Novel phosphorus containing poly (arylene ethers) as flame retardant additives and as reactant in organic synthesis

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″Everything is theoretically impossible,
until it is done″
--- ***Robert. A. Heinlein***

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Abbreviations

BPA	4, 4′-(Propane-2, 2-diyl) diphenol
DHB	4, 4′-Biphenyldiol
SDP	4,4′-Sulfonyldiphenol
AcOH	Acetic acid
DCM	Dichloromethane
DMAc	N, N- Dimethyl acetamide
DMS	Dimethyl sulfide
DMF	N, N- Dimethylformamide
DMSO	Dimethyl sulphoxide
NMP	N-Methyl-2- pyrrolidone
THF	Tetrahydrofuran
MeOH	Methanol
$CHCl_3$	Chloroform
LiCl	Lithium chloride
BH_3	Borane
$NaBH_4$	Sodium borohydride
BBr_3	Boron tribromide
CsF	Cesium fluoride
TPP	Triphenyl phosphine
DEAD	Ditheyl azodicarboxylate
PPO	Phenyl phosphine oxide
PAPO	Poly(arylene phosphine oxide)
PAEPO	Poly(arylene ether phosphine oxide)
BFPPO	Bis(fluorophenyl)phenylphosphine oxide
BFMPO	Bis(fluorophenyl) methylphosphine oxide
HEIP	4, 4′-(hexafluoropropyldiene)diphenol

PAE	Poly(arylene ether)
PEEK	Polyether ether ketone
EPC	Epoxy resin
PI	Polyimide
PES	Polyether sulfone
PSU	Polysulfone
PVC	Polyvinyl chloride
PMA	Polymethyl acrylate
PE	Polyethylene
PP	Polypropylene
POM	Polyoxamethylene
PTFE	Polytetrafluroethylene
PVA	Polyvinyl alcohol
PMS	Poly-α-methylstyrene
TPP	Triphenyl phosphine
Ar	Aryl groups
Nu	Nucleophile
SCVP	Self-condensing vinyl polymerization
ROMBP	Ring-opening multi-branching polymerization
S_NAr	Nucleophilic aromatic substitution mechanism
DSC	Differential scanning calorimeter
E_B	Elongation at break
GPa	Giga Pascal
GPC	Gel permeation chromatography
SEC	Size exclusion chromatography
MALLS	Multi angle light scattering
IR	Infrared spectroscopy
MHz	Mega hertz
dL /g	Decillitre per gram
M_n	Number average molar mass
MPa	Mega Pascal

M_w	Weight average molar mass
NMR	Nuclear magnetic resonance
Đ	M_w/M_n
DB	Degree of branching
T_d	Weight loss temperature / Decomposition temperature
T_g	Glass transition temperature
TGA	Thermogravimetric analysis
σ_m	Tensile strength
E	Young’s Modulus
DMA	Dynamic mechanical analysis
IFR	Intumescent flame retardant
PCFC	Pyrolysis combustion flow calorimetry
HRC	Heat release capacity
EHC	Effective heat of combustion
HRR	Heat release rate
pHRR	Peak heat release rate
LOI	Limiting oxygen index

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Chapter 1

Introduction

1 Introduction

Organic polymers provide one of the most versatile groups of materials and find widespread use. In between them poly(arylene ethers) (PAE) form one of the most popular families of high performance engineering thermoplastics. In recent years a lot of effort has been given for developing high performance polymers to meet the market demand for speciality polymers. Poly(arylene ethers) fulfill all the important criteria that a high performance polymer must have. They possess useful physical properties such as high modulus, toughness, high thermal and thermooxidative stability, chemical resistance as well as good processability and low cost [1]. Poly(arylene ethers) and related structures could be used as moldable or castable tough matrix resins having high glass transition temperatures and good thermal stability. They are very useful in microelectronics as insulating materials and are also used as membrane materials, mainly for gas separation [2] [3] [4] [5]. Commercial engineering plastics, *e.g.* polyether ether ketones (PEEK), polyimides (PI) *etc.* possess superior properties like load bearing, mechanical strength, thermal stability compared to other polymers [6]. Poly(arylene ether ketones) are usually crystalline and therefore resistant to solvents, which is a vital factor for use in aerospace environment. There are certain advantages of poly(arylene ethers) incorporating within the backbone rigid groups (such as biphenyl or naphthalene) over those without these units [7] [8] [9] [10].

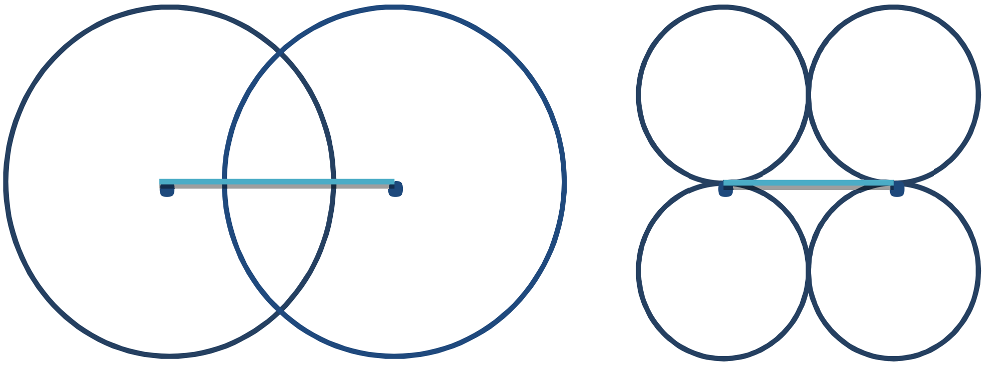
1.1 Historical background of phosphorus containing polymers

Phosphorus-containing organic polymers are relatively few in number compared to other organic polymers. Polyphosphazene, known as ‘inorganic rubber’ [11] was the first known synthetic phosphorus containing polymer. Although its synthesis was first reported by Stokes in 1897, the potential of this class of polymer is only now being realized. Today commercial applications for polyphosphazene speciality polymers [12] exist in the aerospace, marine, oil exploration and a few other industries. Today various other phosphorus-containing polymers such as polyphosphonates, polyimides, and polyoxadiazoles have been prepared and some of them have also become commercially important. Most of these polymers are not only flame retardant but also thermostable. However, polymers having P-N and P-O-C linkages suffer from hydrolytic instability. Phenoxaphosphine ring containing polymers and polymers having P-C linkages in the main chain exhibit good hydrolytic stability.

1.2 Uniqueness of phosphorus

Phosphorus forms many types of compounds, viz. trivalent (lone pair present, pyramidal), tetravalent (sp^3, tetrahedral), pentavalent (sp^3d, trigonal bipyramidal) and hexavalent (sp^3d^2, octahedral) compounds.

The atomic orbitals of phosphorus atoms overlap with atoms of higher electron density, thereby forming covalent bonds. In general, this overlap may 'end on' corresponding to σ- bonding, or π- bonding as shown below.



σ- bonding

π- bonding

Figure 1: Orbital overlapping

In the case of phosphorus the 3s→3d promotional energy is small enough to allow the vacant d orbitals to participate in chemical bonding. The ready availability of 3d atomic orbitals of phosphorus accounts for its different chemical nature. The high energy d-orbitals contribute to reduce electronegativity and greater polarizability of phosphorus compared to other group elements.

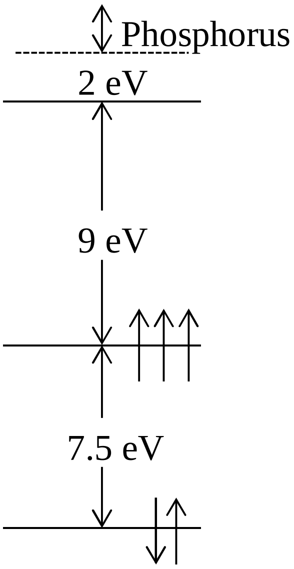
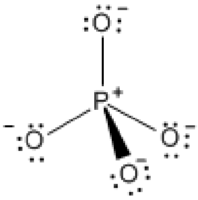


Figure 2: Atomic energy level for phosphorus

In addition to the basic σ- bonding, multiple π- bonding occurs in some phosphorus compounds. For this the element utilizes either d- or p-orbitals and may form bonds of the p_π(P)- p_π(X), d_π(P)- p_π (X) type, where X is most commonly C, N. Analyzing the structure of PO_4^{3-} it is crucial to recognize its symmetry, which is tetrahedral (sp^3 hybridized). A natural bond orbital analysis revels that there are four equal P-O σ bonds and each oxygen has three lone pairs. The contribution of d orbital in bonding is well below 1%. Therefore a more accurate Lewis formula is with charge separation (consistent with the partial charges, i.e. q(P)=2.2, q(O)=−1.3).



In general phosphorus compounds prefer to react by pair mechanisms, using the nucleophilic reactivity of the lone pair electrons in the case of trivalent compounds and the electrophilicity of the phosphorus atom in pentavalent derivatives. As nucleophilic reagents, trivalent phosphorus compounds can rapidly react with both electron deficient centers and also with electronically saturated carbon centers. The nucleophilicity of the phosphorus atom has been observed in various organic reactions.

1.3 The bond strength and its effect on polymer structure

Phosphorus forms various polymeric compounds having P-P, P-C, P-N and P-O-C linkages. The stability of the given bond is dependent on the atmosphere to which it is subjected. High bond strength does not means high stability of the compounds under all conditions. From the bond strength values it is expected that P-C, P-O and P-N linkages in the main chain may give rise to thermostable polymers (272, 360 and 230 kJ/mol respectively). The P-C bond is very resistant towards oxidation and hydrolysis, and in respect it is more stable than C-C bond. The phosphoryl P=O linkage is quite strong but when oxygen is involved in a bridge form, e.g. on P-O-P or P-O-C linkages, this generally results in hydrolytic instability.

1.4 Requirement of flame retardancy

Now-a-days polymer derived products have own a place in our daily life. Composite materials are replacing steel and aluminum alloys slowly but effectively over the past decades [13] [14]. Composite materials consist of an organic polymer matrix reinforced with glass, carbon, aramid, or natural fibres. They offer great physical, thermal, chemical and mechanical properties but due to the organic nature of the polymer matrix composite materials suffer poor fire resistance [15] [16]. That’s why it is essential to incorporate aromatic ring or to introduce fire retardants into the polymer or composite material to meet its application standards. Flame resistance in polymers is achieved by two different approaches, viz.

(i) The desired level of flame resistance is achieved by incorporation of a suitable flame retardant additive system

(ii) The base polymer is designed to have built-in flame resistance by virtue of its chemical structure and composition

Flame retardant additives can be either halogenated [17] [18] [19] [20] [21] [22] [23] or non-halogenated such as

(i) Inorganic flame retardants

(ii) Nitrogen based flame retardants

(iii) Phosphorus based flame retardants.

Because of the environmental reasons the use of halogenated flame retardants became limited in the recent years. The majority of literature on halogen free flame retardants focus on phosphorus based products. Here in **Figure 3** shows a worldwide usage of different flame retardant additives.

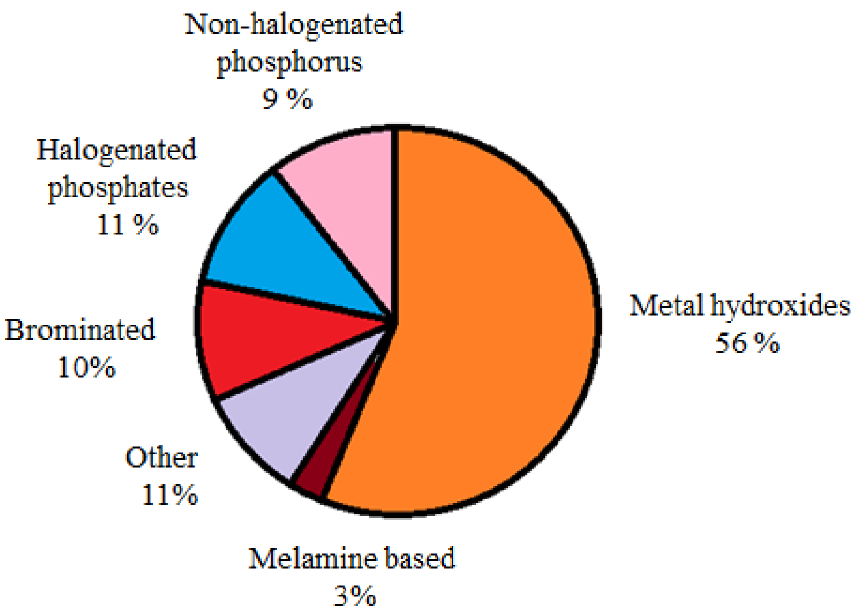


Figure 3: Worldwide usage of flame retardant

It has been found that phosphorus, present either as a constituent in the polymer chain or incorporated as an additive, in the form of a phosphorus compound to the polymer system, can make polymers flame retardant. They are not harmful in the sense of toxic gases since phosphorus stays most likely locked in the char [24].

Chapter 2

State of the art

2 State of the art

2.1 Classical theory of polycondensation

The classical theory of polycondensation is based on the work of Carothers [25] and Flory [26]. They described the polycondensation of bifunctional linear monomers as step-growth process, which means the linear monomers first react with each other step by step yielding linear oligomers and finally linear polymers. One important hypothesis of Carothers theory was that the reactivity of the end groups was assumed to be independent of chain length. That means all reactive species including monomers and linear oligomers had the chance to react with each other at any time and at any concentration. The degree of polymerization ($\overline{\mathrm{DP}}$) as given by Carothers's equation (1) was considered as a function of conversion (P), whereby the ($\overline{\mathrm{DP}}$) increases with the conversion (P) of the functional groups.

$$\overline{\mathrm{DP}} = \frac{1}{1-\mathrm{P}} \quad \text{with } \mathrm{P} = \frac{\mathrm{N_0} - \mathrm{N_t}}{\mathrm{N_0}} \qquad (1)$$

$\overline{\mathrm{DP}}$： Average degree of polymerization
P: conversion of functional groups
N_0, N_t: Number of functional groups

Flory explained that polymers with identical composition but different molar mass exhibit different physical properties. After reaching certain $\overline{\mathrm{DP}}$, properties remain unchanged. In general, increasing degree of polymerization correlates with higher melting temperature and higher mechanical strength [26].

2.2 Synthesis of poly(arylene ether)

Poly(arylene ethers) consist of aromatic rings and ether linkages and are important class of high performance polymeric materials with excellent combination of thermal and mechanical properties [27] [28] [29]. Adding to that they have high chemical resistance [30] [31] [32] [33]. Since early days various synthetic approaches had been followed for the synthesis of poly (arylene ether)s [34] [35] [2] [36] [37] such as Ullmann condensation, aromatic nucleophilic substitutions (S_NAr), ring opening of cyclic arylene ether, silyl ether displacement, electrophilic substitution and catalytic coupling reactions.

2.2.1 Ullmann Condensation

One of the general procedures of synthesizing poly(arylene ether) was Ullmann condensation. This is a procedure where bisphenols and bis-hallide monomers took part in presence of Cu (1) salt/ pyridine as catalyst [35]. General Electrical is the first company which developed commercial poly(arylene ether) which was poly (2, 6-Dimethyl phenylene oxide) [36]. The synthesis procedure involved oxidative coupling of 2, 6-Dimethyl phenol. But this procedure had its own limitation. It neither allowed much structural variation nor incorporation of any electron withdrawing group into the polymer backbone.

2.2.2 Nucleophilic aromatic substitution mechanism (S_NAr)

After some period the most well explored method of synthesizing poly(arylene ether) is highlighted [38] [39]. It involves the nucleophilic displacement of an activated dihalo or dinitro compound with an activated bisphenoxide salt at high temperature [34] [2]. However in this process an activation of the leaving group by an electron withdrawing group at the para-position is essential, e.g. sulfone, ketone or imide groups.

2.2.2.1 Theory behind nucleophilic aromatic substitution mechanism (S_NAr)

It is well known that both sulfone and ketone groups are very effective in activating aryl halides toward nucleophilic displacement. In S_NAr reaction, the first step is the formation of Meisenheimer complex is the rate determining step **Figure 4.** Then in the next step from that intermediate complex, a halogen atom is eliminated and the product is formed. **Figure 5** clearly shows that the activating groups present at 2 and 4 position stabilizes the negative charge by hyperconjugation and/ or by the negative inductive (-I) effect.

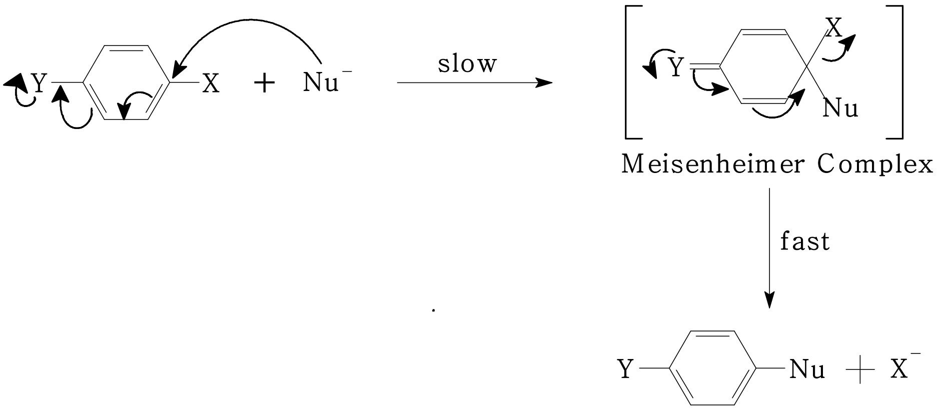


Figure 4: Formation of Meisenheimer complex

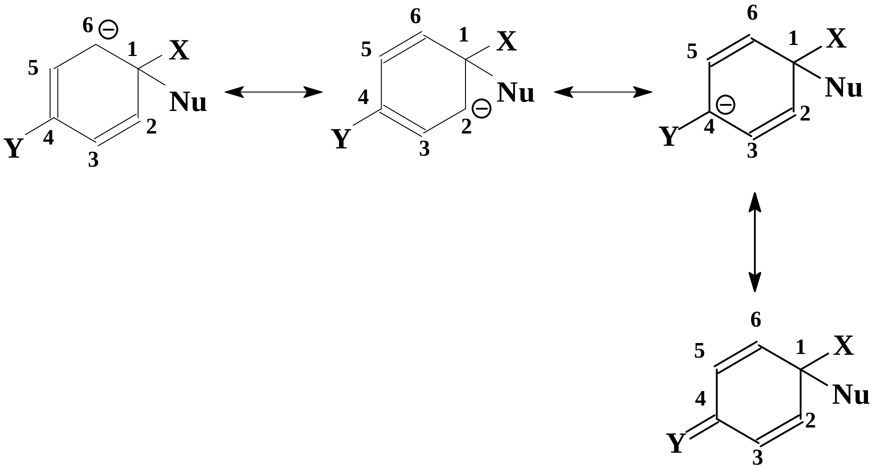


Figure 5: Stabilization mechanism of negative charge by activating group at position 2 and 4

Here, Nu = nucleophile; X = leaving group and Y = electron-withdrawing group (activating group).

From the mechanism shown in **Figure 6** it can be understood why fluorine containing dihalides react faster and preferred in nucleophilic aromatic substitution compared to other halogen containing compounds.

In the two-step mechanism the first step is slower (as aromaticity is being disturbed) and is the rate-determining step. In this first step, the nucleophile attacks on ipso position of the activated di-halide. Fluorine is the strongest electron withdrawing atom compared to other halogen atoms, so the fluorine containing monomer is more reactive than other di-halide monomers. The second step is fast and involves elimination of the halogen atom, through which it maintains the aromaticity. It has no effect on the rate of the reaction. Although fluorine slows down the second step relative to chlorine, it accelerates the first step simply by its enormous inductive effect. So the overall reactivity is very high.

Another advantage of using fluorine is its less probability to undergo any side reaction. These side reactions can limit the molecular weight build up in a step growth polymerization.

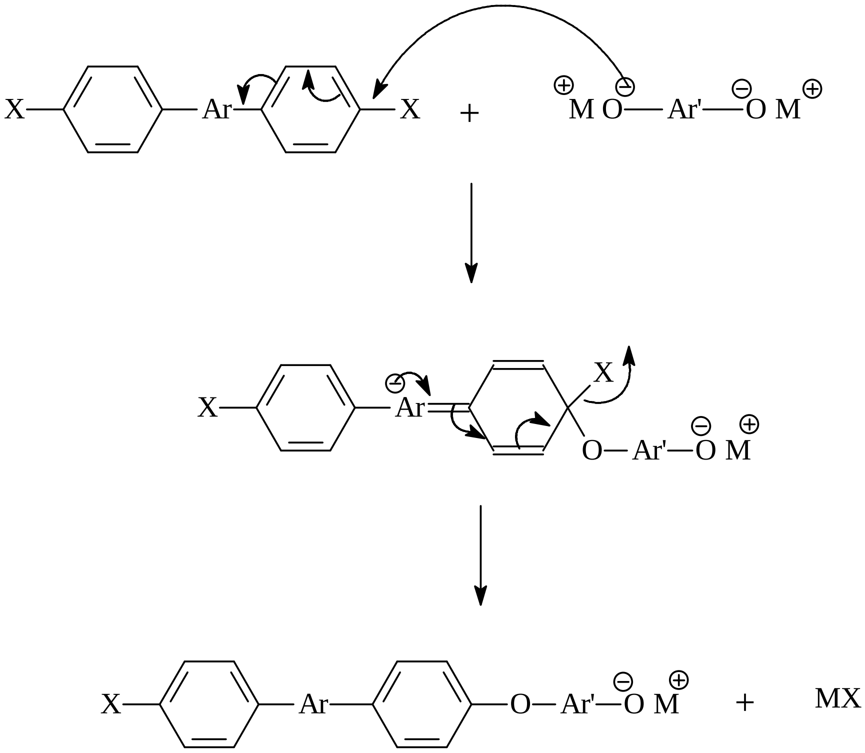


Figure 6: S_NAr mechanism for poly(arylene ethers) synthesis

Johnson et al. [34] first demonstrated the importance of such electron withdrawing groups at para position to synthesize a polymer with higher molecular weight. In between all halogens, fluorine seems to be the most reactive in undergoing nucleophilic displacement reaction. There could be several reasons for that, it might be due to the smaller size of the fluorine atom or due to the strongly polar C-F bond. The phenoxide reactivity depends on the alkali metal. The $–O^- K^+$ is more reactive compared to $–O^-Na^+$ due to higher electrovalent nature of the former bond. Dipolar aprotic solvents such as DMSO, DMF, NMP, DMAc led to higher yield of the final polymer. The reaction medium should be anhydrous otherwise a trace of water present in the reaction mixture could lower the concentration of phenoxide ion and hence affect the reaction efficiency as well.

