CHAPTER II
LITERATURE REVIEWS

2.1 Type of flame retardants

Flame retardants are generally designed to provide a particular level of resistance to ignition flame spread.[1] Good flame retardants should:

- be stable under the production processes and use
- be nontoxic
- blend well with plastic
- give low effect on polymer property changes
- produce a low amount of smoke when burn
- be non-corrosive
- be inexpensive

The products commercially available can be classified as one of the main three types: inorganic and melamine flame retardants; halogen-base flame retardants; and phosphorus-based flame retardants.[1]

2.1.1 Inorganic and melamine flame retardants

The largest group in terms of volume is the inorganic flame retardants comprising, for example, ATH (aluminium trihydroxide), antimony oxide, magnesium hydroxide, zinc borate, zinc stannate, zinc hydroxy stannate and melamine. There are problems associated with this type of flame retardants because they produce carbon monoxide rather than carbon dioxide. For instance, PVC samples protected with antimony oxide generate more smoke than unprotected sample and antimony oxide is potentially toxic.[1]

2.1.2 Halogen-based flame retardants

Halogen-based flame retardants work by inhibiting the free radical flame reactions responsible for sustaining combustion. HET acid (hexachlorobicyclo[2,2,1]-hept-5-one-2,3-dicarboxylic acid) is the only chlorine compound commonly used as a flame retardant and is used, together with antimony oxide, in unsaturated polyester

resin. Some polymers that are inherently flame also contain halogens. PVC, for example, will not sustain combustion because it contains over 50% chlorine. Soft PVC (with added plasticizers), however, does not have the same flame retardant performance characteristics.

Halogen-based flame retardants have caused some controversies in recent years. The Green movement, particularly in Germany and Sweden, argues that these compounds are problematic to dispose of and are a significant source of dioxins and furans from waste incinerators.[1]

2.1.3 Phosphorus-based flame retardants

The discovery in the early 1950's that the incorporation of phosphorus into a polymer backbone gives it flame-retardant properties,[8] sparked great interest in phosphorus polymer chemistry. However, because of the high cost of synthesizing these polymers in comparison to carbon analogues, their low molecular weight, and their perceived hydrolytic instability, research interests have faded since the 1960's. Recently, organophosphorus polymers have regained interest. The versatility of the phosphorus atom can be exploited to synthesize a wide range of polymers. In particular, these polymers might possess potential as a new class of degradable biomaterials whose properties can be modified to match a specific application.

Although the thermal stability and flame retardancy may not be related, interestingly, it has recently been shown that phosphate containing polymers exhibit a better nonflammable characteristics, when they are thermally stable.[9] When compared to halogen-based flame retardants, lower amount of phosphorus can show high flame retardancy (Figure 2.1).[10]
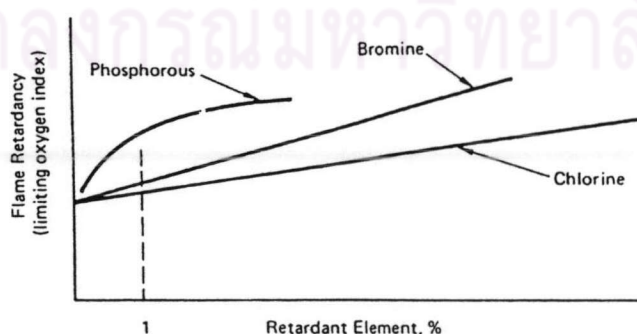

Figure 2.1 The relationship between the amount of flame retardant chemicals in polyurethane and limiting oxygen index.

Phosphorus-based flame retardant additives can be classified into four groups[11] including: a) inorganic phosphates such as red phosphorus and ammonium phosphates; b) organic phosphorus such as amine phosphates and trialkyl phosphates; c) halogenated alkyl phosphates and phosphonates; d) reactive organic phosphorus compounds such as phosphorus-containing diol and polyols. An alternative to introducing phosphorus into polymers by means of physical mixing is a utilization of phosphorus containing polymers.

2.2 Mechanism of action

Mode of action of flame retarding agents can be classified as listed below. Usually a flame retardant can show one or more of the following actions:[1, 11]

1. Cooling of the combusting material (endothermic processes).
2. Shielding of the combustible layer from the gaseous phase with a solid or gaseous protective layer such as char and intumescent coatings.
3. Evolution of inert gases from the substances and additives upon decomposition, thus diluting the fuel in the solid and gaseous phases.
4. Reduction of viscosity favoring by the flow or drip of molten polymer from the combustion zone.

