,7-trioxa-1-phosphabicyclo[2.2.2] octane-1-oxide (18)

The product crystallised from solution and the crude material was recrystallised from ethanol to produce a white powder of 0.91 g (74%), melting point 164-168°C.

IR (mull) 1740 and 1380. ^{1}Hnmr (D_6-acetone) 4.9 (d, 6H), 4.0 (s, 2H), 2.0 (s, 3H). ^{31}Pnmr (D_6-acetone) -9.0 (s). ^{13}Cnmr (D_6-acetone) 206 (s), 20 (s). MS 222 (M^+). Microanalysis; found: C, 37.54; H, 4.96; $C_7H_{11}O_6P$ requires: C, 37.89; H, 4.99%.

Synthesis of mono[1-oxo-2,6,7-trioxa-1-phosphabicyclo[2.2.2]oct-4-ylmethyl]maleate (21)

On extraction with ether a white powder was recovered which recrystallised from glacial acetic acid with yield 1.04 g (71%), melting point 184-187°C.

IR (KBr) 2700-3100 (broad), 1725 and 1650. ^{1}Hnmr (D_6-acetone) 6.8 (s, H), 6.4 (s, H), 4.8 (d, 6H), 4.2 (s, H), 3.8 (s, 2H). ^{31}Pnmr (D_6-acetone) -8.9 (s). ^{13}Cnmr (D_6-acetone) 206 (s), 165 (s), 130 (s), 131 (s). MS 261 (M-OH), 260 ($M-H_2O$). Microanalysis; found: C, 38.48; H, 4.04; $C_9H_{11}O_8P$ requires: C, 38.86; H, 3.99%.

Synthesis of 1-oxo-2,6,7-trioxa-1-phosphabicyclo[2.2.2]oct-4-ylmethyl crotonate (23)

PEPA was dissolved in hot crotonic anhydride at 125°C to form a yellow solution which turned deep orange in five hours. On cooling, a precipitate formed which was recrystallised from glacial acetic acid to give a white powder of yield 0.70 g (52%), melting point 163-165°C.

IR (KBr) 1725, 1650, 1100, 900 and 720. ^{1}Hnmr (D_6-acetone) 6.0 (broad s, H), 5.7 (broad s, H), 4.7 (d, 6H), 4.1 (s, 2H), 1.8 (d, 3H). ^{31}Pnmr (D_6-acetone) -9.0 (s). ^{13}Cnmr (D_6-acetone) 205 (s), 132 (s), 129 (s). MS 248 (M^+), 233 ($M-CH_3$). Microanalysis; found: C, 43.53; H, 5.32; $C_9H_{13}O_6P$ requires: C, 43.46; H, 5.28%.

Reaction with methacrylic anhydride

PEPA was dissolved in hot methacrylic anhydride (125°C) but the solution soon solidified to produce a yellow glass. The reaction was repeated at 120°C and remained as a liquid solution for the duration of the reaction. On cooling, no precipitate was formed so the solution was poured into ether to give a white powder which was found to be unreacted PEPA, yield 0.86 g (86%), melting point 206-210°C.

Synthesis of mono[1-oxo-2,6,7-trioxa-1-phosphabicyclo[2.2.2]oct-4-ylmethyl]endo-5-norbornene-2,3-dicarboxylate (28)

PEPA and endo-5-norbornene-2,3-dicarboxylic anhydride were heated together at 165°C due to the high melting point of the anhydride. The resulting mixture was extracted with ether for forty-eight hours and recrystallised from glacial acetic acid to yield a white powder of 0.57 g (30%), melting point 280-286°C.

IR (mull) 3400 (broad), 1770, 1730, 1570, 1430 and 720. ^{1}Hnmr (D_6-acetone) 6.2 (broad s), 5.6 (s), 4.5 (m), 4.0 (d), 3.4 (m), 2.0 (t), 1.4 (broad s), 1.1 (t). ^{31}Pnmr (D_6-acetone) -8.9 (s). MS 344 (M^+), 330 ($M-CO_2$). Microanalysis; found: C, 48.70; H, 4.88; $C_{14}H_{17}O_8P$ requires: C, 48.85; H, 4.98%.

Synthesis of mono[methyl]endo-5-norbornene-2,3-dicarboxylate (27)

Endo-5-norbornene-2,3-dicarboxylic anhydride (2.0 g, 1.2 x 10^{-2} moles) was heated in methanol (20 mls) under reflux conditions for two and a half hours during which a clear solution formed. The solvent was evaporated to leave a sticky white solid which, on heating at 30°C under vacuum produced a white solid of needle-like crystals, yield 2.35 g (93%), melting point 81-85°C.

IR (mull) 1740, 1700, 1570 and 720. ^{1}Hnmr (D_6-acetone) 10.0 (broad s, H), 6.2 (m, 2H), 3.6 (s, 3H), 3.4 (m, 2H), 3.1 (broad s, 2H), 1.4 (s, 2H). ^{13}Cnmr (D_6-acetone) 207 (s), 174 (s), 136 (s), 134 (s), 51 (s), 48 (d). MS 196 (M^+). Microanalysis; found: C, 61.12; H, 6.15; $C_{10}H_{12}O_4$ requires: C, 61.22; H, 6.17%.

Synthesis of 1-oxo-2,6,7-trioxa-1-phosphabicyclo[2.2.2]oct-4-ylmethyl propanoate (30)

PEPA was heated with propionic anhydride which is a liquid at room temperature. No solid formed on cooling, but on pouring into ether, a white precipitate appeared. This recrystallised from toluene to yield a fine white powder of 0.90 g (69%), melting point 91-93°C.

IR (mull) 1740 and 1100. ^{1}Hnmr (D_6-acetone) 4.7 (d, 6H), 4.0 (s, 2H), 2.4 (q, 2H), 1.1 (t, 3H). ^{31}Pnmr (D_6-acetone) -9.0 (s). ^{13}Cnmr (D_6-acetone) 210 (s), 13 (s). MS 236 (M^+), 208 ($M-CH_2=CH_2$). Microanalysis; found: C, 40.56; H, 5.53; $C_8H_{13}O_6P$ requires: C, 40.68; H, 5.55%.

Synthesis of 4-trimethylacetoxymethyl-2,6,7-trioxa-1-phosphabicyclo [2.2.2]octane-1-oxide (32)

PEPA did not dissolve in trimethylacetic anhydride when heated at 150°C. The temperature was therefore raised until the PEPA did dissolve (at 170°C) to give a clear, colourless solution. On cooling, crystals appeared which were recrystallised from toluene to provide a white solid of 1.06 g (72%), melting point 195-197°C.

IR (mull) 1720 and 1395. ^{1}Hnmr (D_6-acetone) 4.7 (d, 6H), 4.0 (s, 2H), 1.2 (s, 9H). ^{31}Pnmr (D_6-acetone) -9.1 (s). ^{13}Cnmr (D_6-acetone) 205 (s), 26.8 (s). MS 264 (M^+), 249 ($M-CH_3$), 207 ($M-(CH_3)_3C$). Microanalysis; found: C, 45.52; H, 6.46; $C_{10}H_{17}O_6P$ requires: C, 45.46; H, 6.48%.

Synthesis of 1-oxo-2,6,7-trioxa-1-phosphabicyclo[2.2.2]oct-4-ylmethyl benzoate (34)

PEPA and benzoic anhydride were treated under the standard conditions to afford a grey powder which recrystallised from glacial acetic acid to give a white powder of yield 1.20 g (75%), melting point 229-232°C.

IR (mull) 1720, 1590, 1570 and 1500. ^{1}Hnmr (D_6-acetone) 7.8 (m, 5H), 4.9 (d, 6H), 4.3 (s, 2H). ^{31}Pnmr (D_6-acetone) -9.1 (s). ^{13}Cnmr (D_6-acetone) 205 (s), 133 (s), 130 (s), 128 (s). MS 284 (M^+). Microanalysis; found: C, 50.44; H, 4.64; $C_{12}H_{13}O_6P$ requires: C, 50.71; H, 4.61%.

Synthesis of mono[1-oxo-2,6,7-trioxa-1-phosphabicyclo[2.2.2]oct-4-ylmethyl]succinate (36)

Succinic anhydride was not sufficiently soluble in ether so the solidified reaction mixture was extracted with chloroform for forty-eight hours. This afforded a white powder of yield 0.98 g (63%), melting point 162-164°C.

IR (mull) 3100 (broad), 1750, 1710 and 1200. ^{1}Hnmr (D_6-acetone) 8.8 (broad s, H), 4.7 (d, 6H), 4.0 (s, 2H), 2.6 (m, 4H). ^{31}Pnmr (D_6-acetone) -3.0 (s). ^{13}Cnmr (D_6-acetone) 206 (s), 174 (s), 172 (s). MS 280 (M^+), 236 (M-CO_2). Microanalysis; found: C, 38.21; H, 5.12; $C_9H_{13}O_8P$ requires: C, 38.58; H, 4.68%.

Synthesis of mono[1-oxo-2,6,7-trioxa-1-phosphabicyclo[2.2.2]oct-4-ylmethyl]phthalate (38)

PEPA was treated with phthalic anhydride under the usual conditions to afford a white solid which recrystallised from glacial acetic acid to yield a fine white powder of 1.56 g (80%), melting point 188-193°C.

IR (mull) 3400, 1720, 1690, 1600, 1570, 1350, 1110 and 900. ^{1}Hnmr (D_6-acetone) 8.6 (broad s, H), 7.6 (m, 4H), 4.8 (d, 6H), 4.3 (s, 2H). ^{31}Pnmr (D_6-acetone) -8.7 (s). ^{13}Cnmr (D_6-acetone) 206 (s), 168 (s), 132 (d), 129 (d). MS 180, 150 (both PEPA). Microanalysis; found: C, 47.47; H, 4.00; $C_{13}H_{13}O_8P$ requires: C, 47.57; H, 3.99%.

Synthesis of mono[1-oxo-2,6,7-trioxa-1-phosphabicyclo[2.2.2]oct-4-ylmethyl]1,2,3,6-tetrahydrophthalate (40)

PEPA reacted with cis-1,2,3,6-tetrahydrophthalic anhydride under the standard conditions to give a white solid which recrystallised from acetic acid to produce a white powder of yield 1.08 g (58%), melting point 204-209°C.

IR (mull) 3100, 1720 and 900. ^{1}Hnmr (D_6-acetone) 8.2 (broad s, H), 5.6 (t, 2H), 4.7 (d, 6H), 4.1 (s, 2H), 3.1 (m, 2H), 2.0 (m, 4H). ^{31}Pnmr (D_6-acetone) -9.0 (s). ^{13}Cnmr (D_6-acetone) 211 (d), 130 (s), 31 (s). MS 332 (M^+), 298 ($M-CO_2$). Microanalysis; found: C, 46.89; H, 5.13; $C_{13}H_{17}O_8P$ requires: C, 47.00; H, 5.16%.

Reactions with naphthalic anhydride and 1,2,3-benzenetricarboxylic anhydride

In both cases, addition of PEPA to the molten anhydride produced a viscous, black material which was found to be a mixture of degradation products from both starting materials.

Synthesis of mono[1-oxo-2,6,7-trioxa-1-phosphabicyclo[2.2.2]oct-4-ylmethyl]glutarate (44)

PEPA was treated with glutaric anhydride under the standard conditions to give a white powder which recrystallised from glacial acetic acid. Yield 1.17 g (72%), melting point 169-173°C.

IR (mull) 3150 (broad), 1720 (broad). ^{1}Hnmr (D_6-acetone) 7.8 (broad s, H), 4.7 (d, 6H), 4.1 (s, 2H), 2.1 (m, 6H). ^{31}Pnmr

(D_6-acetone) -8.9 (s). ^{13}Cnmr (D_6-acetone) 206 (s), 174 (s), 33 (s), 26 (s). MS 294 (M^+). Microanalysis; found: C, 40.70; H, 5.06; $C_{10}H_{15}O_8P$ requires: C, 40.83; H, 5.14%.

Synthesis of mono[1-oxo-2,6,7-trioxa-1-phosphabicyclo[2.2.2]oct-4-ylmethyl]2,2′-oxydiacetate (46)

PEPA reacted with diglycolic anhydride under the usual conditions to give a solid which recrystallised from glacial acetic acid to produce a white powder of yield 1.20 g (73%), melting point 145-152°C.

IR (mull) 3200 (broad), 1750, 1720 and 1090. ^{1}Hnmr (D_6-acetone) 8.2 (broad s, H), 4.7 (d, 6H), 4.3 (m, 6H). ^{31}Pnmr (D_6-acetone) -8.9 (s). ^{13}Cnmr (D_6-acetone) 206 (s), 171 (s), 68 (s), 60 (s). MS 252 ($M-CO_2$), 237 ($M-CH_3CO_2^-$). Microanalysis; found: C, 36.41; H, 4.46; $C_9H_{13}O_9P$ requires: C, 36.50; H, 4.42%.

Treatment of PEPA with epichlorohydrin

1 PEPA (0.5 g, 2.8×10^{-3} moles) was added to excess epichlorohydrin (10 mls) and the mixture heated under reflux conditions for two and a half hours during which all the PEPA dissolved to afford a colourless solution. On cooling no solid appeared so the cold solution was poured into ether to afford a white precipitate. This was found to be PEPA by TLC and infrared spectroscopy. Yield 0.42 g (84%), melting point 204-210°C.

2 As above but heating continued for eight hours. On pouring into ether a white precipitate formed which was again found to be PEPA. Yield 0.39 g (78%), melting point 210-212°C.

3 As above, but continually heated for twenty-four hours. Unchanged PEPA was isolated on pouring into ether. Yield 0.43 g (86%), melting point 203-207°C.

4 PEPA (0.5 g, 2.8 x 10^{-3} moles) and triethylamine (0.28 g, 2.8 x 10^{-3} moles) were added to epichlorohydrin (10 mls) and the mixture heated under reflux conditions for four hours during which the solution turned orange. No solid formed on cooling therefore the solution was poured into ether to give a yellow oil. Yield 0.12 g (24%).

5 As above, using epichlorohydrin (7.0 g) in dry acetonitrile (15 mls). The mixture was heated under reflux conditions but on cooling, the solution yielded unreacted PEPA.

Reactions with acid chlorides

Synthesis of 4-acetoxymethyl-2,6,7-trioxaphosphabicyclo[2.2.2]octane-1-oxide (18)

1 Acetyl chloride (0.5 g, 6.4 x 10^{-3} moles) and triethylamine (0.64 g, 6.4 x 10^{-3} moles) were added to dioxan (15 mls) to produce a cloudy mixture with heat given off. PEPA (1.2 g, 6.4 x 10^{-3} moles) was added and the mixture heated to reflux for half an hour. After cooling, the mixture was filtered to produce a dirty white solid which, on washing with water, became tacky. Yield 1.4 g, melting point not distinct.

^{1}Hnmr ($CDCl_3$) 4.7 (d), 4.1 (s), 3.6 (s), 3.3 (q), 1.4 (t).

2 Acetyl chloride (0.55 g, 7.04 x 10^{-3} moles) and triethylamine (0.64 g, 6.4 x 10^{-3} moles) were added to dry acetonitrile (10 mls). A white precipitate formed in an exothermic reaction.

To this mixture was added PEPA (1.2 g, 6.4×10^{-3} moles) and the resulting mixture heated under reflux conditions for half an hour during which a red solution formed. On cooling, white crystals appeared. The whole mixture was poured into saturated sodium bicarbonate solution (100 mls), stirred, filtered and washed with water (3 x 20 mls). The final crude product was a light pink powder which recrystallised from glacial acetic acid to give a white powder of yield 0.98 g (69%), melting point 163-165°C.

IR (mull) 1740, 1380. ^{1}Hnmr (D_6-acetone) 4.6 (d, 6H), 3.9 (s, 2H), 1.8 (s, 3H). ^{31}Pnmr (D_6-acetone) 206 (s), 20 (s). MS 222 (M^+).

Synthesis of 1-oxo-2,6,7-trioxa-1-phosphabicyclo[2.2.2]oct-4-ylmethyl methacrylate (50)

Methacryloyl chloride (1.18 g, 1.13×10^{-2} moles) was added to a solution of triethylamine (1.00 g, 1.00×10^{-2} moles) in dry acetonitrile (10 mls). PEPA (1.80 g, 1.00×10^{-2} moles) was added and the resulting solution heated under reflux conditions for half an hour. On cooling the entire mixture was poured into a saturated solution of sodium bicarbonate (100 mls), stirred, filtered and washed with water (3 x 25 mls). The red solid isolated was recrystallised from glacial acetic acid to yield 1.32 g (53%), melting point 186-189°C.

IR (mull) 1710, 1630 and 1410. ^{1}Hnmr (D_6-acetone) 6.1 (broad s, H), 5.6 (broad s, H), 4.6 (d, 6H), 3.9 (s, 2H), 1.8 (s, 3H). ^{31}Pnmr (D_6-acetone) -9.1 (s). ^{13}Cnmr (D_6-acetone) 206 (s), 135 (s), 130 (s). MS 248 (M^+). Microanalysis; found: C, 43.47; H, 5.31; $C_9H_{13}O_6P$ requires: C, 43.53; H, 5.28%.

Attempted reactions with acryloyl chloride

1 Acryloyl chloride (0.5 g, 5.5×10^{-3} moles) was added to a solution of triethylamine (0.55 g, 5.5×10^{-3} moles) in dry acetonitrile (10 mls). PEPA (0.9 g, 5.0×10^{-3} moles) was added to the mixture and heated under reflux conditions for half an hour. On cooling, a white solid formed. The whole mixture was poured into a saturated solution of sodium bicarbonate (100 mls) to yield a dark brown oil. This was filtered and triturated with ether but never solidified and was found to be a complex mixture by TLC and infrared spectroscopy.

2 As above, but under reflux for only quarter of an hour to yield an identical result.

3 As above, but with dioxan as the solvent to yield the same result.

Synthesis of 1-oxo-2,6,7-trioxa-1-phosphabicyclo[2.2.2]oct-4-ylmethyl acetoacetate (55)

1 PEPA (1.0 g, 5.5×10^{-3} moles) was added to diketene (15 g, 1.78×10^{-1} moles) and the mixture heated on an oil bath at 130°C for four hours. After fifteen minutes all the PEPA had dissolved to form an orange solution which soon turned a deep red. After cooling no precipitate had formed so the solution was poured into cold ether to produce a dark red oil. This was analysed by TLC and infrared spectroscopy as a complex mixture. Yield 0.57 g.

2 PEPA (1.0 g, 5.5×10^{-3} moles) and diketene (0.46 g, 5.5×10^{-3} moles) were heated in dry acetonitrile (18 mls) under reflux conditions for three hours during which a pale yellow

solution formed. On cooling, the solution was poured into ether to precipitate a fine white powder which was shown to be unreacted PEPA by TLC and infrared spectroscopy. Yield 0.8 g (80%), melting point 205-207°C.

IR (mull) 1720 (v faint).

3 PEPA (1.0 g, 5.5×10^{-3} moles) and an excess of diketene (1.2 g, 1.4×10^{-2} moles) were heated in dry acetonitrile (12 mls) under reflux conditions for five and a half hours before being cooled and poured into ether. A pale pink powder was recovered which on analysis proved to be mainly PEPA though it did exhibit characteristics of the desired product by showing evidence of a carbonyl functionality. Yield 0.78 g (78%), melting point 150°C and 199-202°C.

IR (mull) 1710 and 1750.

4 PEPA (1.0 g, 5.5×10^{-3} moles) and an excess of diketene (3.0 g, 3.6×10^{-2} moles) were heated in dry acetonitrile (12 mls) under reflux conditions for twenty-four hours. On cooling the solution was poured into cold ether with vigorous stirring to yield a pink solid which was filtered, then washed with cold ether (3 x 20 mls) before being dried under vacuum at room temperature. The crude product recrystallised from ethanol to produce a white crystalline material of yield 0.69 g (47%), melting point 145-148°C.

IR (mull) 1710 and 1750. ^{1}Hnmr (D_6-acetone) 4.8 (d, 6H), 4.2 (s, 2H), 3.7 (s, 2H), 2.2 (s, 3H). ^{31}Pnmr (D_6-acetone) -9.1 (s). ^{13}Cnmr (D_6-acetone) 206 (s), 167 (s), 49 (s). MS 265 (M^+), 222 ($M-C(O)CH_3$). Microanalysis; found: C, 41.00; H, 4.98; $C_9H_{13}O_7P$ requires: C, 40.92; H, 4.96%.

Attempted reactions between PEPA and diphenyl chlorophosphate

1 PEPA (1.0 g, 5.5 x 10^{-3} moles) and diphenyl chlorophosphate (1.48 g, 5.5 x 10^{-3} moles) were dissolved in acetonitrile (15 mls) and the solution heated under reflux conditions for four hours. On cooling, a white precipitate formed which was characterised as PEPA by TLC and infrared spectroscopy. Yield 0.68 g (68%), melting point 204-208°C.

2 PEPA (1.0 g, 5.5 x 10^{-3} moles), diphenyl chlorophosphate (1.48 g, 5.5 x 10^{-3} moles) and triethylamine (0.56 g, 5.5 x 10^{-3} moles) were heated in dioxan (15 mls) under reflux conditions for eighteen hours to form a colourless solution. On cooling, a white precipitate formed which was characterised by TLC and infrared spectroscopy to be PEPA. Yield 0.76 g (76%), melting point 199-205°C.

3 This was repeated, in the absence of a base, with nitrogen bubbled continuously through the mixture. A white precipitate formed on cooling the reaction mixture which was found to be unreacted PEPA by TLC, ^{1}Hnmr and infrared spectroscopy. Yield 0.75 g (75%), melting point 204-210°C.

4 Again a repetition of the above, but in the presence of an inorganic base, anhydrous sodium carbonate (0.59 g, 5.5 x 10^{-3} moles). The base did not dissolve during the reaction and the mixture was filtered hot to remove any inorganic material. On cooling the filtrate, a white precipitate formed which was found to be unreacted PEPA of yield 0.65 g (65%), melting point 204-208°C.

5 The above reaction was repeated in acetonitrile but gave identical results, yield 0.72 g (72%), melting point 205-210°C.

6 Finally, PEPA (0.25 g, 1.4 x 10^{-3} moles) was heated in diphenyl chlorophosphate (5.0 g, 1.86 x 10^{-2} moles) on an oil bath at 120°C for half an hour after which the PEPA had not dissolved. The temperature was raised to 160°C whereupon the PEPA did dissolve and the solution was maintained at this temperature for three hours. On cooling, a white precipitate formed which was filtered and washed with ether before being analysed by infrared spectroscopy, TLC and ^{1}Hnmr and found to be unreacted PEPA, yield 0.22 g (88%), melting point 198-206°C.

Attempted reactions between PEPA and phenyl dichlorophosphate

1 PEPA (1.0 g, 5.5 x 10^{-3} moles) and phenyl dichlorophosphate (0.58 g, 2.76 x 10^{-3} moles) were heated in acetonitrile (15 mls) under reflux conditions for eighteen hours. On cooling, a white precipitate formed which was characterised by infrared spectroscopy and TLC to be unreacted PEPA of yield 0.70 g (70%), melting point 202-207°C.

2 The above reaction was repeated in the presence of triethylamine (0.56 g, 5.5 x 10^{-3} moles). After eighteen hours the solution was allowed to cool and unchanged PEPA was recovered. Yield 0.79 g (79%), melting point 205-210°C.

3 PEPA was dissolved in excess of neat phenyl dichlorophosphate and the solution kept at 160°C for four hours. Unreacted PEPA was recovered on cooling. Yield 0.21 g (84%), melting point 206-209°C.

Attempted reactions between PEPA and phenylphosphonic dichloride

PEPA (1.0 g, 5.5 x 10^{-3} moles) and phenylphosphonic dichloride (1.07 g, 5.5 x 10^{-3} moles) were heated in both acetonitrile and dioxan, the latter in the presence of triethylamine (0.55 g, 5.5 x 10^{-3} moles). Both experiments yielded unreacted PEPA after four hours of reflux. The respective yields were 0.81 g (81%) and 0.74 g (74%). The respective melting points being 203-209°C and 201-207°C.

Hydrogenation of compounds (21), (23) and (50)

Synthesis of mono[1-oxo-2,6,7-trioxa-1-phosphabicyclo[2.2.2]oct-4-ylmethyl]succinate (36)

The maleate ester of PEPA, (21), (1.0 g, 3.59 x 10^{-3} moles) was dissolved in acetone (15 mls) and a catalytic amount (100 mg) of palladium on carbon (10% loading) added. The mixture was stirred under hydrogen at room temperature for twenty-four hours. The catalyst was filtered off using Hyflo super cell filter aid and the filtrate evaporated on a rotary evaporator to produce a grey solid. The crude material was recrystallised from toluene to yield a fine white powder of 0.84 g (84%), melting point 162-164°C.

IR (mull) identical to that of (21) except for the loss of the peak at 1650. ^{1}Hnmr (D_6-acetone) 8.8 (broad s, H), 4.7 (d, 6H), 4.1 (s, 2H), 2.6 (s, 4H). ^{31}Pnmr (D_6-acetone) -3.0 (s). ^{13}Cnmr (D_6-acetone) 206 (s), 175 (s). MS 280 (M^+), 236 ($M-CO_2$). Microanalysis; found: C, 38.31; H, 4.68; $C_9H_{13}O_8P$ requires: C, 38.58; H, 4.68%.

Synthesis of 1-oxo-2,6,7-trioxa-1-phosphabicyclo[2.2.2]oct-4-ylmethyl n-butanoate (56)

The crotonate ester of PEPA, (23), (1.0 g, 4.1 x 10^{-3} moles) was treated as above to again produce a grey solid which recrystallised from toluene to give a white powder of yield 0.85 g (85%), melting point 90-92°C.

IR (mull) identical to (23) but without the peak at 1650. ^{1}Hnmr (D_6-acetone) 4.6 (d, 6H), 4.1 (s, 2H), 2.3 (t, 2H), 1.6 (sextet, 2H), 0.9 (t, 3H). ^{31}Pnmr (D_6-acetone) -9.1 (s). ^{13}Cnmr (D_6-acetone) 206 (s), 36 (s), 19 (s), 14 (s). MS 250 (M^+). Microanalysis; found: C, 43.20; H, 6.00; $C_9H_{15}O_6P$ requires: C, 43.21; H, 6.04%.

Synthesis of 1-oxo-2,6,7-trioxa-1-phosphabicyclo[2.2.2]oct-4-ylmethyl t-butanoate (57)

The methacrylate ester of PEPA, (50), (1.0 g, 4.1 x 10^{-3} moles) was treated as above and recrystallised from toluene to give a white powder of yield 0.87 g (87%), melting point 119-123°C.

IR (mull) as for (50) but without the peak at 1630. ^{1}Hnmr (D_6-acetone) 4.8 (d, 6H), 4.0 (s, 2H), 2.5 (m, H), 1.1 (d, 6H). ^{31}Pnmr (D_6-acetone) -9.0 (s). ^{13}Cnmr (D_6-acetone) 206 (s), 34 (s), 19 (s). MS 250 (M^+). Microanalysis; found: C, 43.31; H, 6.03; $C_9H_{15}O_6P$ requires: C, 43.21; H, 6.04%.

REACTIONS OF PEPA WITH NITRIC ACID

Synthesis of 4-nitratomethyl-2,6,7-trioxa-1-phosphabicyclo[2.2.2] octane-1-oxide (60)

PEPA (1.0 g, 5.5 x 10^{-3} moles) was dissolved in concentrated nitric acid (20 mls) to form a yellow solution which was allowed to stand, at room temperature, for four hours. The solution was then poured into deionised water (200 mls) and extracted with dichloromethane (3 x 150 cm^3). The organic layer was dried ($MgSO_4$) and evaporated to provide a yellow powder which recrystallised from ethanol to produce a very pale yellow powder of yield 0.37 g (30%), melting point 161-167°C.

IR (mull) 1630 and 1260. ^{1}Hnmr (D_6-acetone) 4.9 (d, 6H), 4.6 (s, 2H). ^{31}Pnmr (D_6-acetone) -9.4 (s). ^{13}Cnmr (D_6-acetone) 79 (d), 60 (s), 41 (s). MS 225 (M^+), 179 (M-NO_2). Microanalysis; found: C, 26.80; H, 3.55; N, 5.96; $C_5H_8NO_7P$ requires: C, 26.67; H, 3.55; N, 6.22%.

Synthesis of 2,6,7-trioxa-1-phosphabicyclo[2.2.2]octane-1-oxide (61)

PEPA (1.0 g, 5.5 x 10^{-3} moles) and ammonium vanadate (0.01 g) were dissolved in 60% nitric acid solution (3 mls) to give a yellow solution. This solution was stirred and heated at 60°C for seven hours during which it turned green with the evolution of much brown gas, before turning blue with the cessation of the gas evolution. On cooling, white crystals formed, the yield of which was increased by pouring the solution into ice cold water (20 mls). The crude product was washed with ice cold water (3 x 10 mls) before being recrystallised from boiling water to yield a white powder of 0.62 g (83%), melting point >300°C.

^{1}Hnmr (CF_3COOD) 4.9 (d, 6H), 4.4 (m, H). ^{31}Pnmr (CF_3COOD) -9.4 (s). ^{13}Cnmr (CF_3COOD) 80 (s), 40 (s). MS 150 (M^+). Microanalysis; found: C, 31.81; H, 4.56; $C_4H_7O_4P$ requires: C, 32.01; H, 4.70%.

Synthesis of 1-oxo-2,6,7-trioxa-1-phosphabicyclo[2.2.2]oct-4-ylmethanoic acid (58)

The reaction for the synthesis of (61), see above, was repeated to the recrystallisation stage, where, in place of boiling water, the crude product was recrystallised from hot water (60°C). This afforded a white solid (needle-like crystals). Yield 0.69 g (64%), melting point 265°C (dec), (lit[47] >260°C).