The beneficial effect of trifluoromethyl group ($-CF_3$) was also studied by several groups. *Labadie et al*. [40] [41] studied the effect of $–CF_3$ group at ortho and para position with respect to a leaving group in a S_NAr reaction to prepare a totally aromatic poly(arylene ether) where polar groups such as ketone or sulfone were not present. They explained in their work how the $–CF_3$ group is very effective in activating a fluoride or nitro group at the ortho and para position towards nucleophilic substitution by phenoxide ion. In their work they reported the synthesis of poly(arylene ether) using $–CF_3$ activated dinitro monomer reacting it with bisphenols [40]. Solvent used for this process was NMP and toluene and K_2CO_3 was used as base to convert phenol into phenoxide. Authors reported only high thermal stability of the polymer; however, further details regarding the properties of these polymers were unknown.

Kim et al [42] [43] [44] [45] reported successful synthesis of poly(aryl ether ketone) using $–CF_3$ activated nitro-displacement reaction. High molecular weight polymers were reported only after reaction at temperature 80-120 °C. This process was believed to be the most facile process for the synthesis of poly(arylene ether) under relatively milder condition. The whole process was very special because it was useful for introducing fluorine into the polymer chain that was responsible for several property advantages e.g. lower dielectric constant [46], lower moisture absorption and higher processability.

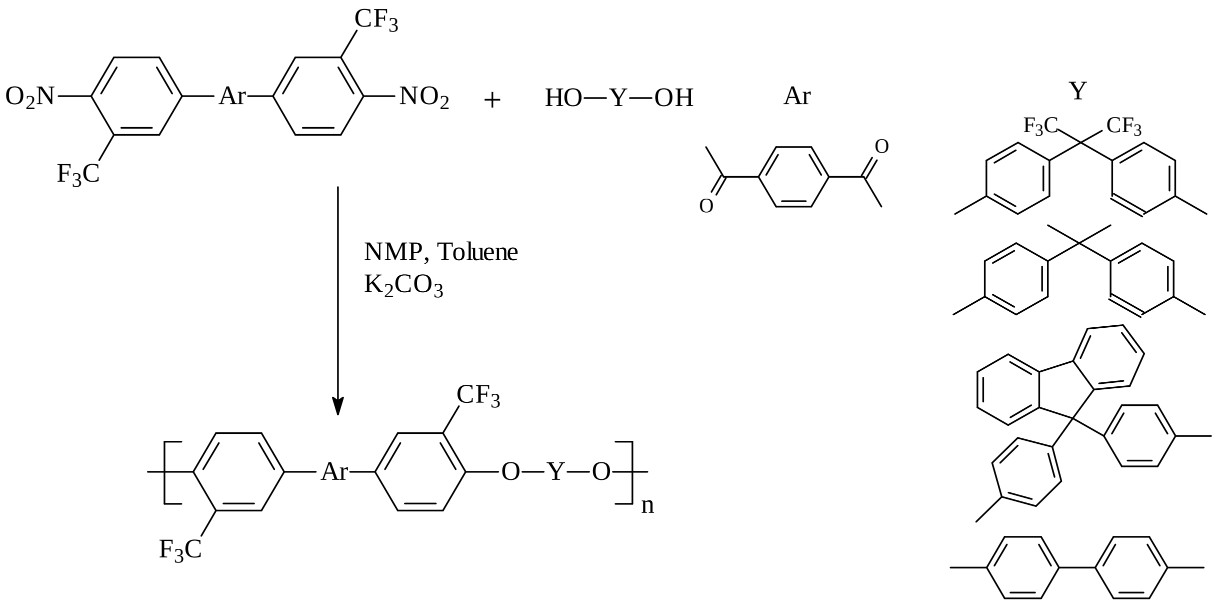


Figure 7: Synthesis of poly(aryl ether) and poly(aryl ether ketone) from $–CF_3$ substituted dinitro monomer

They reported the synthesis of high molecular weight poly(biphenylene oxide) (PBPO). The monomers containing $–CF_3$ substituent (ortho to the nitro group) were prepared by Pd-catalysed Suzuki coupling reaction between 5-bromo-2-nitro benzotrifluoride and p- and m-(methoxyphenyl) boronic acid followed by demethylation using BBr_3. Compared to the doubly activated monomer described earlier, higher temperature was required for completion of reaction in this case.

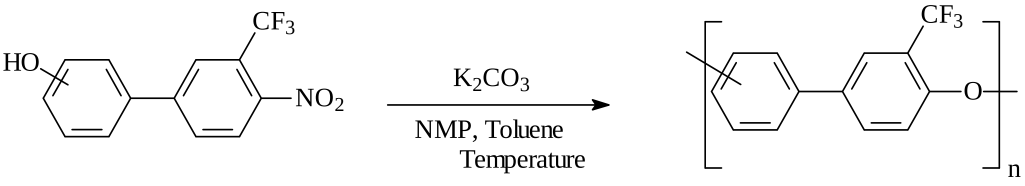


Figure 8: Synthesis of high molecular weight PBPO

Takekoshi and Kim et al. [47] synthesized poly(phenylene oxide) with pendent $–CF_3$ groups by selective and sequential nucleophilic aromatic substitution reaction of both fluoro and nitro groups using AA and BC type monomers. The PPO exhibited high solubility in organic solvents with T_g at around 108°C. TGA analysis revealed reasonably high thermal stability with $T_{d,5}$ at around 529°C. These studies were restricted mainly on synthesis and characterization of the polymers but no data were given on mechanical properties.

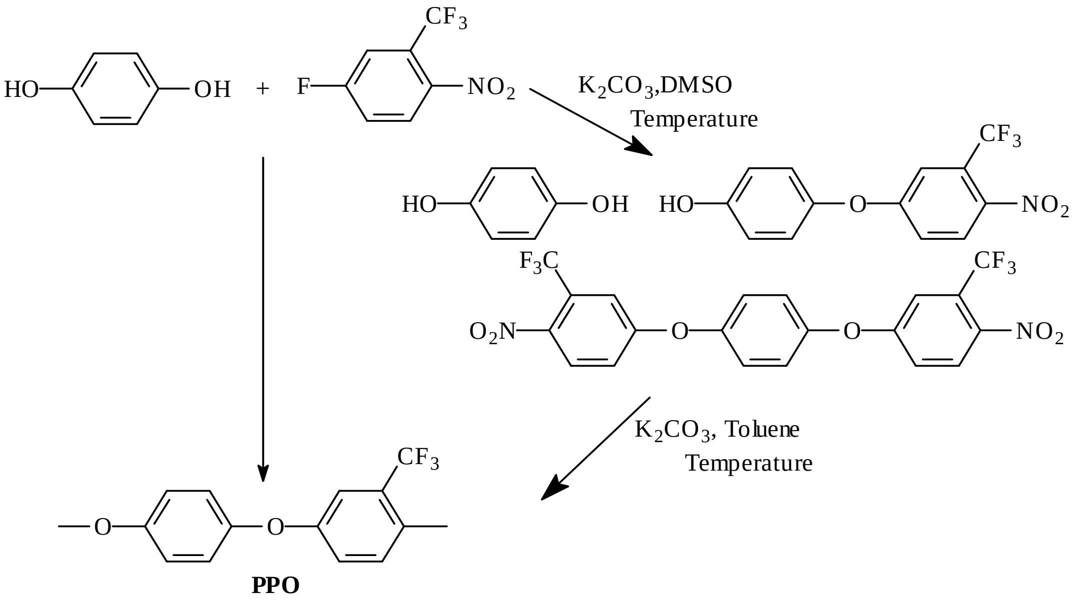


Figure 9: Synthesis of PPO by selective and sequential polymerization of AA and BC monomer

The majority of poly(arylene ethers) were synthesized utilizing fluoro substitution through S_NAr mechanism from bisfluoro compounds by bisphenoxides. Halogen atoms, directly substituted onto heteroaromatic rings were believed to be strongly activated towards nucleophilic displacement reaction [48] [49] [50]. Introduction of five membered heteroaromatic rings impart high thermo oxidative stability along with good mechanical properties [51] [52] [53].

Maier et al. [54] [55] [56] studied the combining effect of heteroaromatic rings and $–CF_3$ substitution. They have synthesized poly(aryl ether oxazoles) and poly(aryl ether thiazoles) containing $–CF_3$ substitution on the heteroaromatic ring. They followed the same fluoro displacement synthetic procedure. Thiazole rings were more aromatic that the oxazole ring and so they were expected to be more thermally stable compared to oxazole ring [57].

Based on the above observation *Banerjee et al.* [58] [59] [60] [61] [62] synthesized new $–CF_3$ containing monomers that would result in a series of more thermally stable, high strength polymers with low dielectric constant. The monomer synthesis followed Suzuki coupling reaction [63]. Thermal studies revealed that the T_g for the phenyl-containing polymers were higher than the corresponding heteroaromatic ring such as pyridine and thiophene moieties. A lower catenation angle (Fig 5) of the pyridine and thiophene groups led to higher bond mobility and hence lowering the T_g of the polymers containing them.

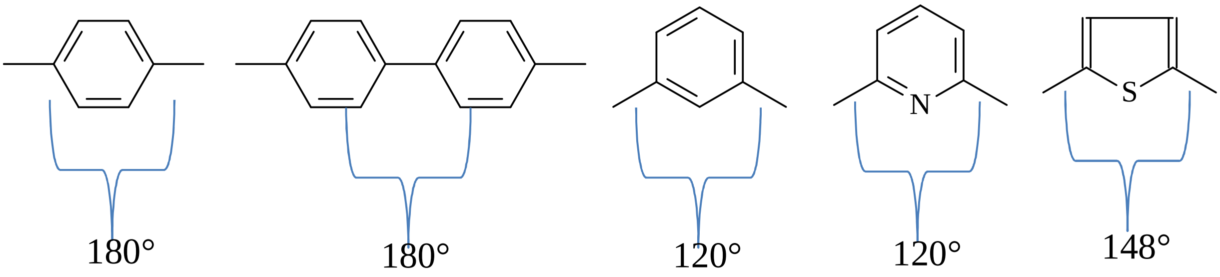


Figure 10: Catenation angle for different aromatic unit

Fluorinated poly(arylene ether sulfides) containing ethynyl end groups were synthesized by *Lee and Lee* [64] via nucleophilic aromatic substitution using pentafluorophenyl sulfide and –CF_3 substituted triphenyl dihydroxy monomer. For fabrication of optical wave-guides with desired properties the dihydroxy monomer was end capped with 3-ethynyl phenol to provide cross linkable groups **(Figure 11**)

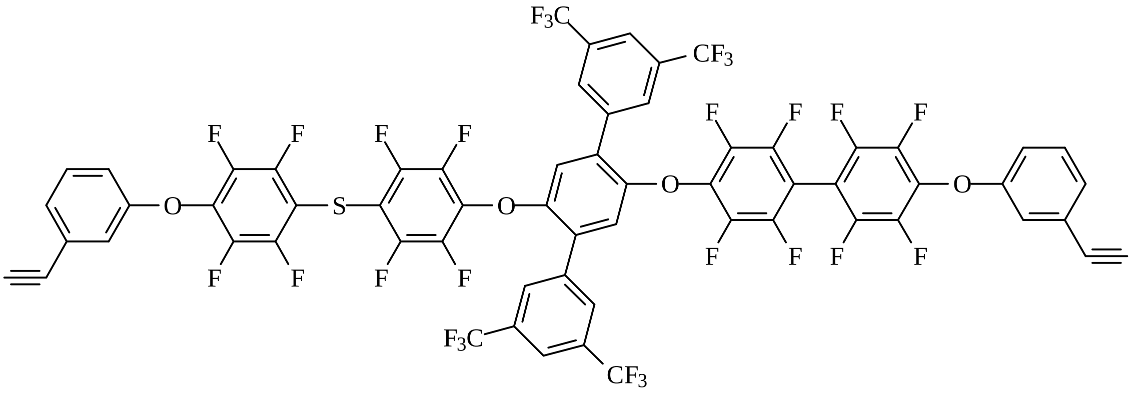


Figure 11: Poly(aryl ether sulfide) containing cross linkable moieties [64]

Kim et al. [65] reported similar cross linkable fluorinated poly(arylene ether sulfones) with terminal ethynyl moieties. They were synthesized via S_NAr using 4, 4'-(hexafluoroisopropylidene) diphenol (HFIP) and pentafluorophenyl sulfone, followed by capping with 3-ethynyl phenol.

Ding et al. [66] reported the synthesis of highly fluorinated aromatic aliphatic copolymers containing sulfone moieties by copolycondensation of decafluorodiphenylsulfone with 6F-BPA and a highly fluorinated branched diol using different feed ratios. *Qi et al.* synthesized bromo-fluorinated poly(arylene ether ketone) having HFIP groups as well as crosslinkable moieties [67]. These polymers exhibited very high processability and formed optically clear thin films and therefore were suitable for use in wavelength sensitive photonic devices. Liquid crystalline poly(arylene ether ketone) copolymers with pendant 3-(trifluoromethyl) phenyl groups were also synthesized using phenyl hydroquinone derivative [68].

2.2.3 Properties imparted by trifluoromethyl groups in polymers:

Incorporation of fluorine as $–CF_3$ groups [69] in polymers affects the following properties :

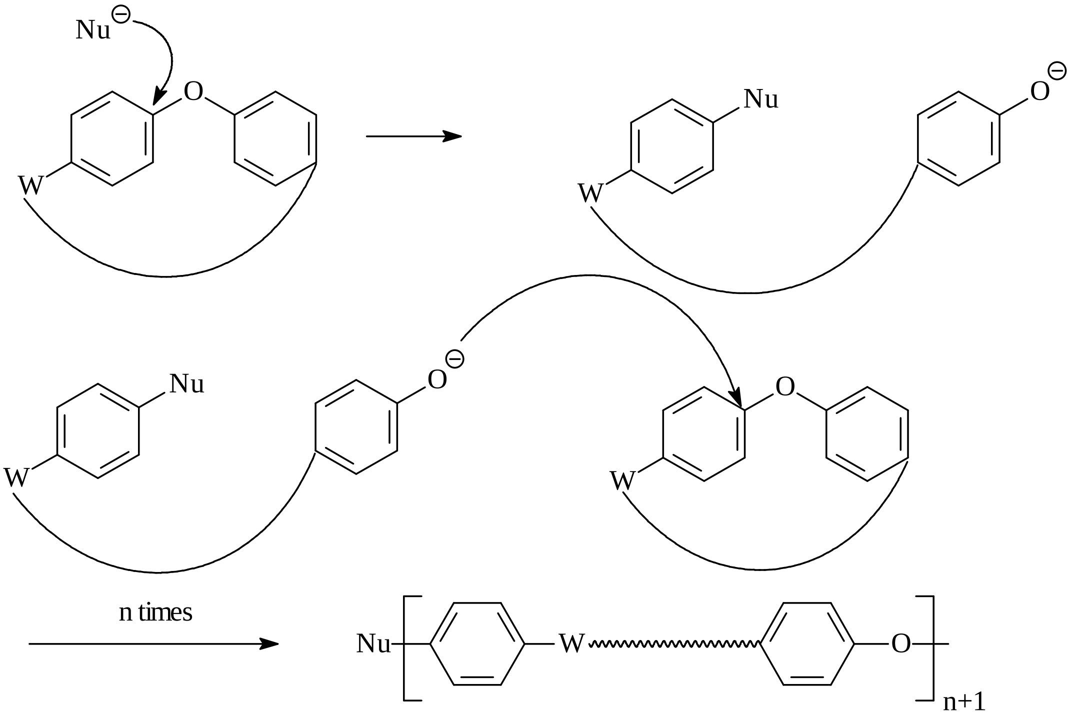
- Increases fractional free volume of the repeating unit
- Increases thermal stability
- Decreases dielectric constant
- Decreases moisture absorption
- Increases solubility, hence enhances the processability

Increase in free volume can be explained by the larger steric volume of fluorine relative to hydrogen, which might interfere with efficient chain packing. Moreover, the mutual repulsion between fluorine atoms on different chains might increase the free volume.

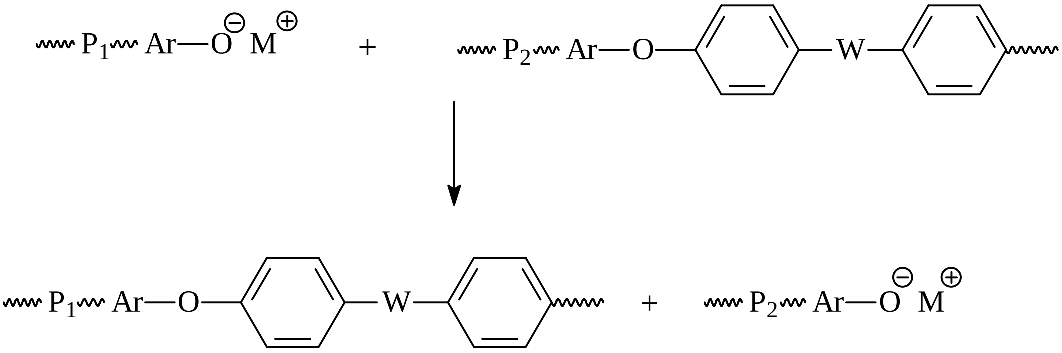
The electronic polarization decreases with fluorine substitution because of less electronic polarizability of the C-F bond compared to C-H. However, when fluorine is positioned non-symmetrically, dipole moment is increased. Therefore at low frequency dipole orientation polarizability is increased with a subsequent increase in low frequency dielectric constant. The steric congestion due to a bulky trifluoromethyl group might also facilitate the formation of a stable Meisenheimer complex with release of steric strain [70] [40] [42] [44] [43] [45].

2.2.4 Theory of ring opening reaction of cyclic polyethers

Arylene ether macrocycles having ether linkages can be ring opened through nucleophile inducing ether exchange reactions. Ether linkages between aryl nuclei which are activated by electron withdrawing groups are labile to attacks by nucleophiles. This is responsible for ether exchange in poly(arylene ether) synthesis via nucleophilic aromatic substitution reaction. In presence of various nucleophilic initiators these macrocycles are readily converting into high molecular weight polymers. In large sized oligomeric cyclics ring strain is always less and that is why the whole polymerization process is actually driven by entropy (**Figure 12**).



Nu = nucleophile, W = electron withdrawing group



W = electron withdrawing group, Ar = aryl group, P_1, P_2 = polymer chains

Figure 12: Ring opening reaction of cyclic polyethers via nucleophile inducing ether exchange reaction

2.2.5 Polycondensation of silylated monomers

Silylated monomers useful for polycondensations are normally compounds with one or more trimethylsilyl groups replacing protons. The monomers most widely used for polycondensations in the form of trimethylsilyl derivatives are:

(i) Aliphatic and aromatic diamines
(ii) Aminophenols
(iii) Aliphatic or aromatic amino acids
(iv) Diphenols
(v) Bisthiophenols or hydroxythiophenols
(vi) Aromatic hydroxy acids; aliphatic or aromatic dicarboxylic acids

There are several advantages of using silylated monomers instead of the protonated precursors. Firstly, polycondensation of silylated monomers with halogen containing electrophiles avoids the liberation of free hydrochloride or hydrofluoric acid, and thus, acid catalysed side reactions. Secondly, the liberated trimethylsilyl derivatives, such as fluoro or chloromethylsilane, trimethylsilylacetate, or hexamethyldisiloxane are highly volatile and easy to remove from the reaction mixture. Thirdly, silylation improves the solubility of the monomers and also reduces the melting point. This later aspect is, for instance, of interest for bulk or melt polycondensation of high melting aromatics whose T_m usually greater than 300°C. Fourthly, due to silylation the volatility of monomers enhances.

In almost all polycondensations silylated monomers mostly act as nucleophiles. Actually electropositive silicon enhances the nucleophilicity of the heteroatoms attached to silicon. In this connection it is noteworthy that the silylation of heteroatoms may have a significant influence in their reactivity. The influence of the silyl group is based on two somewhat opposite interactions with the attached heteroatom:

a) the positive inductive effect via the σ bond
b) the electron withdrawing effect of a $p\pi$-$d\pi$ bond

Silyl groups play the role of protecting groups for O- or S- functionalities because they prevent deprotonation, and thus, the formation of nucleophilic anions. On the other hand, silylation of poorly nucleophilic functional groups (aromatic amines) may enhance their nucleophilicity.

2.2.5.1 Melt polycondensation using silylated diphenols and CsF

This approach basically opens the possibility of synthesizing a broad number of aromatic polyethers in a one pot procedure. Condensation reaction occurs at high temperature (around 350°C). But with proper activation of the siloxy group polycondensation can result at somewhat lower temperature. CsF is the most effective catalyst for polycondensation of silylated diphenols and difluoro aromatics. **Figure 13** is the reaction mechanism proposed by Kricheldorf and Bier.