The action of phosphorus-based flame retardants has been shown to involve several concurrent or alternative mechanisms, exerted in the condense phase (i.e. the pyrolyzing polymer phase) and in the vapor phase (i.e. the flame zone).

2.2.1 Condensed-phase mechanism

2.2.1.1 Charring and related mechanism

There are evidences that in oxygen-containing polymers such as cellulose and rigid polyurethane foam, phosphorus compounds can increase the char yield. The conversion of the combustible substance to char is beneficial from a flame retardancy standpoint in several ways.[12] First of all, it represents material which escaped conversion to gaseous fuel. In addition, the char-forming reactions 'often' produce water, so that any gasified fuel is diluted with high heat-capacity noncombustible water vapor. Moreover, the char can form a heat and mass transfer barrier protecting the underlying polymer. Lastly, the char-forming reactions are often endothermic.

For example, cellulose when heated to its pyrolysis temperature, normally depolymerizes to a tarry product which further breaks down to alkanes, alkenes, alcohols, ketones, and other low molecular weight fuels. When an effective phosphorus-containing flame retardant is present in cellulose, upon fire exposure, breakdown of the retardant generally yields phosphoric and polyphosphoric acid. In some cases where nitrogen components are present, phosphorylating agents are formed having P-N bonds. The formation of P-N bonded compounds may also prevent loss of phosphorus from the condensed phase. These reactive phosphorus species phosphorylate the cellulose, generally with release of water. The phosphorylated cellulose then undergoes thermal elimination. The flame retardant effect results from the endothermicity, the formation of a non-combustible outward-flowing vapor (water), the reduction in fuel release, and in some cases the protective barrier effect of the char. Further flame retardancy results if the char is not burned to carbon oxides. Moreover, if the char does smolder, the presence of a phosphorus compound may inhibit complete conversion to carbon monoxide.

The phosphorus flame retardant may, by coating the char, tend to prevent smoldering by mechanical obstruction of the surface. Smoldering is not only subject to chemical effects but, especially in the case of permeable materials such as open-cell foam, it is strongly favored by air flow through the material. For example, in flexible polyurethane foams, where smoldering is sometimes made worse by the presence of a phosphorus flame retardant.

The enhancement of char in rigid polyurethane foams by phosphorus flame retardants has been determined to be the likely basis of the flame retarding action of phosphorus in these foams.[12] In such systems, phosphorus appears to be largely retained in the char; also, the char appears to be more coherent and more effective as a physical barrier.

In poly(ethylene terephthalate) and in poly(methyl methacrylate) phosphorus flame retardants produce an increase in the amount of residue and a retardation of the release of volatile fuel. Plausible acid-catalyzed crosslinking reactions involving C-O-C, C-C, or C-O-P-O-C linkages have been postulated.[12]

For substantially oxygen-free polymers which form char less readily, such as polyolefins and styrenics, phosphorus flame retardants typically are ineffective unless supplemental char forming additives are also present. However, even in the absence of any char-forming adjuvant, there is some action which may be a combination of

vapor phase activity, melt-drip effects, plus some interaction of the phosphorus additive with oxygenated functional group and/or with sites of unsaturaion produced by oxidative reactions at or near the surface of the polymer prior to gasification.[12]

Phosphorus can also inhibit the glowing combustion of char and carbon fibers. The mechanism of action is not proven but may involve some sort of polyphosphorus acid coating and/or deactivation of the active centers on the solid carbon with diversion of the oxidant away from production of CO_2.

A further mechanism of action of phosphorus was revealed by Russian workers[12] who have recently shown that a phosphorus flame retardant can reduce permeability of the char thus providing an improved barrier to air and fuel passage.

2.2.1.2 Coating mechanisms

Condensed phase mechanisms of action based on coating the burning surface with a phosphorus-rich barrier such as polyphosphoric acid or the like have often been proposed. Bruman[12] proposed that a phosphorus acid physically retards the vaporization of fuel from a hydrocarbon polymer flame retarded by ammonium polyphosphate or triphenyl phosphate. Some infrared evidences were adduced in support of the postulate of a polyphosphoric acid coating.

2.2.1.3 Effect on melt viscosity

Phosphorus compounds can also perform as flame retardants by the opposite of char induction, namely, by catalyzing thermal breakdown of the polymer melt under fire exposure conditions, reducing the melt viscosity and favoring the flow or drip of the molten polymer from the combustion zone. In polystyrene, a bromoalkyl phosphate was shown to work in this manner.