IR (mull) 3510 and 1730. ^{1}Hnmr (CF_3COOD) 4.7 (d, 6H), 6.2 (broad s, H). ^{31}Pnmr (CF_3COOD) -9.1 (s). ^{13}Cnmr (CF_3COOD) 174 (s), 78 (s), 62 (s). MS 194 (M^+), 150 ($M-CO_2$).

2.8 REFERENCES

1 W. D. Emmons and W. S. Wadsworth, US Patent 3,155,703.

2 W. Chang and M. Wismer, US Patent 3,189,633.

3 M. A. Gradsten, US Patent 3,134,662.

4 R. F. W. Ratz, US Patent 3,287,448.

5 I. Hechenbleikner, US Patent 3,293,327.

6 Y. Halpern, R. H. Niswander and I. Skokie, US Patent 4,454,064.

7 B. S. Ainsworth, US Patent 3,000,850.

8 W. A. Hills, US Patent 3,873,496.

9 Y. Halpern and I. Skokie, US Patent 4,154,930.

10 Y. Halpern, I. Skokie and C. T. Fleenor, US Patent 4,201,705.

11 Y. Halpern and I. Skokie, German Patent 29,10,746.

12 Y. Halpern, I. Skokie and C. T. Fleenor, US Patent 4,253,972.

13 Y. Halpern, D. M. Mott and R. H. Niswander, European Patent 01,26,491.

14 Y. Halpern and I. Skokie, US Patent 4,341,694.

15 Y. Halpern, D. M. Mott and R. H. Niswander, US Patent 4,478,998.

16 Y. Halpern, I. Skokie and D. M. Mott, US Patent 4,480,093.

17 E. M. Ballet and J. E. Casida, Science, 1973, 182, 1135.

18 J. H. Petajan, K. J. Voorhees, S. C. Packham, R. C. Baldwin, I. N. Einhorn, M. L. Grunnet, B. G. Dinger and M. M. Birky. Science, 1975, 187, 742.

19 K. J. Voorhees, I. N. Einhorn, F. D. Hileman and L. H. Wojcik, Polymer Letters, 1975, 13, 293.

20 Y. Ozoe, K. Mochida and M. Eto, Agric. Biol. Chem., 1982, 46, 555.

21 T. Fanni, K. Taira, D. G. Govenstein, R. Vaidyanathaswany and J. G. Verkadi, J. Am. Chem. Soc., 1986, 108, 6311.

22 N. A. Mukmeneva, V. K. Kadyrova, V. M. Zharkova and E. T. Mukmenev, J. of General Chem. of USSR, 1987, 57, 2494.

23 L. C. Thomas in "Interpretation of the Infrared Spectra of Organophosphorus Compounds", Heyden and Son Ltd, London, 1974.

24 J. R. Dudley, J. T. Thurston, F. C. Schaefer, D. Holm-Hansen, C. J. Hull and P. Adams, J. Am. Chem. Soc., 1951, 73, 2986.

25 J. Barry, G. Bram and A. Petit, Tetrahedron Letters, 1988, 29, 4568.

26 S. R. Sandler, J. Org. Chem., 1970, 35, 3967.

27 S. R. Sandler, Chem. and Ind., 1971, 1416.

28 Y. Ozoe and M. Eto, Agric. Biol. Chem., 1982, 46, 411.

29 Lancaster Synthesis Ltd, Organic Research Chemicals Catalogue, 1989/90, p 1020.

30 R. Appel, Angew Chem. Internat. Edn., 1975, 14, 801.

31 W. Ried and R. Appel, Justus Liebigs Ann. Chem., 1964, 51, 679.

32 R. Appel, F. Knoll, W. Michel, W. Morbach, H. D. Wihler and H. Veltmann, Chem. Ber., 1976, 58, 109.

33 W. Michel, PhD Dissertation, University of Bonn, 1974.

34 J. B. Lee and T. J. Nolan, Can. J. Chem., 1966, 44, 1331.

35 "Organic Phosphorus Compounds", vol 6, Ed G. M. Kosolapoff and C. Maier, Wiley Interscience, New York, 1973, p 269.

36 Hooker Chem. Corp., British Patent 889,338.

37 O. Neunhoeffer and W. Maiwold, Chem. Ber., 1962, 95, 108.

38 W. S. Wadsworth and W. D. Emmons, J. Am. Chem. Soc., 1962, 84, 610.

39 D. C. Ayres and H. N. Rydon, J. Chem. Soc., 1957, 1109.

40 H. Kaye and L. Todd, J. Chem. Soc., 1967, 142.

41 J. R. Cox, R. E. Wall and F. H. Westheimer, Chem. and Ind., 1959, 929.

42 J. R. Cox, R. E. Wall and F. H. Westheimer, J. Am. Chem. Soc., 1958, 80, 5441.

43 S. Ropuszynski and J. Perka, Polish Patent 92,253.

44 Y. Tamura and R. Tanaka, European Patent 01,16,200.

45 The Merck Index, Edition 9, p 5795, Ed M. Windoholz, Merck and Co Inc, New Jersey, USA.

46 E. Fischer, O. Mauz and N. Mayer, German Patent 25,05,152.

47 Y. Li, J. Wang, T. Han and Y. Liu, Acta Chimica Sinica, 1988, 46, 679.

48 T. H. Lowry and K. S. Richardson in "Mechanism and Theory in Organic Chemistry", third edition, Harper and Row, New York, 1987, p 377.

49 C. N. Hinshelwood, K. J. Laidler and E. W. Timm, J. Chem. Soc., 1938, 848.

50 P. B. D. de la Mare, L. Fowden, E. D. Hughes, C. K. Ingold and J. D. H. Mackie, J. Chem. Soc., 1955, 3200.

51 H. J. Hinze and H. H. Jaffe, J. Am. Chem. Soc., 1963, 85, 148.

52 D. Cook and A. Parker, J. Chem. Soc. B, 1968, 142.

53 M. Charton, J. Am. Chem. Soc., 1975, 97, 3694.

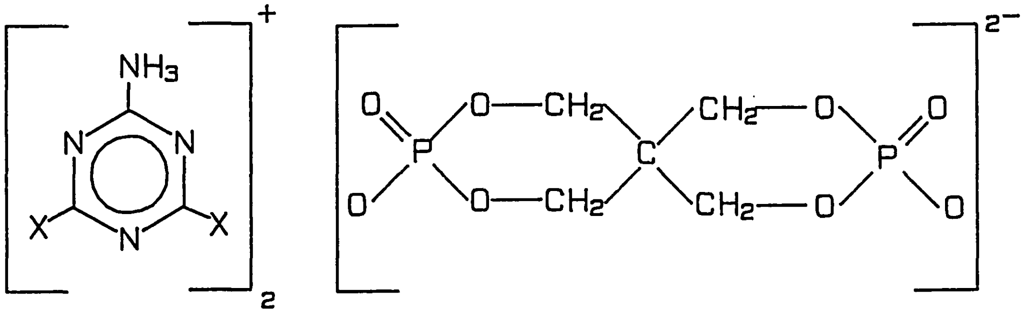
54 H. Holz and L. M. Stock, J. Am. Chem. Soc., 1965, 87, 2404.

CHAPTER 3 : INTUMESCENT SALT SYSTEMS

3.1 INTRODUCTION

The potential of intumescent salt systems as fire retardant additives was first realised by Halpern and Skokie when searching for a compound that contained spumific, carbonific and catalytic entities within the same structure.[1]

Their first patent was published in 1979 and claimed the usefulness, as flame retardants, of ditriazine salts of pentaerythritol diphosphate:



(1)

The triazines covered in the patent were melamine ($X = NH_2$) and ammelide ($X = OH$). The salts were claimed as flame retardants for polymers, though the only polymer to be specified by name and with test data to prove the effect, was polypropylene.

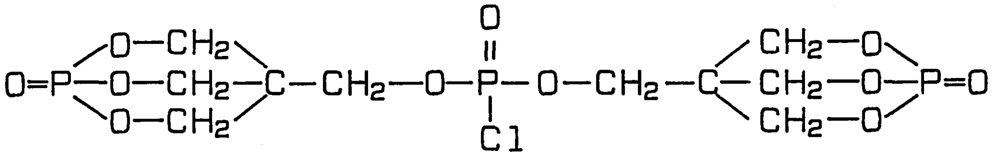
Within a year another patent was published for the same flame retardants described above, but this time as additives for polyolefins.[2] This patent also suggested the addition of a polyol to increase the amount of foam produced.

These flame retardants were again repatented in 1985 by the same authors, this time in Germany.[3]

One year after the original patent, a colleague of Halpern published a patent describing the same flame retardants, but this time with the addition of specific quantities of named polyhydric alcohols.[4] It was claimed that increased flame retardancy was observed on the addition of polyhydric alcohols in a ratio (by weight) to the salt from 1:9 to 1:5. When lesser amounts of the polyhydric alcohol was used, so that the ratio became less than 1:10, the improvement in the char formation became negligible. When the polyhydric alcohol was used in greater amounts, ie when the ratio was more than 1:4, then the flame retardant effect was reduced as the excess polyhydric alcohol supplied fuel to the flame.

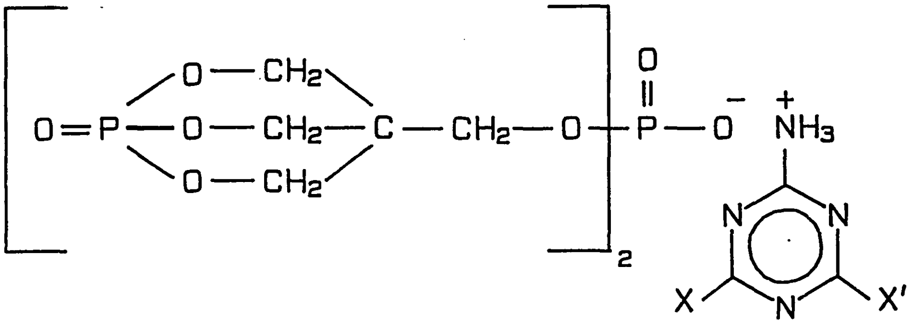
It was not until four years later that a patent was published, this time in Europe, in which an intumescent salt was used as a flame retardant additive with no extra additives required.[5] This patent was closely followed by an American patent repeating the claims.[6]

The work involved another complex organic phosphoric acid which was treated with an s-triazine to produce an intumescent salt. The actual acid was never isolated as it was produced <u>in situ</u> from the oxychloride, compound (2).



(2)

This was treated with the s-triazine under aqueous conditions to produce the salt (3) via the acid.



(3)

Although the patent covered s-triazines in general, the test data quoted in the patent was only for the melamine salt ($X = X' = NH_2$).

Another patent, published a week later by the same authors, covered specific salts, ie (3) where $X = X' = NH_2$ and $X = NH_2$, $X' = OH$.[7]

Once all this work was covered by patents, a comprehensive paper was published in which the two novel intumescent fire retardants were described, ie compounds (1) and (3).[8] These were referred to as "b-MAP" and "Melabis" respectively. There has been no advance on these flame retardants published in the literature since then and "Melabis" is still regarded as the state of the art in intumescent flame retardant additives.

Once a compound is produced that has potential as a flame retardant, it undergoes three initial tests to determine its suitability as an additive and its effectiveness as a flame retardant. First of all it is processed into a polymer. This is very important as it shows whether or not the additive will remain stable at the processing temperature, whether or not the additive will adversely affect the curing of the polymer and whether or not the additive has any detrimental effects on the physical and mechanical properties of the resulting polymer. This done, the additive-containing polymer undergoes two flammability tests which show how effective the additive is as a flame retardant. These tests are the limiting oxygen index and UL-94 tests.

Limiting oxygen index

The limiting oxygen index (L.O.I.) can be used as a comparative method for studying one aspect of polymer flammability, a parameter related to extinguishment.[9] The method described here was developed by Fenimore and Martin and is widely used.[10, 11] The L.O.I. of any polymer is defined as the percentage of oxygen in a mixture of oxygen and nitrogen which is just sufficient to keep the material burning.[12]

A strip or bar of the test sample is placed vertically in the centre of a glass chimney. A mixture of oxygen and nitrogen of known composition is passed through the chimney at a rate of about 4 cm^3s^{-1}. Before reaching the combustion zone, the gaseous mixture is homogenised by passing through a bed of glass balls situated at the base of the chimney. Once the apparatus has been purged, the test sample is ignited at the top by means of a burner. If the sample is extinguished before three minutes, the oxygen concentration is increased and the experiment repeated with a fresh sample. When the sample burns for three minutes, or when the flame propagates a length of 50 mm, the oxygen content of the gaseous mixture corresponds to the L.O.I. of the sample and is expressed as a percentage.

$$\text{L.O.I.} = \frac{[O_2]}{[O_2 + N_2]} \times 100\%$$

UL-94

The Underwriter's Laboratory vertical burning test (UL-94), unlike the L.O.I. test, has to be performed on a sample of specified dimensions.[13] The sample strip is held vertically in ambient atmosphere. A flame (of specified dimensions) is applied to the bottom of the strip for ten seconds then removed. The burning time is noted. If the sample burns for less than thirty seconds, the flame is applied again for a further ten seconds. The second burning time is noted and added to the first. A classification is then made on the basis of the observations. The samples measure 120 mm x 6 mm x 2 mm. The flame is supplied by a gas burner and must be a blue flame, 19 mm high. The flame is placed centrally under the unclamped end of the sample so that the tip of the flame just touches the sample.[14]

The following are noted:

(1) the duration of flaming after the removal of the first flame;

(2) the duration of flaming after the removal of the second flame;

(3) the duration of flaming and glowing after the removal of the second flame;

(4) whether or not the sample burns all the way up to the point at which it is clamped;

(5) whether or not the sample drips flaming particles which ignite a piece of cotton placed 300 mm beneath the sample.

The samples are awarded a grading of "V-0", "V-1", "V-2" or "fail" depending on their performance from the above observations. For most health and safety regulations, only those samples gaining the highest grade ("V-0") are considered successful. Therefore only the criteria for "V-0" are listed here.

These are:

(1) the sample must not burn for more than ten seconds after the removal of each flame;

(2) the sample must not burn for more than fifty seconds in total for ten applications for a set of five specimens;

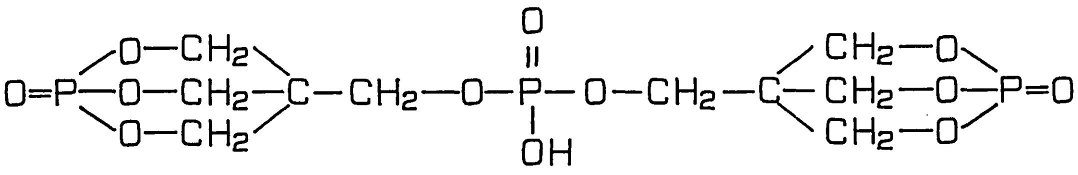
(3) the sample must not burn with flaming or glowing combustion up to the clamp;

(4) the sample must not drip burning particles that ignite the piece of cotton under the sample;

(5) the sample must not glow for more than thirty seconds after the removal of the flame.

3.2 SYNTHESIS OF STARTING MATERIALS

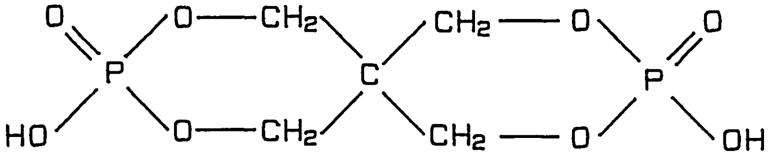
When Halpern et al published their work on intumescent salts, one of the acids used, ie compound (4), was never isolated and characterised, the reactions always being performed using the oxychloride (2) which was hydrolysed to (4) in situ.



(4)

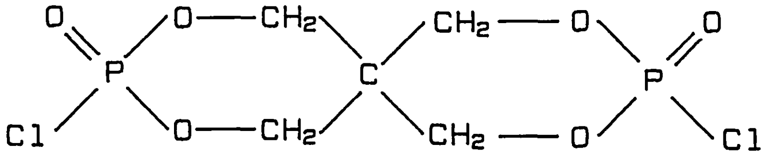
For the purposes of the work covered in this thesis, a fully isolated and characterised acid was needed. Therefore the method for the synthesis of (2) was followed with an extra step, hydrolysis, being added. This afforded a white powder for which analysis was encouraging. Although no molecular ion was observed by mass spectrometry, there was no peak splitting due to chlorine which suggested complete conversion from the oxychloride. Microanalysis results gave values close to the theoretical. The ^{13}Cnmr spectrum showed a carbon skeleton identical to PEPA, as would be expected, and ^{31}Pnmr showed a clean doublet at $\delta = -0.7$ and -3.7 ppm. The ^{1}Hnmr spectrum showed a pair of doublets as expected as both sets of protons will be split by phosphorus as both are in the P-X-CH_2 environment. The ratios of these doublets were unhelpful as one peak was masked by a much larger one due to proton exchange from the very acidic P-OH group to the solvent (D_2O). However, when this spectrum was re-recorded using CF_3COOD as the solvent, the problem did not arise and the spectrum showed two clean doublets of the expected ratio 6 : 2 with a singlet at δ = 11.0 ppm of integral 1 from the OH proton (see Figure 3.1). The structure was therefore characterised as (4) ie bis(4-hydroxymethyl-2,6,7-trioxa-1-phosphabicyclo[2.2.2]octane-1-oxide) phosphate and is referred to hereafter as bis-PEPA acid.

The other principal acid used by Halpern et al was 3,9-bis (hydroxy)-2,4,8,10-tetraoxa-3,9-diphosphaspiro[5.5]undecane-3,9-dioxide, compound (5), referred to as pentaerythritol diphosphate.



(5)

This again was prepared via the oxychloride intermediate, compound (6), though this time the free acid had been isolated.[8]



(6)

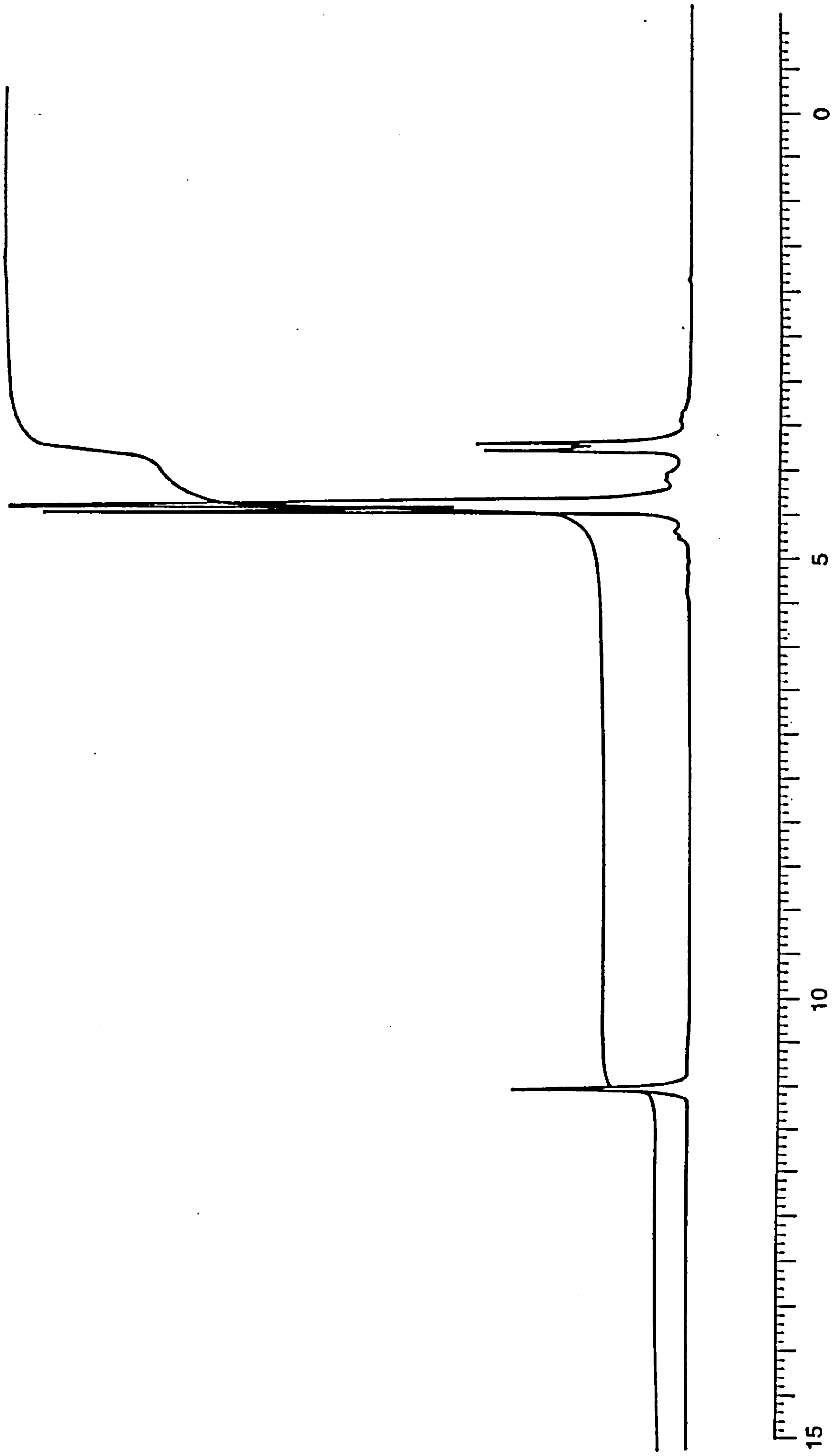


Figure 3.1

^{1}Hnmr Spectrum of Bis-PEPA Acid (4)

For the purposes of the work described in this thesis, compound (6) was originally prepared following the same route used by Halpern <u>et al</u>, ie a method originally developed by Ratz and Sweating.[15] However, it was found that this method, despite being quoted as giving an 80% yield, repeatedly gave very poor yields of below 25%. The product was also found to be of poor quality, with nmr and infrared spectra showing many impurities. Ratz and Sweating[15] claimed to recrystallise the product from glacial acetic acid, but here, this was found to give rise to a brown oil. Therefore an alternative method for the synthesis of (6) was found[16] and employed with satisfactory results, the product obtained in an 82% yield and on recrystallisation from glacial acetic acid yielded a white crystalline solid. From this it was a simple process to hydrolyse the product to give the desired acid (5).[17] Spectral analysis and microanalysis were consistent with those of the literature.[8, 15]

All the other acids employed as anions in the production of intumescent salts described in this chapter were half-esters of PEPA (derived from carboxylic acids), their syntheses and characterisations being detailed in Chapter 2.

All the bases used were available commercially except hexamethylmelamine, trimethylolmelamine, hexacyanomethylmelamine and hexabenzylmelamine, compounds (10), (14), (12) and (13) respectively, the structures of which are given in section 3.4.

Hexamethylmelamine is a known compound and was synthesised by the treatment of cyanuric chloride with dimethylamine, the properties of the product being consistent with those described in the literature.[18] Mass spectrometry showed the molecular ion (at m/z = 210, the proton nmr spectrum showed a singlet at $\delta = 6.9$ ppm; the melting point (171°C) and infrared spectrum also agreed with the literature.

Methylolated melamines have been known since 1947,[19] with trimethylolmelamine first mentioned in 1952.[20] The method for making this compound was taken from a more recent paper and used the reaction between melamine and formaldehyde.[21] Spectroscopic data were consistent with the structure (14). Mass spectrometry showed the molecular ion at $m/z = 216$, the ^{1}Hnmr spectrum revealed the expected peaks of correct integration and infrared spectroscopy also showed the expected spectrum.

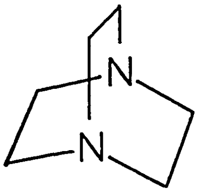
Hexacyanomethylmelamine was first synthesised in 1971, described in a German patent.[22] Cyanuric chloride was treated with iminodiacetonitrile, $HN(CH_2CN)_2$, in acetone. Mass spectrometry showed the molecular ion at $m/z = 360$ which, along with other spectral analyses confirmed the structure.

Hexabenzylmelamine has never previously been synthesised and thus is a novel compound. It was prepared following the same principles for the formation of hexacyanomethylmelamine, ie treating cyanuric chloride with dibenzylamine, $(PhCH_2)_2NH$, in acetone. A white solid was isolated which appeared as a single spot on TLC (with a different R_f value from either starting material, the R_f value in fact being very close to that of hexamethylmelamine). The solid also had a distinct melting point (142-145°C) which was different from that of either starting material. Mass spectrometry showed a molecular ion at $m/z = 666$ with a peak at $m/z = 575$ corresponding to the loss of a benzyl ion. The base peak was at $m/z = 91$ which was for the benzyl ion. The proton nmr spectrum (in D_2O) confirmed the presence of the aromatic and the CH_2 protons by showing the expected chemical shift and ratio. Infrared spectroscopy showed the expected melamine pattern with extra peaks at 1500 and 1610 cm^{-1} confirming the presence of the aromatic rings. The peak at 1650 cm^{-1}, due to $-NH_2$ bending, and the doublets at 3100-3500 cm^{-1}, due to $-NH_2$ stretching (showing the two bands because of symmetrical and unsymmetrical stretching) present in the spectrum of melamine, were absent in the spectrum of the product. Finally, the structure was confirmed by the microanalysis results.

3.3 MODEL SALT SYSTEMS

To gain understanding of the interpretation of analytical results, model salt systems using simpler starting materials were studied.

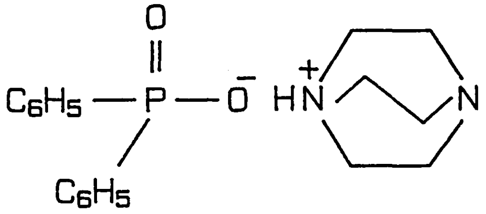
The first model reaction was the salt formation between diphenylphosphinic acid ($HO(O)P(C_6H_5)_2$) and 1,4-diazabicyclo[2.2.2]octane, ie dabco, compound (7).



(7)

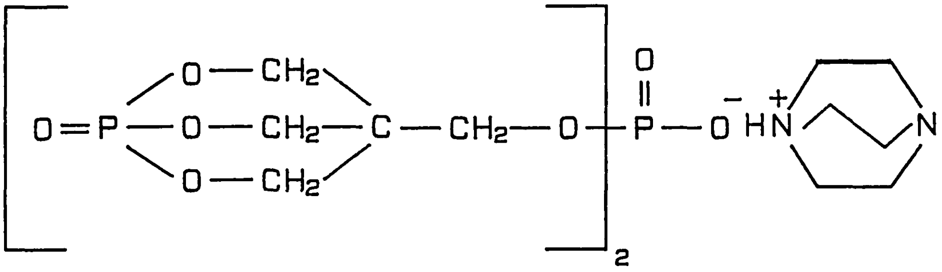
The two starting materials were heated under reflux conditions in acetonitrile whereupon they both dissolved. Dabco on its own does not dissolve in boiling acetonitrile, so this showed some chemical change to have occurred. On cooling, white crystals were precipitated. This product was recrystallisable from acetonitrile, a property which neither starting material possesses individually. Mass spectrometry revealed only the molecular ions for both starting materials but this was not too surprising as the harsh conditions within the mass spectrometer would be sufficient to separate the ions before the salt reaches the detector. The product was not soluble in any common nmr solvent (a fact which itself proves chemical change) so no nmr spectra could be obtained. More evidence of a chemical change was that the melting point of the product was significantly different from that of either starting material. Microanalysis showed results consistent with the theoretical values to show that the overall percentage of atoms remained constant, ie no part of either starting material was eliminated. The final and concluding evidence was the infrared spectrum. The product had been shown to consist of equal proportions of each starting material and it was needed to show that they were chemically bonded. The infrared spectrum of the product was compared to the spectrum of an equimolar physical mixture of the two starting materials. As expected, the two spectra were virtually identical. They did, however, have a couple of differences, namely extra peaks in the reaction spectrum at 2250 and 1160 cm^{-1} due to R_3NH^+ stretching and PO_2^- stretching respectively.

The analysis of the product therefore concluded it to be of structure (8).



(8)

Following the success of this system, the dabco salt of bis-PEPA acid was prepared. The reaction method was the same as before, but this time only one of the starting materials (dabco) appeared to dissolve. However, after heating under reflux for three and a half hours, there was a white solid present which appeared to be of greater volume than that of the initial amount of bis-PEPA acid used. The product was soluble in water and therefore nmr spectra were obtainable in D_2O. The ^{31}Pnmr spectrum showed two clean peaks which matched those of the bis-PEPA acid (δ = -0.7 and -3.7 ppm). Proton nmr showed the same pair of doublets observed for bis-PEPA acid, but with the absence of the -OH proton. There were two additional peaks at δ = 3.3 and 4.2 ppm which confirmed the presence of the protonated dabco and all the peaks were of the correct integral to confirm the equimolar presence of each ion. Mass spectrometry showed no molecular ion for the complete product, but did show a molecular ion for dabco along with its usual fragmentation pattern, plus the usual fragmentation pattern for bis-PEPA acid. Microanalysis values gave a close match to the theoretical values, again showing no loss of either, or part of either starting material. Finally, the infrared spectra of the reaction product and a physical blend were compared. The only differences were at values identical to those differences noted in the dabco-diphenylphosphinic acid work. The product was therefore concluded to be of structure (9)



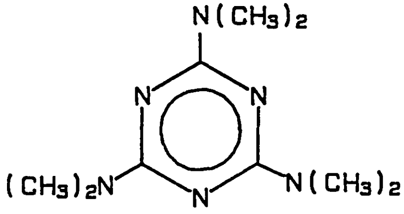
(9)

3.4 SYNTHESIS OF INTUMESCENT SALTS FOR USE AS FLAME RETARDANTS

3.4.1 SYSTEMS BASED ON BIS-PEPA ACID

The first reaction carried out in this area was a repeat of the work developed by Halpern et al in which they synthesised the melamine salt of bis-PEPA acid.[6] This product, compound (3) where $X = X' = NH_2$, is their state of the art flame retardant and is called 'Melabis'. The reaction was carried out in aqueous conditions, with the starting materials being stirred in hot water from which the product crystallised on cooling. Microanalysis, ^{13}Cnmr and mass spectrometry of the product all agreed with the results obtained in the literature. It was thought that these analytical results were not totally conclusive as they would also be obtained if analysing a very fine physical mixture of the two starting materials. Therefore the infrared spectrum of such a mixture was compared to the infrared spectrum of the reaction product. The reaction product showed four extra peaks not present in the spectrum of the physical mixture. These were at 1520 cm^{-1} (due to NH_3^+ bending), 1185 and 1250 cm^{-1} (due to the PO_2^- ion) and an unassigned peak at 780 cm^{-1}. There was also one peak missing from the spectrum of the product which is seen in the spectrum of the mixture at 900 cm^{-1}, caused by vibration of the P-OH bond. The structure was therefore confirmed as that of (3). This material provided a useful standard for comparison in test results (see later).