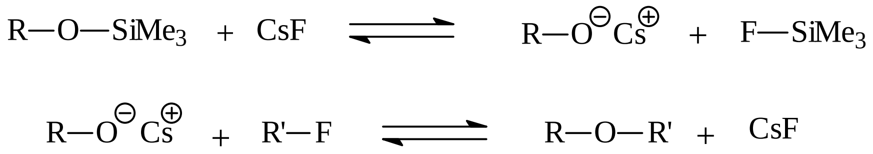


Figure 13: Basic reaction mechanism for polycondensation using trimethyl silyl derivative and CsF [49] [71]

2.3 Polymer burning, combustion and flame retardancy

2.3.1 Polymer burning

To assure public safety most of polymers must pass through regulatory fire and flame tests. That’s why it is very important to know the burning behavior of polymers and then accordingly modifying those (making them less flammable) using flame retardant additives to pass such fire tests. The whole process must proceed without compromising the unique physical properties and the cost of the end products. To burn a polymeric material thermal energy is needed to raise the temperature. This energy could originate from external source or from an adjacent flame. Thermal radiation is the primary mode of heat transfer from the flame to the polymer surface. When the polymer surface temperature rises, thermal degradation starts and small gaseous degradation products evolve which can further support a fire.

2.3.2 Polymer combustion

Combustion of polymers is nothing but a complex coupling between condensed and gas phase phenomena. Characteristics of the critical role in gas phase and condensed phase are briefly described below. Furthermore, the phenomenon in each phase consists of a complex coupling of chemical reactions with heat and mass transfer processes.

Almost everything, pyrolysis products and products of complete combustion are called combustion product of burning polymers. Ultimate products for all hydrocarbon polymers are carbon dioxide and water. The majority of deaths and serious injuries happened due to inhaling smokes and toxic gases. Carbon monoxides is the most important narcotic and toxic gas. All organic compounds form carbon monoxide by incomplete combustion. Hydrogen cyanides and nitrogen dioxides can also be formed nitrogen containing polymers such as polyurethane, polyacrylonitrile etc. which are used widely in domestic furnishing. Hydrogen chloride forms from PVC containing polymers which are used extensively in flooring, cables and pipes.

The heat release rate is one of the key fire hazard components. The heat from oxidation reactions in a flame is released in two components, one is convective and another is radiative. The radiative fraction X_f is normalized by the idealized heat of combustion of the material. This radiative fraction X_f and convective fraction X_c depend strongly on the chemical structure of the material. For large size methane and natural gas flames, roughly 80% of the heat release is convicted and 20% of it is radiated. A small fraction is always fed back to the fuel surface. Combustion efficiency X_a [$(X_f + X_c)/ X_l$, where X_l is the fraction of idealized heat release] (2) decreases with increase in fuel mass flux. Unsaturated materials and aromatic hydrocarbon materials tend to have higher radiative fraction due to an increase in soot particle concentration in their flames. That shows that heat release characteristics and heat feedback rates depend not only on the chemical structure on the materials but also on the diameter of a pool flame and the fiuel mass flux.

$$X_a = \frac{X_f + X_c}{X_l} \qquad (2)$$

Depending on the polymer nature, polymer degradation processes can follow different paths [72] [73] [74]. Some polymers degrade thermally via a free radical chain reaction path, e.g. vinyl polymers. Free radical chain reactions consist of random scission or chain initiated scission, intermolecular or intramolecular transfer, depropagation reaction, termination reactions. Polyethylene (PE), polystyrene (PS), polypropylene (PP), polymethylacrylate (PMA) belong to a group of polymers which undergoes scission at random locations on the main chain to yield many smaller molecular fragments. Polymethylmethacrylate (PMMA), polyoxymethylene (POM), poly-α-methylstyrene (PMS), and also polytetrafluoroethylene (PTFE), undergo a reversal of polymerization reaction after the initial breakage and yield monomer molecules. Above stated two different kinds of polymers undergo almost complete degradation and leaving hardly any char. Char is nothing but a carbonized polymer residue. Polymers with reactive side groups attached to the backbone of a polymer chain may degrade initially as a result of interactions or instabilities of these groups; such reactions may then lead to scission of backbone. Polyvinylchloride (PVC) and polyvinyl alcohol (PVA) are example of such polymers.

These groups tend to undergo cyclization, condensation, recombination or other reactions which ultimately yield some char. Diene polymers, polyacrylonitrile, and many aromatic and heterocyclic backbone polymers also belong to this char forming group. Common to the pyrolysis of all these polymers are the formation of conjugated multiple bonds, transition from a linear to a crosslinked structure, and an increase in the aromaticity of the polymer residue.

Figure 14 illustrates a proposed mechanism for char formation. At first a polymer is thermally decomposed via chain scission. After this step it may go for further decomposition or can react with another polymer chain to form a crosslinked network. If the polymer follows the former path then it may form small molecular weight volatile byproducts which feed the combustion process. But if the initial decomposed polymer radical goes to react with another polymer chain then it may form char. This mechanism is also helpful to explain why the char of many highly aromatic polymers contain graphitic structures on the surface [75].

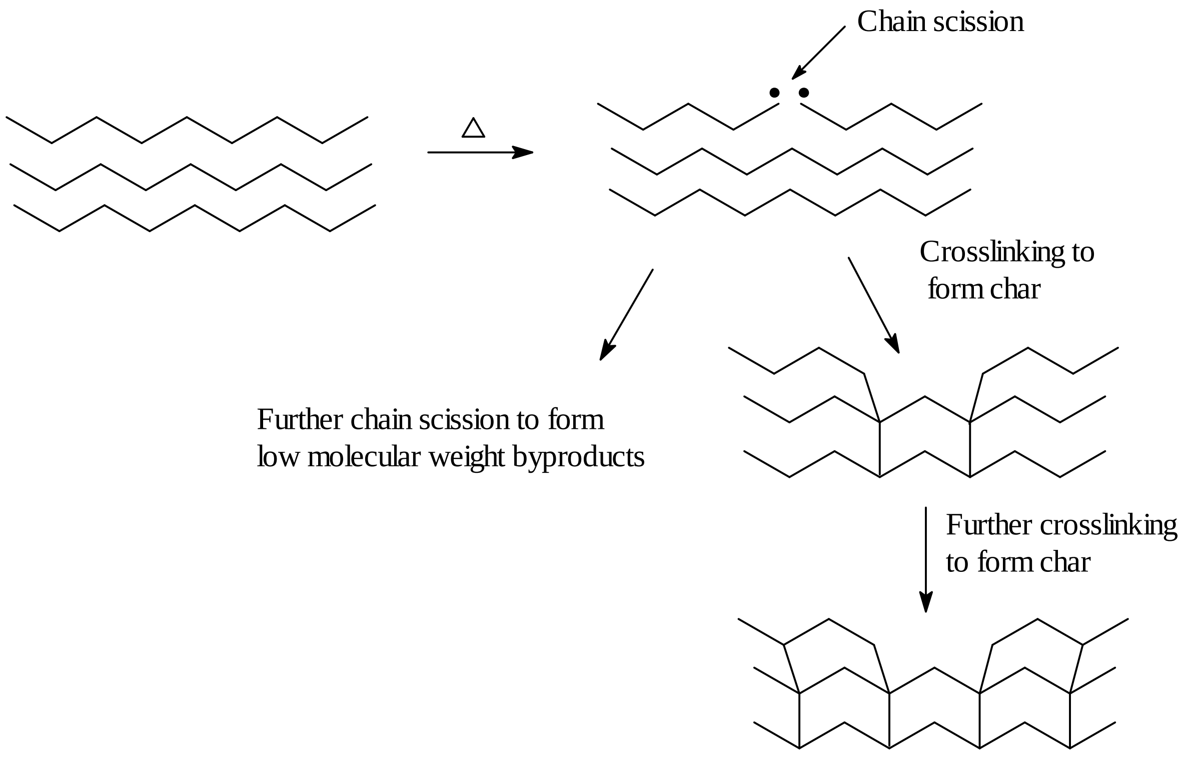


Figure 14: Possible mechanism for char formation [75]

In a fire, the particles may further form complex soot agglomerates. Soot forms in a flame as a result of chain of events, pyrolysis and oxidative pyrolysis of the burning material into small molecules, followed by chemical reactions. Soot particles are not only consisting of carbon but also of considerable amount of hydrogen present earlier in the flame. They absorb hydrocarbon vapors when the combustion products cool and accumulate large quantities of polycyclic hydrocarbons. The presence of soot is the cause of radiative heat transfer.

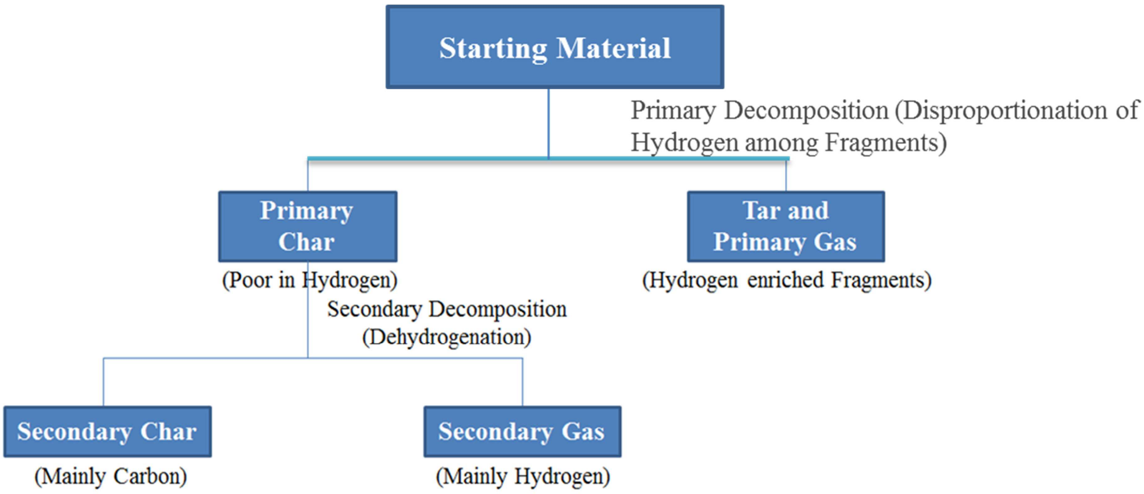


Figure 15: Basic mechanism of pyrolysis [76]

Polymers with reactive side groups attached to the backbone of a polymer degraded initially because of the interaction of these groups, leading to the scission of the backbone. These groups of polymers tend to undergo sometimes cyclization, recombination of other reactions which ultimately yield some char. Polymers containing aromatic and heterocyclic or diene backbones belong to char forming groups. Common features of these polymers are the formation of conjugated multiple bonds, linear to crosslinked structure transition, and an increase of the aromaticity of the polymer residue.

2.3.3 Flame Retardancy

The fire safety of a material means nothing but its increased ignition resistance, reduced flame spread rate, lower heat release rates, less dripping and reduced smoke and toxic product release. Most practical approach for fire safety performance is the addition of flame retardant additives to inexpensive and large commodity polymer. Unfortunately all the commodity polymers have low thermal stability and high heat of combustion.

The flame resistance of polymers has been improved using two different techniques. One way is by physically blending flame retardant additives such as Sb_2O_3 in combination with brominated aromatics [77] [78] [79] [80] [81] [82] or various phosphates with the thermoplastic polymer. And another way is by incorporating flame retardant structures into the polymeric backbone [83] [84] [85] [86] [87] [88] . Flame retardant additives include organic halogen or organic phosphorus compounds [89]. The additive may also degrade endothermally and can absorb energy from the polymer [90] [75]. During the ignition stage these flame retardant additives can deactivate highly reactive reaction propagating species that generated due to the chain scission during combustion process.

The additive must have a minimum impact on physical properties and product costs. Although halogenated flame retardants easily fulfill all the above stated criteria, the future use of these retardants is not clear. Public perception on the environmental impact of combustion of halogenated flame retardant has become an issue in Europe and in USA [91] [83] [92].

Fig 18 shows the role of halogen in combustion cycle.

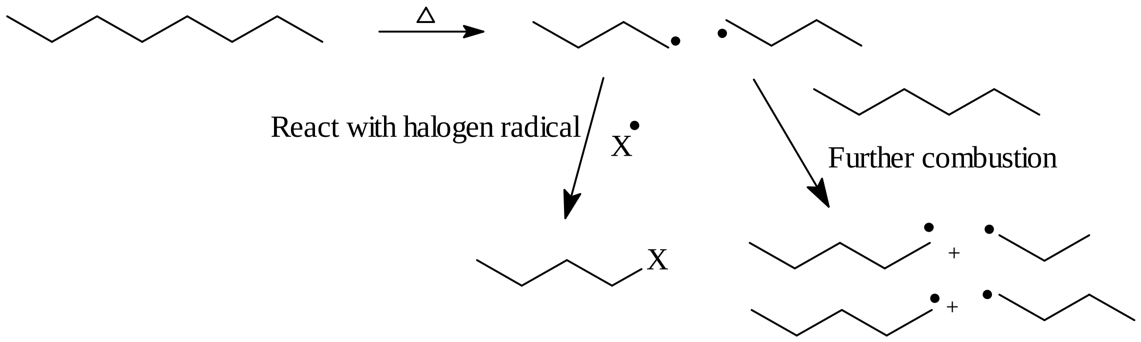


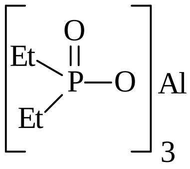
Figure 16: Illustration of how halogen can effect combustion cycle [93]

There are several approaches to non-halogenated flame retardants. Such an attempt is the use of magnesium hydroxides or aluminum trihydrate. In these two cases they generate water during degradation that acts as heat sink. Another approach was to form char during combustion. There are three basic mechanisms whereby the char reduces the flammability.

- Part of carbon and hydrogen stays in the condensed phase and thus reduces the gaseous combustible degradation products evolved.
- The low thermal conductivity of the char layer over the fire exposed surface acts as a thermal insulation to protect the polymer itself [94].

- A dense char acts as a physical barrier to gaseous combustible degradation products [95].

Metal salts of dialkyl phosphinates are known to be effective flame retardants since the late 1970’s. Clariant came out with a wide range of zinc, aluminum ad calcium salts of dialkyl phosphinates as flame retardant. They initiated the production of aluminum diethyl phosphinates which are commonly known as under the brand name of Exolit OP 930 , and are used for glass reinforced polyamide and polyesters. Some of the key aspects of these metal phosphinates are their higher phosphorus content, good thermal stability and less affinity towards moisture.
Schartel et al. [96] investigated aluminum diethyl phosphinates as a flame retardant for polyester but without glass fibre. And they have studied in detail the decomposition mechanism of the polymer composites.



Exolit OP 930/935

Figure 17: Commercially available aluminum phosphinates

The majority of the commodity polymers did not form char during their combustion. The char forming approach is most successful if the polymer chars rapidly and in an earlier burning stage. One possible approach is the use of phosphorus based materials which are well known for their effective flame retardancy. Phosphorus containing flame retardants may also behave as condensed phase inhibitors [83] [97]. However, the mechanism depends entirely on the polymer and the type of phosphorus compound. It was reported that in case of polyurethane, flame retardants operated in condensed phase [98] [79] whereas for polystyrene phosphorus flame retardants act primarily in the gas phase [99]. The use of phosphorus flame retardants was extended to determine effectiveness of phosphine oxides, aromatic phosphine oxides (depending on the structure of the IFR). Condensed phase inhibition involves changes in the polymer substrate to promote crosslinking and the formation of char which serves two purposes. Firstly, it acts as an insulating layer that protects the underlying polymer from the heat and flame and secondly it behaves as a barrier preventing oxygen from reaching the uncombusted polymer.

When phosphorus aryl compound was incorporated into a backbone of a polymer, studies revealed that the phosphorus formed a char that contain phosphorus anhydride type structure which inhibited combustion via a condensed phase mechanism [83]. The condensed phase mechanism was the best choice as it offered the advantage of a material with lower flammability without any release of toxic gases such as HX (main disadvantage of using halogenated flame retardant) and does not require large loading amount which is an essential requirement for vapor phase mechanism.

2.3.4 Properties induced by arylphosphine oxide groups in polymers:

Incorporation of phosphorus in the form of arylphosphine oxides in linear polymers has been studied by many research groups [70] [100] [101] [102]. Their studies revealed that incorporation of such moiety in the polymer chain –

- Increases the thermal stability of the polymer.
- Improves flame retardancy i.e increases its resistance to atomic oxygen [103]
- Increases the organosolubility.

A proposed mechanism for the vapor phase inhibition of phosphine oxide flame retardant additives is provided in the Figure 19 below [97].

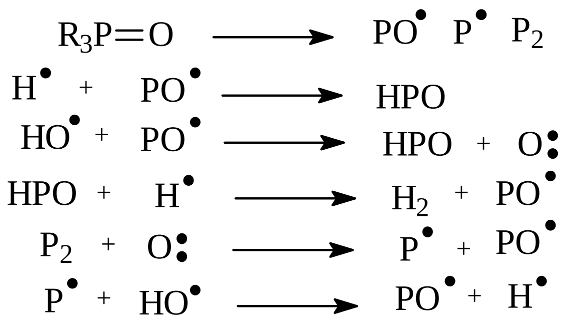
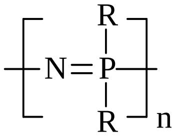
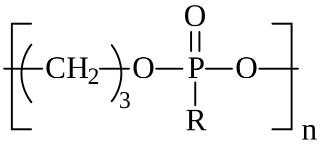
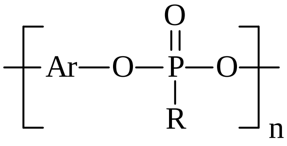
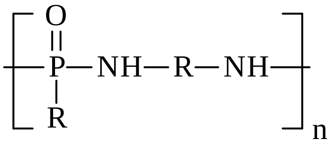


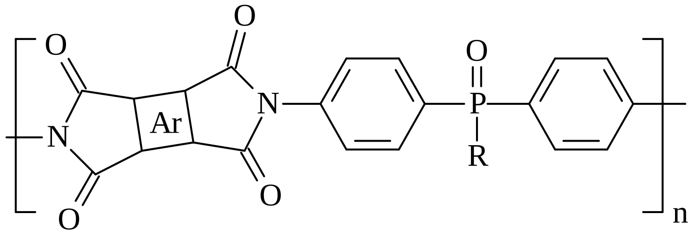
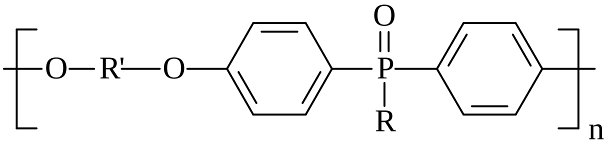
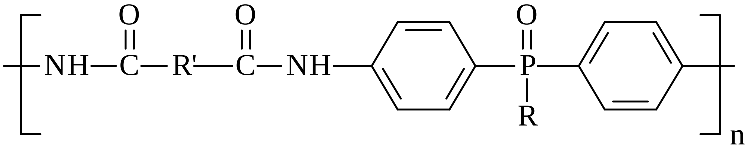
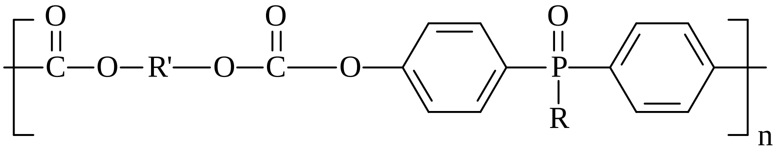
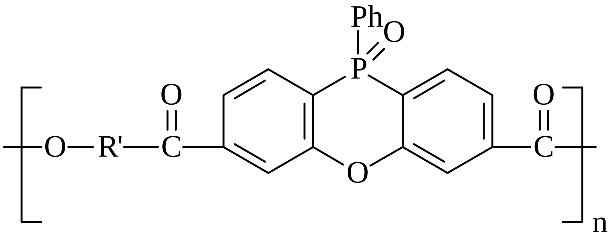
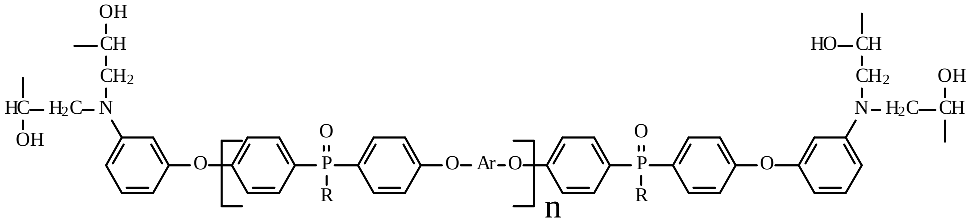
Figure 21: Illustration of the vapor phase inhibition mechanism of phosphine oxide flame retardant [97]

Inagaki et al. [104] showed that there was a linear correlation between the weight percentage of phosphorus in the polymer with the limiting oxygen index (LOI). They studied this with cotton samples treated with phosphorus containing flame retardants. LOI is an empirical technique developed to estimate the amount of oxygen in an O_2-N_2 atmosphere which is required to sustain a blue flame. Therefore higher LOI indicates that the polymer is more flame resistant [76].

Table 1 shows a variety of polymers that have phosphorus incorporated in their backbone.