2.2.1.4 Condensed phase free radical inhibition

Some evidences have been offered in support of a hypothesis of free radical inhibition, or at least of a condensed phase antioxidant effect, by nonvolatile (polymeric or grafted) phosphorus flame retardants. ESR data indicated that aryl phosphate flame retardants could react with alkylperoxy radicals in the polymer surface to form phenoxy radical which was probably less active.[12]

2.2.2 Vapor phase mechanism

2.2.2.1 Chemical mode of action

Introduction of a highly volatile phosphorus compound into a flame can be highly inhibitory. Using mass spectroscopy, it was found that triphenyl phosphate and triphenylphosphine oxide broke down in the flame into small molecular weight species such as P_2, PO, PO_2 and HPO_2. Scavenging of hydrogen atoms and the induction of hydrogen atom recombination were postulated to result from interaction of hydrogen atoms with these phosphorus species. Hydrogen atom concentration in the flame (a rate-controlling species) was thereby reduced.

Vapor phase activity appears to be the basis of the flame retardant utility of phosphates in the commercial blends of polyphenylene oxide with high impact polystyrene; polyphenylene oxide provides protective char while the triaryl phosphate provides the flame inhibition needed to suppress the combustion of the hydrocarbon pyrolysates formed from the styrenic component.

2.2.2.2 Physical mode of action

A physical mode of flame inhibition, base on heat capacity and possibly endothermic dissociation in the vapor phase. The release of water from systems such as phosphorus-catalyzed dehydration/charring of cellulose provides a non-fuel vapor which physically retards the flame by dilution of whatever fuel is produced; the high heat capacity of water vapor makes water particularly effective in this mode of action.

2.2.3 Interaction with other flame retardants

2.2.3.1 Interaction with halogens

Synergism is defined as a combining effect of two or more agents which is greater than additive (by some chosen computational model). Halogen-phosphorus synergism is often postulated by analogy with the strong and well-established halogen-antimony synergism. One reasonably convincing case of phosphorus-halogen synergism was recently reported. A phosphonoalkyldibromophenol used as a retardant in ABS, where the joint action of phosphorus and bromine (in the same molecule) seems to be substantially greater than additive based on a graphical analysis of the data.[12]

2.2.3.2 Interaction with antimony

A careful study of triaryl phosphate and antimony oxide in PVC showed antagonism only in part of the composition range.[10] This antagonistic effect may be related to the formation of antimony phosphate, which is too unreactive to be an effective flame retardant.

2.3 Flammability testing

There are hundreds of methods of evaluating the effects of fire on materials and composite articles. The basic objective of fire testing is to determine the likely contribution of a material or a composite article to the hazards present in a real fire. Fire tests are carried out on various scales, ranging from small-scale tests on the laboratory bench to large or full-scale tests involving whole rooms or buildings. Laboratory-scale tests are used to compare the ignitability and the rate of burning of materials under controlled conditions. They are useful as screening tests for new materials and to ascertain the effects of additives and of minor variations in structure on the combustibility of the polymer. Laboratory-scale fire tests cannot be used to predict the effects in real fires. There are many parameters effecting the course of a real fire and the hazards that result.

Limiting oxygen index (LOI),[13] is a test method which describes a procedure for measuring the minimum concentration of oxygen, expressed as volume percent, in a mixture of oxygen and nitrogen that will just support flaming combustion of a material initially at room temperature. This standard test method has been found applicable for testing various forms of plastic materials including film and cellular plastics.

2.4 Economic aspects

According to a released publication by Business Communication, Inc., the 1998 US consumption of flame-retardant chemicals is estimated to be about 758 million pounds and is projected to increase 5% annually to reach 969 million pounds in 2003. For phosphorus-based flame retardant chemicals, to expand from 89 million pounds in 1998 to reach 125 million pounds in 2003 as phosphorus-based flame retardant chemicals cause reducing smoke obscuration and corrosively help drive the market for phosphorous-based flame retardant chemicals, an annual growth of 7%.