Other s-triazines were investigated for their potential to produce intumescent salts with bis-PEPA acid, the aim being to discover if altering the substituents on a substituted melamine would affect the intumescent properties. Hexamethylmelamine, (10), was easily prepared from cyanuric chloride with an excess of dimethylamine.

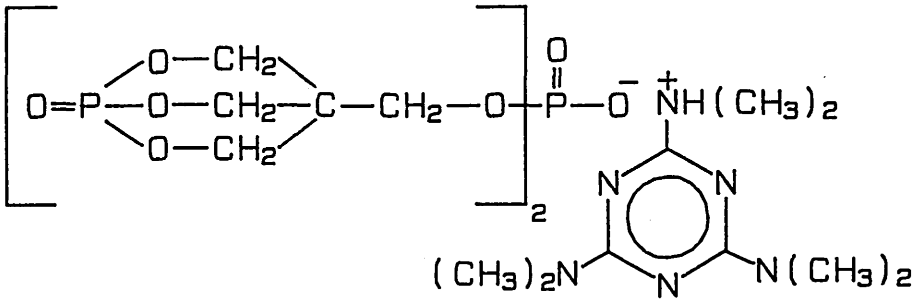


(10)

The hexamethylmelamine was mixed with bis-PEPA acid and treated with boiling water as before. Both starting materials dissolved, a favourable observation as the s-triazine is not soluble in boiling water. The solution was filtered and cooled as before. This time there was no precipitate, even on cooling to 2°C, so the solution was evaporated to dryness, leaving a white solid. This product was not soluble in any common nmr solvent, so no nmr spectra were possible. TLC of the reaction solution before evaporation showed no presence of free acid or free s-triazine. Microanalysis gave values approximate to the theoretical values for carbon and hydrogen, but 1.5% away from the theoretical value for nitrogen. This was not too surprising as there was no way of purifying the product and a crude sample had to be used for analysis. With this in mind, the values were not too discouraging. Infrared spectroscopy of the product showed the same additional peaks when compared to the infrared spectrum of a physical mixture as was observed with 'Melabis'. When placed in an open flame, the product displayed good intumescent properties, far more foam being produced than when the free acid was treated under the same conditions. The product also displayed greater foam formation than an equal amount of the physical mixture of the two starting materials.

However, TGA of the product showed it to be less thermally stable than 'Melabis' (losing 17% of its weight under 100°C as compared to 3% for 'Melabis' but remaining comparable from there on).

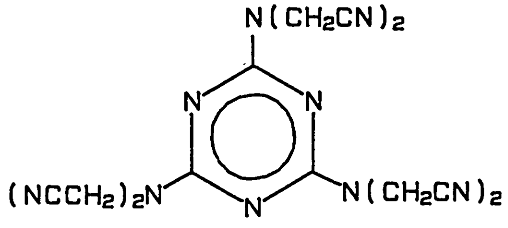
The product was concluded to be of structure (11) and due to its good intumescent properties, was tested for flame retardancy in a polyester (see later).



(11)

The synthesis of (11) was attempted a second time, using a different method, in an endeavour to see if the salt formation was possible in non-aqueous conditions. The method used in the model salt syntheses was employed, ie using acetonitrile as the solvent. During the course of the reaction, the bis-PEPA acid did not dissolve whereas the s-triazine went into solution very quickly. After an extended period of reflux, TLC of the reaction liquor showed the presence of large quantities of unreacted hexamethylmelamine but nothing else. The white solid which had remained during the reaction was analysed by infrared spectroscopy and its melting point to show it was unreacted bis-PEPA acid, so it was concluded that no reaction had occurred.

Due to the above lack of success, the use of aqueous conditions were resumed. Another s-triazine, hexacyanomethylmelamine, (12), was used in an attempted salt synthesis.

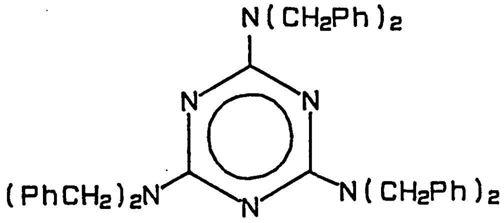


(12)

It was envisaged that this triazine, having twice the nitrogen content of melamine, would provide a greater spumific content to the resulting salt.

After five minutes of stirring the starting materials in boiling water, a large amount of solid remained undissolved. The mixture was filtered and the undissolved solid was analysed by infrared spectroscopy and TLC after which it was shown to be unchanged hexacyanomethylmelamine. Nothing crystallised from the filtrate on cooling so it was evaporated to dryness to yield a white powder which was found to be bis-PEPA acid. Obviously no reaction was taking place between the two starting materials. The experiment was repeated with prolonged stirring in boiling water (twenty minutes) but with the same results. The most likely reason for the failure of this reaction is the electron-withdrawing effect of the cyanomethyl substituents on the amine nitrogen atoms which therefore reduces the basicity of the molecule.

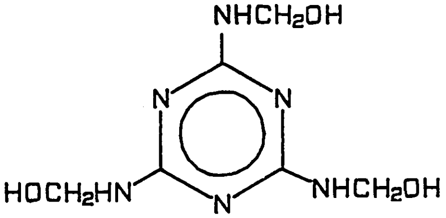
This lack of reaction was also observed with the next s-triazine used, hexabenzylmelamine (13), which was employed to see if a resulting salt would produce more char on burning due to the increased carbon content.



(13)

Again, filtration separated the two starting materials which were identified by infrared spectroscopy and melting point. This time the lack of reaction is most probably due to the effects of steric crowding about the key nitrogen atoms. These last two reactions, although producing no desired product, served as useful controls. They showed that in the absence of salt formation between bis-PEPA acid and a melamine derivative, the two starting materials are separated during the work up procedure (by filtration) and hence was further proof that the salts obtained so far are not just physical mixes of the starting materials.

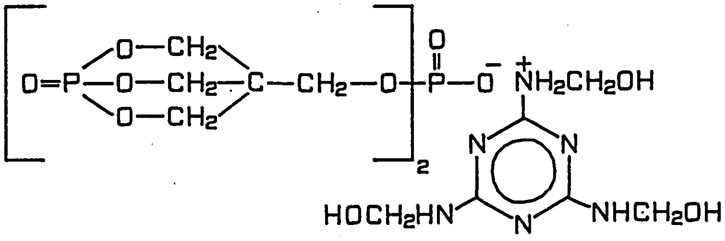
The final s-triazine salt of bis-PEPA acid to be synthesised was with trimethylolmelamine (14).



(14)

Both starting materials dissolved during the reaction, but again no precipitate was produced on cooling the filtrate. On evaporation a white powder was produced with a melting point much higher than that of either starting material. Once isolated by the removal of the water, this product possessed a much lower water solubility - to such an extent that nmr spectra in D_2O were not possible. It was considered that the heat involved in the evaporation procedure was somehow curing the salt to yield a less soluble product. This will be discussed later.

Mass spectrometry of the product showed the molecular ion for the s-triazine and the usual fragmentation pattern for the acid. The infrared spectrum showed both moieties present and again had extra peaks (as observed previously) when compared to the spectrum of a physical mix. Microanalysis gave satisfactory matching to the theoretical values. In order to obtain a proton nmr spectrum, the reaction was repeated on a much smaller scale in D_2O. A spectrum of the final solution before evaporation was thus enabled to be recorded. The spectrum was inconclusive as it was very noisy, but it did show the expected peaks for bis-PEPA acid with an extra peak at $\delta = 3.4$ ppm which was also observed in the spectrum of trimethylolmelamine on its own. The desired salt (15) was concluded to have been synthesised and was eventually found to be a very promising flame retardant, details of which are given in section 3.5.



(15)

As stated above, it appeared that the evaporation temperature was in some way affecting the water solubility of the salt. A cause for concern at this stage was a slight smell of formaldehyde present when the water was evaporated. It was thought possible that during this process the trimethylolmelamine was decomposing to melamine with the liberation of formaldehyde. If this was so, the intumescent salt obtained would in fact be the melamine salt of bis-PEPA acid, in other words 'Melabis', the compound already synthesised and patented by Halpern _et_ _al_.[8]

The trimethylolmelamine salt was heated at 150°C overnight in order to maximise any affect that heat might have on the sample. It was then compared to a sample of 'Melabis' in an attempt to prove that it had a different composition. The first piece of evidence to suggest that the two salts were indeed different was infrared spectroscopy. The infrared spectrum of the trimethylolmelamine salt showed a broad OH peak which was absent on the spectrum of 'Melabis'. This confirmed the existence of at least one methylol group and hence showed the salt not to be simple 'Melabis'. The TGA traces of each salt show notable differences, enough to verify different composition (see Figure 2). The final piece of evidence to show that

'Melabis' had not been formed was the microanalysis results shown in Tables 1 and 2:

Table 1

	Trimethylolmelamine Salt Theoretical Values	Actual Values	Difference
% C	30.09	29.89	0.20
% H	4.54	4.32	0.22
% N	13.20	11.21	1.99

Table 2

	Melamine Salt Theoretical Values	Actual Values	Difference
% C	28.47	29.89	1.42
% H	4.20	4.32	0.12
% N	15.33	11.21	4.12

As observed, the overall composition was a far better match for the trimethylolmelamine salt than for 'Melabis'.

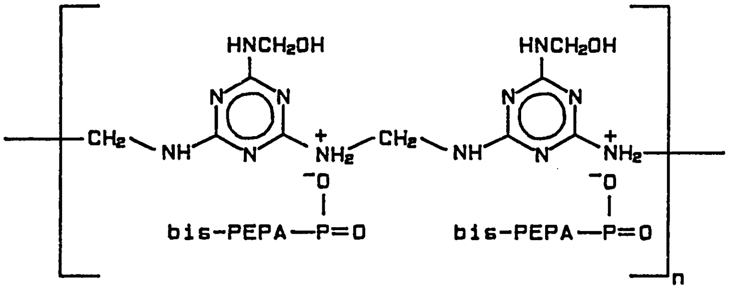
Therefore it was concluded that the product obtained by the treatment of trimethylolmelamine with bis-PEPA acid was structurally different from 'Melabis'.

A large batch of the trimethylolmelamine salt was then synthesised and divided into six samples. One sample was left untreated, the others heated at 100, 125, 150, 175 and 200°C respectively for twenty hours. The sample heated at 200°C had discoloured overnight, turning a dark brown, so this was disregarded. The infrared spectra, TGA traces and microanalysis of the rest were compared. The infrared spectra of all were virtually identical, as were the TGA traces. The % C fell gradually (though slightly) as the samples were heated to higher temperatures, with the final carbon value of 29.30% at 175°C. The % H remained fairly constant whilst the % N dropped by just under 1% over the range.

The relative intumescence of each sample remained constant when put in an open flame. The most noticeable difference between the samples was their water solubility. The untreated salt had a water solubility of 2.80 gl^{-1}. After heating at 175°C for twenty hours, this dropped to 0.084 gl^{-1}.

The only satisfactory explanation for the decrease in solubility, the change in elemental composition, the retention of infrared and TGA characteristics and the smell of formaldehyde noted, was the formation of a polymeric salt.

Such a salt could have a variety of structures, one such example being:



(16)

The microanalysis data would fit such a structure with a decrease in the carbon percentage and an increase in the nitrogen percentage as formaldehyde, $H_2C=O$, is eliminated.

Whatever the actual structure, this salt showed greater intumescence when held in a flame, compared to 'Melabis'. The TGA traces also revealed it to be more thermally stable than 'Melabis' (see Figure 3.2) and hence this salt was one of those assessed for its flame retardancy effect in polymers.

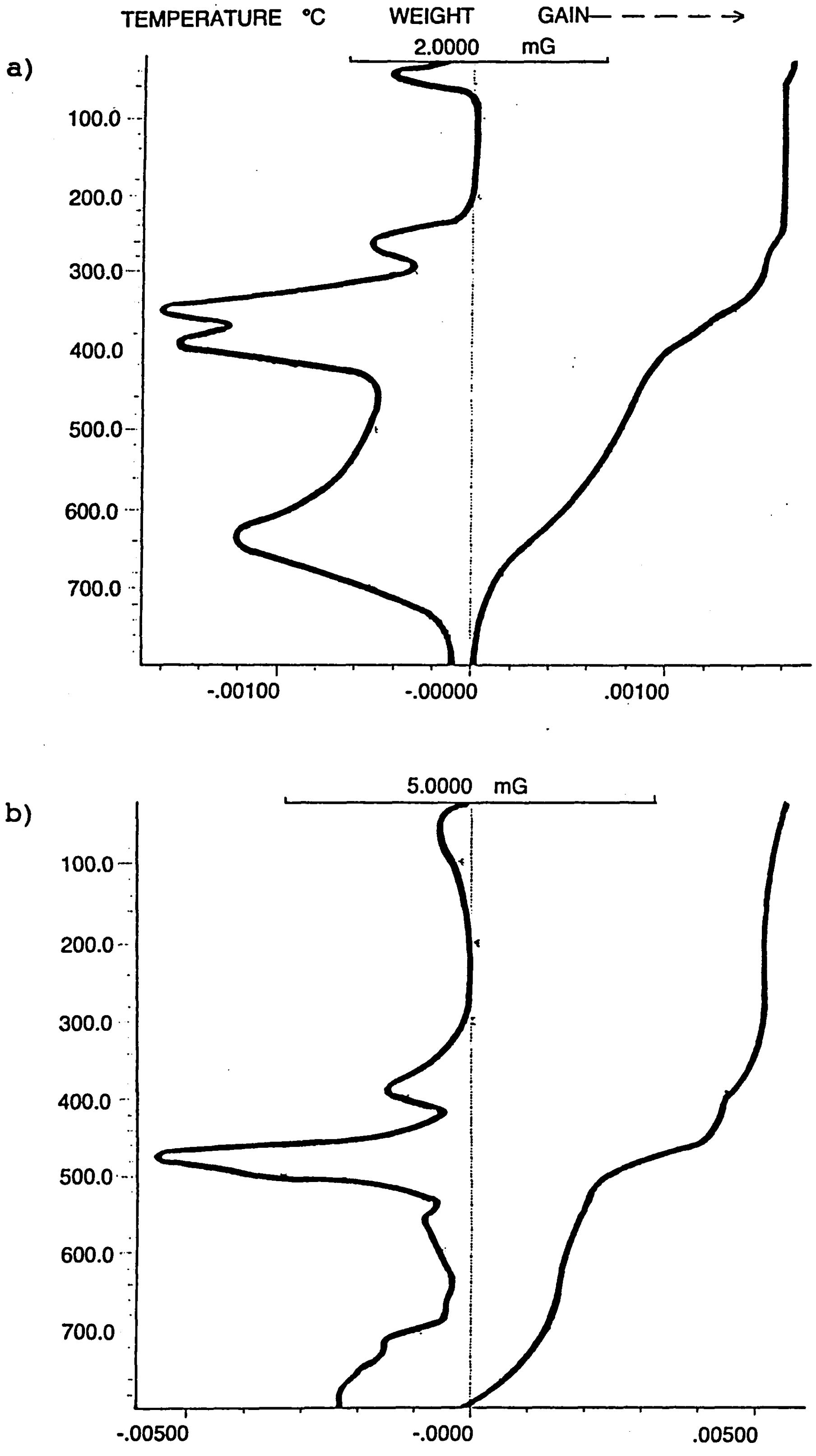


Figure 3.2

Comparison of TGA traces for a) "melabis" and b) trimethylolmelamine salt of bis-PEPA acid

3.4.2 SYSTEMS BASED ON PENTAERYTHRITOL DIPHOSPHATE

Halpern et al synthesised the melamine salt of pentaerythritol diphosphate, calling it 'b-MAP', compound (1), by heating the two starting materials together under reflux conditions in acetonitrile followed by stirring the mixture at room temperature overnight.[8] This method was repeated to yield a white solid with similar characteristics to 'b-MAP'. Analysis showed the product to be identical to that described in the literature.

As this method took far longer (and on an industrial scale would be far more expensive) than the method used in the synthesis of compound (3), the reaction was repeated following the aqueous method previously described. Both starting materials dissolved with the addition of boiling water, and after filtration a white solid precipitated from the filtrate. This was characterised (by mass spectrometry, infrared spectroscopy and melting point measurement) and found to be identical to 'b-MAP', therefore it seemed that, although this method had a lower percentage yield, (65% compared to 98%), it was a quicker and cheaper method of synthesising the salt.

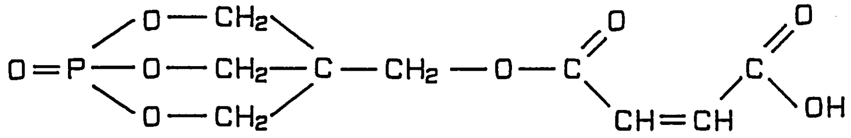
Using this knowledge, the hexamethylmelamine salt of pentaerythritol diphosphate was synthesised using aqueous conditions. Again a white solid precipitated from the filtrate. This was insoluble in all common nmr solvents, but infrared, melting point and microanalysis all confirmed the salt structure. Mass spectrometry again showed no molecular ion, but there was evidence of the two distinct ions as the spectrum showed the molecular ion and the fragmentation pattern for the s-triazine on top of the breakdown pattern for the acid. As confirmation, the reaction was repeated in acetonitrile to yield a white solid with identical infrared and mass spectra as before. This salt had a low melting point (195°C) and when the TGA trace was examined it showed a 44% weight loss below 200°C. The salt was therefore not sufficiently thermally stable at polymer processing temperatures and was impractical for use as a flame retardant additive.

The final s-triazine to be used in salt synthesis with pentaerythritol diphosphate was trimethylolmelamine (14). This reaction did not produce a salt. On grinding the two starting materials together, they coagulated into a sticky mass which had no solubility in boiling water. This sticky mass was then heated under reflux in acetonitrile for five hours but remained unchanged. Trimethylolmelamine is known for its polymerisability to form insoluble, sticky polymers.[23] Obviously the pentaerythritol diphosphate initiates this polymerisation which thus prevents salt formation. The bis-PEPA acid clearly does not have this affect on the s-triazine. It was also observed that if left in a bottle for a couple of weeks, the trimethylolmelamine coagulates into a viscous lump of its own accord.

The salts of pentaerythritol diphosphate were given low priority at this stage in order to concentrate on the more promising results being obtained from the bis-PEPA acid salts.

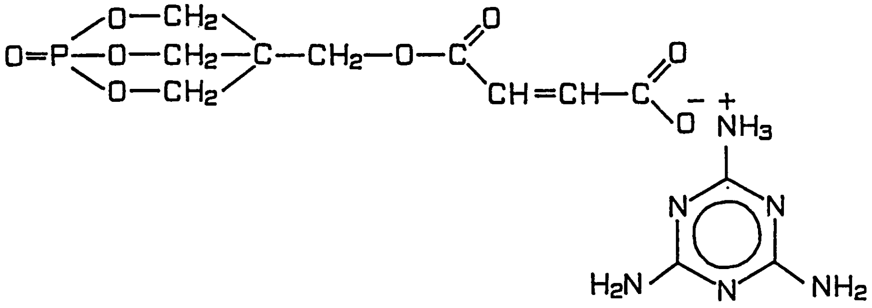
3.4.3 SYSTEMS BASED ON PEPA MALEATE

The synthesis of PEPA maleate, compound (17), is detailed in Chapter 2. This, being a novel acid, would thus give rise to completely novel salt systems.



(17)

The first salt synthesised was the melamine salt. This was produced under the usual aqueous conditions to give a white precipitate. Nmr spectra were unobtainable due to the product's lack of solubility in nmr solvents. Mass spectrometry showed no molecular ion for the product, but a strong peak at m/z = 126 proved melamine to be present (126 = rmm for melamine). Although there was no peak for the molecular ion of PEPA maleate, the spectrum did show the usual fragmentation pattern for the free acid (see Chapter 2). The infrared spectrum showed the product to contain the structures of both starting materials. The melting point was different from that of either starting materials (160°C compared to 187°C and >300°C for the acid and melamine respectively). The TGA trace was different from that of either of the starting materials, showing degradation to start at just over 100°C. Although microanalysis did not show a very close match, it was within reasonable proximity and the product was concluded to be of structure (18).



(18)

This reaction proved to be the only successful synthesis of an s-triazine salt with PEPA maleate.

The synthesis of the hexamethylmelamine salt was attempted, first under the standard aqueous conditions and then in acetonitrile under reflux conditions. Both attempts yielded just the starting materials which were easily identified by TLC and their infrared spectra.

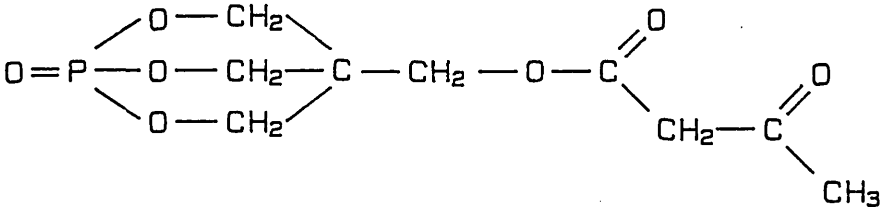
Also attempted was the synthesis of the trimethylolmelamine salt. Again, just the starting materials were recovered and identified by TLC and infrared spectroscopy.

Finally, the synthesis of a metal salt of PEPA maleate was attempted. It was hoped that such a product would act as a good flame retardant though it would probably not be intumescent. Metal salts also have the advantage of being smoke suppressants.[24, 25] PEPA maleate was treated with magnesium ethoxide, first in acetonitrile and then in ethanol (both under reflux). Both times, a white solid was recovered which was found to be PEPA maleate by infrared, melting point and TLC. After this lack of success, this work was given low priority in order to concentrate on systems found to produce salts.

3.4.4 SYSTEMS BASED ON OTHER PEPA ESTERS

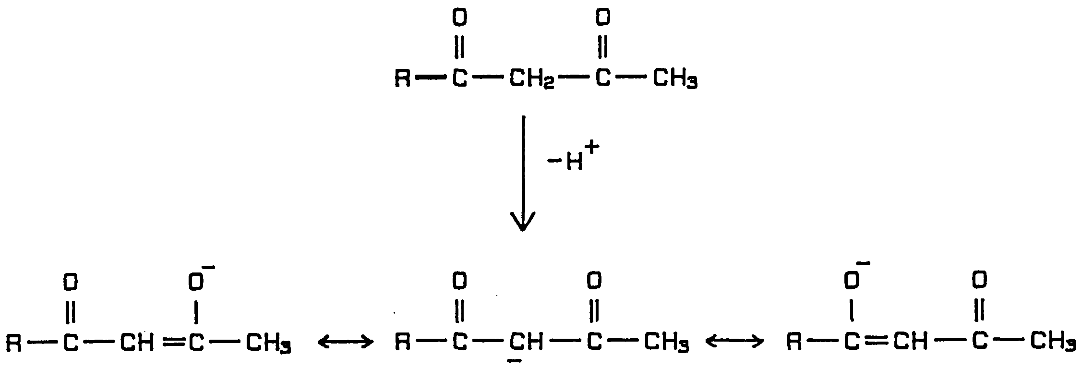
A range of esters based on the PEPA structure were prepared and detailed in Chapter 2. The majority of these were synthesised for use as intermediates. Those containing unsaturation were developed in the area of polymerisation (see Chapter 4), whilst those containing acid groups were developed for their potential in forming intumescent salts. Most work was carried out using PEPA maleate, (17), see section 3.3, but other acidic compounds were also explored.

The ß-keto ester derivative of PEPA, (19), although not containing an acid group, provided a potential anion in salt formation.

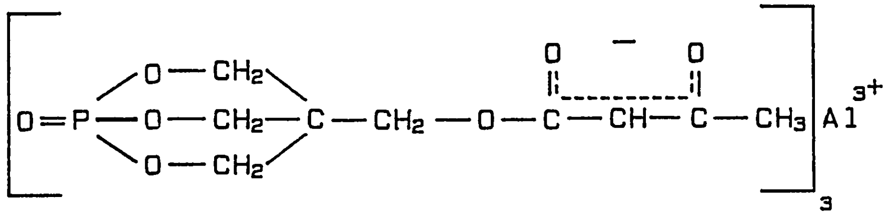


(19)

The reason for this is that having two carbonyl groups attached to the same carbon atom makes that atom more acidic than if it were a simple ketone due to the ability of the resulting anion to undergo resonance and thus spread the charge:



Initial attention was focused on metal salts, with aluminium being the first metal to be used. The ß-keto ester was heated under reflux with aluminium isopropoxide in isopropanol to yield a highly insoluble white powder. Spectral analysis was hindered by its insolubility and mass spectrometry displayed the characteristic of all salts produced so far, ie the highest peak was only for the molecular ion of the ß-keto ester, the salt being decomposed before reaching the detector. The infrared spectrum showed peaks consistent with the ester starting material except for the loss of the carbonyl peaks at 1720 and 1760 cm^{-1}. The spectrum of the product also showed additional peaks at 1520 and 1610 cm^{-1}. These peaks were due to unsaturation and confirmed the presence of the anion in its resonance form (see Figure 3.3). Microanalysis of the product showed its composition to be consistent with the theoretical values for the aluminium salt and, along with the significant change in melting point to above 300°C, confirmed the structure of the product as (20):



(20)

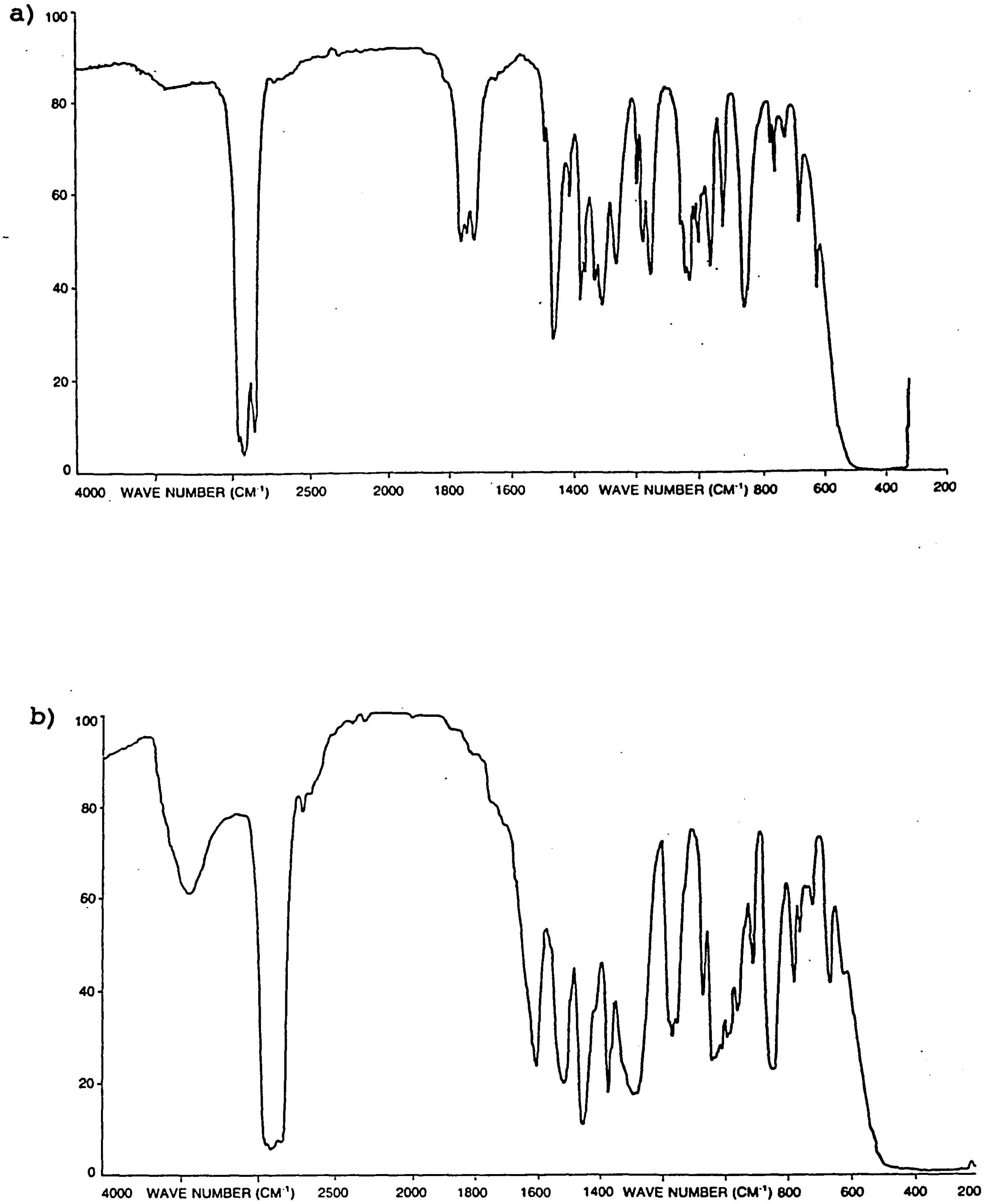


Figure 3.3

Comparison of Infrared Spectra of a) ß-keto ester and b) its aluminium salt

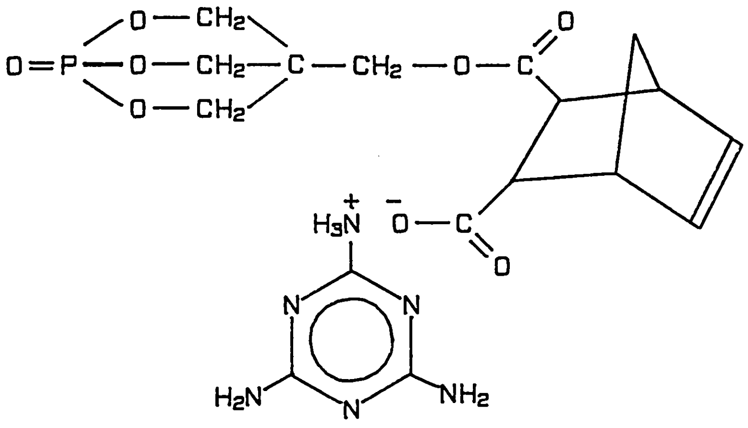
This product was showing ideal characteristics as a flame retardant additive. It was a free flowing white powder, insoluble in water and organic solvents, and possessed a high melting point. When held in an open flame the compound was not intumescent, but neither was it flammable so there was hope that whereas it might not be of use as an intumescent flame retardant, it might exhibit flame retardant properties and even show a degree of smoke suppression. Unfortunately, the TGA trace showed a significant decomposition at low temperatures. About 10% weight loss was observed before 100°C with the main bulk of weight loss starting at around 180°C. This was too unstable to be of use as a polymer additive and therefore the product was not developed further.