Table 1: Polymers with phosphorus incorporated in the backbone

Polymer Class	**Polymer structure**
Polyphosphazine [105] [106] [107] [108] [109] [110]	 $\left[N=\overset{R}{\underset{R}{P}} \right]_n$
Polyphosphonate [111]	 $\left[\left(CH_2 \right)_3 O-\overset{O}{\underset{R}{P}}-O \right]_n$
Aryl polyphosphonate [112] [113] [114] [115]	 $\left[Ar-O-\overset{O}{\underset{R}{P}}-O \right]_n$
Phosphorus amide [116] [117] [118] [119] [120] [121]	 $\left[\overset{O}{\underset{R}{P}}-NH-R-NH \right]_n$

Polyimide [122]	
Poly(arylene ether) [123]	
Polyamide [124]	
Polycarbonate [125]	
Polyester [126]	
Epoxy networks [127]	

A wide variety of phosphorous containing poly(arylene ethers) were synthesized and the relationships between their primary structures and their properties had been extensively studied. High performance polymers containing phosphine oxide are of great importance because of their increased thermal stability and inherent flame resistance property [128]. *McGrath et al.* [129] [130] [131] reported first polymers that contained phosphine oxide in its backbone. They prepared the material simply from phosphine oxide and benzene. They also reported the synthesis and flame-retardant properties of aromatic polyphosphonates and arylene ether-phenylphosphine oxide containing polymers [132] [131]. According to them the presence of phosphorus in the char after high temperature heating implied that these materials should also be resistant to aggressive oxygen plasma environments.

McGrath [133] [134] and *Cabasso* [135] further studied the synthesis of linear poly(arylene ether phosphine oxide)s via metal catalyzed coupling reaction and also studied metal complexation of phosphorous containing polymers**.** Polymers containing PhPO units exhibited excellent adhesion properties to metal substrates. They were usually amorphous and showed a very high refractive index due to the non-coplanar structure of the triarylphosphine oxide units and the highly polar P=O bonds.

Connell et al. [103] [136] reported the high resistance of polymers with PhPO groups against atomic oxygen. The polymers were synthesized by the aromatic nucleophilic displacement reaction of two isomeric bisphenols, 2,5-dihydroxyphenyldiphenylphosphine oxide and bis (4-hydroxyphenyl) phenylphosphine oxide, with activated aromatic difluorides in the presence of anhydrous potassium carbonate in DMAc at 155°C.

Yoon et al. [137] reported that polymers containing the PPO group exhibit excellent adhesion properties to metal substrates and miscibility with many thermoplastic and thermosetting polymers. Due to the noncoplanar structure of triarylphosphine oxide and the intensely polar P=O bond, polymers containing the PPO group are usually amorphous and provide low birefringence and high refractive index.

Laura et al. [138] tried a new way of synthesizing [poly(arylene phosphine oxide] PAPO. They prepared it using Ni(0) catalyzed coupling of bis(4-chlorophenyl)phenylphosphine oxide. A very high glass transition temp (365 ^{o}C) and char yield was reported in nitrogen and air (35% at 750 ^{o}C) for that polymer. Due to some exceptional properties of PAPO they tried to introduce functional groups into the polymer backbone by aromatic nucleophilic substitution of the PAPO system.

Riley et al. [130] synthesized and characterized phosphorous containing poly(arylene ether)s. Their goal was to investigate the effect of phosphine oxide moiety upon thermal stability, mechanical strength, and fire resistance. For that purpose they synthesized phosphorous containing aromatic dihalides and bisphenols. Then these monomers were successfully polymerized *via* S_NAr mechanism. It was determined that by incorporating the phosphine oxide moiety into the polymer backbone certain properties of the resulting poly(arylene ether)s were substantially improved, such as an increase in T_g, thermal stability in air and modulus. The high char yields obtained for these polymers in air, along with observed intumescence indicates that these materials have improved fire resistance.

Jianyong Jin et al. [139] studied further about this topic. They developed phenylphosphine oxide (PPO) containing perfluorocyclobutyl (PFCB) polymers for potential use as multifunctional materials in space environments **(**Figure 20). The reaction of *p*-BrArOCF=CF2 (where Ar = phenyl or biphenyl) with *tert*-butyllithium afforded the lithium reagent smoothly below -20 °C. Subsequent substitution with phenylphosphonic dichloride provided the bis(trifluorovinyl ether) monomer containing the PPO group. Polymerization proceeded thermally above 150 °C to give polymers that exhibited high glass transition temperatures.

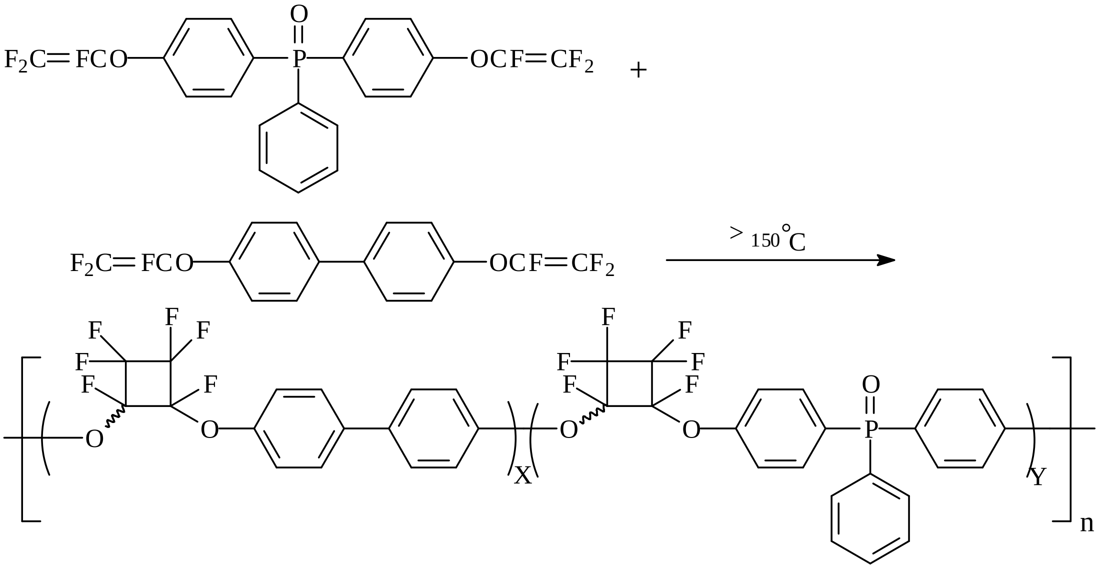


Figure 18: Copolymerization of PPO containing perfluorocyclobutyl monomers [139]

Functionalized phosphorus containing monomers were synthesized using various commonly used methodologies, including nucleophilic substitution of halogenated phosphine, phosphine sulfides or phosphine oxides with Grignard, and organolithium reagents according to *Smith et al* [131] [140]. They synthesized bis (fluorophenyl) phenylphosphine oxide (BFPPO) and bis (fluorophenyl) methylphosphine oxide (BFMPO) by the Grignard reaction of dichlorophenylphosphine oxide or dichloromethylphosphine oxide with 4-bromofluorobenzene.

They further worked on these BFPPO and BFMPO to phosphine oxide bisphenols and then tried to derivatize these compounds into phosphine oxide bisaminophenoxy. Henceforth, flame resistant poly (arylene ether)s, epoxy resins, polyamides, polyimides and bismaleimides were subsequently derived. [141] [142]

Yang et al. [143] reported the synthesis of bis(4- aminophenyl)phenyl phosphine oxide using nucleophilic substitution with organolithium agent in combination with Gabriel reaction in high yield and purity. Polyimides were prepared from this bis(4-aminophenyl)phenyl phosphine oxide and various dianhydrides to produce soluble polyimides, which in some cases exhibited very high glass transition temperatures, and in all cases were thermo-oxidatively stable as observed from TGA in air.

Braun et al. [144] and *Hoffmann et al.* [145] studied the fire behavior of PSUs and blends containing phosphorus-PSUs with different phosphorus environment. The influence of the chemical structure, charring and phosphorus release was discussed based on the mass loss, kinetics and products. They have also studied the phosphorus polyesters with systematically altered phosphorus environment. They have incorporated monomer with phosphorus containing substituents into aromatic-aliphatic polyesters to develop flame retardant as additive for poly (butylene terephthalate).

Voit et al. [146] [147] reported a series of linear poly(arylene ether phosphine oxide)s (PAEPOs) containing trifluoromethyl groups. In pyrolysis combustion flow calorimetry (PCFC) and thermal analysis, indications were found that these polymers behaved as flame retardants.

Wan et al. [148] reported bis (4-carboxyphenyl) phenylphosphine oxide that was synthesized by a Friedel-Craft reaction of dichlorophenyl phosphine sulfide followed by two sequential oxidative reactions. The compound was used to prepare tough, melt processible Nylon 6, 6 copolymers, which exhibited significantly decreased heat release rates, as measured by cone calorimetry, in comparison to the homopolymers.

So a lot of works regarding phosphine oxide containing poly(arylene ether), have been listed above. Mostly halogenated poly(arylene ethers) with phosphine oxide backbone was synthesized using nucleophilic substitution or metal catalized coupling reaction method. Still there are some possibilities to work with non-halogenated PAEPO’s. There are no works stating the comparative effect of phosphine oxide, trifluoromethyl and methoxy groups. For the first time that creates a chance for comparative study. Fresh challenges can be taken for synthesizing higher phosphorus containing PAEPO's which can act as better flame retardant additive in a polymer composite. There are very less information available regarding synthesis of trivalent phosphorus containing poly(arylene ethers). So a lot of scopes are there to explore the trivalent phosphorus chemistry.

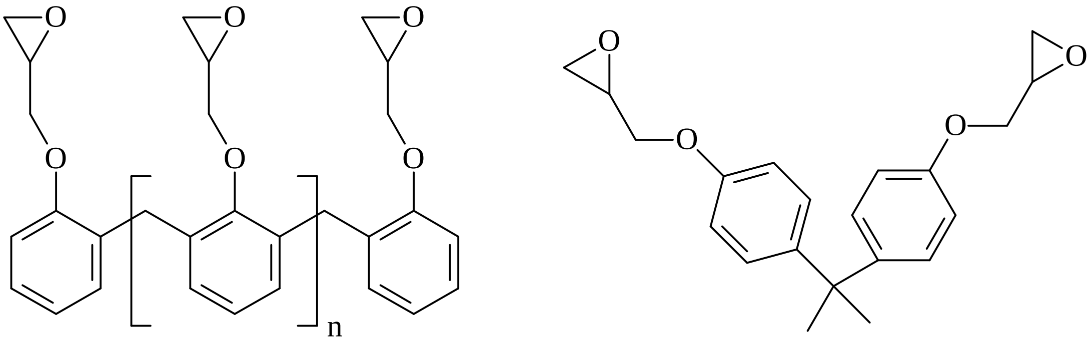
2.3.5 Epoxies and epoxies with flame retardants

The term epoxy has been widely adapted for many uses beyond fiber reinforced polymer composites. Epoxy resins are commonly used in:

(i) General purpose adhesives
(ii) As the binder in cements and mortars
(iii) Rigid foams
(iv) Non-skid coating
(v) Industrial coatings
(vi) Fiber reinforced plastics

Epoxy resin composites find their application also in electronic or electrical sectors. There are some glass reinforced laminates of epoxy available, which meet the defined flame retardant standards. Epoxy resins mixed with curing agents, accelerators, fillers and fire retardants are the most essential component for electrical and electronic application (Printing Wiring Boards) [149] [150] [151] .

The principal epoxy resins used for electrical and electronic application are the bifunctional diglycidyl ester of bisphenols A (DGEBA). These are used for semiconductor encapsulation. Highly functional phenol novolac epoxy resins are used for PWBs.



Phenol novolac epoxy

DGEBA

Figure 19: Commonly used epoxies for electrical and electronic (EE) application

Epoxy resins in EE are commonly cured by reaction of the epoxy end group with amines, phenol novolac or anhydrides [152]. Polyaddition of this hardener with epoxy resin generates a hydroxyl group that increases the crosslinking density of the cured resin.

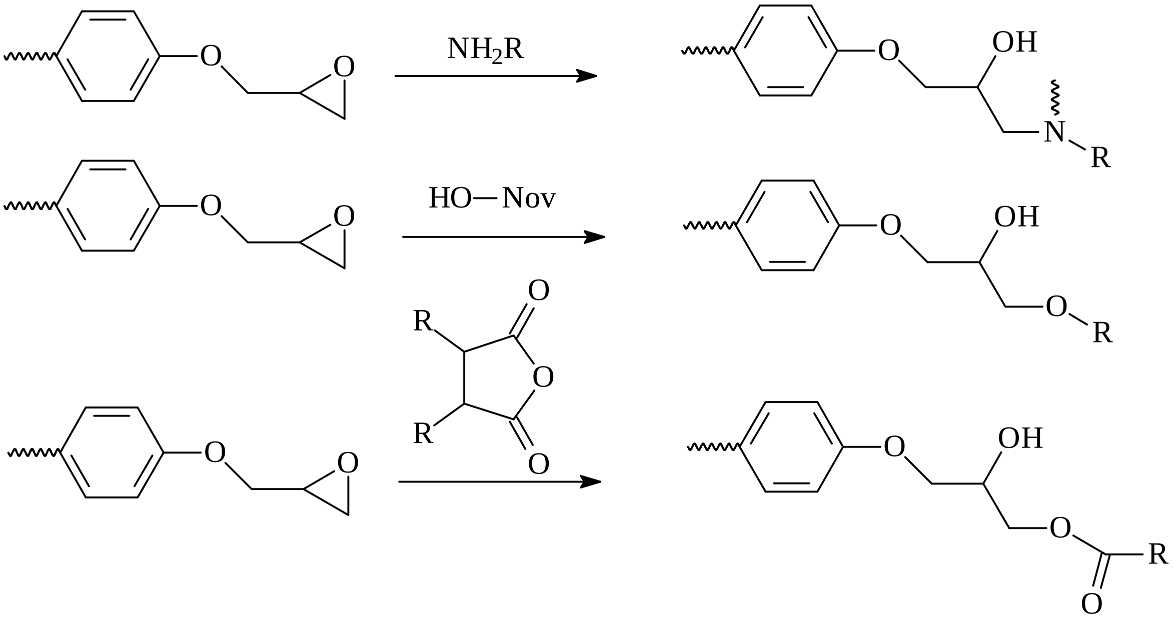
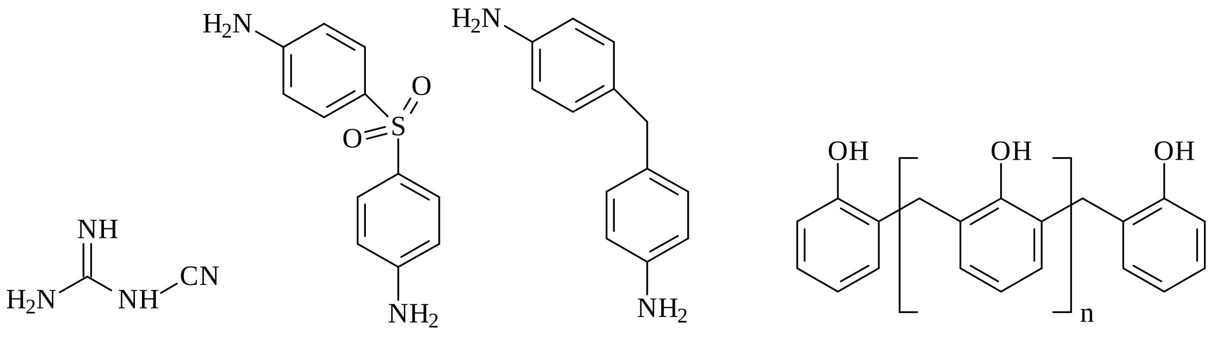


Figure 20: Newly formed bonds during the curing of epoxy resin

Different hardeners are used based on the composite application. Some most commonly used hardeners are shown in **Figure 21** Below [149].



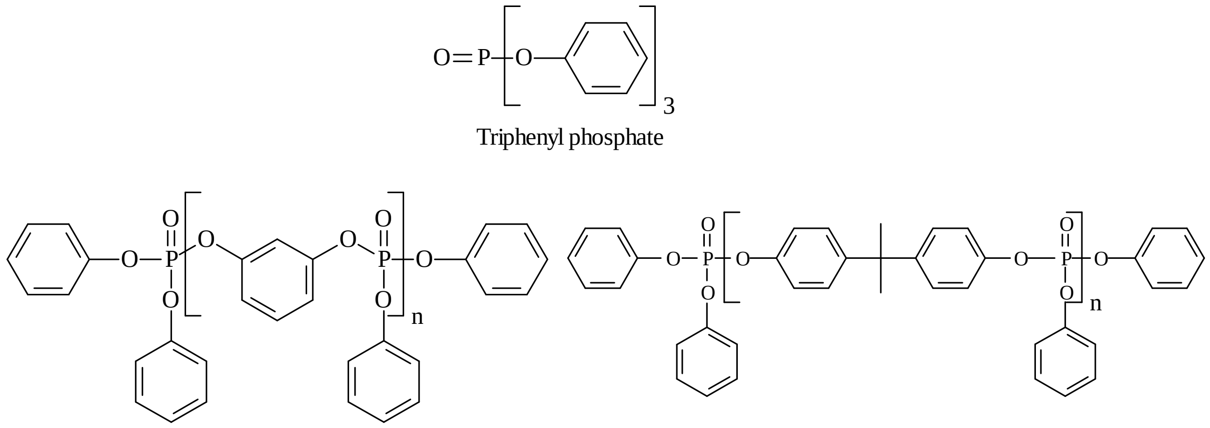
DICY DDS DDM Phenolic novolac

Figure 21: Commonly used curing agents

2.3.6 Epoxies with phosphorus containing flame retardants

Red phosphorus, a long known and very effective flame retardant is mainly used in polyamides, polycarbonates and polyesters [153] [154]. It is actually nontoxic and thermally stable up to 450°C. *Honda et al.* described an adhesive formulation made from bisphenols-A and cresol novolac epoxy using red phosphorus as a flame retardant [155]. A novolac epoxy resin passes the UL-94 test only with 1.6 % phosphorus.

There are several aromatic phosphates which were introduced as flame retardants. One simple example is triphenyl phosphates [156]. One of the major drawbacks of these flame retardants are the loss of clarity of composites. They have negative effect on physical properties of the cured polymer too. This is where the idea of bridged aromatic phosphates comes in. Bisphenol-A bridged diphenyl phosphates and resorcinol bridged diphenyl phosphate are commercially available and can impose good thermal stability, high flame retardancy and low volatility.



Triphenyl phosphate

Resorcinol bridged phosphate

Bisphenol A bridged phosphate

Figure 22: Commercially available flame retardant phosphates

DOPO (9, 10-dihydroxo-9-oxa-10-phospha phenanthrene-10-oxide) is a special phosphorus containing compound that has been introduced. *Schartel et al.* [157] [158] introduced DOPO into epoxy resin and extensively studied the effect of DOPO as flame retardant additive and as anionic hardener (considering gas phase mechanism). *Yang and Kim* [159] used a DOPO derivative and oligo (ethylene terephthalate) to prepare a flame retardant polyester. They reported that the polymers with phosphorus containing pendant groups are more stable against the melt polymerization condition than the polyesters with phosphorus in their backbone. At the same time copolyesters of poly(ethylene terephthalate) and a polymer with phosphorus in their backbone are less stable but better in terms of flame retardancy (having higher LOI). *Pospiech et al.* [160] [161] [162] synthesized polyester with DOPO substituent and their nanocomposites with layered silicates and studied in detail flame retardancy and decomposition mechanism. *Brehme et al.* [163] compared the DOPO substituted polyester with the commercially available Exolit OP 930 as an additive blend with poly(butylene terephthalate). *Chang et al.* [164] synthesized polymers where there was phosphorus in the main chain as well as DOPO attached to the polyester backbone.

There are several approaches where we can observe, tailoring material properties by blending one polymer with another one e.g. blending poly(sulfonyl-diphenylene phenylphosphate) in poly(butylene terephthalates) [165] [166] or in polycarbonates [167].

Due to their outstanding properties poly(arylene ethers) such as poly(sulfone) (PSU) and poly (ether sulfone) (PES) are commonly used for high performance application [168] [169] [170] [171] [172] with epoxy resin. Beside that these polymers show lower fire risk also [76] [173] [174] [175]. *Hoffmann et al.* [145] [176] proposed that the incorporation of phosphorus containing monomers (e.g. DOPO) into the polymer backbone improves the fire behavior of poly(ether sulfone). These materials are useful not only as toughness modifier but also can be used as flame retardant in epoxy resin composite. *Döring et al.* have studied non phosphorus and phosphorus containing poly(ether sulfone) and their corresponding blends with an EP [144].

Above literature review reveals that various works have been done with epoxy resin composites containing phosphorus based flame retardant additives. Those additives are mainly poly(arylene ethers) or polyesters. In some cases they have increased the phosphorus content of the composites (by increasing phosphorus containing additive) to have better flame retardant material (V-0 rating in UL-94 test). Because of that, in every case they deteriorate the material properties of the composites. The new challenge must be to improve that factor. That means to obtain flame retardant epoxy resin composites (with V-0 rating in UL-94 test) with good material properties (keeping additive loading as low as possible).

2.4 Trivalent phosphorus in organic synthesis

Throughout the years one of the main problems that chemists are facing is to deal with trivalent phosphorus containing compounds specially phosphines, because phosphines are not stable towards air, water or acids. Phosphines are proactive and have always a tendency to become oxidized. But after oxidation (pentavalent state) it remains quite useless. Therefore a number of methods were developed in order to overcome the instability of phosphines. One of the best ways was the protection of phosphine lone pair by a protecting group.