In the European market for flame retardant chemicals, phosphorus-based flame retardants are shown (Figure 2.2) to have the highest market share among the three main catagories.[1]

The total European market for flame retardant chemicals
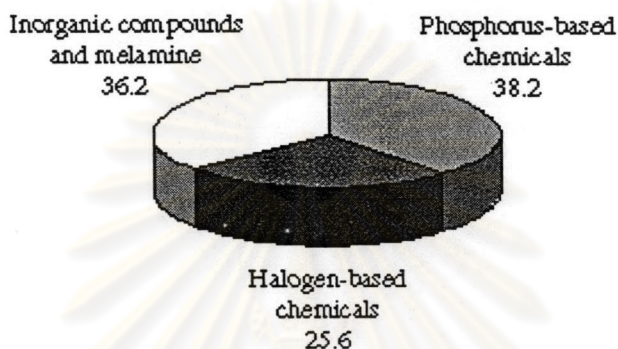*(percent of revenues by product type-forecast for the year 2003)*

Inorganic compounds and melamine
36.2

Phosphorus-based chemicals
38.2

Halogen-based chemicals
25.6

Figure 2.2 The percent of flame retardants produced in Europe for the year 2003.

Trends in research and development of phosphorus flame retardants have been in the direction of volatile, less toxic, more stable compounds, and where feasible, in the direction of built-in phosphorus structures. At the same time, there have been an increasing number of regulatory delays in new compounds, and the existent materials are finding increased exploitation in the form of mixtures.

2.5 Polyphosphates and polyphosphonates

The usual method of preparation of polyphosphates and polyphosphonates is based on the esterification of diols with equimolar amounts of dichlorophosphates and phosphonyl dichlorides, respectively. For polyphosphates, with aliphatic diols, polycondensation proceeds faster than with bisphenols, but some side reactions are difficult to eliminate and lead to low-molecular-weight product formation.[14] Several researchers have published results on the synthesis of polyphosphonates by interfacial polycondensation,[8, 15] by melt,[16] by high or low-temperature polycondensation,[7] or by a phase-transfer-catalyzed method.[17]

In 1983 Kim studied the low-temperature polycondensation of phenyl-phosphonic dichloride with 4,4'-thiodiphenol (TDP) and with 4,4'-sulfonyldiphenol (SDP).[18]
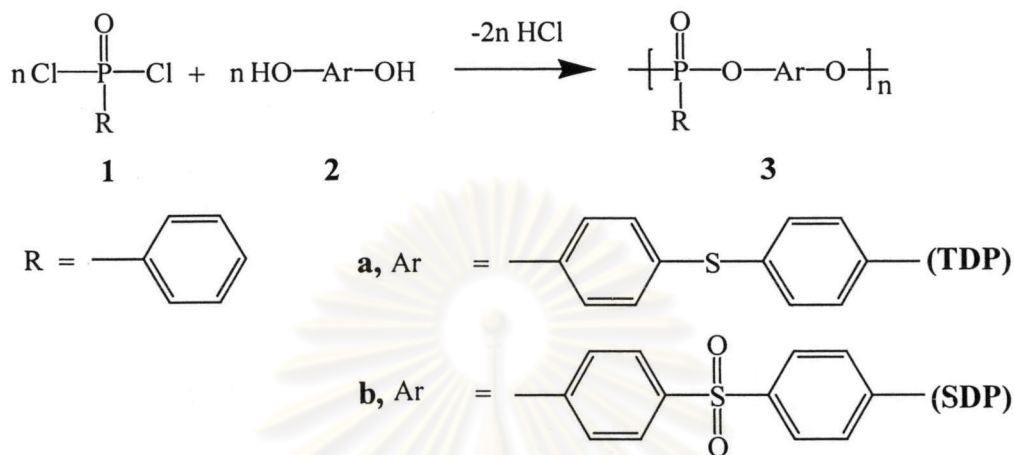
Scheme 2.1 Synthesis of aromatic polyphosphonates for studies factors affecting to $\overline{M}_W$

The effect of solvents (dichloromethane, chloroform, dichloroethane, chlorobenzene) and the effect of acid acceptors (triethylamine, tri-n-butylamine, pyridine, *N,N*-dimethylaniline) were studied in the low-temperature polycondensation of phenylphosphonic dichloride with either SDP or TDP. The reaction in methylene chloride in the presence of an acid acceptor, triethylamine, give high inherent viscosity reflecting high weight average molecular weight ($\overline{M}_W$). Moreover it has been shown that the exclusion of water is an important factor for obtaining a high molecular weight polymer in solution polymerization.