The synthesis of the magnesium salt of the ß-keto ester was attempted. The ester was heated under reflux with magnesium ethoxide, first in ethanol, then, due to the lack of success in that solvent, in acetonitrile. On both occasions the reaction mixture yielded the unreacted ester, identified by TLC, melting point and infrared spectroscopy. The two starting materials were then heated together in the absence of a solvent. The ester melted but the magnesium ethoxide did not dissolve. The temperature was increased but the ester decomposed to give a black viscous residue with the magnesium ethoxide remaining undissolved.

The final metal salt to be investigated using the ß-keto ester involved copper. This was attempted by heating the ester with copper (II) acetate under reflux conditions in ethanol. Again, a product crystallised on cooling the solution, but was found to be the ester starting material by TLC, melting point and infrared spectroscopy.

Finally, the ß-keto ester was treated with melamine in an attempt to produce the corresponding salt. A mixture of the two starting materials would not dissolve in boiling water so the non-aqueous method was attempted. After heating under reflux in acetonitrile overnight, a white precipitate appeared on cooling but was found to be the unreacted ester by infrared, TLC and melting point. It was therefore concluded that melamine was not a strong enough base to form a salt with (19).

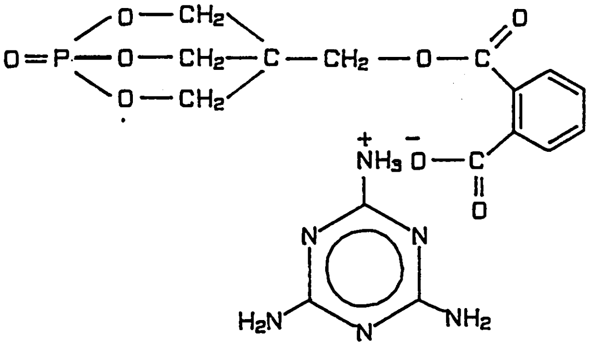
The melamine salt of the PEPA-norbornene ester (21) was successfully synthesised using the aqueous method.



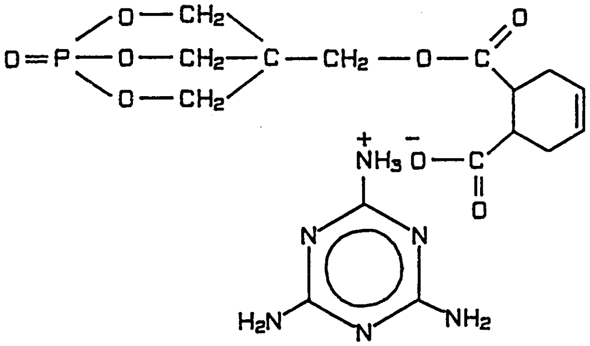
(21)

Again the product was very insoluble, making nmr impossible and mass spectrometry showed the molecular ion and characteristic fragmentation pattern for each ion. Microanalysis confirmed the elemental composition of the salt and the TGA trace was different from that of both starting materials. Unfortunately, the TGA trace showed the salt to be of low thermal stability with 15% weight loss occurring under 180°C and the major weight loss peak starting at 190°C. This, along with the product's relative lack of intumescence when held in an open flame, resulted in the salt not being included in any flame retardancy tests.

Similar results were obtained from the phthalic and the cis-1,2,3,6-tetrahydrophthalic esters of PEPA, compounds (22) and (23), see Chapter 2. Both compounds formed insoluble materials when treated with melamine in aqueous conditions. Both products analysed in the standard way to be the corresponding melamine salt. Again, whilst showing intumescent properties, neither showed sufficient thermal stability to be considered of further interest.

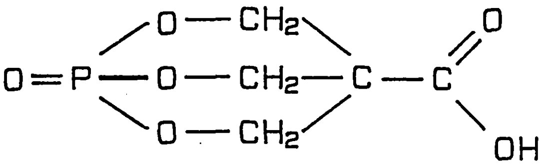


(22)



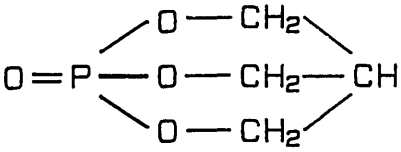
(23)

The final acid to be investigated for salt formation was the PEPA acid, (24).



(24)

Unfortunately, the formation of salts of this compound was hindered by the compound's instability. The addition of boiling water to a mixture of (24) and melamine, or the heating in acetonitrile under reflux conditions with a suitable base, resulted in the decarboxylation of the acid to give structure (25). Details of analysis of (25) are given in Chapter 2.



(25)

3.5 PERFORMANCE DATA

The thermal stability and intumescent properties of all the compounds synthesised in the work described in this chapter have been studied. Intumescence is measured in a relative manner by placing a small amount of sample on the end of a spatula and putting it into a blue gas flame. It is obvious, by observing the decomposition, whether the compound has a high or low degree of intumescence. Thermal stability takes into account the compound's melting point and TGA trace. From these observations certain salts were selected as suitable for testing (ie those with a high degree of intumescence and high thermal stability) and were incorporated into a polyester. However, two of the samples tested were not salts but physical mixtures of bis-PEPA acid and an s-triazine. These were of interest because the physical mixtures appeared highly intumescent and, though not as thermally stable as the corresponding salts, were cheaper to produce and probably not covered by existing patents.

All the samples were tested in Scott Bader Glass A unsaturated polyester resin at 20% loading.

All the samples were ground with a pestle and mortar and passed through a 106 μm sieve before use.

Once the samples were incorporated, the resulting polymers were tested for their limiting oxygen index and their water solubility.

The samples tested were:

1 untreated polyester (control);

2 the PEPA maleate ester (17);

3 the melamine salt of PEPA maleate (18);

4 the hexamethylmelamine salt of bis-PEPA acid (11);

5 the trimethylolmelamine salt of bis-PEPA acid (15);

6 bis-PEPA acid and melamine, a 1:1 mixture;

7 bis-PEPA acid and hexamethylmelamine, a 1:1 mixture.

The additives that comprised of physical mixtures of the starting materials (ie sample nos 6 and 7) were found to interfere with the curing reaction of the polymer. The polymer containing sample no 6 took a week to cure, and for the polymer containing sample no 7, curing was prevented completely.

The limiting oxygen index and water solubility of each polymer was then measured. The water solubility is expressed as the percentage weight change of the polyester samples after stirring in water at 20°C for sixteen hours.

The results were as follows:

Table 3

Sample No	C.O.I. (%)	Weight Change (%)
1	18.1	0.0
2	21.8	- 0.45
3	24.5	- 0.39
4	22.3	+ 0.10
5	29.2	- 0.41
6	23.2	- 0.43

Some of the samples produced respectable increases in the C.O.I. but sample no 5, the trimethylolmelamine salt of bis-PEPA acid was the only one to provide results good enough to be regarded as significant. The water solubility of all samples except sample no 4 were unacceptable so further improvements in that area were required.

As the trimethylolmelamine salt of bis-PEPA acid was the most promising system, further work was concentrated in that area.

The next stage of testing was the incorporation of this salt into polypropylene and polyurethane at various loadings ranging from 20 to 30% for polypropylene and 10 to 20% for polyurethane.

As discussed earlier in this chapter, the water solubility of the trimethylolmelamine salt was greatly reduced on heating at 175°C overnight whilst other, favourable, characteristics were maintained. As one criterion for an effective intumescent flame retardant additive is a low water solubility, the trimethylolmelamine salt was tested twice, once in an untreated form and then in the heated form, which will be referred to subsequently as the 'uncured' and 'cured' salt, respectively.

Also tested in polypropylene and polyurethane at comparable levels was 'Melabis'. This acted as a standard, being the state of the art intumescent flame retardant manufactured by Borg-Warner.

The final additive tested at this stage was pure PEPA maleate, (17). Although not expected to prove an effective flame retardant in polypropylene, due to the results obtained in polyester, it was hoped that this compound, with its functional group, would react during the curing process of the polyurethane to become part of the polymer skeleton rather than just an additive.

All the samples were ground in a ball mill and passed through a 150 μm sieve before use.

RESULTS IN POLYPROPYLENE

The samples were incorporated into ICI GY 545M polypropylene, the results being given in Tables 4 and 5.

Table 4

Sample	C.O.I. (%)	Intumescence Observed on Burning
Pure polypropylene	17.5	NO
+ 20% PEPA maleate	19.1	NO
+ 20% 'Melabis'	23.7	YES
+ 20% uncured salt	24.6	YES
+ 20% cured salt	24.8	YES
+ 30% uncured salt	30.0	YES
+ 30% cured salt	29.5	YES

Table 5

Sample	UL-94 (Vertical) Test Number of Passes in Five Tests
Pure polypropylene	0
+ 20% PEPA maleate	0
+ 20% 'Melabis'	0
+ 20% uncured salt	2
+ 20% cured salt	0
+ 30% uncured salt	5
+ 30% cured salt	5

The water solubility was measured for each polymer sample by stirring the polymer in water at 20°C for sixteen hours then recording the weight loss. For all samples the weight loss was less than 0.08%.

To complete this data, a final sample was prepared and tested. The trimethylolmelamine salt had so far been prepared using equimolar amounts of starting materials. There was a possibility that using different ratios might affect whatever form of cross-linking was occurring to produce a structurally different salt.

Therefore the preparation of the salt was repeated twice, first using a 10% excess of the <u>s</u>-triazine, then a 10% excess of the acid. In the former no salt was produced as the starting materials coagulated on the addition of boiling water, the probable cause being the polymerisation of the triazine before having chance to react with the acid[23] (see section 3.4.2).

A salt was produced using 10% excess of the acid and was processed into polypropylene to give the following results:

Table 6

Sample	C.O.I. (%)	UL-94 (Passes Out of Five)
PP + 20%	23.8	1
PP + 25%	24.6	2
PP + 30%	26.4	4

RESULTS IN POLYURETHANE

The polyurethane was synthesised by the reaction of a mixture of formulated polyols with diphenylmethane-4,4-diisocyanate, (MDI). The additives were mixed into the polyol mixture with a food blender before the addition of MDI.

The resulting polyurethane was a brittle, pale yellow foam with a C.O.I. of 22.2%.

When a 20% loading of the PEPA maleate was added, the polyurethane did not cure properly, taking over twenty-four hours to produce a much denser (with much smaller air bubbles) brown foam. Although this foam had a higher C.O.I. than the untreated foam (25.9%) the chemical interference in the curing and structure of the foam was unacceptable.

The other additives all processed into the polyurethane with no problems and gave the C.O.I. results shown in Table 7.

Table 7

Additive	Loading			
	10%	12.5%	15%	20%
'Melabis'	24.0	24.0	-	24.9
Uncured salt	24.4	24.1	25.0	25.5
Cured salt	23.4	24.0	24.4	24.8

3.6 CONCLUSIONS

Analysis of performance data

The main conclusion from the results described in section 3.5 was that the uncured salt of bis-PEPA acid and trimethylolmelamine showed better flame retardant properties than the cured sample. The solubilities of both samples when stirred in water were negligible, so it was concluded that there was no need to heat this salt overnight before incorporation into a polymer.

The uncured salt, despite showing a greater degree of intumescence when held in an open flame, showed only slightly better flame retardant properties than 'Melabis' when used as an additive in polypropylene. The improvements over 'Melabis' may not be sufficient to justify an attempt to market the salt without further development of trying to increase the flame retardancy even further.

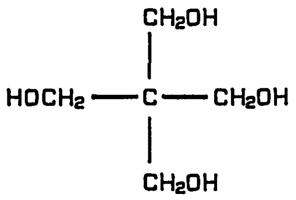
There was no increase in performance when 10% excess of the acid was used in the synthesis of the salt, and this synthesis was prevented if 10% excess of the s-triazine was used. It can therefore be assumed that the optimum molar ratio of the starting materials is 1:1.

The influence of molecular structure on intumescent decomposition

Throughout the work described in this thesis, it was observed that some compounds had a higher degree of intumescence than others, with some compounds possessing no intumescent properties at all. The main factor concerning this was thought to be the ratio of the carbonific and spumific sources within the structure of the molecule.

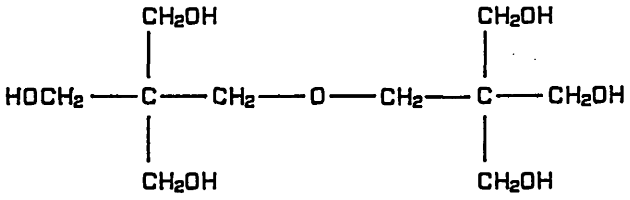
Hence a variety of bases and acids were used in salt synthesis in an attempt to alter these ratios. However, none of the salts produced showed any great improvement on 'Melabis'.

Repeatedly, throughout the patent literature reviewed in Chapter 1, the carbonific source of the intumescent flame retardant additives was a polyol, commonly pentaerythritol (26), dipentaerythritol (27) or tripentaerythritol (28).



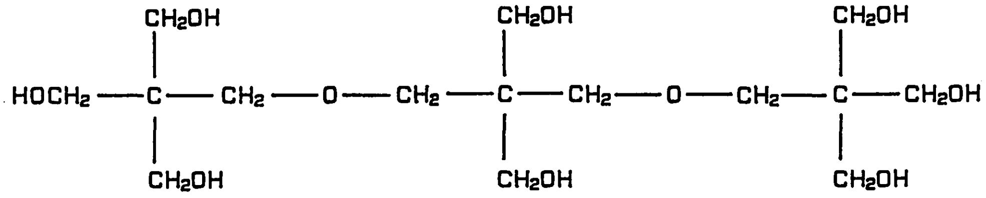
$$\mathrm{HOCH_2}-\overset{\mathrm{CH_2OH}}{\underset{\mathrm{CH_2OH}}{\mathrm{C}}}-\mathrm{CH_2OH}$$

(26)



$$\mathrm{HOCH_2}-\overset{\mathrm{CH_2OH}}{\underset{\mathrm{CH_2OH}}{\mathrm{C}}}-\mathrm{CH_2}-\mathrm{O}-\mathrm{CH_2}-\overset{\mathrm{CH_2OH}}{\underset{\mathrm{CH_2OH}}{\mathrm{C}}}-\mathrm{CH_2OH}$$

(27)

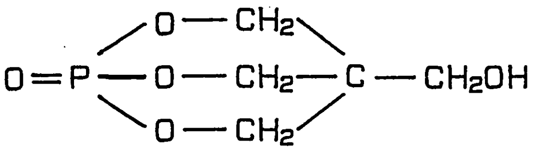


$$\mathrm{HOCH_2}-\overset{\mathrm{CH_2OH}}{\underset{\mathrm{CH_2OH}}{\mathrm{C}}}-\mathrm{CH_2}-\mathrm{O}-\mathrm{CH_2}-\overset{\mathrm{CH_2OH}}{\underset{\mathrm{CH_2OH}}{\mathrm{C}}}-\mathrm{CH_2}-\mathrm{O}-\mathrm{CH_2}-\overset{\mathrm{CH_2OH}}{\underset{\mathrm{CH_2OH}}{\mathrm{C}}}-\mathrm{CH_2OH}$$

(28)

In one of Halpern's original patents,[2] claiming the effectiveness of compound (1) as a flame retardant additive, the addition of a polyol was suggested in order to increase the amount of foam produced.

Not surprisingly, when polyols (eg pentaerythritol) are held in an open flame, they do not show intumescent properties. However, their corresponding phosphates, eg pentaerythritol phosphate, (29), do exhibit intumescence.

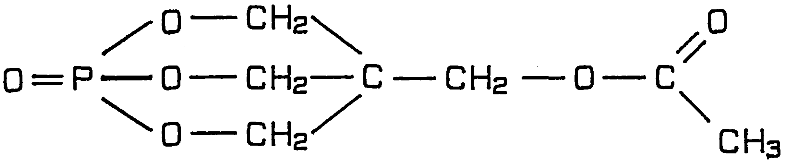


(29)

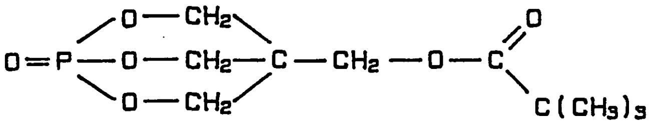
It is the phosphate entity which, on pyrolysis, decomposes to phosphoric acid, the latter acting as an intumescent catalyst (see Chapter 1).

As part of the work described in Chapter 2, a variety of derivatives of PEPA were synthesised. These were produced, not only to be intumescent additives in their own right, but also to be combined with a spumific compound (eg melamine), either physically or chemically, to improve their intumescent performance.

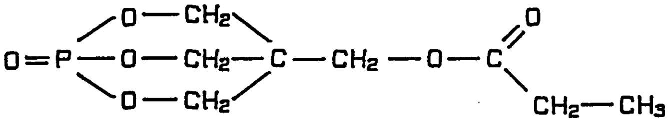
It was noted that one group of derivatives showed no degree of intumescence when held in an open flame. These were the simple alkyl esters of PEPA, ie the acetate (30), the trimethylacetate (31), the propionate (32), the crotonate (33), the methacrylate (34) and the benzoate (35).



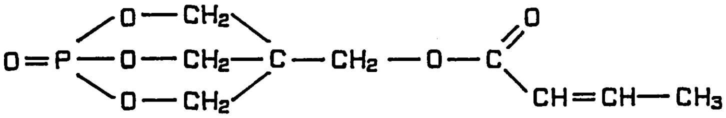
(30)



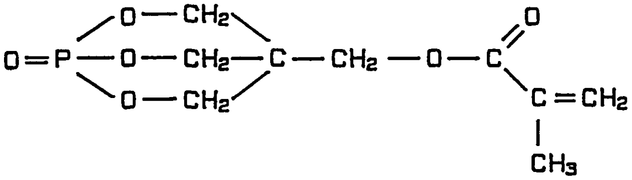
(31)



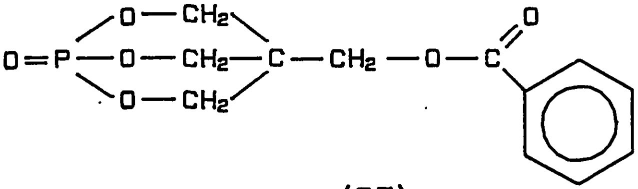
(32)



(33)



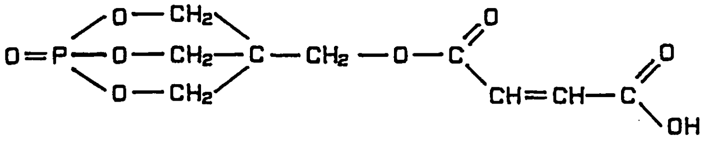
(34)



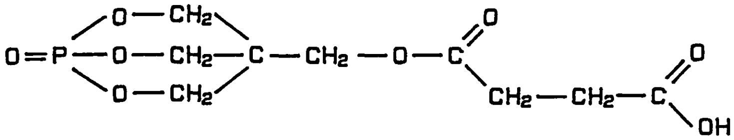
(35)

Even when mixed with an equimolar amount of melamine, these compounds did not show any sign of intumescence.

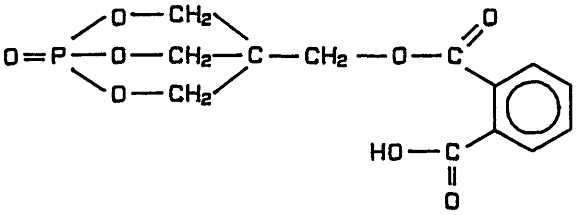
Other derivatives of PEPA, however, were found to be intumescent on their own. These included the maleate, (17), the succinate, (36), the phthalate, (37), and the diglycolate, (38).



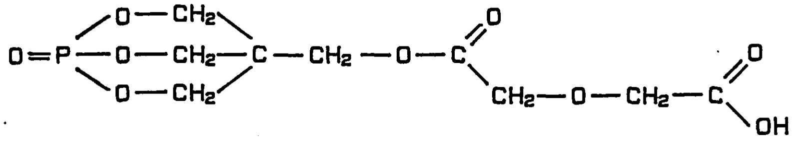
(17)



(36)



(37)



(38)

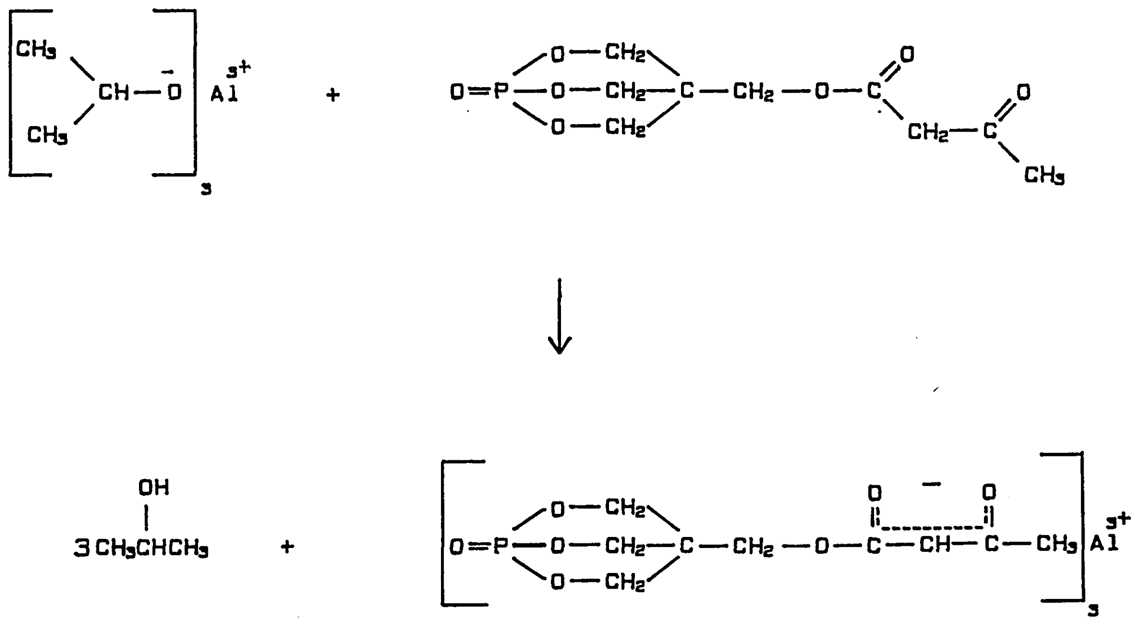
Not only were these derivatives intumescent in their own right, but when mixed with melamine, either physically or chemically, to produce a salt, the degree of intumescence was increased. The only difference between these derivatives and the non-intumescent derivatives was the addition of an acid group, $-CO_2H$. It was thought that this acid functionality was in some way initiating the intumescent performance. However, PEPA itself is intumescent yet this does not contain an acid group. It does, however, have a hydroxy group, -OH, which provides a fairly acidic proton.

Therefore it would seem that in order for intumescent behaviour to be displayed, it is necessary to have a 'free' proton, ie a reasonably acidic hydrogen atom in the system.

In the case of the majority of the intumescent salts produced in the work described in this chapter, the base is an amine which is protonated to form R_3NH^+. This N-H bond is sufficiently weak to provide a 'free' proton on thermal decomposition of the salt.

This phenomenon could explain the results observed on the trimethylolmelamine salt of the bis-PEPA acid. As stated, this salt exhibited a greater degree of intumescence than did 'Melabis'. The trimethylolmelamine salt contains not only a greater carbon content than melamine, but also has three extra hydroxy groups and therefore contains three more acidic protons. If this salt does cure on heating, as suggested, then the loss of flame retardancy properties of the 'cured' sample is explained by the loss of some of these hydroxy groups on the formation of the polymer, eg structure (16).

The aluminium salt of the ß-keto ester of PEPA, (20), was the only salt not to show intumescent properties. On examining the structure this is not surprising as there is no free proton within the system, the proton having been lost to form isopropanol:



Electron Microscopy

In order to examine the structure of the foams produced on intumescent decomposition, electron microscopy was employed.

Two salts were studied, namely 'Melabis', (3), and the trimethylolmelamine salt of bis-PEPA acid, (15). In order for valid comparisons to be made, the salts were decomposed under identical, controlled conditions. This was achieved in the TGA furnace, both samples being heated to 800°C at a rate of 10°C min^{-1} under a constant flow of nitrogen. The foams thus produced were frozen in liquid nitrogen and then cut to reveal a cross section of the internal structure. The micrographs were recorded at two hundred times magnification (Figure 3.4) and one thousand times magnification (Figure 3.5).

As can be seen from Figure 3.4, the internal structures of the two are quite different. The foam produced by the trimethylolmelamine salt of bis-PEPA acid appears to be more dense than that produced by 'Melabis', ie the micrograph shows a greater amount of char per unit area. This is also evident in Figure 3.5 where the micrograph of the foam produced by 'Melabis' shows a view deeper into the structure before being obstructed by a wall of the char than does the micrograph of the trimethylolmelamine salt of bis-PEPA acid in which the view is almost immediately obstructed by the dense wall.

Thus it would appear that the foam produced on the intumescent decomposition of the trimethylolmelamine salt of bis-PEPA acid is more closely packed than that produced by 'Melabis', and as such would be expected to provide a more effective insulating barrier between the substrate and the heat source. This is evident from the results obtained in section 3.5 of this chapter where the trimethylolmelamine salt does show slightly better flame retardant properties than does 'Melabis'.

The increased density of the char structure supports the theory that the degree of intumescence is governed by the molecular structure of the original salt. As previously stated, intumescent behaviour appears to be linked to the presence of a 'free' proton. Trimethylolmelamine contains three extra hydroxy groups not present in melamine and therefore its salt with bis-PEPA acid contains three more acidic protons per molecule than 'Melabis'. These extra protons increase the degree of foam formation, resulting in a much denser foam.