It was discovered through the years that the best protecting group for phosphines is borane. *Burg et al.* [177] first reported the synthesis of phosphine-borane complex and from then this method was easily introduced into the chemistry family to prepare a wide range of phosphine-borane compounds. It was shown that the phosphine-borane complexes are quite stable showing inertness towards air and most acids [178] [179]. *Frisch et al.* showed that triphenyl phosphine could easily react with borane to form triphenylphosphine-borane [180]. Most frequently used methods include $BH_3 \cdot THF$ and $BH_3 \cdot DMS$ as reagents [181] [182] [183]. *McNulty et al. [184]*

showed that the use of sodium borohydride together with AcOH in THF provided the highest yielding phosphine-borane adduct for a range of aryl or alkyl phosphines. *Imamoto et al.* [185] [186] made use of sodium borohydride as borane source but in their case they have used cerium trichloride as a reaction starter. This methodology was powerful enough for some phosphine oxide to convert into phosphine-borane adduct.

$$Ar_3P \quad + \quad BH_3{\bullet}THF \xrightarrow{THF} Ar_3P{\bullet}BH_3$$

Figure 23: Formation of phosphine-borane complex

In 1967, Oyo Mitsunobu reported a method for the condensation of a carboxylic acid and an alcohol, using a mixture of triphenylphosphine (TPP) and diethyl azodicarboxylate (DEAD), to provide an ester [187] [188].

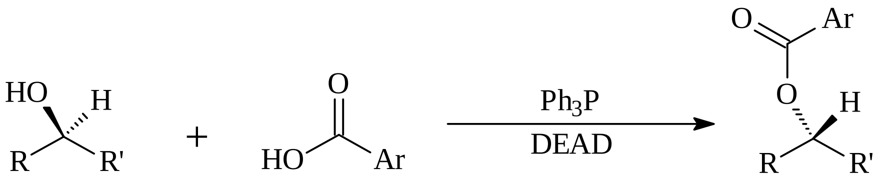


Figure 24: Basic Mitsunobu reaction

After the reaction triphenyl phosphine (Ph_3P) and DEAD transformed into triphenyl phosphine oxide and dicarboalkoxy hydrazine, respectively. The biggest challenge for the Mitsunobu reaction is the isolation of pure product from the crude mixture, because the crude mixture contains some excess reagents along with several byproducts.

Always there is a possibility of a side reaction. In the intermediate state negatively charged N of DEAD can go either way (**Figure 25**).

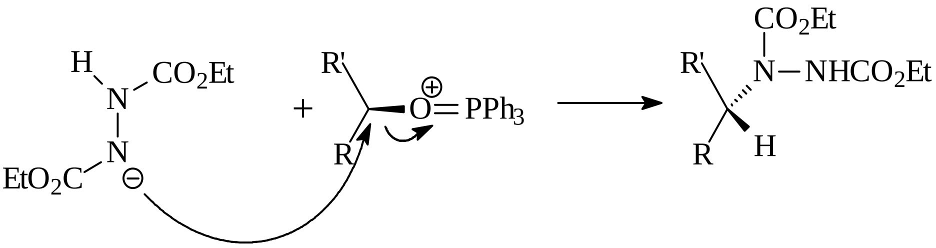


Figure 25: Formation of the side product

Over the years because of its scope, stereo specificity and mild reaction condition, Mitsunobu reaction established its significance in organic synthesis and in medicinal chemistry [189]. To sort out the separation problem and reaction yield a lot of work has been done or reviewed [190] [191].

There are a number of ways to get rid of the separation problem. In some approaches some additional reactions were required after the Mitsunobu reaction itself only to effect separation process. Fluorous approach was attractive among them because of comparatively easier separation technique involved [192] [193]. Fluorous approach is nothing but an approach where either fluorous DEAD or fluorous triphenyl phosphine is used to make separation easier. But still the result was not satisfactory and the cost of separation was higher.

Curran et al. [194] reported the use of both fluorous DEAD (F-DEAD-1) and fluorous phosphine (F-TPP) in Mitsunobu reaction. That reaction combination was responsible for relatively better purification of the final product by solid phase extraction process. *Dobbs and McGregor-Johnson* reported the synthesis and application of fluorous DEAD reagent (F-DEAD-1) (**Figure 26**) in Mitsunobu reactions [195].

Dandapani and Curran further worked on to sort out the limitations of first generation Mitsunobu reagents. They have synthesized a series of fluorous hydrazides and studied their separation properties by fluorous HPLC [196].

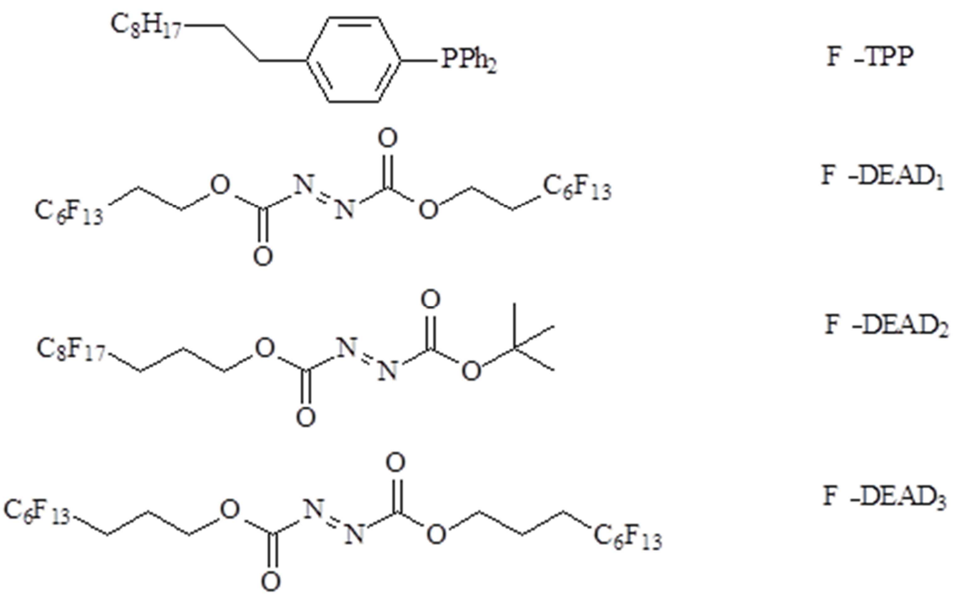


Figure 26: First and second generation Mitsunobu reagents

So it is clear that various groups have worked to solve the separation problems occur during Mitsunobu reaction. They have tried different approaches. Using fluorinated triphenyl phosphine, fluorinated DEAD or sometimes using both of them, they can get rid of the side products. But it is quite clear that the process is time consuming and complex too. The idea comes here is the use of trivalent phosphorus moiety with higher molar mass (trivalent phosphorus containing polyarylene ether). When it get transformed into the poly(arylene ether phosphine oxide), it will be easily separable. To do this approach it is necessary to perform one model reaction using triphenyl phosphine first and then to replace the triphenyl phosphine with trivalent phosphorus containing polymer, keeping other reactants same.

Chapter 3

Aim of the work

3 Aim of the work

The aim of the present research contained three different segments. In the first segment the work was planned on the synthesis, characterization and the discussion of probable application of phosphine oxide containing poly(arylene ethers). In the second the research was oriented on the application of poly(arylene ether phosphine oxides) as flame retardant additive in an epoxy resin matrix. And the third segment was based on synthesizing trivalent phosphorus containing polymers and its application in organic synthesis.

The past research revealed some important and interesting properties of poly(arylene ethers) having phosphine oxide groups. Inspired from that, the preparations of new classes of polymers or improvement of the properties of the existing polymers by judicious selection of new monomers were planned. Their properties were aimed to compare with the other poly(arylene ethers).

The approach was firstly to synthesize three different kinds of phosphine oxide containing monomers.

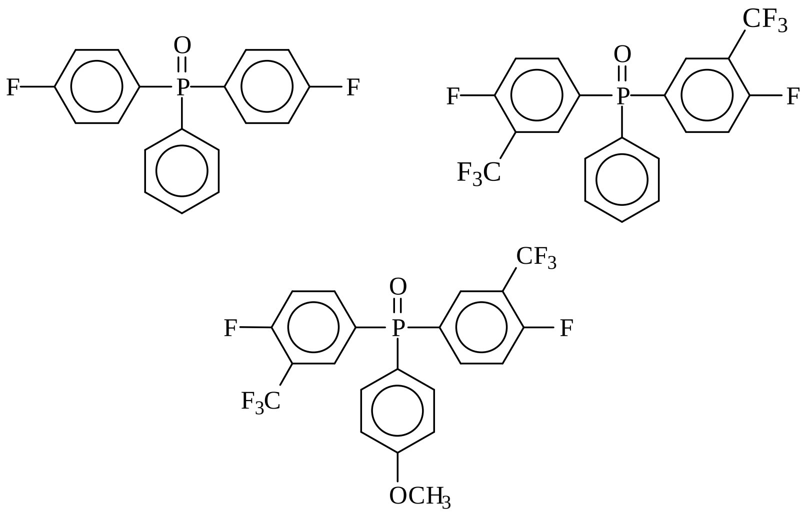


Figure 27: Monomers synthesized in this work

The technique used for synthesizing the monomers was Grignard reaction. Freshly prepared corresponding Grignard reagents reacted with the phenylphosphonic dichloride to produce above monomers.

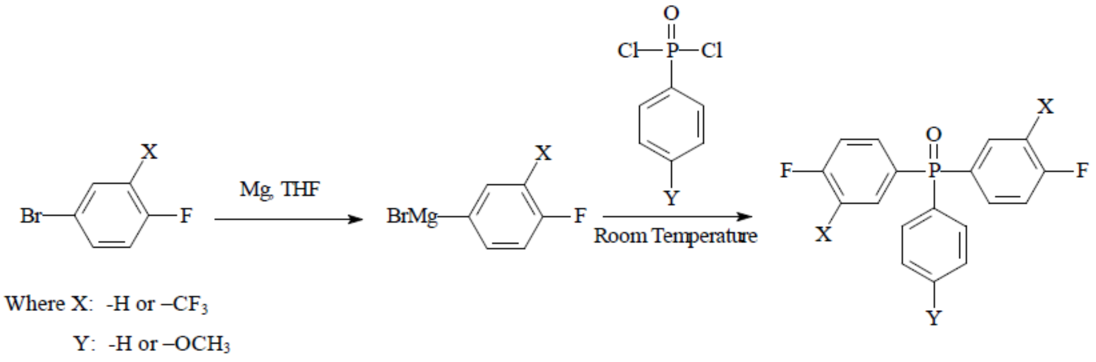
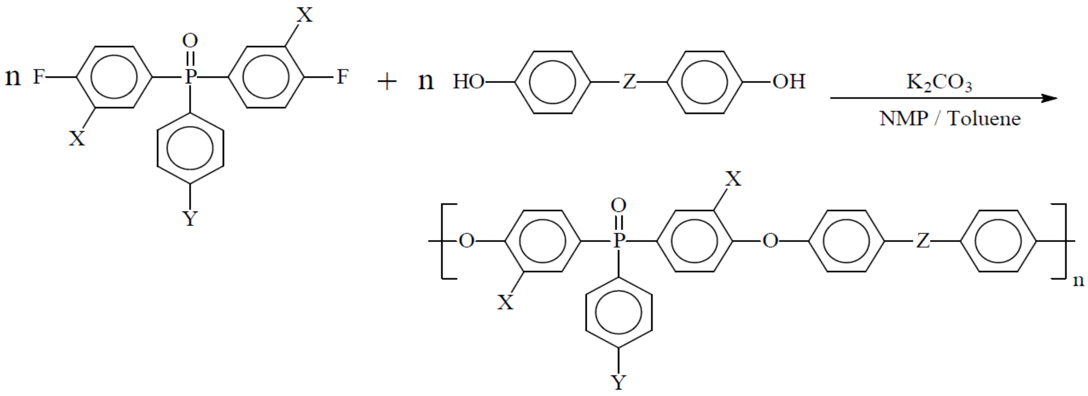


Figure 28: Reaction method for synthesizing monomers

These monomers were further aimed to use for synthesizing corresponding polymers. The reaction planned was basically a $A_2 + B_2$ step growth polymerization using aromatic nucleophilic substitution reaction (S_NAr) technique in presence of a mild base (K_2CO_3). The solvent used for this reaction was dry NMP and dry toluene. The purpose of using toluene was to take out the byproducts azeotropically from the reaction mixture.



Where X: -H or $–CF_3$

Y: -H or $–OCH_3$

Z: - , $-SO_2$, Ar, $-C(CH_3)_2$

Figure 29: A_2+B_2 step growth polymerization

The synthetic strategy led to a series of PAEPOs allowing for the first time a direct comparison of the effect of phosphine oxide, trifluoromethyl- and methylether groups. The thermal decomposition and combustion behavior and the burning behavior of selected samples were extensively studied. Based on the characterization results, decomposition mechanisms were derived in order to select a proper structure suitable to improve the physical and flame retardant properties of high performance polymers.

The new class of high performance poly(arylene ethers) by polycondensation of A_2 and B_2 monomer should fulfill the following criteria

- The polymers should have high T_g, good mechanical and flame retardant properties.
- The polymers should have highly processability.
- Thermal stability of the polymers should be high enough for its application.

By combination of the different monomers, the knowledge on high performance phosphine oxide containing poly(arylene ethers) with higher phosphorus content could be expanded and extensively studied whether the phosphorus content had any significant value to prepare a better flame retardant polymer or not. Higher phosphorus containing poly(arylene ether phosphine oxides) were planned to synthesize following the same aromatic nucleophilic substitution reaction mechanism. To increase the phosphorus content of the polymer repeating unit bis(4-fluorophenyl) phenylphosphine oxide monomer was undergone polycondensation reaction with 10-(2, 5-Dihydroxypheny), 10-H-9-Oxa-10-Phosphaphenanthrenelo-oxide (DOPO-HQ).

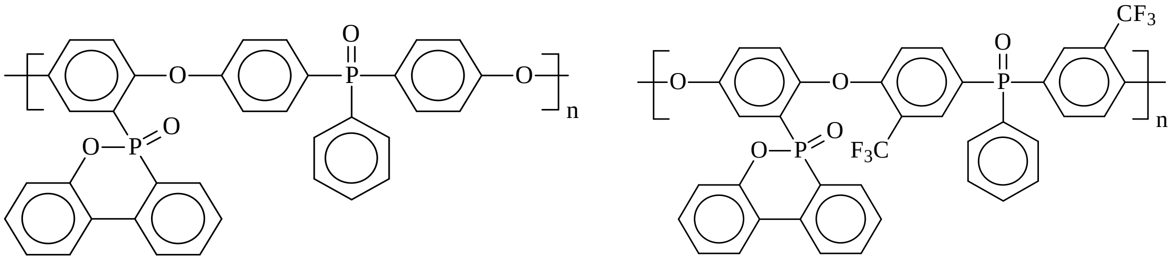


Figure 30: Higher phosphorus containing poly(arylene ether phosphine oxides)

Phosphorus containing fire retardants show always different mechanisms in the condensed and gas phase, regardless of whether an additive or reactive approach was used. Keeping in mind this earlier knowledge, in next segment the aim was to use the synthesized poly(arylene ether phosphine oxides) as an intumescent flame retardant (IFR) in epoxy resins.

In the present study PSU control (BPA based polysulfone) with four different PAEPO's and their corresponding blends with an EP were planned to investigate.

- Epoxy resin – C (EPC) + Bis(4-aminophenyl) sulfone (DDS) + Polymer **P1** (wt %)
- Epoxy resin – C (EPC) + Bis(4-aminophenyl) sulfone (DDS) + Polymer **P2** (wt %)
- Epoxy resin – C (EPC) + Bis(4-aminophenyl) sulfone (DDS) + Polymer **P3** (wt %)
- Epoxy resin – C (EPC) + Bis(4-aminophenyl) sulfone (DDS) + Polymer **P4** (wt %)
- Epoxy resin – C (EPC) + Bis(4-aminophenyl) sulfone (DDS) + Polymer **P9** (wt %)

The pyrolysis and the fire retardancy mechanisms of blends with epoxy resin were tackled by means of a comprehensive thermal analysis (thermogravimetry (TG)) and the fire tests [limiting oxygen index (LOI), cone calorimeter, UL 94]

After that the last segment of the research work was concentrated with trivalent phosphorus chemistry. Normally trivalent phosphorus is very unstable to air and moisture. So necessary precaution was needed to synthesize the monomer. Trivalent phosphorus containing monomer was synthesized using Grignard reaction from dichlorophenyl phosphine and 4-bromo fluorobenzene and it was investigated whether or not it could be successfully polymerized maintaining higher trivalent phosphorus content.

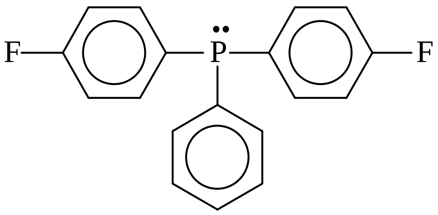


Figure 31: Trivalent phosphorus containing monomer (A_2)

Highly reactive trivalent phosphorus containing monomer can easily get oxidised in presence of any mild base which is basically a common reactant during A_2 + B_2 polycondensation reaction

(B_2 = diphenols). So the research was concentrated to find out a useful way of synthesizing linear trivalent phosphorus containing polymer. To do that the idea of protecting the free electron of phosphorus came in. The easiest way was to do that by preparing a phosphine borane adduct. And after the polymerization reaction it was necessary to do one deprotection reaction. Another way was to prepare first silylated bisphenol A and then to polymerize it with trivalent phosphorus monomer using melt polymerization technique in presence of catalytic CsF.

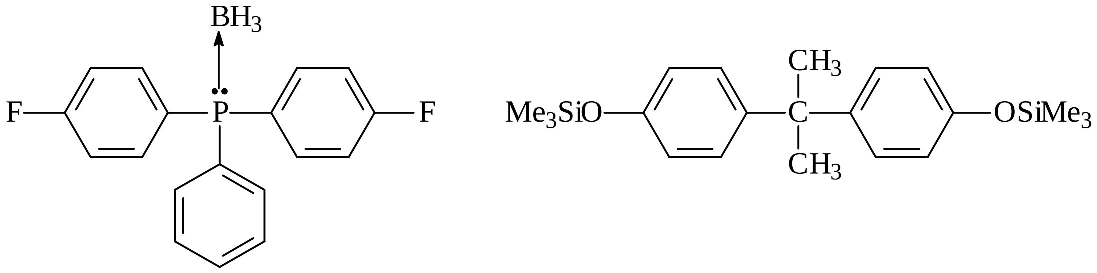


Figure 32: Structure of the intermediates (phosphine borane complex and silylated bisphenol A)

After preparing the respective polymer next aim was to utilize this polymer in organic synthesis. A lot of researcher worked to solve the separation problems occur during Mitsunobu reaction. Because the main obstacle for Mitsunobu reaction is in its separation process. Always there is a possibility of getting lower yields because of the complicated separation system. Different researchers tried different approaches. Using fluorinated triphenyl phosphine, fluorinated DEAD or sometimes using both of them, they could get rid of the side products. The idea came here was to use trivalent phosphorus moiety with higher molar mass (trivalent phosphorus containing polyarylene ether). When it got transformed into the poly(arylene ether phosphine oxide), then it would be easily separable. To do this approach it was necessary to perform one model reaction using triphenyl phosphine first and then to replace the triphenyl phosphine with trivalent phosphorus containing polymer, keeping other reactants same.

The Mitsunobu reaction of dimethyl-5-hydroxyisophthalate and a long chain semifluorinated alcohol was planned as a model reaction. It requires triphenyl phosphine as a reactant. Then the reaction was repeated replacing triphenyl phosphine with triphenyl phosphine containing polymer keeping other reactant identical. The study strictly concentrated on the separation of Mitsunobu adducts and on the yield of the reaction after adding the polymer as a reactant.

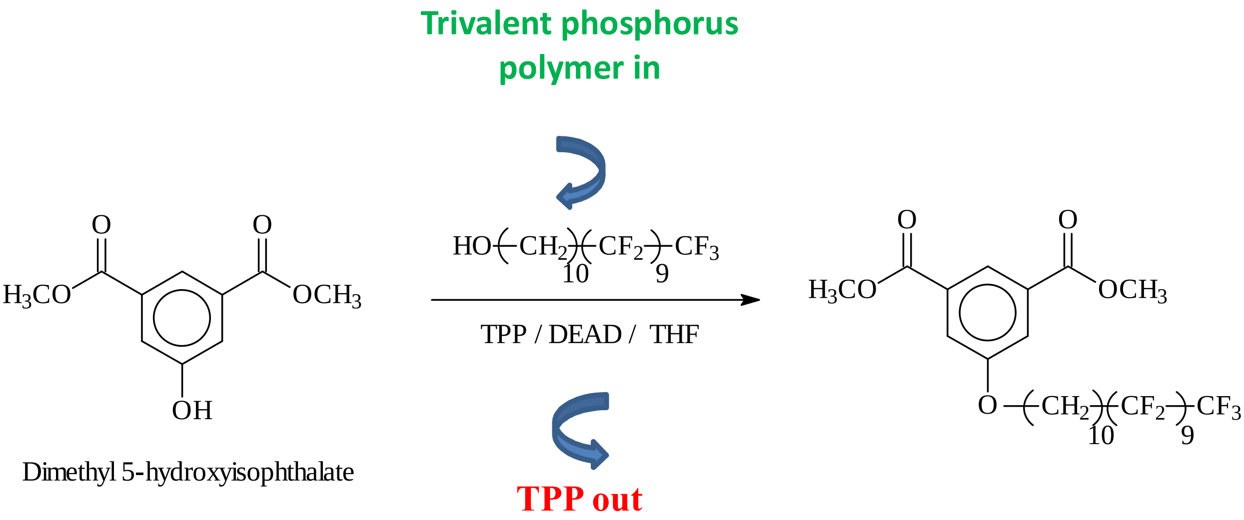


Figure 33: Mitsunobu reaction of dimethyl-5-hydroxyisophthalate and a long chain semifluorinated alcohol according to [197]

Chapter 4

Results and discussion

4 Results and Discussion

4.1 Poly(arylene ether phosphine oxide)

The research work was fully based on the synthesis, characterization and the discussion of probable application of phosphine oxide containing poly(arylene ethers). Considerable attention had been devoted to the preparation of new classes of polymers or improvement of the properties of the existing polymers by judicious selection of new monomers and then comparing their properties with the other poly(arylene ethers). The synthetic strategy led to a series of PAEPOs allowing for the first time a direct comparison of the effect of phosphine oxide, trifluoromethyl- and methylether groups.