In 1986, Natansohn synthesized aromatic polyphosphonates from reaction of chloromethylphosphonic dichloride (CMPD) with a series of bisphenols: 4,4'-sulfonyldiphenol (SDP), tetrabromobisphenol A (TBBA), 4,4'-bisphenol (BP) and 2,7-dihydroxynaphthalene (2,7 DHN). Three methods of preparation, namely, melt, solution, and phase transfer catalyzed polycondensation were compared.[16]
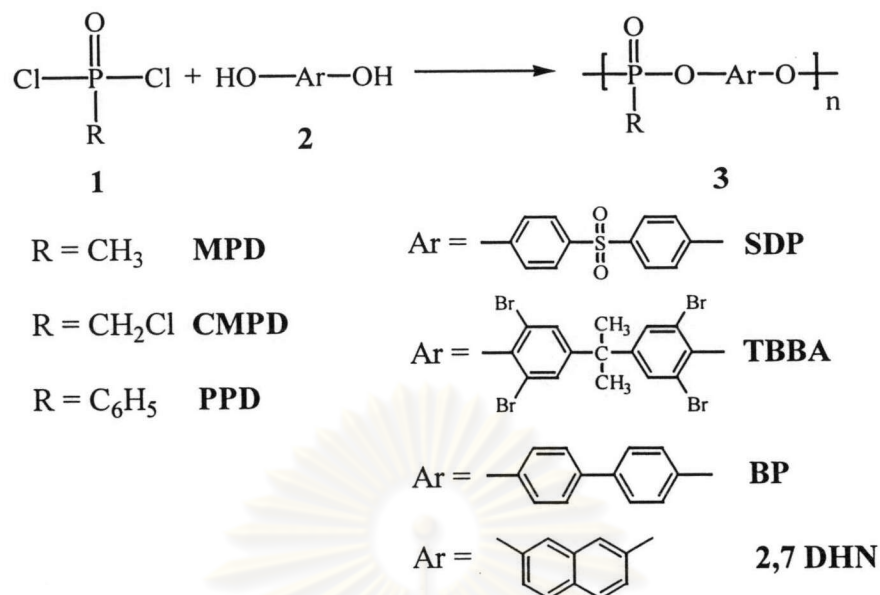
Scheme 2.2 Aromatic polyphosphonates synthesized by melt, solution, and phase-transfer catalyzed polycondensation.

This report revealed the general increase in $\overline{M}_W$ from melt to solution and to phase transfer catalyzed polycondensation. Moreover, BP along with SDP and 2,7 DHN are supposed to increase the probability of generating a crystalline structure and TBBA could improve the fire retardant ability of the polyphosphonate, due to the presence of bromine.

In 1987, Kishore and coworkers studied the effect of alkyl pendent groups on thermal stability of synthesized polyphosphate esters.[19] The reactions of six different alkylphosphorodichloridates with bisphenol A by solution polycondensation were carried out.
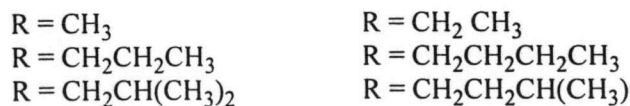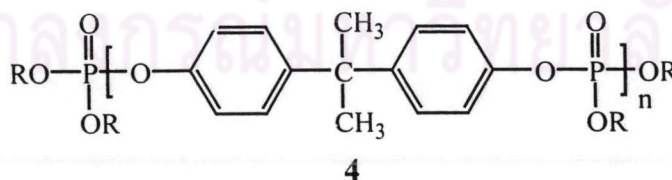
Figure 2.3 Polyphosphates with various alkyl pendent groups.