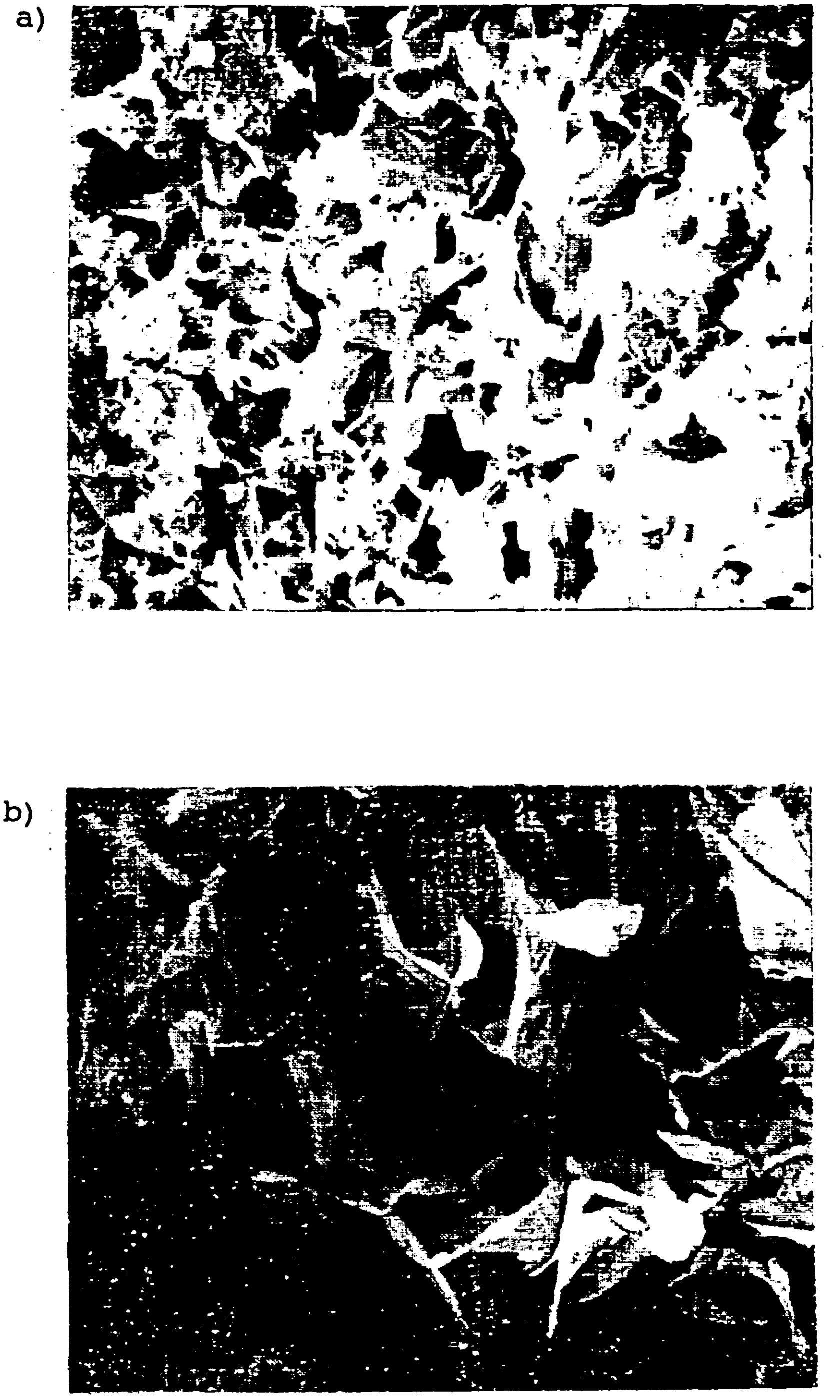


Figure 3.4

Electron micrographs of the foam produced after heating

a) trimethylolmelamine salt of bis-PEPA acid

and b) "melabis"

at x200 magnification

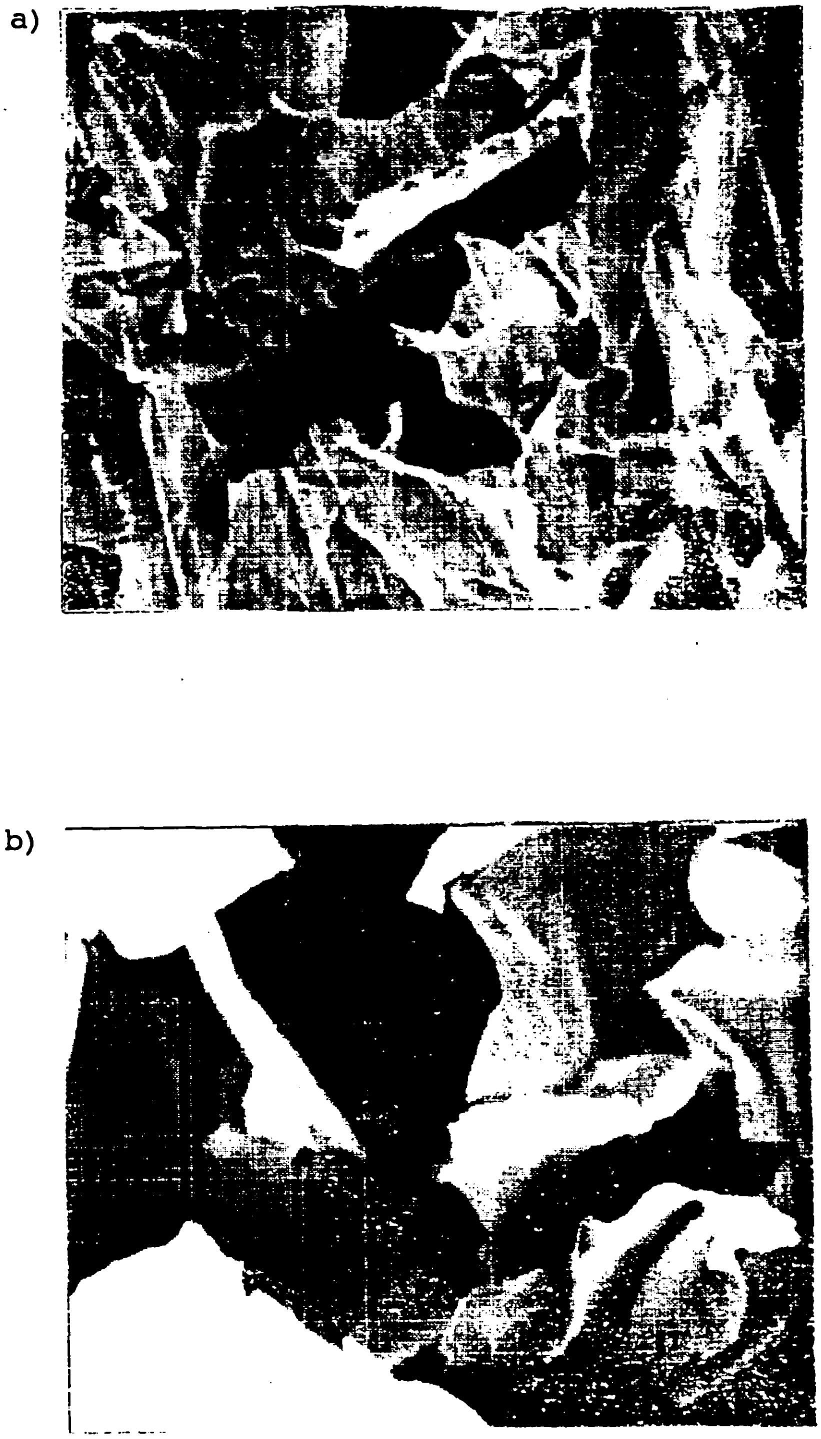


Figure 3.5

Electron micrographs of the foam produced after heating

a) trimethylolmelamine salt of bis-PEPA acid

and b) "melabis"

at x1000 magnification

It is not possible to determine the nature of the pore structure of these foams from the micrographs obtained. Discrete pores within the foam structure would obviously provide better insulation against heat than would interconnecting pores through which heat would flow more easily.

3.7 EXPERIMENTAL

General information

Details of the instruments and chemicals used are given in Chapter 2. All abbreviations used are identical to those in Chapter 2.

The polypropylene samples were mixed in a Brabender torque rheometer research system.

The limiting oxygen index tests were carried out on a Stanton Redcroft FTA flammability unit.

Thermogravimetric analyses were obtained from a Metter TG 50 thermobalance, the data being processed on a Metter TC 10A TA-processer.

Electron micrographs were obtained from an ISI Mini-SEM.

All the salts described in this experimental section were formed by the exchange of a proton from one starting material to the other. Subsequently the starting material structures remained basically unaltered in the products. As such the infrared spectra of all the products showed a strong similarity to spectra of simple physical mixtures of their starting materials. Therefore, only peaks in the infrared spectra which were not in the individual spectra of either starting material, and so correspond to a chemical change, are quoted.

STARTING MATERIALS

Synthesis of bis(4-hydroxymethyl-2,6,7-trioxa-1-phosphabicyclo[2.2.2] octane-1-oxide)phosphate bis-PEPA acid (4)

PEPA (2.64 g, 1.47 x 10^{-2} moles) and phosphorus oxychloride (0.63 mls, 6.9 x 10^{-3} moles) were heated in acetonitrile (30 mls) under reflux conditions, in an inert atmosphere, with mechanical stirring, for twenty hours. Deionised water (0.124 g, 6.9 x 10^{-3} moles) was injected and the mixture maintained at 80°C for a further six hours. After this a white solid had formed which was filtered before being washed with acetonitrile (2 x 10 mls) followed by 1,1,1-trichloroethane (3 x 20 mls) and subsequently dried at 100°C. The crude product was recrystallised from glacial acetic acid to yield a white solid, 2.32 g (37%), mpt 249 - 251°C.

IR (KBr) 3400, 2900, 1320, 1265, 1060, 1040, 1020, 990 and 950. ^{1}Hnmr (CF_3COOD) 3.7 (d, 4H), 4.4 (d, 12H), 11.0 (s, H). ^{31}Pnmr (D_2O) -0.7 (s), -3.7 (s). ^{13}Cnmr (D_2O) 79 (d), 64 (s), 41 (d). Microanalysis; found: C, 29.04; H, 4.38; $C_{10}H_{17}O_{12}P_3$ requires: C, 28.45; H, 4.06%.

Synthesis of 3,9-bis(chloro)-2,4,8,10-tetraoxa-3,9-diphosphaspiro[5.5]undecane-3,9-dioxide (6)

Method 1[15]. Pentaerythritol (2.72 g, 2.0 x 10^{-2} moles) and phosphorus oxychloride (6.6 g, 4.3 x 10^{-2} moles) were protected from atmospheric moisture and heated at 90°C for two hours, then held at 100°C for twenty hours by which time the mixture had become a grey solid. This solid was crushed, dispersed in phosphorus oxychloride (5.0 g, 3.3 x 10^{-2} moles) then heated under reflux conditions for two hours, during which vast quantities of HCl were evolved. On cooling, most of the excess phosphorus oxychloride was removed by decantation, the rest being removed by distillation at 10 mm. The crude solid was washed with carbon tetrachloride (4 x 10 mls), absolute ethanol (25 mls), then rinsed with ether (40 mls). The product was a grey powder, yield 1.38 g (23%), mpt 265 - 278°C, (lit[15] 229 - 232°C). On recrystallisation from glacial acetic acid, a brown oil was obtained.

^{31}Pnmr (D_6-DMSO) 8.1 (d), - 0.3 (s), - 4.4 (s), - 8.8 (s).

Method 2[16]. Pentaerythritol (2.72 g, 2.0 x 10^{-2} moles) was added to phosphorus oxychloride (10 mls, 1.09 x 10^{-1} moles) and heated in a steam bath with stirring. The pentaerythritol dissolved after about twenty minutes and a white solid formed gradually over the next five hours. The mixture was cooled and the solid filtered, washed with dichloromethane (3 x 10 mls) then vacuum dried at 100°C. The crude product was recrystallised from glacial acetic acid to yield a white solid of 3.96 g (66%), mpt 245 - 250°C (lit[16] 243 - 245°C).

IR (KBr) 2900, 1320 and 1020. ^{31}Pnmr (CF_3COOD) - 1.8 (s).

Synthesis of 3,9-bis(hydroxy)-2,4,8,10-tetraoxa-3,9-diphosphaspiro[5.5]undecane-3,9-dioxide ie pentaerythritol diphosphate (5)

Compound (6) (2.5 g, 8.4 x 10^{-3} moles) was added to acetonitrile (15 mls) and the resulting slurry heated to 80°C. Deionised water (0.3 mls, 1.62 x 10^{-2} moles) was injected and the mixture maintained at a slow reflux for twenty-two hours. The resulting mixture was filtered, washed with acetonitrile (2 x 20 mls) and dichloromethane (3 x 10 mls) before being dried in a vacuum oven at 100°C. The crude product recrystallised from glacial acetic acid to yield a white crystalline solid, yield 2.08 g (95%), mpt 305 - 310°C (lit[8] 314°C).

IR (mull) 1260 and 1000. ^{1}Hnmr (CF_3COOD) 4.2 (d, 8H), 9.8 (s, 2H). ^{31}Pnmr (CF_3COOD) -2.4 (s), -7.2 (s). ^{13}Cnmr (D_2O) 70 (d), 38 (s). MS 260 (M^+). Microanalysis; found: C, 22.79; H, 4.09; $C_5H_{10}O_8P_2$ requires: C, 23.09; H, 3.88%.

Synthesis of hexamethylmelamine (10)

Cyanuric chloride (10.0 g, 5.8 x 10^{-2} moles) was dissolved in dry acetone (60 mls). This solution was added slowly to a 40% aqueous solution of dimethylamine (80 mls) with the evolution of much heat. On slight cooling, a white solid began to crystallise. The mixture was poured into cold water to produce more precipitate which was filtered and washed with aqueous acetone (2 x 30 mls). The final product was a white powder of yield 10.27 g (84%), mpt 170 - 172°C, (lit[26] 172 - 174°C).

IR (KBr) 3300 and 2900. ^{1}Hnmr (CD_3CN) 6.9 (s). MS 210 (M^+), 195 ($M - CH_3$).

Synthesis of trimethylolmelamine (14)

Melamine (12.6 g, 1.0 x 10^{-1} moles) was treated with formaldehyde (24.3 mls of 37% aq formalin solution, 3.0 x 10^{-1} moles). The mixture was stirred cold for two hours then heated to 70°C for five minutes during which all the solid went into solution. On cooling, a white solid formed which was triturated with methanol, filtered, washed with methanol (3 x 20 mls) and dried under vacuum at room temperature to yield a white powder of 19.2 g (88%), mpt 134 - 139°C.

IR (mull) 3380, 1550 and 960. ^{1}Hnmr (D_2O) 4.3 (s, 6H), 4.8 (s, 6H). MS 216 (M^+), 199 (M - OH), 184 (M - CH_3OH).

Synthesis of hexacyanomethylmelamine (12)

Cyanuric chloride (1.84 g, 1.06×10^{-2} moles) and iminodiacetonitrile (5.70 g, 6.36×10^{-2} moles) were dissolved in acetone (35 mls) and the resulting solution heated under reflux conditions for three hours during which a white solid began to form. The mixture was cooled and filtered to yield a white solid of 2.03 g, (53%), mpt 194 - 199°C.

MS 360 (M^+), 320 (M - CH_2CN).

Synthesis of hexabenzylmelamine (13)

Cyanuric chloride (1.84 g, 1.06×10^{-2} moles) and dibenzylamine (12.00 g, 6.36×10^{-2} moles) were added to acetone (35 mls). A large quantity of solid formed in an exothermic reaction. The mixture was heated under reflux conditions for six hours during which the colour of the supernatant liquid changed from yellow to green. The mixture was then cooled and poured into methanol before being filtered to give a white solid of needle-like crystals, yield 3.7 g (52%), mpt 142 - 145°C.

IR (mull) 1660, 1600, 1560 and 1500. ^{1}Hnmr (D_2O) 4.5 (s, 2H), 7.4 (s, 5H). MS 666 (M^+), 575 (M - $CH_2C_6H_5$).

Microanalysis; found: C, 80.44; H, 6.69; N, 11.98; $C_{45}H_{42}N_6$ requires: C, 81.05; H, 6.36; N, 12.60%.

MODEL SALT SYSTEMS

Synthesis of the 1,4-diazabicyclo[2.2.2]octane salt of diphenylphospinic acid (8)

1,4-diazabicyclo[2.2.2]octane (1.03 g, 9.2×10^{-3} moles) and diphenylphosphinic acid (2.0 g, 9.2×10^{-3} moles) were heated in acetonitrile (15 mls) under reflux conditions for three hours during which the solution became clear. On cooling, white needles crystallised which were filtered and washed with cold acetonitrile (2 x 20 mls). The product recrystallised from acetonitrile to yield 2.51 g (83%), mpt 179 - 183°C.

IR (KBr) 2250 and 1160. Microanalysis; found: C, 64.89; H, 6.91; N, 8.03; $C_{18}H_{23}N_2O_2P$ requires: C, 65.44; H, 7.02; N, 8.48%.

Synthesis of the 1,4-diazabicyclo[2.2.2]octane salt of bis(4-hydroxymethyl-2,6,7-trioxa-1-phosphabicyclo[2.2.2]octane-1-oxide) phosphate (9)

1,4-diazabicyclo[2.2.2]octane (0.11 g, 9.5×10^{-4} moles) and bis-PEPA acid (0.40 g, 9.5×10^{4} moles) were heated in acetonitrile (15 mls) under reflux conditions for three hours during which the amine appeared to dissolve but not the acid. After the three hours a white solid remained in the solvent which was of greater quantity than that of the acid originally used. This was filtered and washed with acetonitrile (2 x 10 mls) to yield a white powder of 4.8 g (94%), mpt 295 - 298°C (dec).

IR (mull) 1160 and 2450. ^{1}Hnmr (D_2O) 3.3 (s, 12H), 3.8 (d, 4H), 4.2 (broad s, H), 4.9 (d, 12 H). ^{31}Pnmr (D_2O) -0.7 (s), -3.7 (s). Microanalysis; found: C, 35.70; H, 5.42; N, 5.20; $C_{16}H_{29}N_2O_{12}P_3$ requires: C, 35.97; H, 5.47; N, 5.24%.

Salts of bis(4-hydroxymethyl-2,6,7-trioxa-1-phosphabicyclo[2.2.2] octane-1-oxide) phosphate ie bis-PEPA acid (4)

Synthesis of the melamine salt of bis-PEPA acid ie 'Melabis' (3)

Melamine (0.38 g, 3.0 x 10^{-3} moles) and bis-PEPA acid (1.25 g, 3.0 x 10^{-3} moles) were stirred together to ensure a good degree of dispersion before boiling water (15 mls) was added. This mixture was stirred for five minutes during which most of the solids dissolved. The hot solution was then filtered and the filtrate left to cool. A white solid precipitated which was filtered to yield 0.68 g (44%), mpt >300°C, (lit[8] >250°C).

IR (mull) 1520, 1185, 1250 and 780. ^{13}Cnmr (D_2O) 81 (d), 68 (s), 38 (d).

Synthesis of the hexamethylmelamine salt of bis-PEPA acid (11)

1 **Aqueous conditions.** Hexamethylmelamine (0.2 g, 9.5 x 10^{-4} moles) and bis-PEPA acid (0.4g, 9.5 x 10^{-4} moles) were stirred together before the addition of boiling water (10 mls). After stirring for five minutes, a clear solution had formed which was filtered and

allowed to cool. The filtrate was left overnight but did not produce a precipitate. It was cooled in a fridge for five hours but still did not yield any crystals. The solution was poured into an evaporating basin and heated on a steam bath until all the water had evaporated to leave a white solid of yield 0.44 g (73%), mpt 197 - 204°C.

IR (mull) 1250, 1185 and 780. Microanalysis; found: C, 34.01; H, 4.84; N, 12.42; $C_{19}H_{32}N_6O_{12}P_3$ requires: C, 34.13; H, 4.21; N, 14.04%.

2 **Non-aqueous conditions.** Hexamethylmelamine (0.1 g, 4.7×10^{-4} moles) and bis-PEPA acid (0.2 g, 4.7×10^{-4} moles) were heated in acetonitrile (15 mls) under reflux conditions for twenty-four hours. A white solid remained in the mixture throughout the reaction and no extra solid precipitated on cooling. The solid was analysed and found to be bis-PEPA acid by mpt 249 - 251°C and IR (KBr) 3400, 2900, 1320, 1265, 1060, 1040, 1020, 990 and 950. The solvent was analysed by TLC to reveal it contained the unreacted s-triazine.

Attempted synthesis of the hexacyanomethylmelamine salt of bis-PEPA acid

Hexacyanomethylmelamine (0.34 g, 9.5×10^{-4} moles) and bis-PEPA acid (0.4 g, 9.5×10^{-4} moles) were stirred together in a beaker and boiling water (15 mls) added. Stirring was continued for five minutes after which not all of the solid had dissolved and on filtering the hot solution a white powder was collected which was analysed as the unreacted triazine by TLC, mpt 195 - 200°C and MS 360 (M^+). The filtrate was evaporated to leave a white powder which was shown to be bis-PEPA acid by mpt and IR.

Attempted synthesis of the hexabenzylmelamine salt of bis-PEPA acid

Hexabenzylmelamine (0.63 g, 9.5×10^{-4} moles) and bis-PEPA acid (0.4 g, 9.5×10^{-4} moles) were treated as above with the same result, the recovered solids being identified as hexabenzylmelamine and bis-PEPA acid by mpt and IR.

Synthesis of the trimethylolmelamine salt of bis-PEPA acid (15)

Trimethylolmelamine (0.2 g, 9.5×10^{-4} moles) and bis-PEPA acid (0.4 g, 9.5×10^{-4} moles) were mixed together, boiling water added (10 mls) and the resulting solution filtered. On cooling, no precipitate formed so the solution was evaporated to dryness to leave a white solid, yield 0.45 g (70%), mpt >300°C.

IR (mull) 3200 and 1190. ^{1}Hnmr (D_2O) 1.3 (t), 3.4 (s), 3.7 (d), 4.8 (d) spectrum too noisy for conclusive integration. Microanalysis; found: C, 29.89; H, 4.32; N, 11.21; $C_{16}H_{29}N_6O_{15}P_3$ requires: C, 30.09; H, 4.54; N, 13.20%.

Salts of 3,9-bis(hydroxy)-2,4,8,10-tetraoxa-3,9-diphosphaspiro[5.5] undecane-3,9-dioxide, ie pentaerythritol diphosphate (5)

Synthesis of the melamine salt of pentaerythritol diphosphate, ie 'b-MAP' (1)

Melamine (3.02 g, 2.4×10^{-2} moles) and pentaerythritol diphosphate (3.1 g, 1.2×10^{-2} moles) were ground together in a mortar and pestle and added to acetonitrile (50 mls). The mixture was stirred and heated to reflux for five hours. The mixture was allowed to cool to room temperature and stirring was continued for a further sixteen hours. The resulting mixture was filtered and dried under vacuum to yield a white powder, 6.04 g (98%), mpt >300°C.

IR (mull) 1510, 1225, 1190 and 760.

This product was also synthesised under the usual aqueous conditions, see synthesis of (3), to yield a white powder of identical characteristics, 3.70 g (65%), mpt >300°C.

IR (mull) 1510, 1225, 1190 and 760.

Synthesis of the hexamethylmelamine salt of pentaerythritol diphosphate

1 **Non-aqueous conditions.** Hexamethylmelamine (5.04 g, 2.4×10^{-2} moles) and pentaerythritol diphosphate (3.1 g, 1.2×10^{-2} moles) were treated in acetonitrile, as above, to produce a white solid of yield 6.5 g (80%), mpt 195 - 199°C.

IR (mull) 1220, 1150 and 750. Microanalysis; found: C, 29.92; H, 4.59; N, 25.17; $C_{17}H_{34}N_2O_{14}P_2$ requires: C, 29.48; H, 4.91; N, 24.28%.

2 **Aqueous conditions.** The starting materials (as above) were treated under the usual aqueous conditions to yield a white powder of yield 7.25 g (85%), mpt 195 - 199°C.

IR (mull) 1220, 1150 and 750.

Attempted synthesis of the trimethylolmelamine salt of pentaerythritol diphosphate

Trimethylolmelamine and pentaerythritol diphosphate were treated, in equimolar amounts, first in the aqueous and then in the non-aqueous conditions described above. In both cases, an insoluble sticky mass was formed due to polymerisation of the s-triazine.

Salts of the PEPA maleate ester (17)

Synthesis of the melamine salt of PEPA maleate (18)

Melamine (0.47 g, 3.76 x 10^{-3} moles) was mixed with PEPA maleate (1.0 g, 3.76 x 10^{-3} moles) before boiling water (15 mls) was added. Stirring was continued for five minutes during which most of the solid mixture went into solution. The hot solution was filtered and a fine white precipitate appeared on cooling. The crude product was washed with cold water (2 x 20 mls) and recrystallised from water to give a fine white powder of yield 1.02 g (70%), mpt 162 - 168°C.

IR (mull) 1600 and 1520. Microanalysis; found: C, 34.20; H, 4.51; N, 20.14; $C_{12}H_{17}N_6O_8P$ requires: C, 35.65; H, 4.24; N, 20.79%.

Attempted synthesis of the magnesium salt of PEPA maleate

PEPA maleate (0.1 g, 3.8 x 10^{-4} moles) and magnesium ethoxide (0.02 g, 1.9 x 10^{-4} moles) were heated in acetonitrile and ethanol under reflux conditions.

1 **In acetonitrile.** The ester dissolved but not the magnesium ethoxide. After heating under reflux conditions for four hours the mixture was cooled and filtered. The filtrate contained unreacted

PEPA maleate by TLC. The filtrate evaporated to leave a white solid which was shown to be PEPA maleate by melting point and IR.

2 **In ethanol.** The magnesium ethoxide dissolved in ethanol but the PEPA maleate did not. After twenty hours the undissolved residue was filtered from the solution and found to be PEPA maleate by TLC, melting point and IR. The ethanol was evaporated to yield unreacted magnesium ethoxide (IR identification).

Salts of the ß-keto ester

Synthesis of the aluminium salt of the ß-keto ester (20)

Aluminium isopropoxide (0.1 g, 4.9×10^{-4} moles) and the ß-keto ester (0.39 g, 1.47×10^{-3} moles) were heated in dry isopropanol (20 mls) under reflux conditions for three hours during which a white solid appeared. The solvent was evaporated to leave a white powder which was dried under vacuum at 80°C. The product was insoluble in all common solvents. Yield 0.45 g (92%), mpt >300°C.

IR (mull) 1520 and 1610. Microanalysis; found: C, 38.72; H, 4.63; $C_{27}H_{36}O_{21}P_3Al$ requires: C, 39.37; H, 4.44%.

Attempted synthesis of the magnesium salt of the ß-keto ester

1 Magnesium ethoxide (0.043 g, 3.75×10^{-4} moles) and the ß-keto ester (0.20 g, 7.55×10^{-4} moles) were heated in dry ethanol (10 mls) under reflux conditions for four hours. On cooling, white crystals formed which were filtered and washed with cold ethanol (3 x 10 mls). TLC and infrared spectroscopy of the

crystals showed them to be the unreacted ester, a fact confirmed by their melting point (148°C).

2 The starting materials (as above) were heated in acetonitrile under reflux conditions for four hours. The magnesium ethoxide did not dissolve and the mixture was filtered. No precipitate formed on cooling so the filtrate was evaporated to yield a white powder which was confirmed as the unreacted ester by TLC and infrared, mpt 145 - 147°C.

3 The starting materials (as above) were heated, in the absence of a solvent, on an oil bath under nitrogen at 150°C. The ester melted but the magnesium ethoxide did not dissolve. On increasing the temperature to 165°C, the ester decomposed leaving the magnesium ethoxide unreacted and intact.

Attempted synthesis of the copper salt of the ß-keto ester

Copper acetate (0.30 g, 1.5×10^{-3} moles) and the ß-keto ester (0.40 g, 3.0×10^{-3} moles) were heated in ethanol under reflux conditions for four hours. The mixture was filtered hot which separated a green solid from the solution. On cooling the filtrate, crystals appeared which were identified as the unreacted ester by TLC, melting point and infrared spectroscopy.

Attempted synthesis of the melamine salt of the ß-keto ester

1 **Aqueous conditions.** Melamine (0.28 g, 5.26×10^{-3} moles) and the ß-keto ester (0.50 g, 5.26×10^{-3} moles) were mixed together. Boiling water was added but the two solids did not dissolve and were

recovered by filtration and found to be a mixture of the two starting materials by TLC and melting point.

2 **Non-aqueous conditions.** The starting materials (as above) were heated in acetonitrile under reflux conditions overnight. The melamine did not dissolve and was filtered off. The filtrate was evaporated to leave a white solid which was identified as the ester by TLC, infrared and melting point.

The synthesis of melamine salts of other derivatives of PEPA

All the derivatives of PEPA were mixed in equimolar proportions with melamine. Boiling water was poured on and stirring continued for five minutes before the hot solutions were filtered. In all cases a white precipitate formed on cooling which was filtered and washed with cold water.

1 **Synthesis of (21).** The PEPA-norbornene ester (1.00 g, 2.9×10^{-3} moles) was treated with melamine (0.36 g, 2.9×10^{-3} moles) to produce a white powder of yield 1.1 g (81%), mpt 260°C (dec).

IR (mull) 1500 and 1300. Microanalysis; found: C, 41.35; H, 4.93; N, 19.85; $C_{17}H_{23}N_6O_8P$ requires: C, 43.41; H, 4.93; N, 17.87%.

2 **Synthesis of (22).** The PEPA-phthalic ester (1.3 g, 3.97×10^{-3} moles) was treated with melamine (0.50 g, 3.97×10^{-3} moles) to yield a product of 1.43 g (79%), mpt 210°C.

IR (mull) 1510 and 1310. Microanalysis; found: C, 43.51;

H, 3.99; N, 18.42; $C_{16}H_{19}N_6O_8P$ requires: C, 42.29; H, 4.19; N, 18.50%.

3 **Synthesis of (23).** The PEPA-tetrahydrophthalic ester (1.32 g, 3.97×10^{-3} moles) was treated with melamine (0.5 g, 3.97×10^{-3} moles) to give a white powder of yield 1.39 g (76%), mpt 180°C.

IR (mull) 1510 and 1310. Microanalysis; found: C, 41.04; H, 5.72; N, 19.77; $C_{16}H_{23}N_6O_8P$ requires: C, 41.92; H, 5.02; N, 18.34%.

REFERENCES

1 Y. Halpern and I. Skokie, US Patent 4,154,930.

2 Y. Halpern, I. Skokie and C. T. Fleenor, US Patent 4,201,705.

3 Y. Halpern and I. Skokie, German Patent 29,10,746.

4 C. T. Fleenor, US Patent 4,253,972.

5 Y. Halpern, D. M. Mott and R. H. Niswander, European Patent 01,26,491.

6 Y. Halpern, D. M. Mott and R. H. Niswander, US Patent 4,478,998.

7 Y. Halpern, I. Skokie and D. M. Mott, US Patent 4,480,093.

8 Y. Halpern, D. M. Mott and R. H. Niswander, Ind. Eng. Chem. Prod. Res. Dev., 1984, 23, 233.

9 G. Camino, L. Costa, E. Casorati, G. Bertelli and R. Locatelli, J. of App. Polym. Science, 1988, 35, 1863.

10 C. P. Fenimore and F. J. Martin, Combust. Flame, 1966, 10, 135.

11 C. P. Fenimore in 'Flame-Retardant Polymeric Materials', vol 1, ed M. Lewin, S. M. Atlas and E. M. Pearce, Plenum Press, New York, 1975, p 371.