4.1.1 Synthesis of Poly (arylene ether phosphine oxide)

Polymerization reactions for the synthesis of PAEPOs were carried out with stoichiometric amounts of the respective bisfluorophosphine oxide monomer and the bisphenol in presence of an excess of K_2CO_3 in NMP as solvent according to the protocol reported in experimental section..

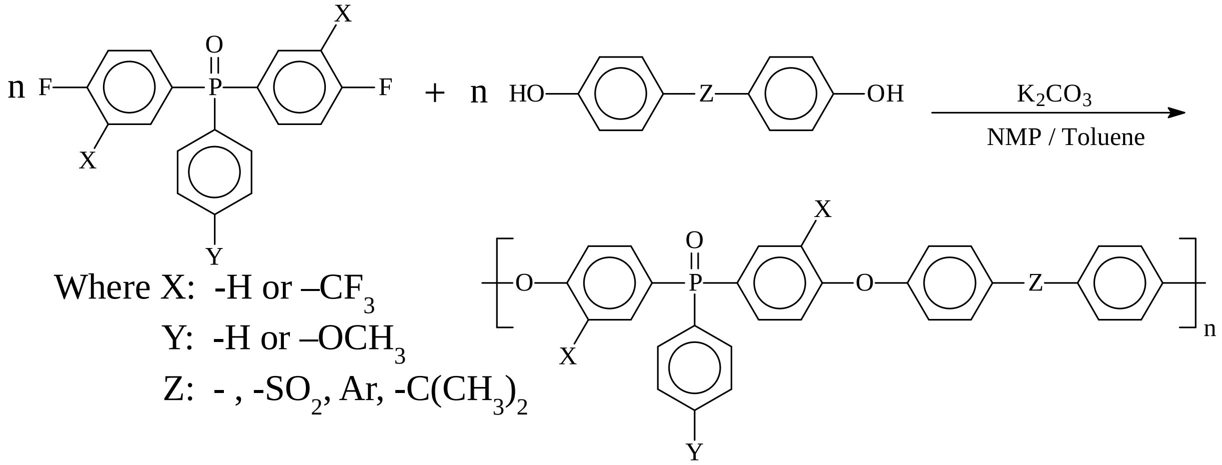


Figure 34: Synthesis route for the PAEPOs studied (e.g. polymer **P7** where X= CF_3, Y= $-OCH_3$, and Z= $-C(CH_3)_2$

Above in **Figure 34** is the basic reaction scheme followed for synthesizing poly (arylene ether phosphine oxide) s. Two phosphine oxide containing bisfluoro-derivatized monomers were synthesized successfully by the reaction of phenylphosphonic dichloride with 4-bromofluorophenol, and 5-bromo-2-fluorobenzotrifluoride, respectively. Another one was synthesized by the coupling reaction of 4-methoxy phenylphosphonic dichloride with 5-bromo-2-fluorobenzotrifluoride

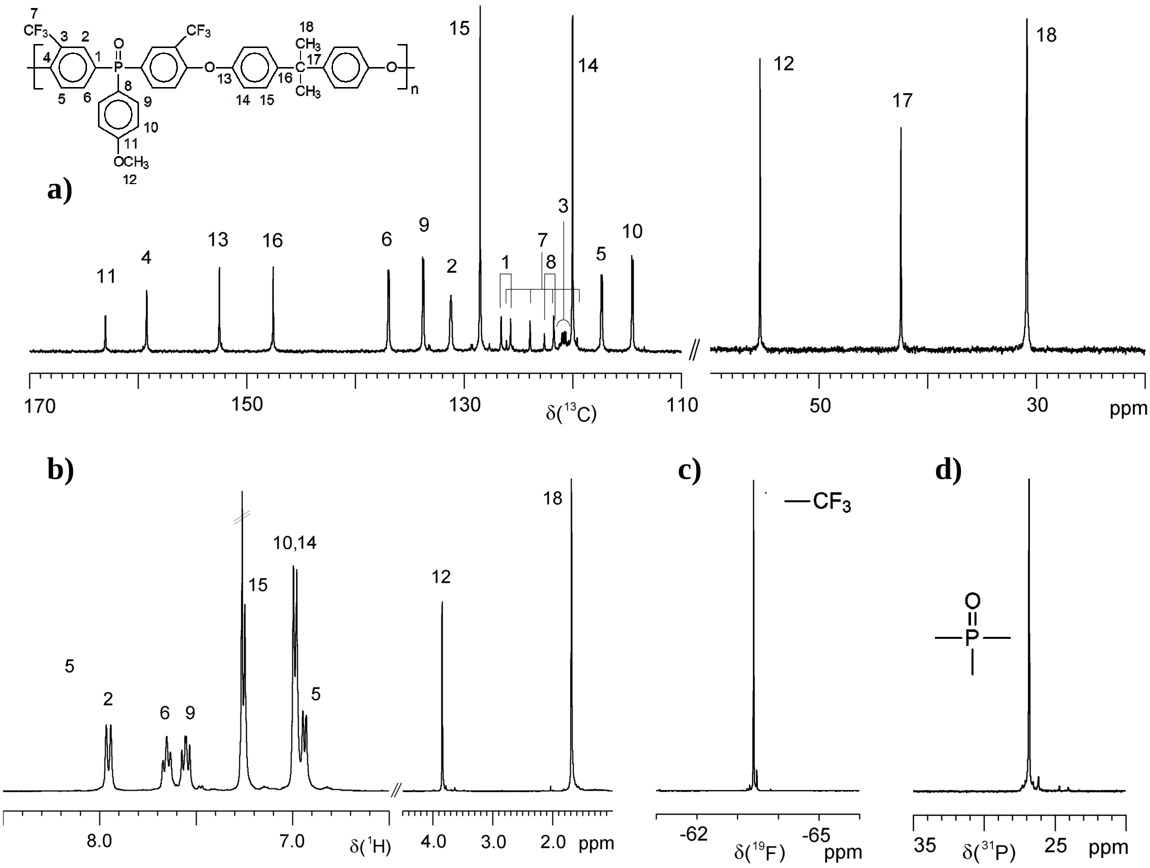


Figure 35: ^{13}C (a), ^{1}H (b), ^{19}F (c), and ^{31}P NMR spectrum (d) of the linear poly(arylene ether phosphine oxide) **P7** (solvent: $CDCl_3$)

The present study focused on the comparison of PAEPOs with bisphenol-A and 4, 4'-dihydroxybiphenyl moieties, respectively, as summarized in Table 2. All the phosphine oxide derivatives were characterized by FTIR and ^{1}H, ^{13}C, ^{19}F and ^{31}P NMR spectroscopy, confirming the desired structures as described in the experimental part. The data from FTIR and NMR spectroscopy supported the formation of the desired structure of the linear poly(arylene ether phosphine oxide)s. The FTIR spectra showed the bands of aryl ether linkages which were generated in the polymer forming reaction in the region of 1140–1055 cm^{-1}, as well as bands in the region of 1254–1152 cm^{-1} corresponding to -CF$_3$ groups [147]. The polymer structures were also characterized by NMR spectroscopy. The detailed signal assignment for all monomers and polymers (P2-P8) are given in the experimental section. Due to the scalar coupling with the phosphorus and fluorine atoms splitting of the ^{1}H and ^{13}C NMR signal occurs. For all polymers except P2, ^{1}H and ^{13}C NMR spectra did not show any signals corresponding to terminal –OH groups whereas the ^{19}F NMR spectra of the polymers show complete conversion of the 4-fluoro groups, suggesting a high degree of overall conversion and formation of high molar mass polymers. In case of P2, the terminal –OH signal remains together with some other signals corresponding to side reactions. Their low content did not allow elucidating the formed by-products. However, these reactions and non-converted educts lowered the molar mass of the final polymer.

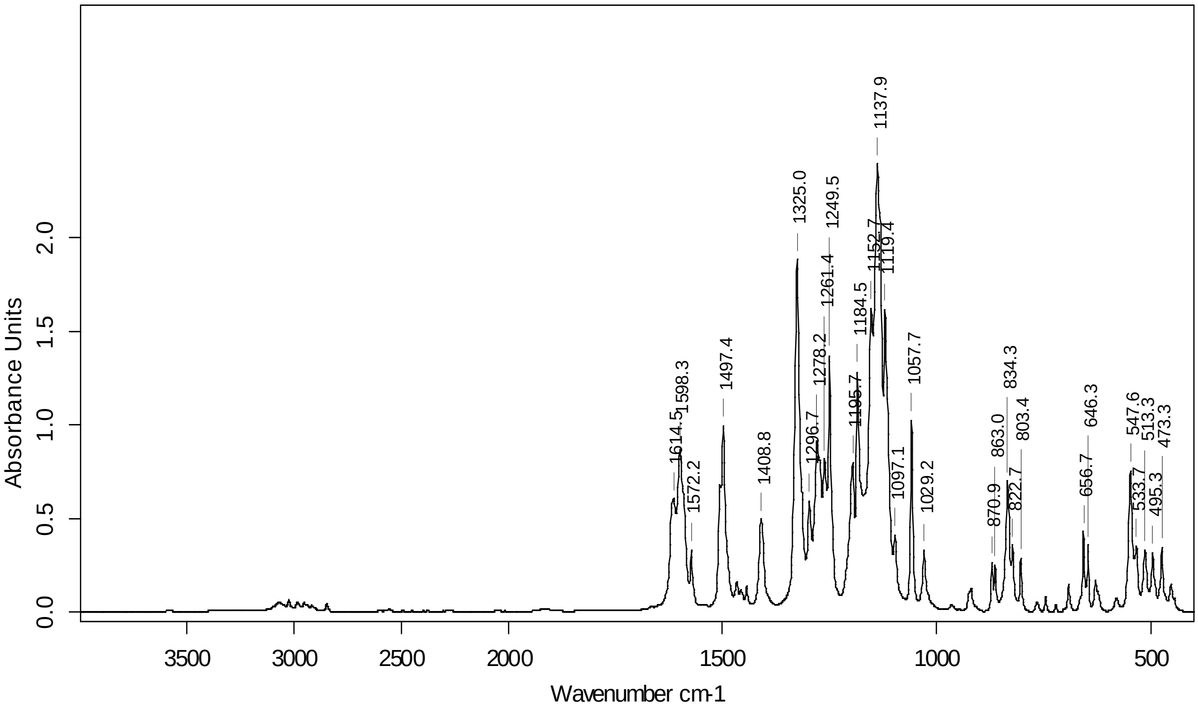
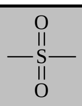
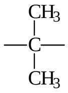
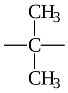
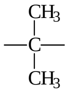


Figure 36: FTIR spectra of **P7** polymer

The ^{1}H and ^{13}C NMR spectra (not depicted; signal assignments are given in the experimental part) are characterized by significant broadening of the polymer backbone signals whereas the non-reacted 4–fluoro-3-trifluoromethylphenyl moieties of the linear and terminal subunits show narrower signals in the ^{13}C NMR spectrum.

Table 2: Chemical structure of the synthesized PAEPOs

Polymer	X	Y	Z
P 2	H	H	 $-\mathrm{SO_2}-$
P 3	H	H	 $-\mathrm{C(CH_3)_2}-$
P 4	H	H	—
P 5	$-CF_3$	H	 $-\mathrm{C(CH_3)_2}-$
P 6	$-CF_3$	H	—
P 7	$-CF_3$	$-OCH_3$	 $-\mathrm{C(CH_3)_2}-$
P 8	$-CF_3$	$-OCH_3$	—

All the synthesized poly(arylene ether phosphine oxide)s exhibited good solubility in common organic solvents such as chloroform, dichloromethane, tetrahydrofuran and in dipolar aprotic solvents like N,N'-dimethylformamide, N-methylpyrrolidone. Interesting differences occurred in case of DMSO and acetone. Surprisingly, polymers P5, P6, P7 and P8 showed excellent solubility in DMSO and acetone. Polymer P3 and P4 did not dissolve in acetone, but showed solubility in DMSO upon heating. It is assumed that the phosphine oxide unit is responsible for the solubility of polymer P2, P3 and P4 in DMSO which makes the difference to previous findings where no phosphine oxide groups were present [58]. Phosphine oxide groups present in the polymers provided increased solubility because of two reasons: first, the phosphine oxide groups cause strong intermolecular forces with solvent molecules and second the tetrahedral geometry of the triaryl phosphine oxide moiety typically increases the solubility characteristics.

Table 3: Solubility chart for all the synthesized PAEPOs

Polymer	NMP	DMF	DMSO	THF	CH_2Cl_2	$CHCl_3$	Acetone
P2 (X=H,Y=H, Z=-SO_2)	+	+	±	+	+	+	_
P3 (X=H,Y=H, Z=-CMe_2)	+	+	±	+	+	+	_
P4 (X=H,Y=H, Z=-$(CH_2)_2$-)	+	+	±	+	+	+	_
P5 (X=CF_3,Y=H, Z=-CMe_2)	+	+	+	+	+	+	+
P6(X=CF_3,Y=H, Z=-$(CH_2)_2$-)	+	+	+	+	+	+	+
P7 (X=CF_3,Y=OCH_3, Z=-CMe_2)	+	+	+	+	+	+	+
P8 (X=CF_3,Y=OCH_3, Z=-$(CH_2)_2$-)	+	+	+	+	+	+	+

'+' = soluble at room temperature; '±' = soluble after heating; *'-' = insoluble at room temperature;*

Molar masses of the synthesized PAEPOs were determined by SEC with MALLS detection (**Table 4**). The molar masses of all polymers except P2 were in the range or higher than the BPA-polysulfone control. The dispersities M_w/M_n were in some cases lower than expected for polycondensation, mutually due to work-up procedure and loss of low molar mass fractions caused by the high solubility of the polymers.

Table 4: Molar masses and film forming behavior of synthesized PAEPOs

Polymer	η_{inh} ^{a} **(dL/g)**	**M_w ^{b} (g/mol)**	**D^c (M_w/M_n)**	**Film Quality**
(PSU Control) (BPA based Polysulfone)	0.41	45000	1.82	Flexible
P2 (X=H,Y=H, Z=-SO_2)	0.08	6100	1.18	Brittle
P3 (X=H,Y=H, Z=-CMe_2)	0.38	59800	3.10	Flexible
P4 (X=H,Y=H, Z=-$(CH_2)_2$-)	0.28	41300	2.83	Flexible
P5 (X=CF_3,Y=H, Z=-CMe_2)	0.35	123600	2.92	Flexible
P6 (X=CF_3,Y=H, Z=-$(CH_2)_2$-)	0.28	40500	1.28	Flexible
P7 (X=CF_3,Y=OCH_3, Z=-CMe_2)	0.80	57100	1.13	Flexible
P8 (X=CF_3,Y=OCH_3, Z=-$(CH_2)_2$-)	0.67	41300	1.30	Flexible

a. *Inherent viscosity of poly(arylene ethers) in DMAc at room temperature; concentration 0.5 %(w/v)*

b. *Weight-averaged molar mass detected by SEC; PolarGel-M column (PL); DMAc + 3g/l LiCl ;Agilent Technologies; Knauer-RI - detector K2301; MiniDAWN -LS - detector from Wyatt Technology; Flow rate 1.0 ml/min.*

c. *Đ; Dispersity M_w/M_n*

4.1.2 Film casting and mechanical properties of the films

From all polymers except P2 free-standing films were casted from dichloromethane to evaluate their mechanical properties. Clear flexible films were obtained, as outlined in **Table 4**. The low molar mass of P2 gave reason to the observed brittle behavior.

Stress-strain experiments were carried out on selected samples to evaluate mechanical properties. The results are presented in **Table 5**. The mechanical properties of PAEPOs containing 4, 4’-oxybiphenylene groups and different phosphine oxide containing moieties in the polymer chain on samples in comparable molar mass range were examined and compared.

Only slight differences in mechanical properties between the polymers were observed which are caused by both, differences in chemical structure as well as slight deviations in film preparation. The data obtained for P8 reproduce the data for this polymer given in [146]. The highest Young's modulus, i.e. stiffness, was found as expected for the non-substituted polymer P4. CF_3-substituents at the flanking phenylene groups slightly improve tensile strength (in P6), but not elongation at break as measure for toughness. The elongation at break is the highest in the non-substituted polymer (P4).

Table 5: Mechanical properties of 4,4'-biphenyl-containing PAEPO films

Polymer	**M_w** (g/mol)	**Tensile strength** (MPa)	**Young's modulus** (GPa)	**Elongation at break** (%)
P4 (X=H,Y=H, Z=-$(CH_2)_2$-)	41300	56.7±0.5	2.44±0.03	31±2.0
P6 (X=CF_3,Y=H, Z=-$(CH_2)_2$-)	40500	63.01±1.0	2.39±0.02	20±1.0
P8 (X=CF_3,Y=OCH_3, Z=-$(CH_2)_2$-)	41300	51.82±1.0	2.13±0.03	15±0.5

4.1.3 Glass transition temperatures of the PAEPOs

The heat flow behavior of the polymers was investigated by DSC. The second heating run was used to calculate T_g in order to avoid influence of thermal history and preparation effects. The DSC curves are shown in **Figure 37**. All PAEPOs did not exhibit melting and crystallization transitions. The curves showed only a clearly distinguishable glass transition.

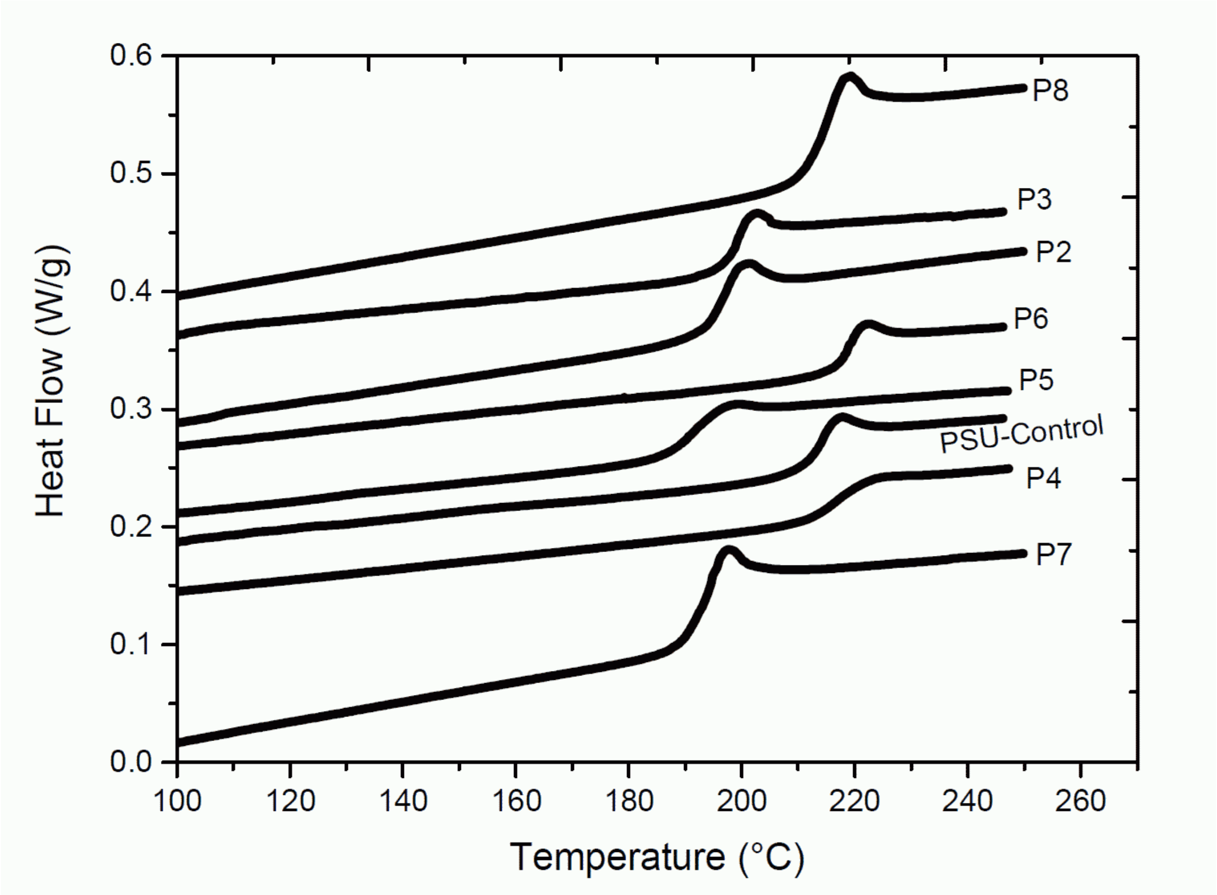


Figure 37: DSC curves (2^{nd} heating) of all PAEPOs under study

The glass transition temperatures of the PAEPOs related to the chemical structure are summarized in **Table 6**. The T_g's of all PAEPOs are higher than those of the BPA-PSU control without P=O units. The glass transition temperatures of BPA-containing PAEPOs with PO units range up to 200 °C while biphenylene-containing PAEPOs show T_g's about 20-30 °C higher (rise from 200 °C to 225 °C). This indicates the higher stiffness of these biphenylene-containing aromatic polyethers (compare P2 vs P4, P5 vs P6 and P7 vs P8) whereas methoxy substituents on the phenylene ring do not have a significant effect on T_g.