The thermal stability of the polymers was found not to be affected much by the change in the alkyl pendent group. Moreover, a relationship between the structure and flammability of ten polyphosphate esters was studied (Figure 2.4).[9] It was concluded that the flammability of a polyphosphate is dependent on its thermal stability as well as its phosphorus content.
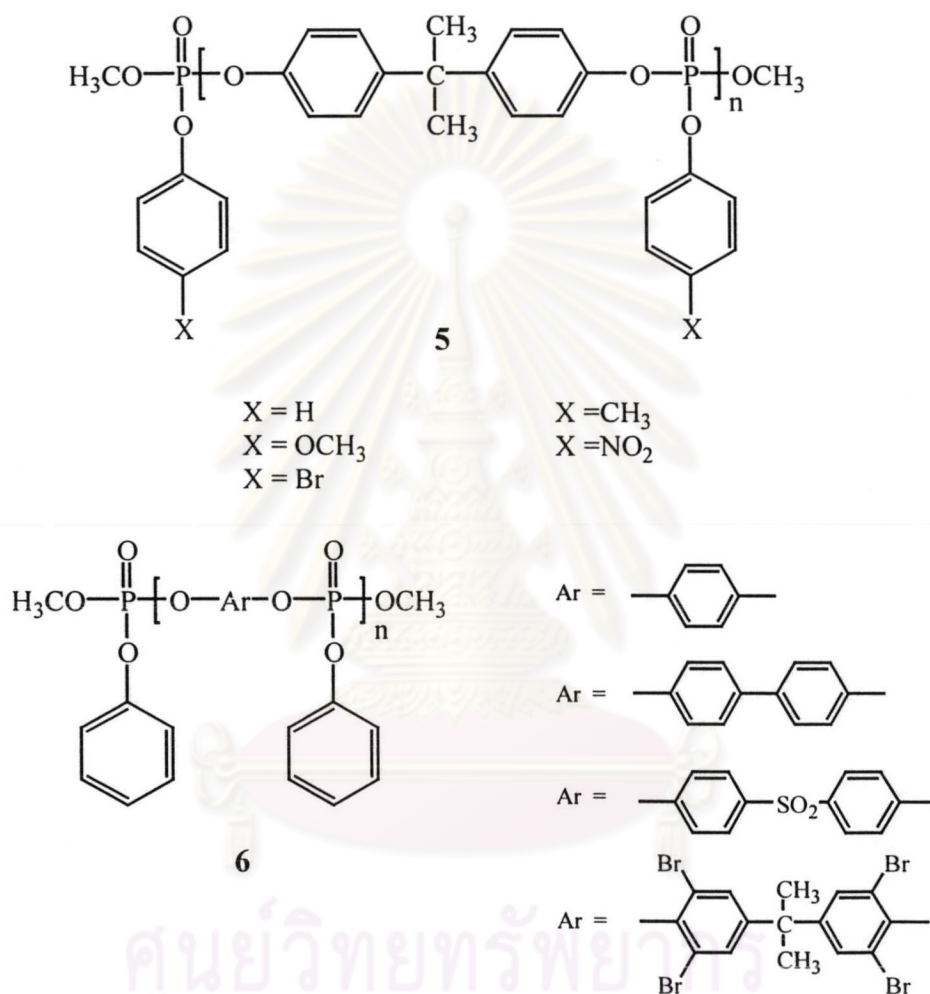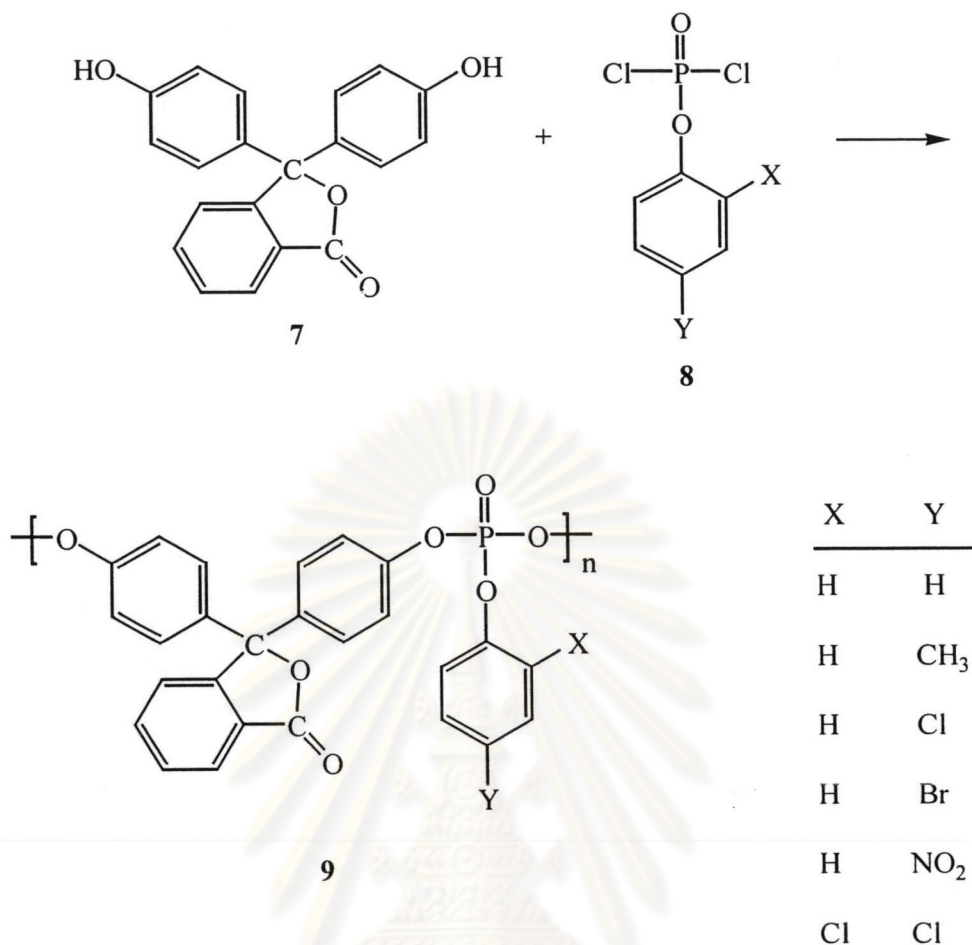