12 J. Brossas, Polymer Deg. and Stab., 1989, 23, 313.

13 A. H. Landrock in 'Handbook of Plastics and Flammability and Combustion Toxicology', Noyes, Park Ridge, New Jersey, 1983.

14 Underwriter's Laboratories, Standard for Safety Manual, 3rd Edition, 1980.

15 R. Ratz and O. Sweating, J. Org. Chem., 1963, 28, 1608.

16 H. Grabhofer, H. Muller, R. F. Posse and H. Ulrich, US Patent 3,342,903.

17 B. Dhawan and D. Redmore, Phosphorus and Sulphur, 1987, 31, 215.

18 S. K. Das, T. Gündüz, R. A. Shaw and B. C. Smith, J. Chem. Soc. (A), 1969, 1403.

19 J. K. Dixon, N. T. Woodberry and G. W. Costa, J. Am. Chem. Soc., 1947, 69, 599.

20 J. Wohnsiedler, Ind. Eng. Chem., 1952, 44, 2679.

21 T. R. Manley, Polym. J., 1973, 4, 111.

22 H. Cordes, German Patent 1,935,010.

23 E. J. Modest in 'Heterocyclic Compounds', vol 2, Chapter 8, ed R. C. Elderfield, Wiley & Sons Inc, New York, 1961.

24 B. Kaur, R. K. Jain, I. S. Gur and H. L. Bhatnagar, J. of Analytical and Applied Pyrolysis, 1987, 11, 465.

25 W. J. Kroenke, J. Appl. Polym. Sci., 1981, 26, 1167.

26 D. W. Kaiser, J. T. Thurston, J. R. Dudley, F. C. Schaefer, I. Hechenbleikner and D. Holm-Hansen, J. Amer. Chem. Soc., 1951, 73, 2985.

CHAPTER 4 : POLYMERIC FLAME RETARDANTS

4.1 INTRODUCTION

4.2 THE POLYMERISATION OF DERIVATIVES OF PEPA

4.3 COPOLYMER SYNTHESIS

4.4 CONCLUSIONS

4.5 EXPERIMENTAL

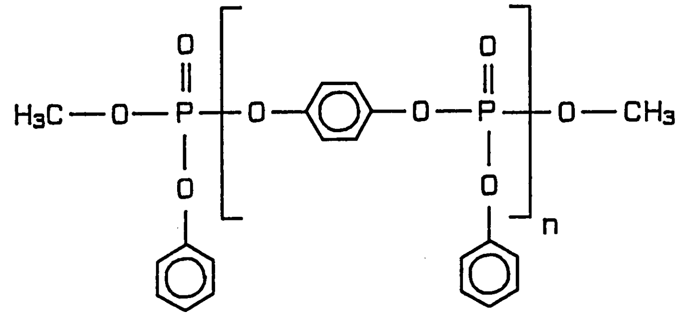
4.6 REFERENCES

4.1 INTRODUCTION

The use of polymers in flame retardant formulations is not a recent development. Halogenated polymers have been used as non-intumescent flame retardant additives since the 1970's.[1, 2] In early intumescent coatings the active ingredients were often bound together by naturally occurring polymers such as cellulose[3] and it was soon discovered that this form of binder was also a good supply of the carbonific source needed for intumescent behaviour.[4-6] In later formulations the intumescent catalyst was also supplied in a polymeric form, such as ammonium polyphosphate.[7, 8]

In recent years it has been claimed that polymeric flame retardant additives are preferable to conventional non-polymeric additives due to their better resistance to extraction, migration, volatile loss, etc, thus making the flame retardancy available on a more permanent basis.[9-11]

Polyphosphate esters have received some attention in this area during the past couple of years, with additives of typical structure (1) being not only effective flame retardants but also possessing attractive plasticising properties.[12-14]

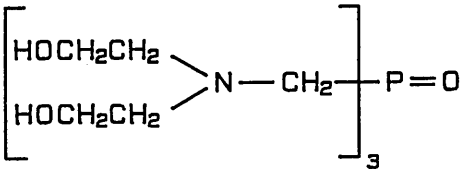


(1)

The most recent development in the production of flame retardant polymers is to synthesise polymers that are flame retardant in themselves, thus eliminating the need for flame retardant additives. This is usually achieved by the inclusion, at some stage during the polymer synthesis, of a compound with flame retardant properties which will act as a crosslinking agent or as a monomer and thus be included in the polymer backbone, rendering some degree of flame retardancy on the resulting product.

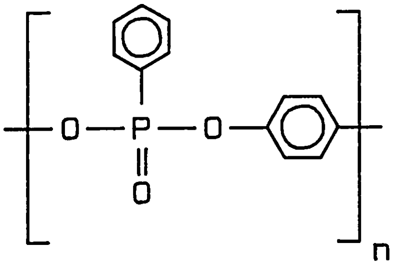
An example of this is the development of flame retardant epoxy resins. Epoxy resins are used in a wide range of applications including adhesives, coatings, etc,[15] but their flammability creates a major hazard. This was counteracted in the past by the use of flame retardant additives including ammonium phosphate and phosphorus mixtures.[16] This has been superseded by the utilisation of fire-retardant crosslinking agents, resulting in fire retardant compositions for various epoxy resins.[17-19]

Polyurethane foams also present problems due to their flammability. Polyurethane foams are the product of a chemical reaction between a polyol and a polyfunctional isocyanate. The addition of a flame retardant additive to either of these starting materials, prior to their reaction, results in the dispersion of the additive throughout the resulting foam. If a polyol with flame retardant properties is treated with an isocyanate, then the resulting polyurethane will have reduced flammability. Such a polyol is tris[N,N-bis(2-hydroxyethyl)aminomethyl]phosphine oxide, (2), which has been successfully utilised in the synthesis of flame retardant polyurethane foams.[20]



(2)

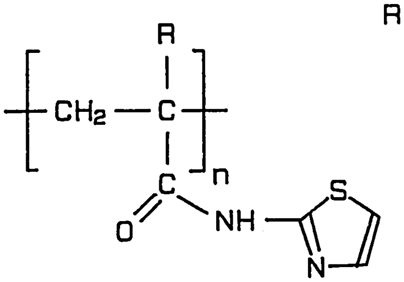
The polymerisation of phenyl phosphonates has resulted in a flame retardant plastic, (3), with useful engineering properties.[21] However, these products have proved to be of more use as fire retardant additives in other polyesters than as engineering plastics in their own right.



(3)

The main area of interest on which the work described in this chapter is concentrated is the production of flame retardant poly(methyl methacrylate). Commercial poly(methyl methacrylate) is a hard, rigid, transparent material.[22] Its major uses arise from its high light transmission and good weathering properties. It is a useful moulding material for applications where good appearance, reasonable toughness and rigidity are requirements which are considered to justify the extra cost of the polymer as compared with the larger tonnage plastics. The polymer is used for many applications including display signs (both internal and external), light fittings and protective screens.

Methacrylic derivatives have been synthesised, an example of which is compound (4) which has been investigated for its potential as a polymeric drug carrier.[23]



R=CH$_3$ or H

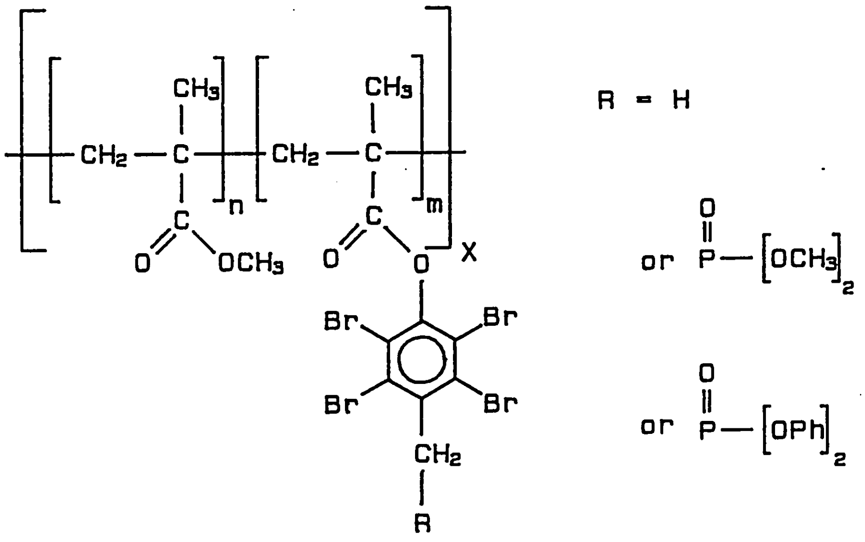
(4)

A rapidly expanding market for the use of poly(methyl methacrylate) is in the manufacture of washbasins, baths, etc. The polymer can be cast to give considerable design versatility, readily accepts pigments (therefore can be available in a wide range of colours) and is much lighter and cheaper than similar products from conventional materials.[24]

For many applications, poly(methyl methacrylate) must contain fire retardants and in order for government legislation to be upheld, the required amounts of flame retardant additives are relatively high, causing problems with the physical and mechanical properties of the polymer. The properties most affected are the Vicat softening temperature, transparency, migration, water absorption and light degradation of the fire retarded polymer. In extreme cases, surface cracking has been observed. Thus, the most commonly used fire retardants, especially systems containing antimony oxides and/or halogenated organic compounds, cannot be used and attention has therefore turned very rapidly to phosphorus-based fire retardants.[25]

For reasons already discussed, recent developments in the field of producing flame retarded poly(methyl methacrylate) have concentrated on the production of copolymers in attempts to introduce a flame retardant entity into the poly(methyl methacrylate) backbone. There are papers in the literature describing copolymers of poly(methyl methacrylate) synthesised for reasons other than imparting flame retardancy to the polymer.[26, 27]

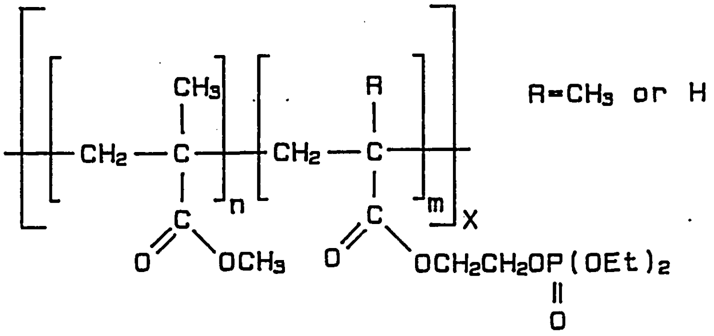
As mentioned in the introduction to this thesis, the Chinese are still pursuing the area of halogenated flame retardants despite their obvious unfavourable environmental effects.[28] A recent Chinese paper claimed that the chemical grafting of flame retardant compounds into the poly(methyl methacrylate) backbone gives better flame retardancy than the physical mixing of the compounds with the polymer.[29] Methyl methacrylate was copolymerised with 4-methacryloxy-2,3,5,6-tetrabromobenzyl phosphonates to produce copolymers of structure (5).



(5)

Such copolymers were reported as showing significant flame retardancy, but doubts must be held as to whether such brominated polymers are safe in a fire situation due to their liberation, on heating, of toxic, obscuring and corrosive smokes caused by the production of hydrogen bromide gas (see Chapter 1).

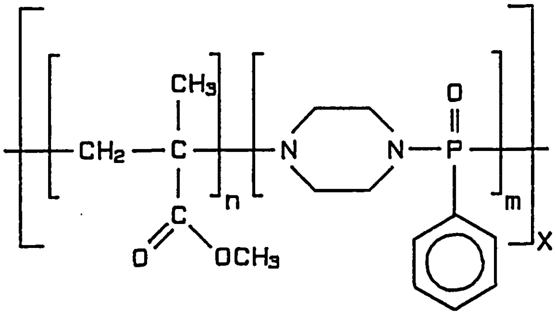
One of the most recent attempts to create flame retardant poly(methyl methacrylate) has been the copolymerisation of methyl methacrylate with diethyl-2-(methacryloyloxy)ethyl phosphate and related compounds.[30-33] The polymers produced were random polymers of the form:



(6)

Such copolymers were found to be less thermally stable than pure poly(methyl methacrylate), yet were significantly flame retardant. This was accounted for by either the formation of a protective char barrier or interference by the degradation products in the vapour phase chain reactions.

Also studied were copolymers of the type (7) with similar results.[32]

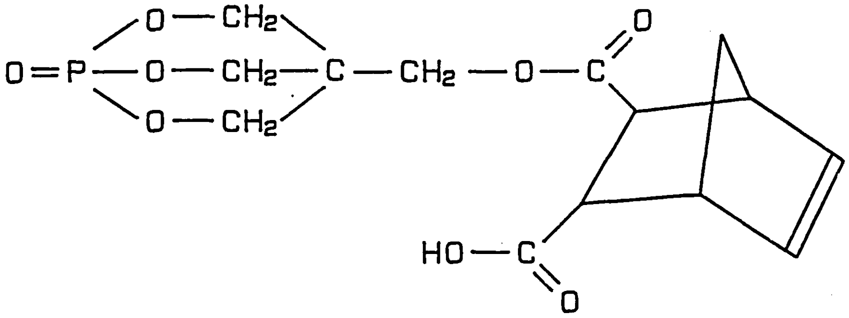


(7)

4.2 THE POLYMERISATION OF DERIVATIVES OF PEPA

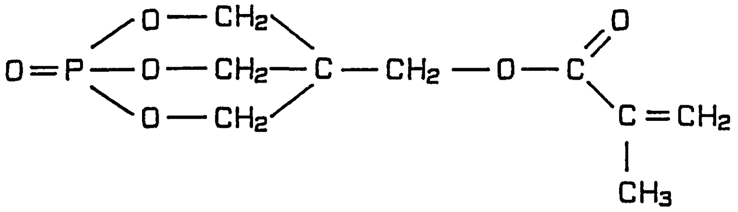
The work described in Chapter 2 provided four derivatives of PEPA with side chains containing a carbon-carbon double bond which therefore had the potential to undergo polymerisation.

The norbornene ester, (8), was not soluble in any solvent, even on heating, and thus polymerisation was not possible.

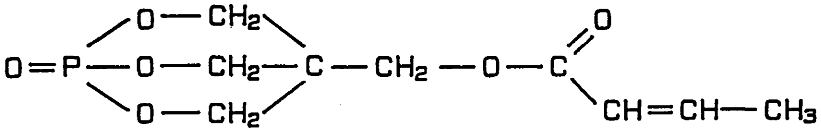


(8)

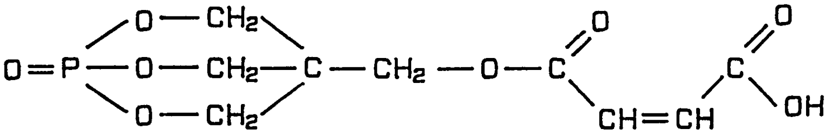
Work therefore concentrated on the remaining three esters, ie the methacrylate, (9), crotonate, (10), and maleate, (11).



(9)

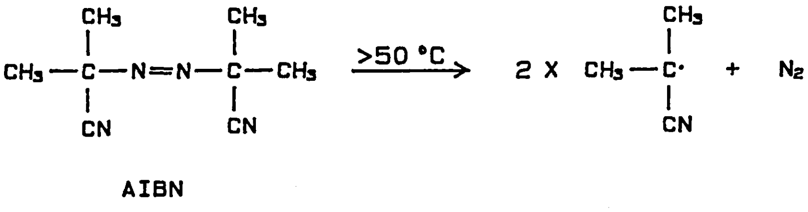


(10)



(11)

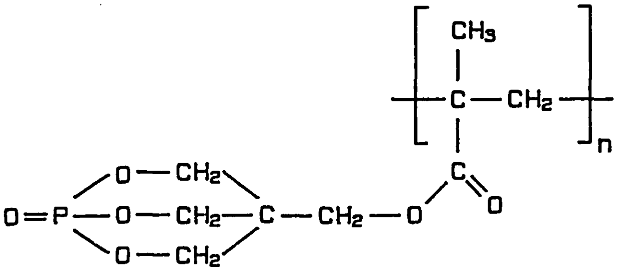
Compounds of these structures would be expected to undergo free radical polymerisation,[34] so this method was adopted. The free radical initiator was α-azo-iso-butyrnitrile (AIBN) which undergoes the following reaction:



Scheme 1

AIBN was added to a solution of the starting material which was then heated to 60°C for twenty-four hours under nitrogen.

This treatment of the methacrylate ester, (9), produced a fine white powder. The infrared spectrum of this product was identical to that of the starting material except for the disappearance of the peak at 1600 cm^{-1} due to the C=C. The melting point of the product was >300°C, significantly higher than that of the starting material (187°C). The product was not mobile on a TLC plate. The ^{1}Hnmr spectrum showed evidence of the PEPA structure along with the typical peaks for polymethacrylates. The ^{1}Hnmr spectrum and its implications are discussed in more detail in section 4.3. The product was therefore confirmed as structure (12):



(12)

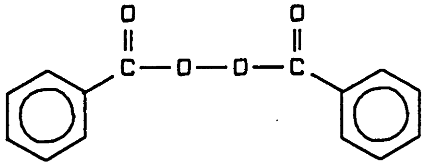
Microanalysis of this polymer gave values close to the theoretical figures and showed the presence of a small amount of nitrogen (0.31%). Each polymer chain will be terminated by one $(CH_3)_2CCN$ group and thus, knowing the percentage of nitrogen in the polymer, the average molecular weight of the polymer can be determined:

$$\text{average rmm of polymer} = \frac{\text{rmm of nitrogen}}{\text{percentage of nitrogen in polymer}} \times 100$$

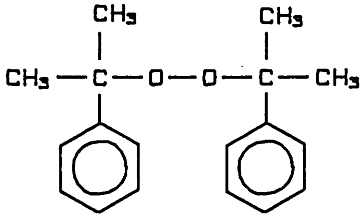
For compound (12) the average molecular weight was found to be 4500. As each monomer has a molecular weight of 248, the average polymer chain of (12) contains about eighteen repeating units.

The polymer had excellent thermal stability, the TGA trace showing no weight loss until 340°C. The TGA trace is provided in Figure 4.8 further in this chapter. The polymer was not intumescent when held in an open flame, nor was a physical blend with melamine. In the light of the observations and conclusions of Chapter 3, this was expected as the polymer contains no acidic proton. However, it was anticipated that the high thermal stability and relatively high phosphorus content (11.65%) would make it a useful non-intumescent flame retardant polymeric additive.

Following this success, a similar polymerisation reaction was attempted on the crotonate ester, (10). However, under identical conditions, this compound did not polymerise and only the recovered starting material was identified after the reaction, characterised by infrared spectroscopy (showing the C=C bond to be intact), melting point and TLC behaviour. Different conditions were employed including higher temperatures and the effects of changing the radical initiator. Both benzoyl peroxide, (13), and dicumyl peroxide, (14), were used, but again no polymer was formed.



(13)



(14)

It was considered that the most probable explanation for the lack of reaction was that the methyl group on the end of the molecule was providing sufficient steric hindrance to prevent free radical attack at the double bond.

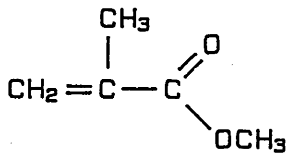
Polymerisation of the maleate ester, (11), was also attempted but again with no success, analysis of the recovered material identifying it as the starting material. The reaction was attempted under various conditions, as discussed above, including a change of solvent to tetrahydrofuran (THF), but still without success. Work therefore concentrated on the polymer formed from the methacrylate ester.

4.3 COPOLYMER SYNTHESIS

Though poly(PEPA methacrylate) is very thermally stable and shows promise as a flame retardant additive in its own right, it was thought that its true potential could be in the area of copolymerisation. As discussed in the Introduction, 4.1, copolymers containing fire retardant monomers in the polymer backbone are preferred to polymers containing the fire retardant entity as an additive.

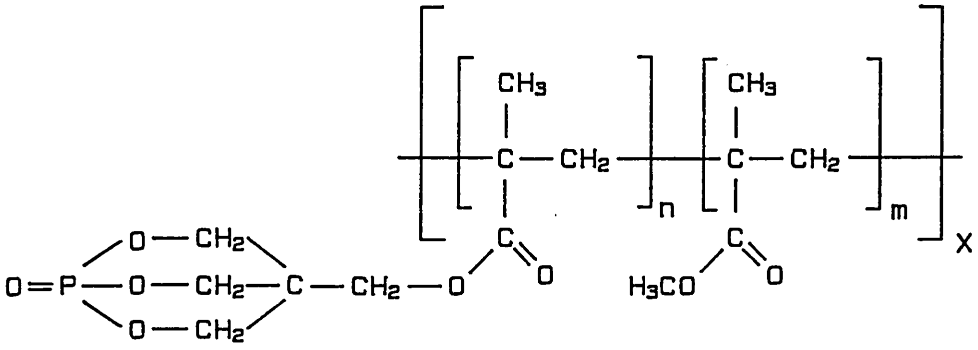
The methacrylate ester, (9), was heated in DMF in the presence of AIBN and styrene added in a series of concentrations from 5 to 50% by weight. In each case, on pouring the resulting solution into methanol, a white polymer was isolated. This polymer proved to be pure poly(PEPA methacrylate), ie compound (12). It revealed no evidence of containing styrene units by either infrared or ^{1}Hnmr spectroscopy, and when the solution was poured into methanol, a strong smell of styrene was noticed. Various conditions were attempted including elevated temperatures and different initiators, (13) and (14), but a copolymer was never isolated and this aspect was left in abeyance in order to concentrate on copolymerisations with methyl methacrylate which were indicating far more potential.

The PEPA methacrylate, (9), shows a structural similarity to methyl methacrylate, (15).



(15)

It was therefore anticipated that the two compounds would successfully copolymerise. An equimolar mixture of the two monomers was treated with AIBN in DMF and heated at 60°C for twenty-four hours. The resulting solution was poured into methanol to produce a white precipitate. As expected, the infrared spectrum of this product was not significantly different from that of pure poly(PEPA methacrylate) except in the carbonyl region where two peaks were observed, at 1660 cm^{-1}, and at 1710 cm^{-1}. This was expected as there will be two carbonyl environments in the copolymer, one as a methyl ester, the other as a PEPA ester. Indeed, the 1710 cm^{-1} peak corresponds to that observed in the infrared spectrum of pure poly(PEPA methacrylate). The ^{1}Hnmr spectrum and TGA trace of the copolymer showed considerable differences from those of pure poly(PEPA methacrylate). Microanalysis revealed the elemental composition to be close to the theoretical values for a 1:1 copolymer, so the structure was confirmed as that of (16, m=n):

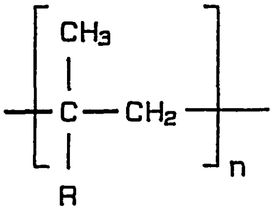


(16)

For comparison, a sample of pure poly(methyl methacrylate) was prepared using the conditions established above. It was observed that on pouring into methanol, the reaction solution was very viscous implying a polymer of much higher molecular weight than those previously prepared. The infrared spectrum of this polymer showed a single carbonyl peak at 1665 cm^{-1} accounting for the additional peak in the infrared spectrum of the copolymer. The ^{1}Hnmr spectrum and TGA trace were also recorded and will be discussed subsequently.

A series of copolymers was synthesised between PEPA methacrylate, (9), and methyl methacrylate, (15), with varying proportions of PEPA methacrylate in the range 5%, 10%, 20%, 30% and 40%, by weight, respectively.

The ^{1}Hnmr spectra of the copolymers showed two very broad signals as $\delta = 1.0$ and 1.9 ppm. These were due to the methacrylate protons from each monomer:



$$-\left[\underset{\displaystyle R}{\underset{|}{\overset{\displaystyle CH_3}{\overset{|}{C}}}}-CH_2\right]_n-$$

A doublet at $\delta = 4.9$ ppm is due to the CH_2 protons within the PEPA cage. This leaves a broad signal at $\delta = 3.6$ ppm. A signal at this value is observed in the spectra of both pure poly(methyl methacrylate) and pure poly(PEPA methacrylate), due to the methoxy protons and the CH_2 protons attached to the PEPA cage, respectively. In the spectrum of pure poly(PEPA methacrylate), the signal at $\delta = 4.9$ and 3.6 ppm are in the ratio 6:2. It is therefore possible to measure the integral signal at $\delta = 4.9$ ppm from the copolymer and hence calculate the proportion of the 3.6 ppm signal that is due to the PEPA structure. The remaining fraction must be due to the methyl methacrylate structure and therefore a value for the true proportion of monomers within the copolymer can be determined. This figure is important to ascertain because the presence of both starting materials in a certain proportion during the reaction does not guarantee the same proportion of monomers in the end product due to the possibility of their possessing different rates of reaction.

The degree of copolymerisation was verified by microanalysis from the percentage of phosphorus present in each polymer. The results obtained are given in Table 1.

Table 1

% PEPA Methacrylate Starting Material	% PEPA Methacrylate in Product Calculated from ^{1}Hnmr	% PEPA Methacrylate in Product Calculated from Microanalysis
0	0	0
5	6	4.7
10	10	10.5
20	22	21.3
30	29	28.0
40	39	40.8
50	47	48.8
100	100	100

As can be observed from Table 1, the results calculated from both the microanalysis data and the ^{1}Hnmr spectra show very close matching to the theoretical values. This indicates that the percentage of each monomer in the copolymers is the same as the percentage of each starting material present. Therefore it can be concluded that PEPA methacrylate and methyl methacrylate have very similar rates of polymerisation.

Microanalysis of these polymers also provided values for the nitrogen content and hence the average molecular weight was determined. Knowing the average molecular weight and percentage composition of the copolymers, the average number of repeating units could be calculated thus determining the average polymer length, see Table 2.

Table 2

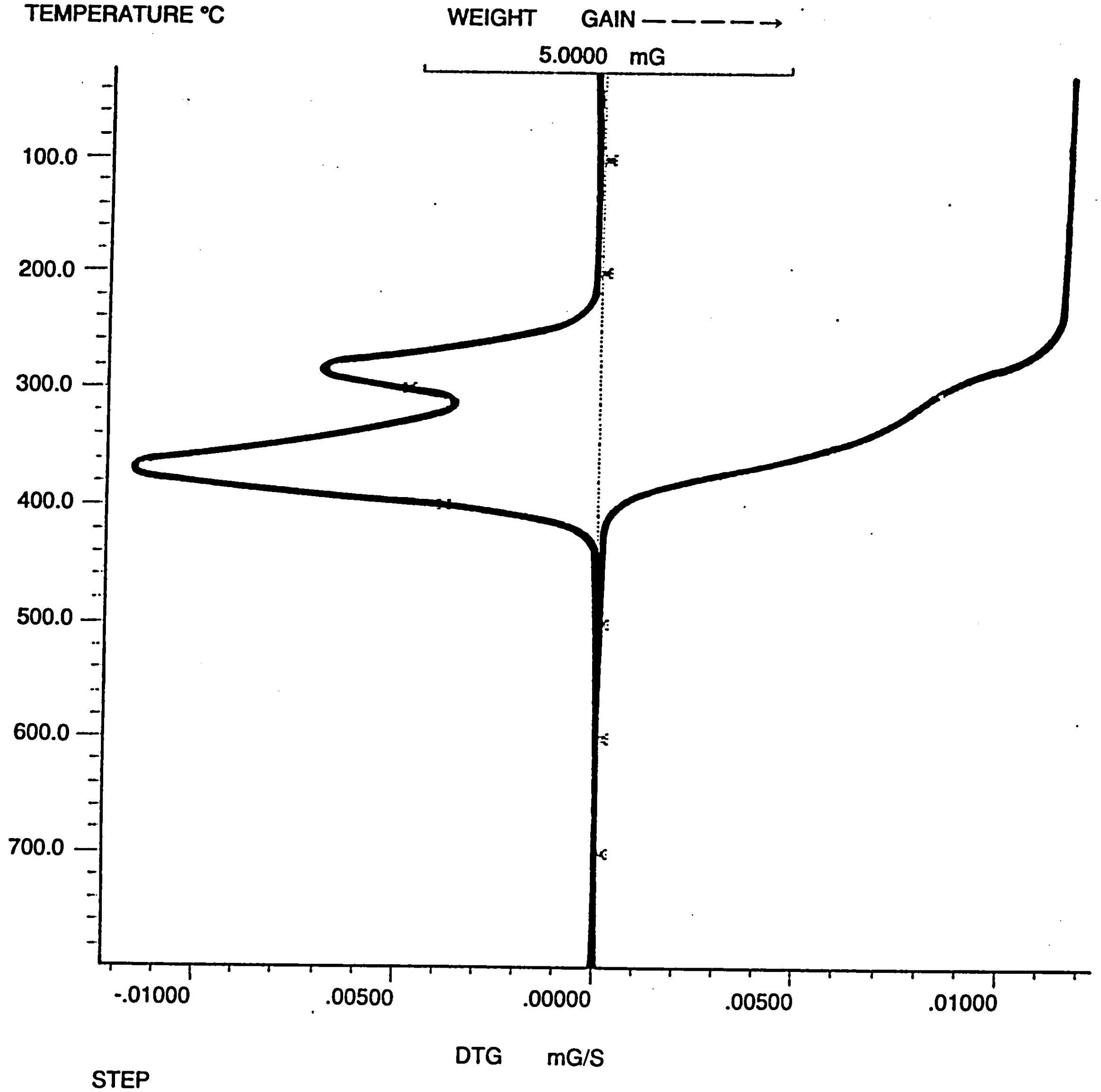
% PEPA Methacrylate Starting Material	Average Molecular Weight of Polymer	Average Number of Repeating Units
0	> 28000	> 280
5	11666	109
10	9333	80
20	7000	54
30	6555	45
40	5777	36
50	3000	17
100	4500	18

The thermal stability of all the polymers was studied using TGA. The traces are all shown in the following pages, their respective numbers being:

% PEPA Methacrylate Starting Material	Figure
0	4.1
5	4.2
10	4.3
20	4.4
30	4.5
40	4.6
50	4.7
100	4.8

As can be seen, pure poly(PEPA methacrylate), Figure 4.8, is stable to around 400°C whereas pure poly(methyl methacrylate) loses 31% of its weight at 285°C, with 68% being lost at 369°C (Figure 4.1). It can be seen that the addition of 5% PEPA methacrylate does not have any significant affect on the thermal properties of the poly(methyl methacrylate). At 10% incorporation, two weight loss peaks were still present, but the first had decreased to only 23% weight loss and the second had increased its decomposition temperature to 391°C. At 20% incorporation, the initial weight loss was down to 19% and the second decomposition temperature was at 402°C. At 30% incorporation, the first decomposition peak had moved close enough to the second to form a shoulder. This shoulder was much less pronounced at 40% incorporation and was insignificant at 50% incorporation.