Table 6: Glass transition temperature for the differently substituted PAEPOs

Polymer	T_g (°C)	X, Y , Z
PSU-Control	187	isopropylidene, SO_2
P2	195	H,H SO_2
P3	198	H,H isopropylidene
P4	217	H,H biphenyl
P5	190	CF_3,H isopropylidene
P6	218	CF_3,H biphenyl
P7	194	CF_3,OCH_3 isopropylidene
P8	225	CF_3,OCH_3 biphenyl

4.1.4 Thermal stability of the polymers

The thermal stability was investigated by means of TGA. The respective TGA curves are displayed in **Figure 38**. The curves illustrate that the thermal stability in general is very high. The decomposition of all polymers started well above 400 °C (note that early mass losses at about 200 °C were caused by residues of solvents, for instance in sample P4), and in all cases, well above the PSU control. The non-substituted sample P4 showed the highest thermal stability, while the introduction of $–CF_3$ and $-OCH_3$ substituents reduces the onset of decomposition.

The char yields at 750 °C (at a heating rate of 10 K/min) were higher than 25 wt. %, except in samples where $–CH_3$ substituents are introduced (P3, P7, P8). In this case, also additional biphenylene units do not support higher char formation, which can be observed at comparison of the BPA series to the DHDP series (**Figure 39**). The respective biphenylene-containing polymers produced higher char amounts than the comparable BPA analogues (compare P2 vs P4 and P5 vs

P6). An additional raise of char yields was observed after incorporation of $–CF_3$ units (compare P4 vs P6 and P2 vs P5). (**Table 7**)

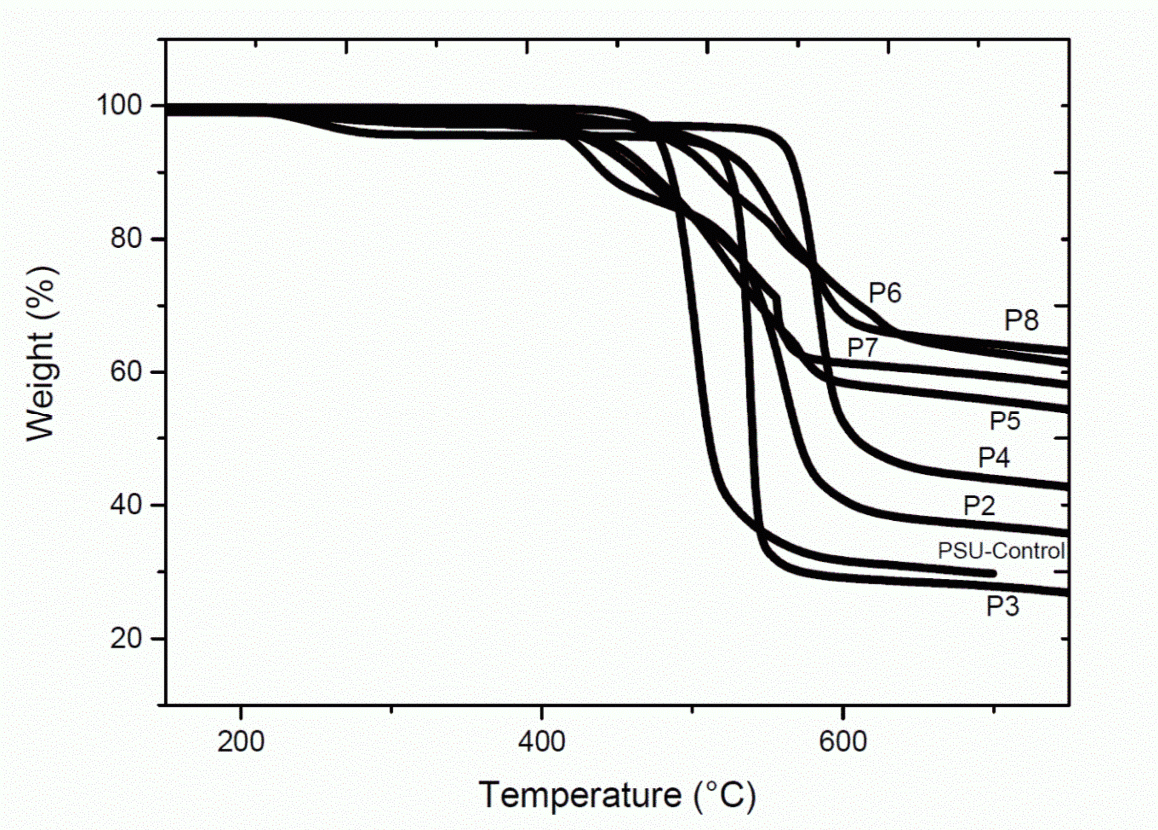


Figure 38: Thermal decomposition of PAEPOs as measured by TGA

Table 7: Thermal stability data for PAEPOs as measured by TGA

Polymer	**P content (wt. %)**	**$T_{d,5\%}$ (°C)**	**$T_{d,10\%}$ (°C)**	**Char residue (wt. %)**
(PSU Control) (BPA based Polysulfone)	0.00	470	493	29.5
P2 (X=H,Y=H, Z=$-SO_2$)	5.91	425	445	34.16
P3 (X=H,Y=H, Z=$-CMe_2$)	6.17	525	532	25.7
P4 (X=H,Y=H, Z=$-(CH_2)_2-$)	6.73	566	575	41.4
P5 (X=CF_3,Y=H, Z=$-CMe_2$)	4.85	470	495	53.1

P6 (X=CF_3,Y=H, Z=-$(CH_2)_2$-)	5.20	510	536	59.9
P7 (X=CF_3,Y=OCH_3, Z=-CMe_2)	4.64	435	470	56.6
P8 (X=CF_3,Y=OCH_3, Z=-$(CH_2)_2$-)	4.95	497	520	62.0

It can be noted that a clear influence of the chemical structure on both onset of decomposition as well as char yield was recognized. Additional factors contributing to the char yield are aromatic content, presence of –CF_3 groups as well as total phosphorus content.

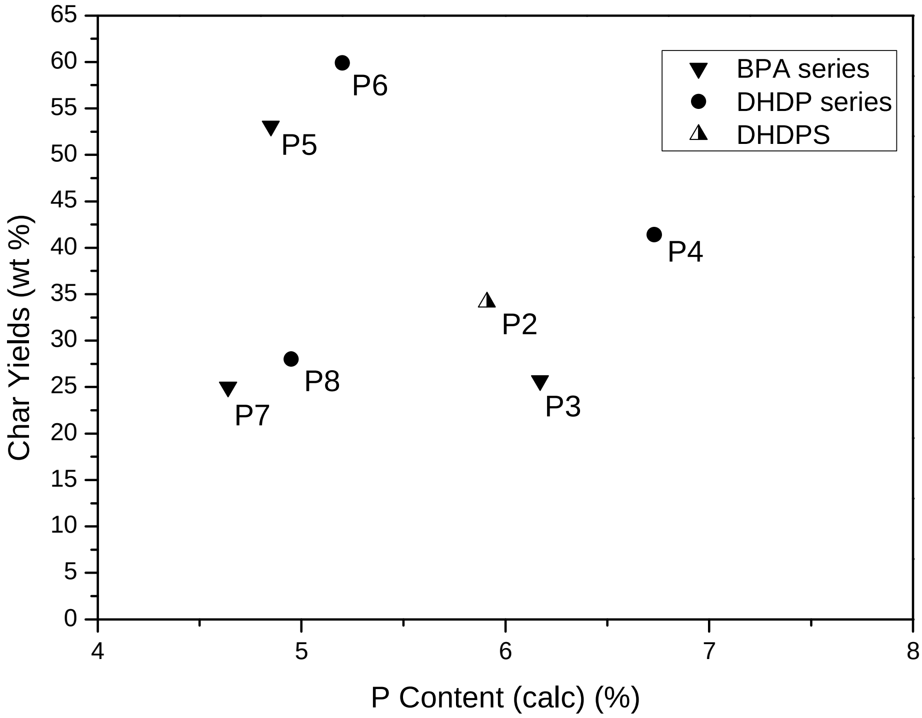


Figure 39: TGA char yields in PAEPOs plotted versus P content

4.1.5 Decomposition of PAEPOs studied by TGA coupled with FTIR

Isothermal TGA was performed at the decomposition steps determined by TGA for each polymer and the structure of the gases evolved there were analyzed by TGA-FTIR coupling. From the FTIR spectra of the gases evolved at the first decomposition step (**Figure 40**), characteristic bands for phosphorus aryl ethers (1506, 1228, 837, 719 cm^{-1}) together with characteristic bands for carbon dioxide (2300-2400, 669 cm^{-1}) were observed in the spectrum. Biphenyl structures further decomposed to phenol or p-cresol (3592, 3010, 1499, 1235, 1170, 835 cm^{-1}). Several other bands characteristic for monosubstituted benzenes could not be identified unambiguously due to superimposition with other bands. Formation of phosphorus-containing combustion products was also observed during the first decomposition step. The bands at 3050, 1455, 1256, 930, 730, 693 cm^{-1} indicated mono-substituted phenyl rings linked to a phosphoryl group which was the only indication that the diphenyl phosphine oxide group was cleaved from the rest of the polymer backbone.

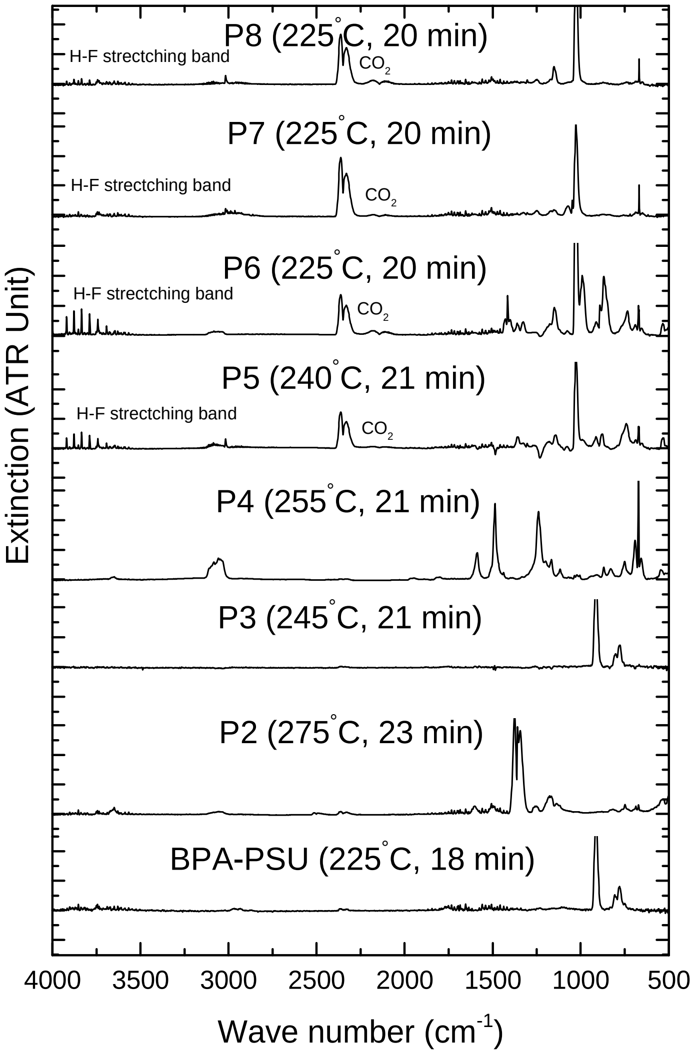


Figure 40: TGA-FTIR spectra of the gases evolved at the first decomposition step

Characteristic FTIR spectra of the gases evolved at the main decomposition step of the polymers under study are illustrated in **Figure 41**. For the PSU control (BPA-PSU) and P2, characteristic bands of SO_2 between 1375 and 1340 cm^{-1} were monitored. For P1, P3 and P5, bands were observed between 3155-2850 cm^{-1} with the characteristic C-H stretching bands of methane at 3015 cm^{-1}.

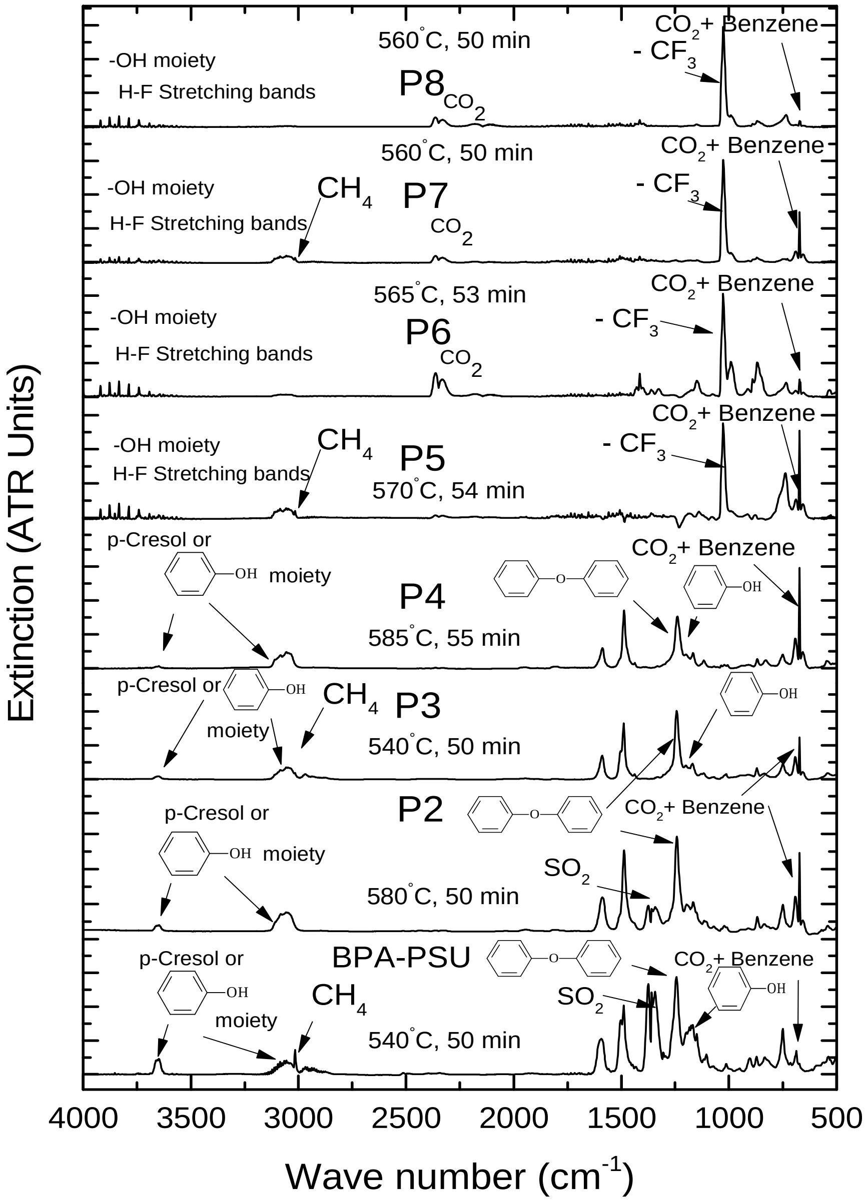


Figure 41: TGA-FTIR spectra of gases evolved at the main decomposition step

Diphenylene ether with a characteristic vibration at 1242 cm^{-1} and characteristic –OH stretching bands of phenol at 3644 and 1183 cm^{-1} were identified keeping in mind that the characteristic –OH stretching bands can originate from phenol, isopropylidene substituted phenols or bisphenol A, respectively. The formation of hydroxyl-substituted aromatics (3650 cm^{-1}) was also observed. However, the –OH stretching band at 1183 cm^{-1} was only weak. Thus, it can be stated that phenol or substituted phenols did not constitute the main decomposition products. The bands at 2300 and 662 cm^{-1} were attributed to CO_2. Determination of the intensities of both bands showed that the band at 662 cm^{-1} peak had a larger intensity than the band at 2300 cm^{-1}. It was concluded that the additional contribution is due to benzene. Phosphorus-related pyrolysis products are reflected by lower intense bands of aryl phosphoryl compounds.

From the data obtained from both TGA and TGA-FTIR, a proposal for the decomposition schemes was drawn. **Figure 42** illustrates the decomposition pathway for P3.

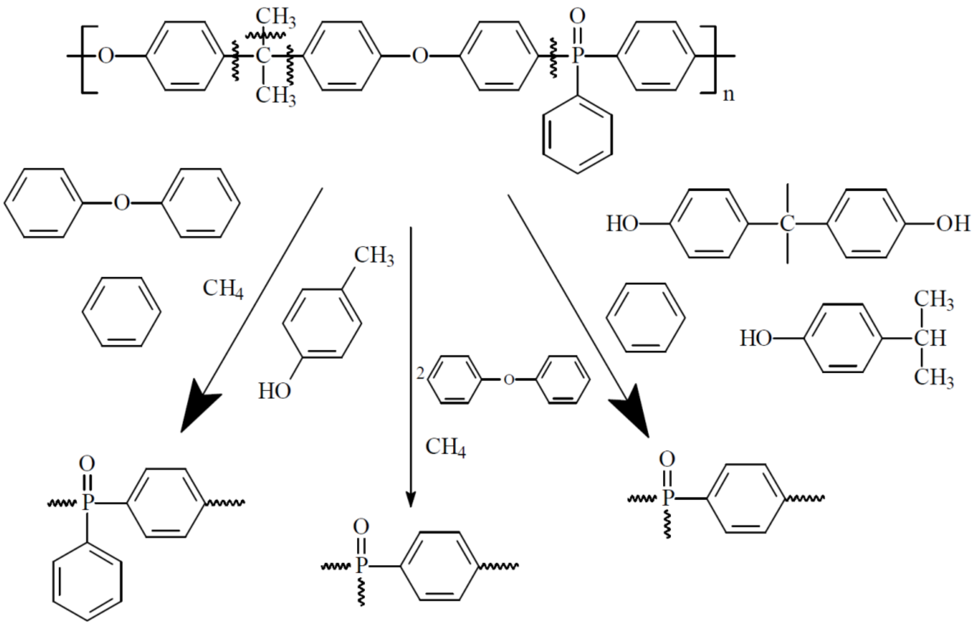


Figure 42: Probable decomposition schemes of P3 polymer

P3 polymer decomposed through different and overlapping processes. The evolved gas analysis too supported this conclusion. The diphenylene ether and benzene detected are caused by scission of phosphorus-aryl and carbon-aryl bonds, respectively. Their formation yields a theoretical mass loss of 59 wt.-%, whereas the formation of two diphenylene ethers results in a theoretical mass loss of 76 wt.-%. That mass loss was quite close to the experimental value of 75%. FTIR spectra of the char showed the presence of phosphorus in the form of phosphine oxide. Considering the experimental mass loss and the FTIR spectrum of the char residue at different temperatures into account several decomposition possibilities can be proposed (**Figure 42**). So from the thermal analysis it was understandable that all materials were char forming and phosphorus mainly locked in the residue.

4.1.6 Combustion behaviour of the PAEPOs

The combustion behaviour of the poly(arylene ether)s was studied by pyrolysis combustion flow calorimetry (PCFC). The PCFC methodology combines constant heating rate and flow characteristics of thermal analysis methods such as thermogravimetry (TGA) with the capability to determine a heat of combustion typical of oxygen bomb calorimetry. Note that the heating rates in TGA and PCFC normally used are different (TGA: 10 K/min; PCFC: 60 K/min). The PCFC method determines the heat release and heat release rate using the oxygen consumption methods, thus yielding values corresponding to a fire calorimeter rather than to thermal analysis [198] [199]. Important parameters determined are total heat released per unit initial mass (HR), the heat release capacity (HRC), specific heat release rate (HRR) and the temperature at the maximum of heat release rate (T_{max}). Of these four parameters, HRC has been proposed as the best single measure of the fire hazard of a material on small scale.

The curves obtained in the PCFC measurements of the PAEPOs are given in **Figure 43**, the data are summarized in **Table 8**. It should be noted that the polymers containing substituted phenylene rings generally show a multistep combustion (P5-P8) with a second main combustion close to 600 °C, indicating a secondary combustion of the char formed in the first step. For multiple decomposition the actual HRC is reported by a peak summation method [199] [200], whereby the separated peaks are added together, i.e. $HRC = HRC_1 + HRC_2 + \ldots\ldots\ldots$

The pHRR of the PSU control was already low compared to other polymers due to the presence of aromatic rings and SO_2 [198]. Adding to these structure TPPO units by replacement of the phenylene unit leads to a further reduction of pHRR in P2. Exchange of the diphenyl sulfone unit by either BPA or biphenylene surprisingly enhances both, pHRR as well as HRC drastically to very high values. In contrast, polymers P5, P6, P7 and P8 show very low pHRR values which can be assigned to both, incorporation of phosphorus as well as to a great extent to incorporation of $-CF_3$ units.