Figure 2.4 The structure of aromatic polyphosphates

In 1990, a new class of phosphate ester polymers based on phenolphthalein and aryl phosphorodichloridates was synthesized by interfacial polycondensation using a phase transfer catalyst.[20] These polymers showed an improvement in thermal properties.

Scheme 2.3 Synthesis of phenolphthalein containing polyphosphates

All the polymers showed good thermal stability in the range of 230-320 °C and thereafter started degrading in air. High LOI values were observed. Among the compounds studied, the polymer with bromine substituted phenyl pendent (**9**, where X=H, Y=Br) gave higher LOI value (51) than the other polymers (LOI = 40-45).

In 1992, Liaw and coworkers[21] synthesized an aromatic polyphosphate (**10**) from the reaction of phenoxydichlorophosphate (PDCP) with 4,4'-sulphonyldiphenol (SDP) in dichloromethane under low temperature conditions. Comparison of glass transition temperature and LOI value were between polymer **3a** synthesized from PPD with 4,4'-thiodiphenol (TDP) polyphosphonate and **3b** synthesized from phenyl phosphonic dichloride (PPD) with 4,4'-sulphonyldiphenol (SDP) polyphosphonate. It was suggestive that a flexible ether linkage at the phosphorus atom affected the thermal behavior and flame retardancy of the polymer.