It is therefore apparent that the inclusion of PEPA methacrylate into the backbone of poly(methyl methacrylate) increases the thermal stability of the latter. The loadings have to be fairly high to make a significant improvement, but such higher loadings also decrease the polymer chain length.



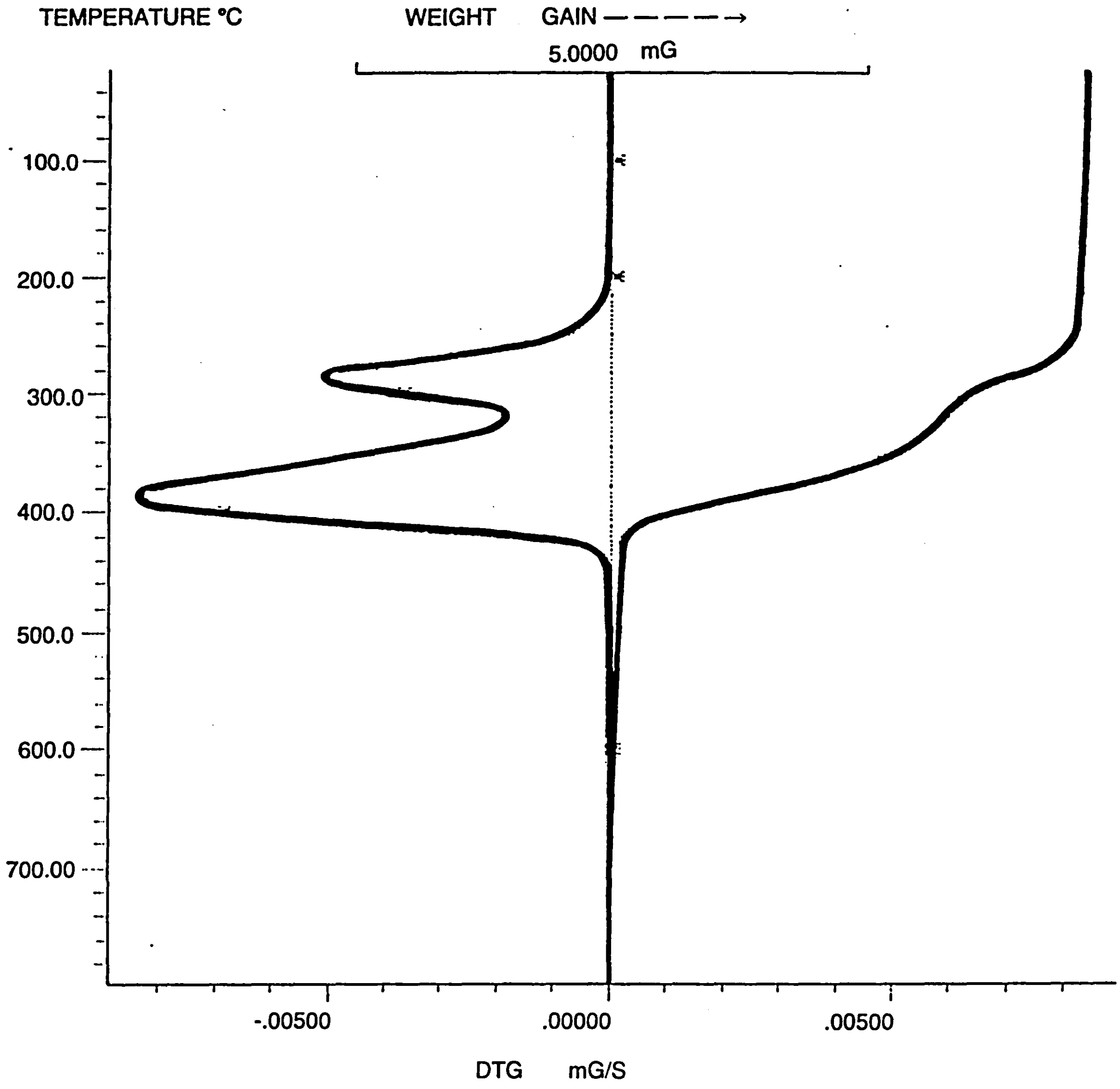
```
STEP
START TEMP.°C          212.7
PEAK TEMP. °C          285.3
END TEMP. °C           314.7
Δm      mG            -1.9410
Δm      %             -31.530

STEP
START TEMP. °C         314.7
PEAK TEMP. °C          369.7
END TEMP. °C           432.0
Δm      mG            -4.2190
Δm      %             -68.535

Δm      mG                        -.02100
Δm      %                         -.34113
```

Figure 4.1

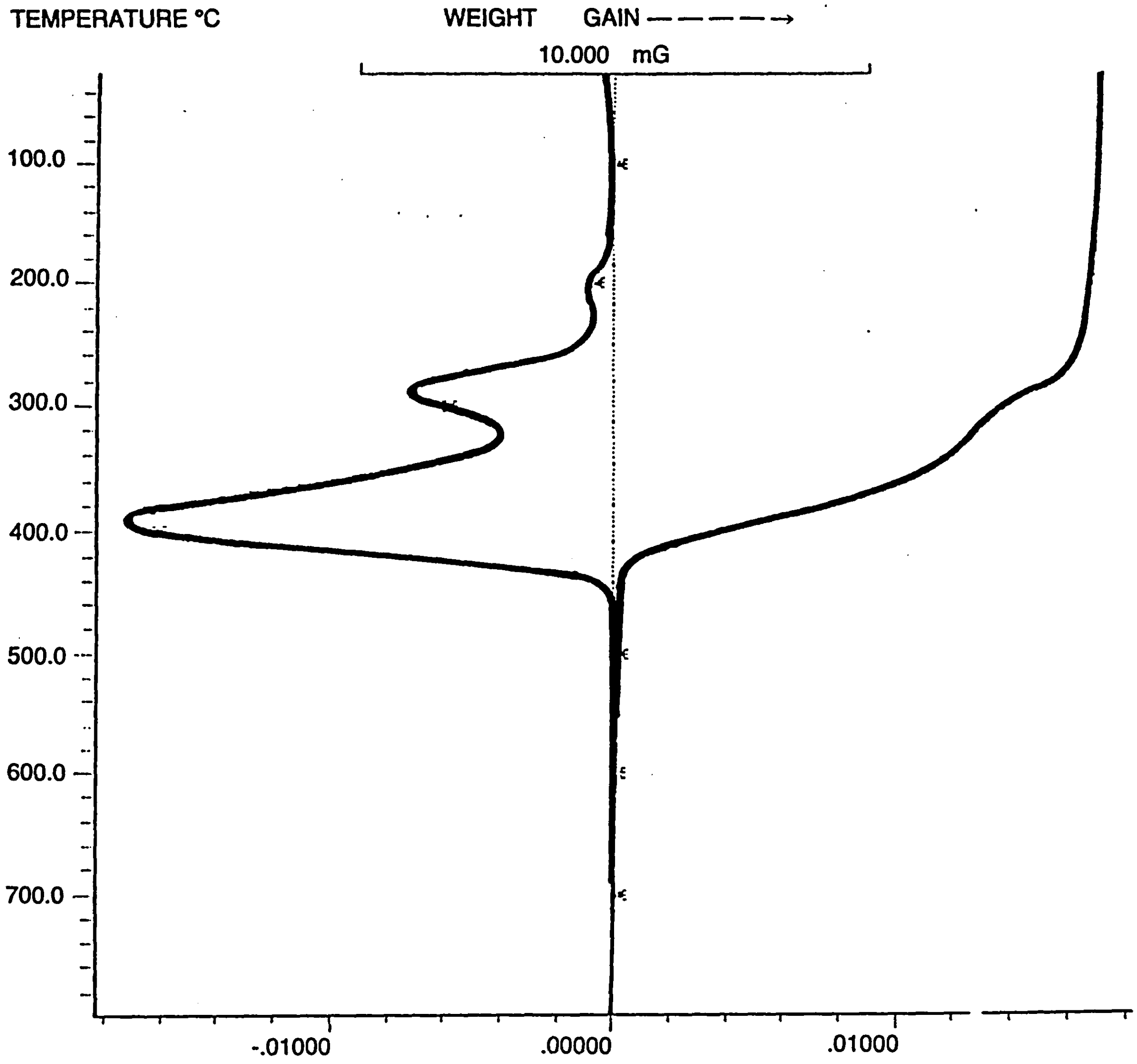
TGA Trace of pure poly(methyl methacrylate)



STEP		
START TEMP.°C	215.7	
PEAK TEMP. °C	289.0	
END TEMP. °C	322.0	
Δm mG	-1.3830	
Δm %	-30.510	
STEP		
START TEMP. °C	322.0	
PEAK TEMP. °C	384.3	
END TEMP. °C	439.3	
Δm mG	-3.1000	
Δm %	-68.387	
Δm mG		-.07800
Δm %		-1.7207

Figure 4.2

TGA Trace of copolymer consisting of 95% methyl methacrylate and 5% PEPA methacrylate



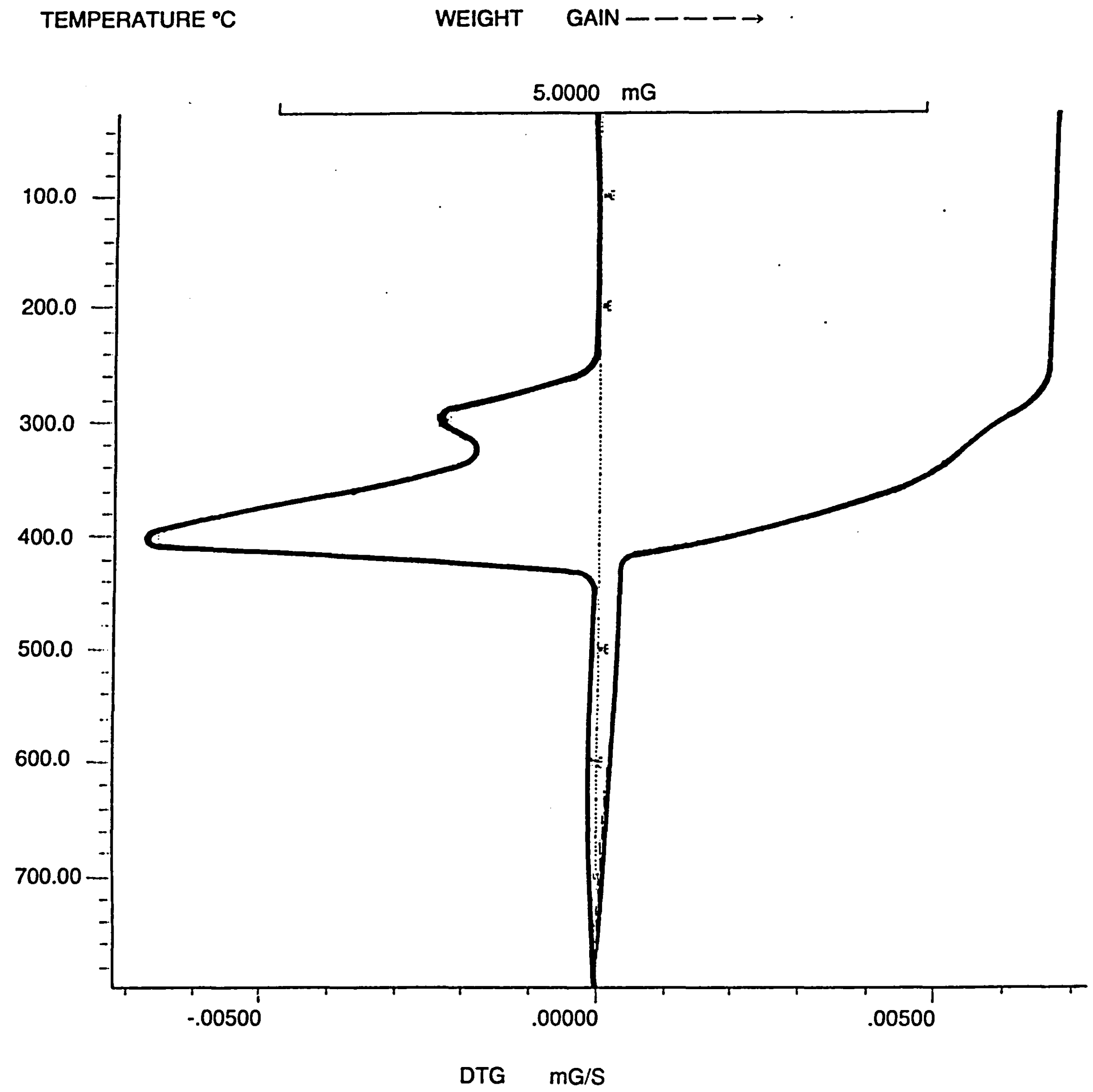
```
                         DTG     mG/S
STEP
START TEMP.°C                     226.7
PEAK TEMP. °C                     289.0
END TEMP. °C                      322.0
Δm      mG                       -2.1930
Δm      %                       -23.224

STEP
START TEMP. °C                    322.0
PEAK TEMP. °C                     391.7
END TEMP. °C                      454.0
Δm      mG                       -6.8810
Δm      %                       -72.869

  Δ     mG                                 -.14900
Δm      %                                  -1.5779
```

Figure 4.3

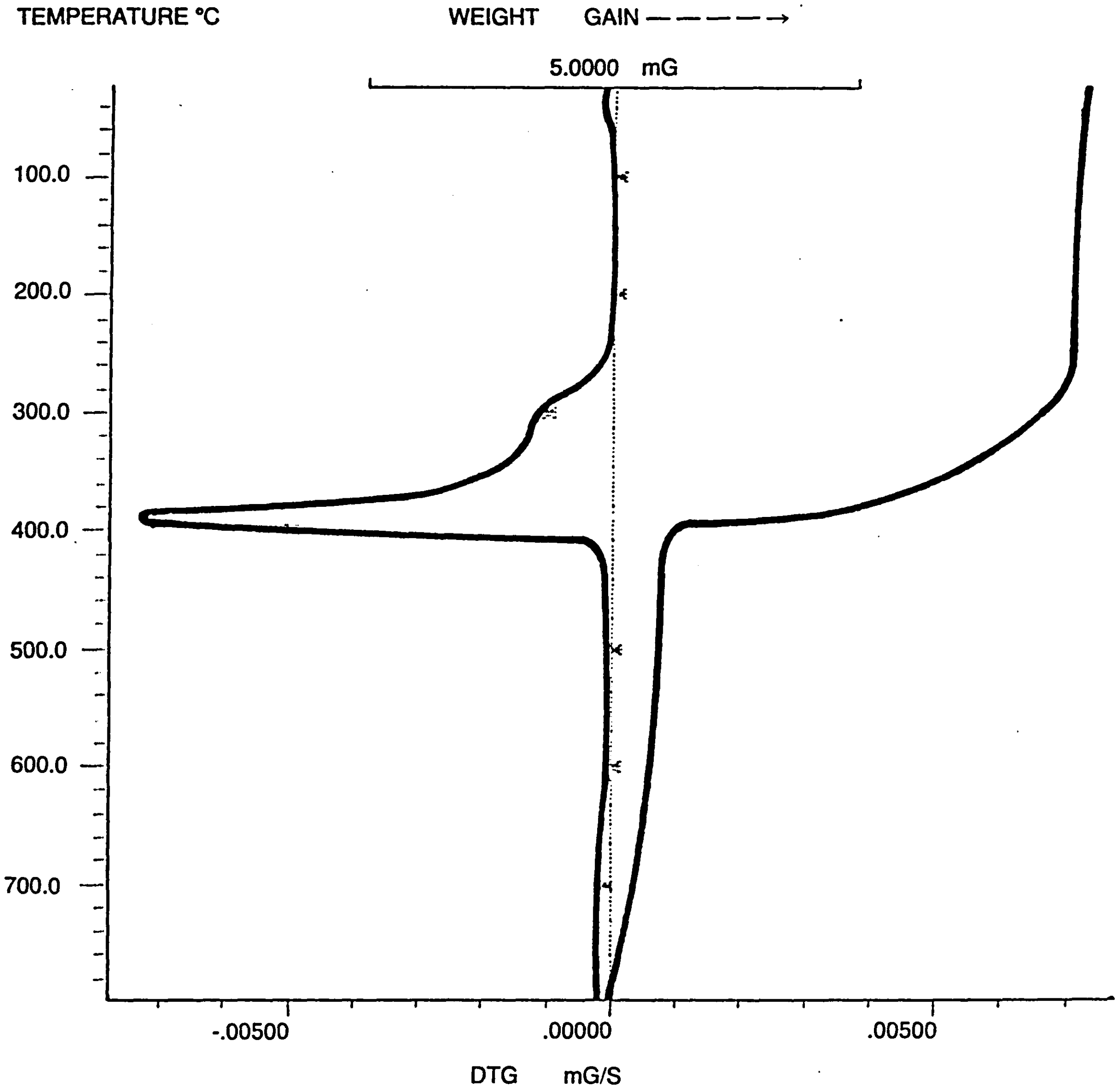
TGA Trace of copolymer consisting of 90% methyl methacrylate and 10% PEPA methacrylate



STEP		
START TEMP.°C	245.0	
PEAK TEMP. °C	296.3	
END TEMP. °C	325.7	
∆m mG	-.68800	
∆m %	-19.573	
STEP		
START TEMP. °C	325.7	
PEAK TEMP. °C	402.7	
END TEMP. °C	439.3	
∆m mG	-2.6170	
∆m %	-74.452	
∆m mG		-.17200
∆m %		-4.8933

Figure 4.4

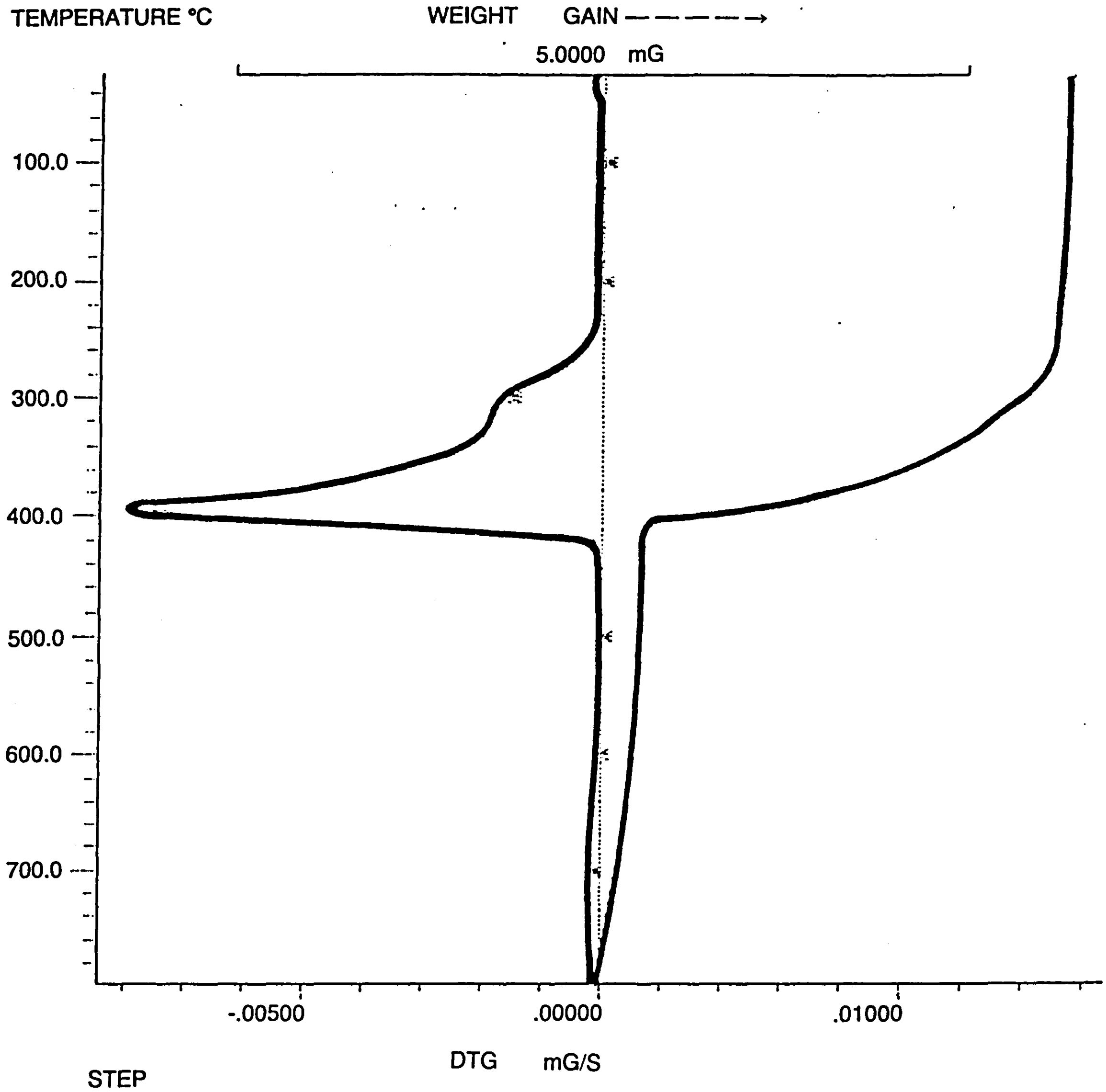
TGA Trace of copolymer consisting of 80% methyl methacrylate and 20% PEPA methacrylate



STEP		
START TEMP.°C	226.7	
PEAK TEMP. °C	395.3	
END TEMP. °C	428.3	
Δm mG	-2.8410	
Δm %	-86.484	
Δm mG		-.07000
Δm %		-2.1309

Figure 4.5

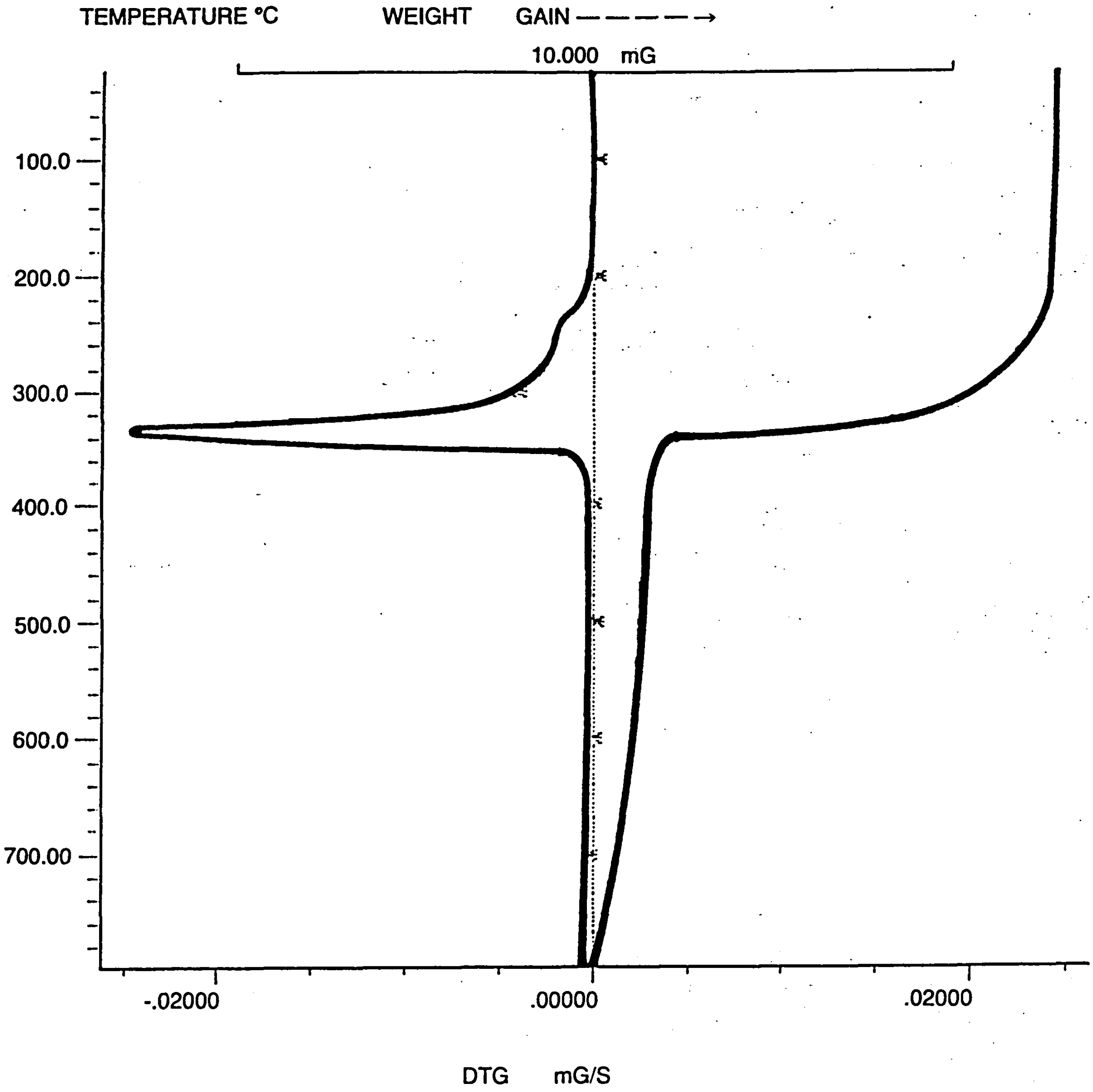
TGA Trace of copolymer consisting of 70% methyl methacrylate and 30% PEPA methacrylate



STEP	
START TEMP.°C	237.7
PEAK TEMP. °C	388.0
END TEMP. °C	553.0
Δm mG	-4.2290
Δm %	-79.284

Figure 4.6

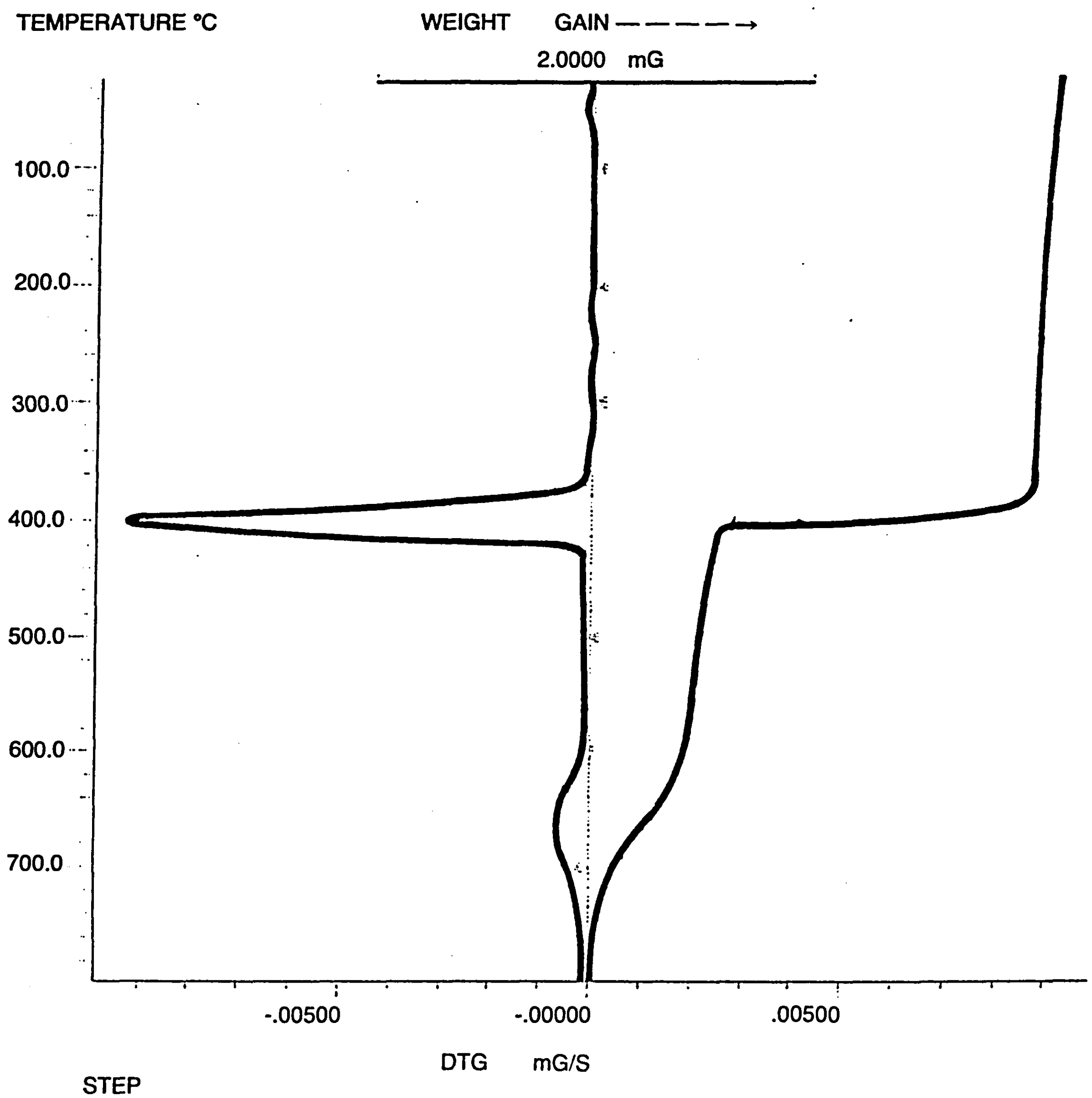
TGA Trace of copolymer consisting of 60% methyl methacrylate and 40% PEPA methacrylate



STEP	
START TEMP.°C	127.7
PEAK TEMP. °C	333.0
END TEMP. °C	479.7
Δm mG	-5.7950
Δm %	-79.221

Figure 4.7

TGA Trace of an equimolar copolymer of methyl methacrylate and PEPA methacrylate



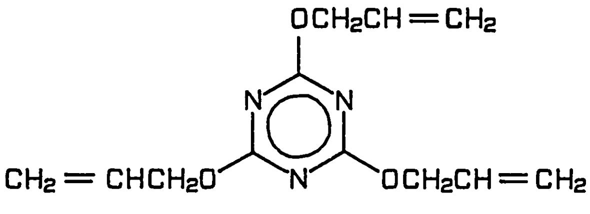
STEP		
START TEMP.°C	340.3	
PEAK TEMP. °C	399.0	
END TEMP. °C	494.3	
∧m mG	-1.517.0	
∧m %	-63.901	
∧ mG		-.02500
∧m %		-1.0531
STEP		
START TEMP. °C	538.3	
PEAK TEMP. °C	670.3	
END TEMP. °C	795.0	
∧m mG	-.48300	
∧m %	-20.345	

Figure 4.8

TGA Trace of pure poly(PEPA methacrylate)

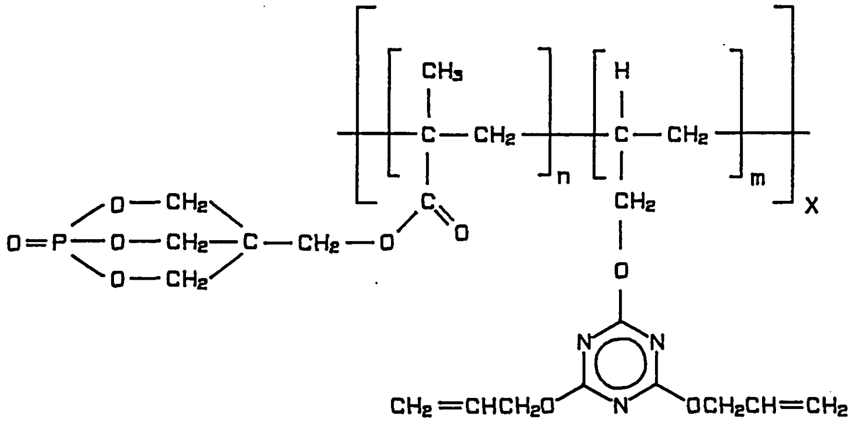
Copolymers containing an s-triazine moiety

The final area of work undertaken in the field of polymeric flame retardants was the synthesis of a polymeric additive containing an s-triazine unit, thus providing a spumific source to the additive. The s-triazine used as the monomer was 2,4,6-triallyoxy-s-triazine, (17).