$X = H$
$X = CH_3$
$X = NO_2$
$X = Br$
$X = OCH_3$

11

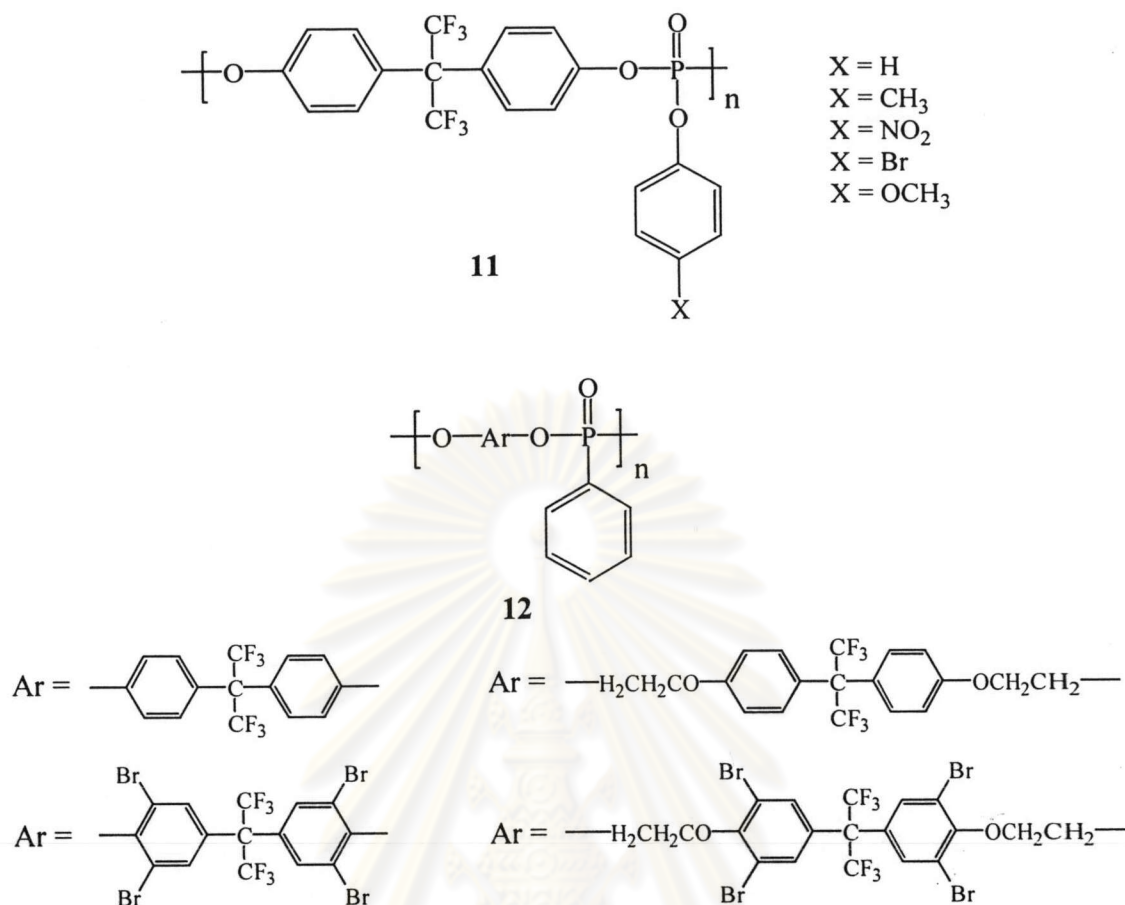**12**

$Ar =$ $Ar =$

$Ar =$ $Ar =$

Figure 2.6 Structure of fluorine containing aromatic polyphosphates and
polyphosphonates which show good solubility and thermal stability

Polyphosphates and polyphosphonates containing fluorine atoms possess good solubility in chlorinated aliphatic hydrocarbons and aprotic solvents. This is due to the fact that fluorine atoms improve the solubility of polymers, enhance their high performance, and increase their thermal stability. Moreover, the incorporation of halogen substituents into the polymer chain leads to increased flame retardancy and decreased thermal stability. Thus, polymers containing bromine and fluorine atoms should be excellent candidates to improve flame retardancy while retaining good thermal stability. In 1997, they synthesized polyphosphate esters from low temperature solution polycondensation of various aryl phosphorodichloridates with 3,3',5,5'-tetrabromobisphenol AF.[7]
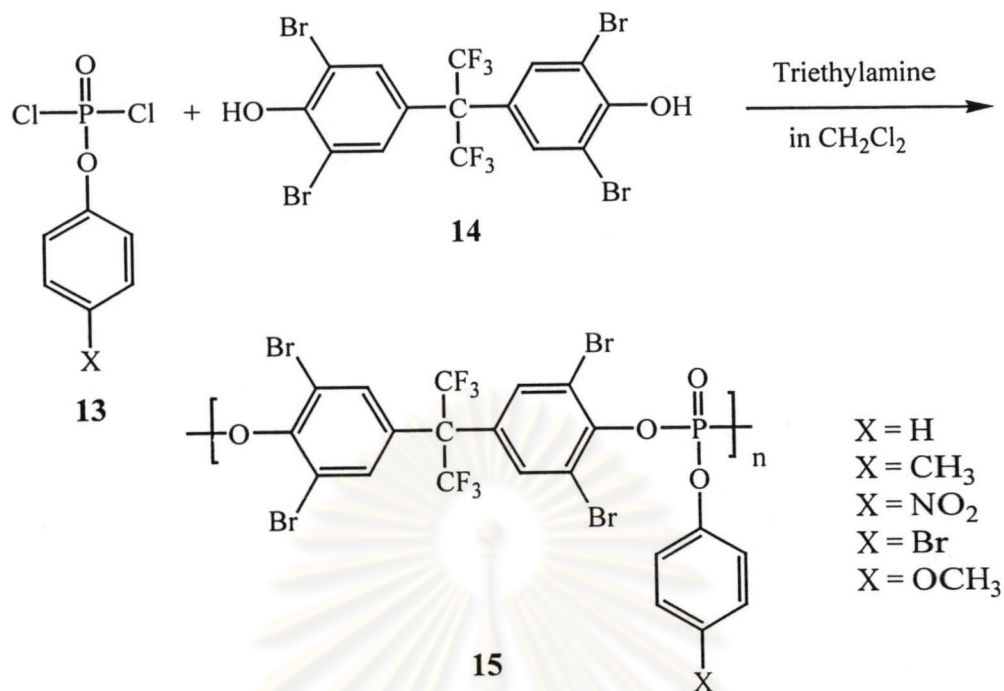
Scheme 2.4 Synthesis of bromine and fluorine containing polyphosphates which shown high T_g and LOI value

The incorporation of bromine atoms into the polymer chain led to high glass transition temperature and increased flame retardancy. Moreover polyphosphates incorporating bromine atoms on the ring led to decreased crystallinity in terms of their larger van der waals radius.