(17)

Attempts to form a pure polymer of (17) were unsuccessful; however, using the conditions established in the synthesis of methyl methacrylate copolymers, two copolymers with PEPA methacrylate were synthesised in which the s-triazine was present at molar concentrations of 5% and 10%, by weight respectively. The infrared spectra of these copolymers showed evidence of an s-triazine ring and also of an alkene functionality. This implies that at least one of the double bonds of the monomer remains intact and the copolymer formed is therefore not totally cross-linked as might be expected. The copolymer structure will, at its simplest, be that of structure (18) though it could also be polymerised across one other alkene bond.



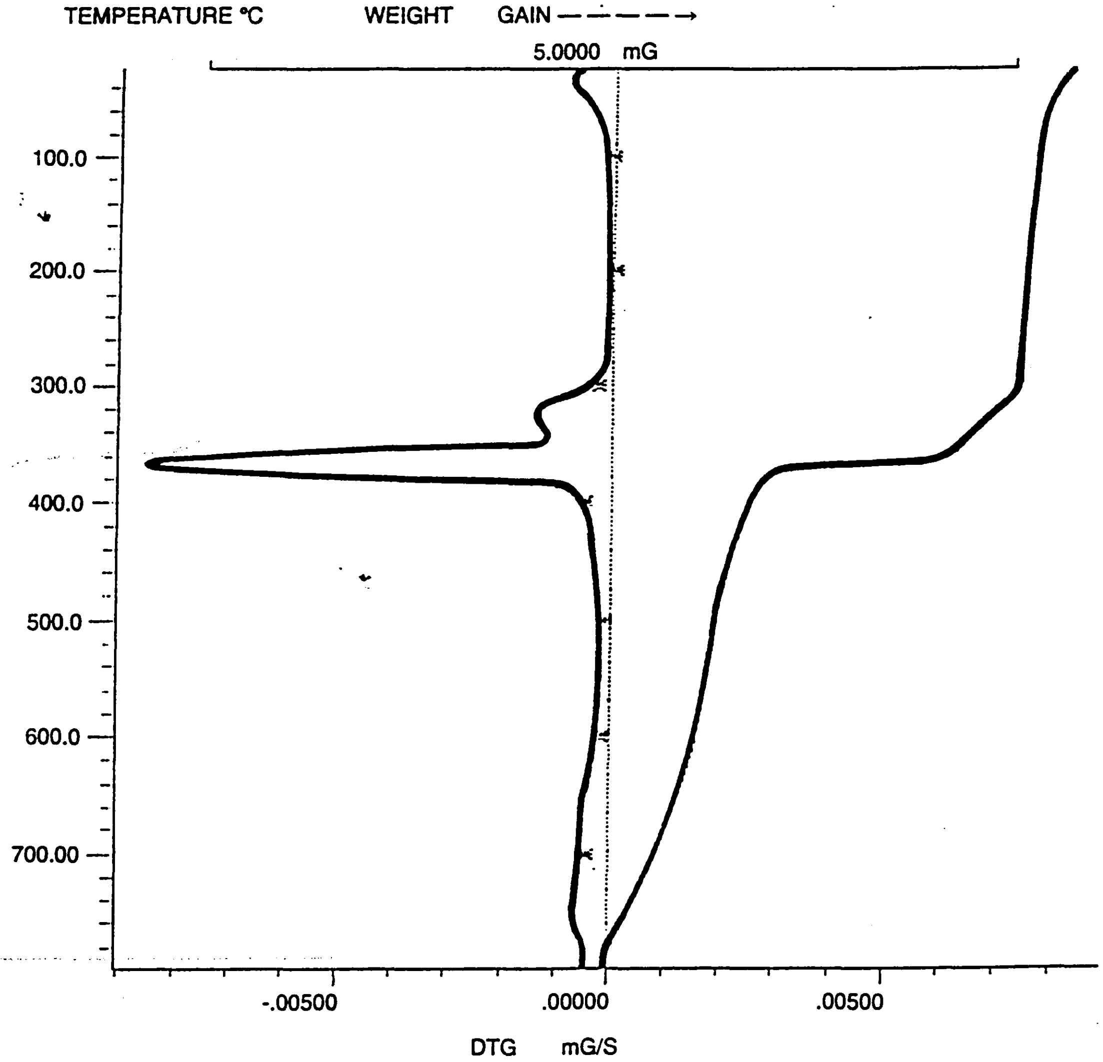
(18)

These copolymers again showed high thermal stability by TGA (see Figure 4.9) but were not intumescent when held in open flame. Again, this lack of intumescence was anticipated due to lack of an acidic proton within the structure.

Microanalysis data of the two copolymers provided evidence of their true composition, see Table 3.

Table 3

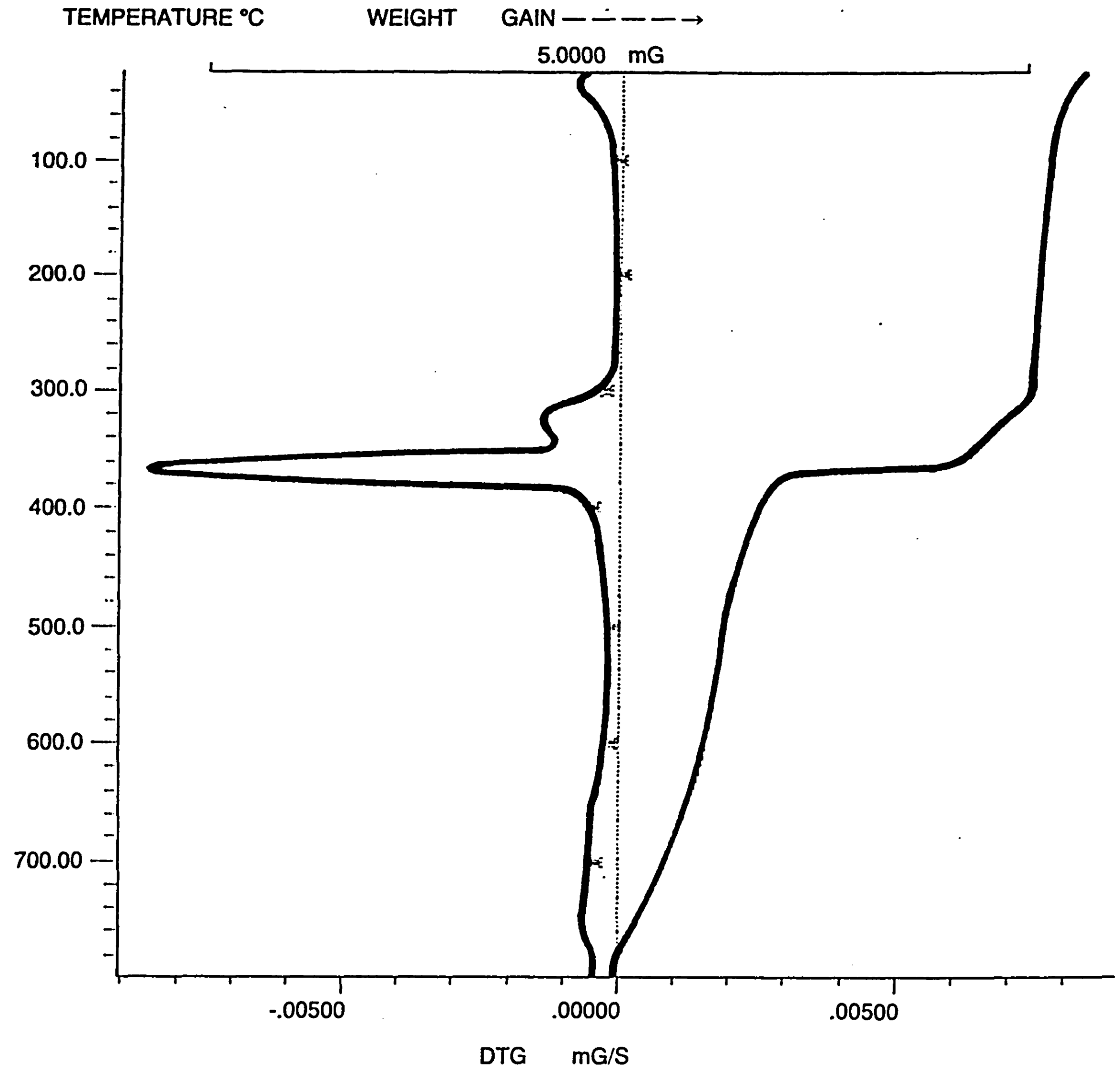
% s-Triazine, Theoretical	% s-Triazine Indicated by Microanalysis
10	9.5
5	4.4



STEP			
START TEMP.°C		28.7	
PEAK TEMP. °C		36.0	
END TEMP. °C		146.0	
Δm	mG	-.21400	
Δm	%	-6.1143	
Δm	mG		-.05800
Δm	%		-1.6571
STEP			
START TEMP. °C		267.0	
PEAK TEMP. °C		366.0	
END TEMP. °C		538.3	
Δm	mG	-1.9200	
Δm	%	-54.857	
STEP			
START TEMP. °C		538.3	
PEAK TEMP. °C		751.0	
END TEMP. °C		795.0	
Δm	mG	-.62800	
Δm	%	-17.943	

Figure 4.9

TGA Trace of copolymer consisting of 95% PEPA methacrylate and 5% 2,4,6-triallyoxy-s-triazine



```
STEP
START TEMP.°C                28.7
PEAK TEMP. °C                36.0
END TEMP. °C                146.0
Δm      mG              -.21400
Δm      %               -6.1143

Δm       mG                              -.05800
Δm       %                               -1.6571

STEP
START TEMP. °C              267.0
PEAK TEMP. °C               366.0
END TEMP. °C                538.3
Δm      mG              -1.9200
Δm      %               -54.857

STEP
START TEMP. °C              538.3
PEAK TEMP. °C               751.0
END TEMP. °C                795.0
Δm      mG              -.62800
Δm      %               -17.943
```

Figure 4.9

TGA Trace of copolymer consisting of 95% PEPA methacrylate and 5% 2,4,6-triallyoxy-s-triazine

4.4 CONCLUSIONS

PEPA methacrylate, (9), was successfully polymerised to produce a white polymer with an average chain length of eighteen repeating units which showed good thermal stability. This polymer has potential for use as a non-intumescent flame retardant additive in its own right. The monomer can be incorporated into the backbone of poly(methyl methacrylate) to produce a copolymer of increased thermal stability. The copolymers are pure white in colour, therefore the appearance of the poly(methyl methacrylate) will not be affected. At the present stage, a large amount of PEPA methacrylate needs to be added in order to impart a significant increase in the thermal stability. This had the disadvantage of shortening the average polymer chain length.

PEPA methacrylate also copolymerises with 2,4,6-trialloxy-s-triazine to form a non-intumescent copolymer with good thermal stability. The s-triazine units within this copolymer still possess at least one substituent containing a carbon-carbon double bond. It should be possible, in the future, for this double bond to be exploited and a functional group added across that contains an acidic proton. The resulting polymer should then be intumescent, providing even greater scope as a fire retardant additive.

4.5 EXPERIMENTAL

General Information

Details of the instruments and chemicals used are given in the Experimental sections of Chapters 2 and 3. All abbreviations used are listed in Chapter 2.

Synthesis of poly(1-oxo-2,6,7-trioxa-1-phosphabicyclo[2.2.2]oct-4-ylmethyl methacrylate) (12)

PEPA methacrylate (0.5 g, 2.0 x 10^{-3} moles) and AIBN (3.0 x 10^{-3} g) were added to DMF (2.5 mls) in which they dissolved. The solution was stirred and heated to 60°C, under nitrogen, for twenty-four hours during which it turned yellow. On cooling, the solution was poured into methanol to produce a white precipitate which was filtered and washed with methanol (6 x 25 mls) before being dried under vacuum at 120°C. The final product was a white powder of yield 0.44 g (88%), melting point > 320°C.

IR (mull) 1710 and 1410. ^{1}Hnmr (D_7-DMF) 4.8 (d, 6H), 3.5 (s, 2H), 2.0 (very broad m). Microanalysis; found: C, 42.92; H, 5.69; N, 0.31; P, 11.65; $C_9H_{13}O_6P$ requires: C, 43.53; H, 5.28; N, 0.00; P, 12.50%.

Attempted polymerisation of 1-oxo-2,6,7-trioxa-1-phosphabicyclo[2.2.2]oct-4-ylmethyl crotonate (10)

The crotonate ester (0.5 g, 2.0 x 10^{-3} moles) was treated as above, but on pouring into methanol, no precipitate was produced. The methanol was then evaporated and the solution poured into ether to yield a white solid which was washed with ether (3 x 10 mls) before being dried under vacuum at 50°C. The final product was a white powder of yield 0.33 g (67%), melting point 166-168°C.

IR (mull) 1725, 1650, 1100, 900 and 720. Product found to be unchanged starting material.

Attempted polymerisation of mono[1-oxo-2,6,7-trioxa-1-phosphabicyclo[2.2.2]oct-4-ylmethyl] maleate (11)

The maleate ester (0.5 g, 1.8×10^{-3} moles) was treated as above and afforded no precipitate on pouring into methanol. On pouring into petrol, a pale orange oil was formed which solidified overnight to give a pale orange solid of yield 0.21 g (42%), melting point 182-188°C.

IR (mull) 2700-3100 (broad), 1730 and 1660. Product found to be unchanged starting material.

COPOLYMER SYNTHESIS

Attempted copolymerisation between 1-oxo-2,6,7-trioxa-1-phosphabicyclo[2.2.2]oct-4-ylmethyl methacrylate and styrene

PEPA methacrylate (0.5 g, 2.0×10^{-3} moles), styrene (0.21 g, 2.0×10^{-3} moles) and AIBN (3.0×10^{-2} g) were stirred in DMF (3.5 mls) under nitrogen for twenty-four hours at 65°C. After cooling, the solution was poured into methanol to give a white precipitate which was washed with methanol (6 x 20 mls) and dried under vacuum at 75°C. On pouring the solution into methanol, a smell of styrene was noticed. The final white powder was of yield 0.42 g (59%), melting point >300°C.

IR (mull) 1710 and 1410. ^{1}Hnmr (D_7-DMF) 4.8 (d, 6H), 3.6 (s, 2H), 2.0 (broad s), 1.0 (broad m).

This attempted copolymerisation was repeated at higher temperatures (80 and 110°C), first using benzoyl peroxide then dicumyl peroxide instead of AIBN. In all cases only the methacrylate ester starting material was recovered.

Synthesis of a range of copolymers between methyl methacrylate and 1-oxo-2,6,7-trioxa-1-phosphabicyclo[2.2.2]oct-4-ylmethyl methacrylate

1 Containing 50% PEPA methacrylate

PEPA methacrylate (0.37 g, 1.49×10^{-3} moles) and methyl methacrylate (0.15 g, 1.5×10^{-3} moles) were added to DMF (3 mls) containing a catalytic amount of AIBN (3.0×10^{-2} g). The resulting solution was stirred under nitrogen and heated at 60°C for twenty-four hours. On cooling, the solution was poured into methanol to yield a white precipitate which was filtered and washed with methanol (6 x 20 mls) before being dried under vacuum at 100°C. The final product was a white powder of yield 0.44 g (85%), melting point >300°C.

IR (mull) 1710, 1660 and 1410. ^{1}Hnmr (D_7-DMF) 5.0 (broad d, 6H), 3.8 (broad s, 5H), 2.0 (broad s), 1.0 (broad m). Microanalysis; found: C, 45.47; H, 6.38; N, 0.48; P, 8.79; $C_{14}H_{21}O_{10}P$ requires: C, 44.20; H, 5.52; N, 0.00; P, 8.16%.

2 Containing 40% PEPA methacrylate

PEPA methacrylate (0.66 g, 2.66×10^{-3} moles) and methyl methacrylate (0.4 g, 4.0×10^{-3} moles) were treated as above to yield a white powder of 0.87 g (82%), melting point 280°C.

IR (mull) 1715 and 1665. ^{1}Hnmr (D_7-DMF) 4.8 (broad s, 12H), 3.5 (broad s, 13H), 2.0 (broad s), 1.0 (broad m). Microanalysis; found: C, 58.35; H, 6.58; N, 0.24; P, 7.89; $(C_9H_{13}O_6P)_4(C_5H_8O_2)_6$ requires: C, 59.02; H, 5.12; N, 0.00; P, 6.35%.

3 Containing 30% PEPA methacrylate

PEPA methacrylate (0.43 g, 1.73 x 10^{-3} moles) and methyl methacrylate (0.4 g, 4.0 x 10^{-3} moles) were treated as above to yield a white powder of 0.63 g (72%), melting point 280°C.

IR (mull) 1710 and 1665. ^{1}Hnmr (D_7-DMF) 4.7 (broad d, 17H), 3.5 (broad s, 27H), 1.8 (broad s), 0.9 (broad m). Microanalysis; found: C, 52.32; H, 6.79; N, 0.21; P, 6.11; $(C_9H_{13}O_6P)_3(C_5H_8O_2)_7$ requires: C, 51.52; H, 6.58; N, 0.00; P, 6.44%.

4 Containing 20% PEPA methacrylate

PEPA methacrylate (0.31 g, 1.25 x 10^{-3} moles) and methyl methacrylate (0.5 g, 5.0 x 10^{-3} moles) were treated as above to yield a white powder of 0.52 g (64%), melting point 260°C.

IR (mull) 1702 and 1660. ^{1}Hnmr (D_7-DMF) 4.7 (broad d, 3H), 3.4 (broad s, 7H), 1.9 (broad s), 1.0 (broad s). Microanalysis; found: C, 54.04; H, 7.14; N, 0.20; P, 5.02; $(C_9H_{13}O_6P)(C_5H_8O_2)_4$ requires: C, 53.70; H, 6.94; N, 0.00; P, 4.78%.

5 Containing 10% PEPA methacrylate

PEPA methacrylate (0.14 g, 5.65 x 10^{-4} moles) and methyl methacrylate (0.5 g, 5.0 x 10^{-3} moles) were treated as above to give a white powder of yield 0.42 g (66%), melting point 220°C.

IR (mull) 1715 and 1650. ^{1}Hnmr (D_7-DMF) 4.7 (broad s, 3H), 3.5 (broad s, 15H), 1.8 (broad s), 0.9 (broad s). Microanalysis; found: C, 56.92; H, 7.66; N, 0.15; P, 2.58; $(C_9H_{13}O_6P)(C_5H_8O_2)_9$ requires: C, 56.44; H, 7.40; N, 0.00; P, 2.70%.

6 Containing 5% PEPA methacrylate

PEPA methacrylate (0.07 g, 2.82×10^{-4} moles) and methyl methacrylate (0.5 g, 5.0×10^{-3} moles) were treated as above to afford a white powder of yield 0.32 g (56%), melting point 200°C.

IR (mull) 1710 and 1660. ^{1}Hnmr (D_7-DMF) 4.8 (broad d, H), 3.5 (broad s, 10H), 1.8 (broad s), 0.9 (broad s). Microanalysis; found: C, 57.97; H, 7.69; N, 0.12; P, 1.37; $(C_9H_{13}O_6P)(C_5H_8O_2)_9$ requires: C, 58.10; H, 7.68; N, 0.00; P, 1.44%.

Synthesis of pure poly(methyl methacrylate)

Methyl methacrylate (0.5 g, 5.0×10^{-3} moles) was treated as above to afford a white powder of yield 0.43 g (86%), melting point 267-275°C.

IR (mull) 1665, 1250, 1150, 970 and 840. ^{1}Hnmr (D_7-DMF) 3.6 (s), 2.0 (broad s), 1.0 (broad d). Microanalysis; found: C, 57.79; H, 8.08; N, 0.05; $C_5H_8O_2$ requires: C, 60.00; H, 8.00; N, 0.00%.

Attempted synthesis of poly(2,4,6-triallyoxy-s-triazine)

2,4,6-Triallyoxy-s-triazine (0.6 g, 2.4×10^{-3} moles) and AIBN (3.0×10^{-2} g) were added to DMF (3 mls) in which they both dissolved. The solution was stirred and heated to 65°C, under nitrogen, for twenty-four hours during which it turned orange. On cooling, the solution was poured into methanol but produced no precipitate. The methanol was evaporated and the solution poured into ether but still provided no precipitate. TLC of the solution showed it to contain the unreacted starting material.

Various other conditions were employed including higher reaction temperatures and changing the AIBN for benzoyl peroxide and dicumyl peroxide but still no polymer resulted.

Synthesis of copolymers between 2,4,6-triallyoxy-s-triazine and 1-oxo-2,6,7-trioxa-1-phosphabicyclo[2.2.2]oct-4-ylmethyl methacrylate

1 Containing 5% 2,4,6-triallyoxy-s-triazine

PEPA methacrylate (0.5 g, 2.0 x 10^{-3} moles) and 2,4,6-triallyoxy-s-triazine (0.026 g, 1.05 x 10^{-4} moles) were added to DMF (4 mls) containing a catalytic amount of AIBN (3.0 x 10^{-2} g). The resulting solution was stirred under nitrogen and heated at 60°C for twenty-four hours. On cooling, the solution was poured into methanol to provide a white precipitate which was filtered and washed with methanol (8 x 20 mls) before being dried under vacuum at 80°C. The final product was a white powder of yield 0.37 g (70%), melting point >300°C.

IR (mull) 1710, 1640, 1590, 1510 and 1410. Microanalysis; found: C, 44.18; H, 5.28; N, 0.74; $(C_9H_{13}O_6P)_{19}C_{12}H_{15}N_3O_3$ requires: C, 44.86; H, 5.35; N, 0.88%.

2 Containing 10% 2,4,6-triallyoxy-s-triazine

PEPA methacrylate (0.5 g, 2.0 x 10^{-3} moles) and 2,4,6-triallyoxy-s-triazine (0.056 g, 2.22 x 10^{-4} moles) were treated as above to yield a white powder of 0.41 g (74%), melting point >300°C.

IR (mull) 1710, 1640, 1590, 1510 and 1410. Microanalysis; found: C, 44.91; H, 5.30; N, 1.61; $(C_9H_{13}O_6P)_9C_{12}H_{15}N_3O_3$ requires: C, 44.98; H, 5.32; N, 1.69%.

4.6 REFERENCES

1 H. L. Vandersall, J. Fire and Flammability, 1971, 2, 97.

2 H. R. Buser, H. P. Bosshardt and C. Rappe, Chemosphere, 1978, 7, 109.

3 J. Gay-Lussac, Ann. Chim. (Paris), 1821, 18, 211.

4 G. Jones, W. Juda and S. Soll, US Patent 2,452,054.

5 G. Jones, W. Juda and S. Soll, US Patent 2,452,055.

6 G. Jones, W. Juda and S. Soll, US Patent 2,566,964.

7 P. G. Sears and H. L. Vandersall, Canadian Patent 822,594.

8 F. J. Hahn and H. L. Vandersall, US Patent 3,513,114.

9 J. K. Sears and N. W. Touchetti in "Encyclopedia of Chemical Technology", ed K. Othmer, Wiley, New York, 1982.

10 J. H. Troitzsch, Prod. Org. Coat., 1983, 11, 41.

11 R. Burkhardt, E. N. Peterson and N. Volkommer, Chemiker Ztg., 1978, 102, 11.

12 K. S. Annakutty and K. Kishore, Polymer, 1988, 29, 756.

13 K. S. Annakutty and K. Kishore, Polymer, 1988, 29, 762.

14 K. S. Annakutty and K. Kishore, Polymer, 1988, 29, 1273.

15 H. Lee and K. Neville in "Handbook of Epoxy Resins", McGraw-Hill, New York, 1967.

16 M. Lewin, S. M. Atlas and E. M. Pearce in "Flame Retardant Polymeric Materials", Plenum Press, New York, 1975, p 362.

17 J. A. Mikroyannidis and D. A. Kourtides, J. of Applied Polymer Science, 1984, 29, 197.

18 M. Hosoda and E. Kashiwagi, Japanese Patent 73,56229.

19 D. F. W. Cross, German Patent 2,212,390.

20 H. Sivriev, V. Kaleva, G. Borissov, L. Zabski and Z. Jedlinski, Eur. Polymer J., 1988, 24, 365.

21 H. R. Kricheldorf, H. Koziel and E. Witek, Makromol. Chem. Rapid Commun., 1988, 9, 217.

22 J. A. Brydson in "Plastic Materials", 4th Edition, Butterworth Scientific, London, 1982.

23 J. Montheard, J. Vergnaud and N. Chafi, Polymer Bulletin, 1988, 20, 177.

24 B. A. Chemicals Ltd, advertising brochure, publication no M300, 3K, August 1989.

25 B. Bredemeier, J. P. Kehrli and R. Wolf in "Flame Retardants 90", The Plastics and Rubber Institute, London, 1990, Chapter 17.

26 C. W. Allen, J. C. Shaw and D. E. Brown, Macromolecules, 1988, 21, 2653.

27 A. Ryttel, Acta Polymerica, 1989, 40, 690.

28 C. P. Yang and T. M. Lee, J. of Applied Polymer Science, 1987, 34, 2733.

29 C. P. Yang and S. Wang, J. of Polymer Science A, 1989, 27, 3551.

30 C. P. Reghunadhan and G. Clouet, Polymer, 1988, 29, 1909.

31 C. P. Reghunadhan, G. Clouet and J. Brossas, J. of Polymer Science, 1988, 26, 1791.

32 C. P. Reghunadhan, G. Clouet and Y. Guilbert, Poly. Deg. and Stab., 1989, 26, 305.

33 C. P. Reghunadhan and G. Clouet, Eur. Polymer J., 1989, 25, 251.

34 G. Moad and D. H. Solomon, Aust. J. Chem., 1990, 43, 215.

Courses and Conferences Attended

1 Phosphorus Chemistry, eight lectures, Dr. D. W. Allen, Sheffield City Polytechnic, 1987.

2 Nuclear Magnetic Resonance, eight lectures, Dr. D. J. Mowthorpe, Sheffield City Polytechnic, 1988.

3 Organic Symposia:

   i) Leicester, Dec. 1987

   ii) Loughborough, Dec. 1988.

4 Society of Chemical Industry, Phosphorus '88 conference, Old Trafford, Manchester.