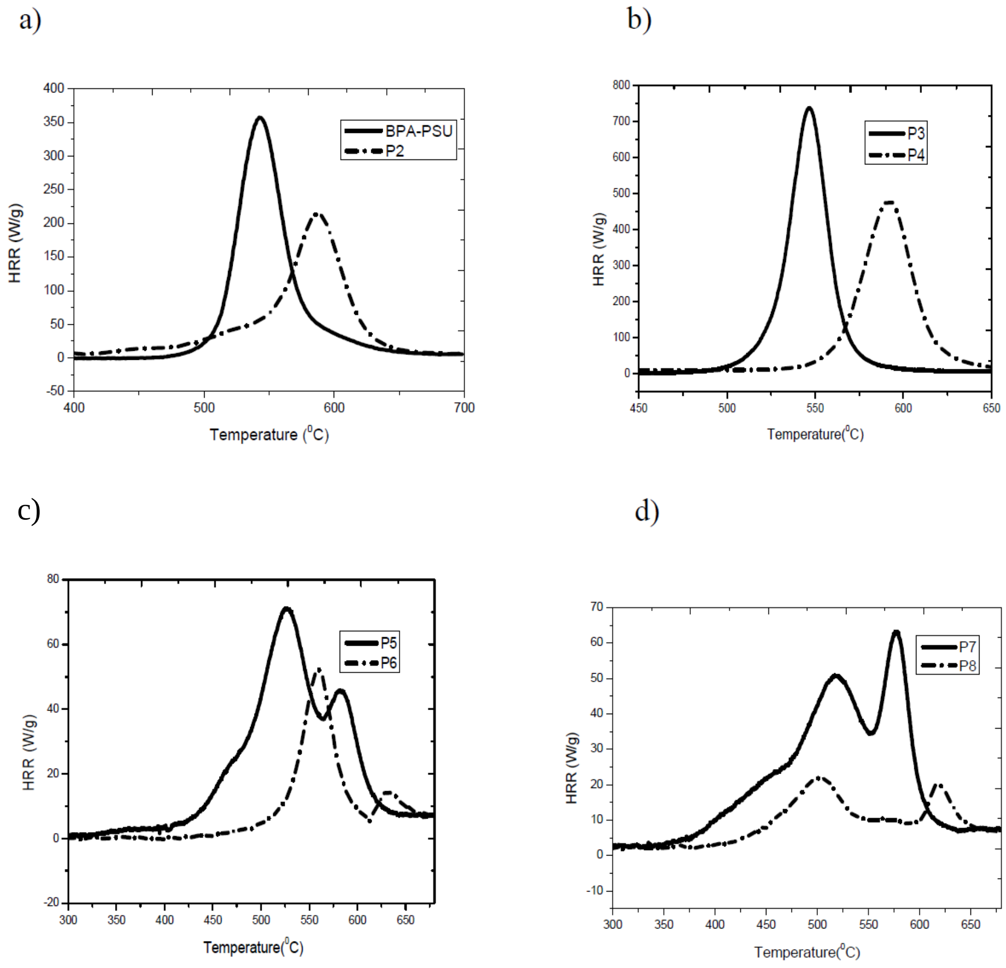


Figure 43: Heat release rate curves obtained by PCFC for a) BPA-PSU control and P2; b) for P3 and P4; c) for P5 and P6; d) for P7 and P8

These low pHRR values mean that the polymer releases less combustionable gas than the other polymers, indicating the flame retarding effect of halogens as expected.

THR calculated from the total area under the HRR peaks is also an important parameter for evaluation of fire hazards. Comparing all THR values, it is indicated that the combustion behaviour is strongly influenced by both halogen and phosphorus.

Table 8: PCFC data for PAEPOs

Polymer	**T_{max}(^{o}C)**	**pHRR** **(J g^{-1} s^{-1})**	**THR** **(kJ g^{-1})**	**HRC** **(J g^{-1} K^{-1})**	**Char residue** **(wt.-%)**
(PSU Control) (BPA based Polysulfone)	544	372	16.30	367	31.34
P2 (X=H,Y=H, Z=-SO_2)	589	214	12.7	238	43.15
P3 (X=H,Y=H, Z=-CMe_2)	544	734	20.90	737	31.61
P4 (X=H,Y=H, Z=-$(CH_2)_2$-)	589	481	17.00	474	43.12
P5 (X=CF_3,Y=H, Z=-CMe_2)	526, 581	71	6.20	101(53+48)	53.87
P6 (X=CF_3,Y=H, Z=-$(CH_2)_2$-)	562, 634	52	2.40	59(45+14)	60.00
P7 (X=CF_3,Y=OCH_3, Z=-CMe_2)	520, 570	63	3.50	79(34+45)	56.27
P8 (X=CF_3,Y=OCH_3, Z=-$(CH_2)_2$-)	498, 610	23	1.80	32(17+15)	65.01

The proportion of phosphorus and fluorine in the polymer chain is regarded as the most important factor for improving the flame retardancy of the polymer. This is illustrated by **Figure 44**. **Table 9** summarizes the calculations of the heat of combustion of the pyrolysis gases [199] [200], which show that the heat of combustion of the volatiles decreases by a factor of 2-5 when –CF_3 is a substituent on the phosphine oxide containing polymer.

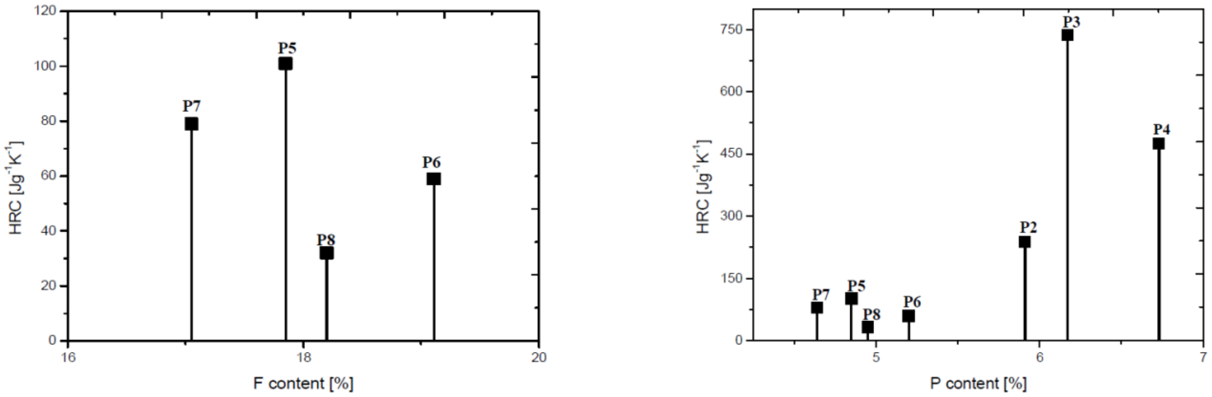


Figure 44: Influence of fluorine and phosphorus content on HRC

Table 9 shows that the THRdecreases dramatically when –CF_3 was a substituent on the phosphine oxide unit, i.e., P5-P8. It was illustrative to compute the heat of combustion of the pyrolysis gases to see whether the chemical composition of these gases were changing with the chemical structure of the polymer.

$$H_{c,gas} = {}^{THR}/_{1-\mu} \tag{3}$$

where μ is the char yield.

The table below summarizes these calculations, which show that the heat of combustion of the volatiles decreases by a factor of 2-5 when –CF_3 is a substituent on the PO. Good results were expected for all of the phosphine oxide polymers in tests of flaming combustion (e.g., UL 94, LOI, etc.)

Table 9: Heat of combustion values of the pyrolysis gases

Polymer	**THR (kJ/g-sample)**	**Char Yield, μ (g/g-sample)**	**$H_{c,gas}$ (kJ/g-volatile)**
(PSU Control) (BPA based Polysulfone)	16.3	0.31	23.7
P2 (X=H,Y=H, Z=-SO_2)	12.7	0.43	22.3

P3 (X=H,Y=H, Z=-CMe_2)	20.9	0.32	30.6
P4 (X=H,Y=H, Z=-$(CH_2)_2$-)	17.0	0.43	29.9
P5 (X=CF_3,Y=H, Z=-CMe_2)	6.20	0.54	13.4
P6 (X=CF_3,Y=H, Z=-$(CH_2)_2$-)	2.40	0.60	6.0
P7 (X=CF_3,Y=OCH_3, Z=-CMe_2)	3.50	0.56	8.0
P8 (X=CF_3,Y=OCH_3, Z=-$(CH_2)_2$-)	1.80	0.65	5.1

4.1.7 LOI measurement of the PAEPO

LOI measusurements were carried out for polymer P3 which could not be afforded for all the polymers because synthesis of large amount of the necessary monomers was not possible under the limited lab conditions. P3 polymer which shows surprisingly high pHRR and HRC values exhibit flame reatardancy in the LOI test. LOI value of polymer P3 having phosphine oxide in main chain came in direct comparison with some of previous works where phosphorus is in the side chain [144] [145].

Table 10: LOI of PSU and PAEPO (P3)

Polymer	P %	LOI
(PSU Control) (BPA based Polysulfone)	6.17	33.2
P3(X=H,Y=H, Z=-CMe_2)	6.17	33.2

4.2 Synthesis of higher phosphorus containing poly(arylene ether phosphine oxides)

The second segment of research was about synthesizing higher phosphorus (increasing phosphorus content in each polymer repeating unit) containing poly(arylene ether phosphine oxide) and application of several synthesized PAEPO's as intumescence flame retardant (IFR) additive in epoxy resin composite.

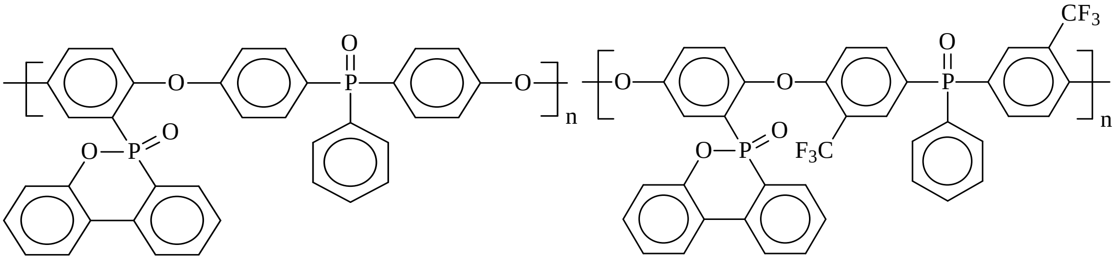


Figure 45: Newly synthesized higher phosphorus containing PAEPO's

Higher phosphorus containing poly(arylene ether phosphine oxides) were synthesized following the same aromatic nucleophilic substitution reaction mechanism. To increase the phosphorus content of the polymer repeating unit bis(4-fluorophenyl) phenylphosphine oxide monomer was undergone polycondensation reaction with 10-(2, 5-Dihydroxypheny), 10-H-9-Oxa-10-Phosphaphenanthrenelo-oxide (DOPO-HQ). From the reaction mixture the polymer was precipitated in a 1:1 mixture of methanol and distilled water.

Table 11: Polymerization recipe of the synthesized polymers P9 and P10

Polymer	Diol (mole) (g)	Bisfluoro (mole) (g)	NMP (ml)	Toluene (ml)	K_2CO_3 (g)
P9	0.002004 0.650	0.002004 0.902	16.1	32.1	0.833
P10	0.00251 0.815	0.00251 0.789	15.5	31.1	0.664

Table 11 represents batch polymerization recipe (monomers, base and the solvent used) for synthesizing higher phosphorus containing PAEPOs. The polymerization at the lab scale performed under comparable condition, yielded higher phosphorus containing polymers with number average molar masses of 48900 and 83100 g/mol. The resulting polymer products were brittle at room temperature. The synthesis results obtained are summarized in **Table 12**.

Table 12: Physical properties of the polymers P9 and P10

Polymer	**P Content Mass (%)**	**M_n**	**PDI**	**Film quality**	**T_g (°C)**
P9	8.43	48900	1.38	Brittle	175
P10	10.35	83100	1.93	Brittle	174

Before we started describing characterization results of DOPO-HQ containing polymers it is necessary to show the reversibility of the DOPO-HQ structure in reaction medium.

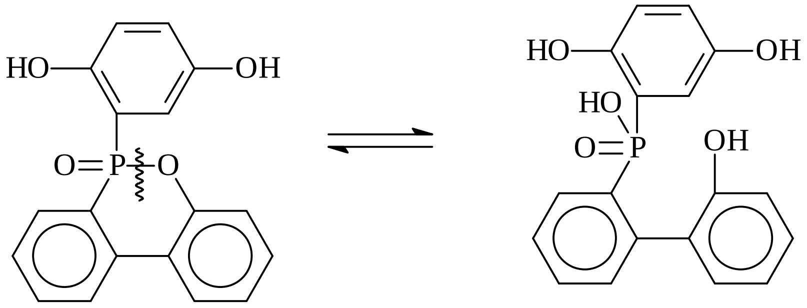


Figure 46: Reversibility of the DOPO-HQ structure

Due to the complexity of the DOPO-HQ structure it was very difficult to characterize the polymer structure using ^1H NMR. In DOPO structure the weakest linkage is the P-O linkage. In presence of mild base this linkage is getting broken and in the solution closed and open structures are present at the same time. This is one of the reasons for getting complicated ^1H NMR structure. MALDI-TOF was used to further clarify the chemical structure of the polymers.

The samples were purified before analysis by re-precipitation from chloroform to methanol to remove any impurities. Below in **Figure 47** illustrate the results obtained with polymers P10 and **Figure 48** illustrate polymer P10. It should be noted that the spectra contain only information about the polymeric structure of the samples with lower molar masses between 1200 to 5000 Da. The periodicity in these distributions (as marked in the figure) corresponding to the mass of the repeating units is the same. This fact proves the formation of the desired phosphorus polymer.

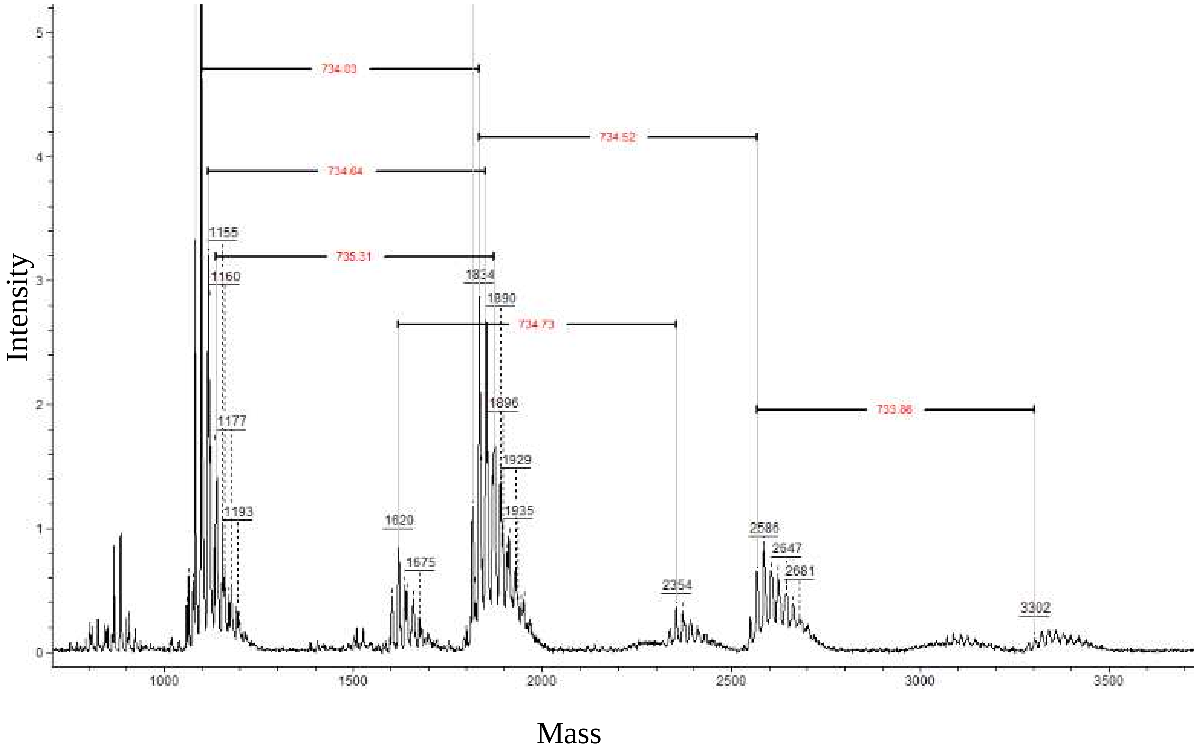


Figure 47: MALDI-TOF spectra of polymer P10

For the sample preparation, the polymer P 10 was mixed with 2-(4-hydroxy-phenylazo) benzoic acid (HABA) as matrices dissolved in THF. In the mass spectrum of P 10 different major and minor distributions were shown. All of them showed the average peak-to-peak distance of 734-735 Da. However, that was in a good agreement with the molar mass of the monomer repeat unit of 734.52 gmol^{-1}. That means there were different combinations of end groups with or without salt.

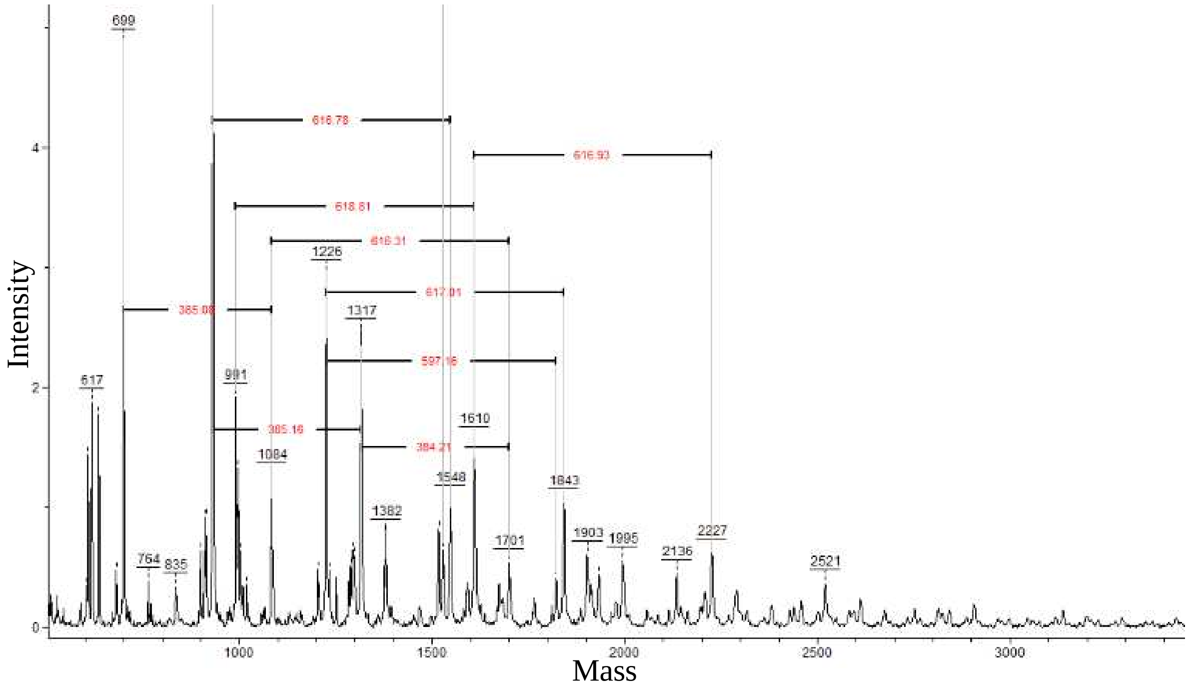


Figure 48: MALDI-TOF spectra of polymer P9

For the sample preparation, the polymer P9 was mixed with dithranol as matrices dissolved in THF. In case of P9 different peak-to-peak distances e.g. of 617 Da, 597 Da, 385 Da was found. The expected monomer repeating unit amounts 598.52 gmol^{-1}.

4.3 Preparation of EP-PAEPO composite

In the present study PSU control (P1/ BPA based polysulfone) with four different PAEPO's and their corresponding blends with an EP were investigated.

- Epoxy resin – C (EPC) + Bis (4-aminophenyl) sulfone (DDS) + Polymer **P1** (10 wt %)
- Epoxy resin – C (EPC) + Bis (4-aminophenyl) sulfone (DDS) + Polymer **P2** (10 wt %)
- Epoxy resin – C (EPC) + Bis (4-aminophenyl) sulfone (DDS) + Polymer **P3** (10 wt %)
- Epoxy resin – C (EPC) + Bis (4-aminophenyl) sulfone (DDS) + Polymer **P4** (10 wt %)
- Epoxy resin – C (EPC) + Bis (4-aminophenyl) sulfone (DDS) + Polymer **P9** (10 wt %)

All epoxy formulations with 10 wt% of PAEPO's in the final product were prepared according to the following identical experimental procedure. DGEBA (epoxy equivalent weight 173 g eq^{-1}, Solvay, Spain) was placed in a glass flask and heated to 130^{0}C in an oil bath connected to a temperature controller. Desired amount of the respective PAEPO's (10 wt % of P1, P2, P3, P4 and P9) was then added slowly into the EP and mixed thoroughly using a mechanical stirrer until the mixture became completely homogeneous. Keeping the temperature fixed at around 130°C the anionic hardener (4, 4'-DDS, eq. weight of 62 g eq^{-1}, synthesis grade, Sigma Aldrich, Germany) was added into the mixture in a substoichiometric ratio (DGEBA/DDS, 1: 0.4). After mixing, the hot mixture was poured into preheated aluminum mold at 433K and placed in a vacuum oven for 1 hr for degassing. The EP system was then cured following a curing cycle. Curing cycle started from room temperature to 453K with a fixed temperature rising rate (2K min^{-1}). This temperature was maintained for 2 h and curing was completed with the same temperature reduction rate from 453K to room temperature. For easy release of the cured EP, the mold surface was coated with a thin layer of Frecote-700 NC. Thus 100mm × 100mm × 3-4 mm EP composite sheet was obtained and was subsequently machine cut to the desired specimen size for further testing. One control sample of DGEBA/ DDS without PAEPO's (same specimen size) was prepared following an identical procedure.

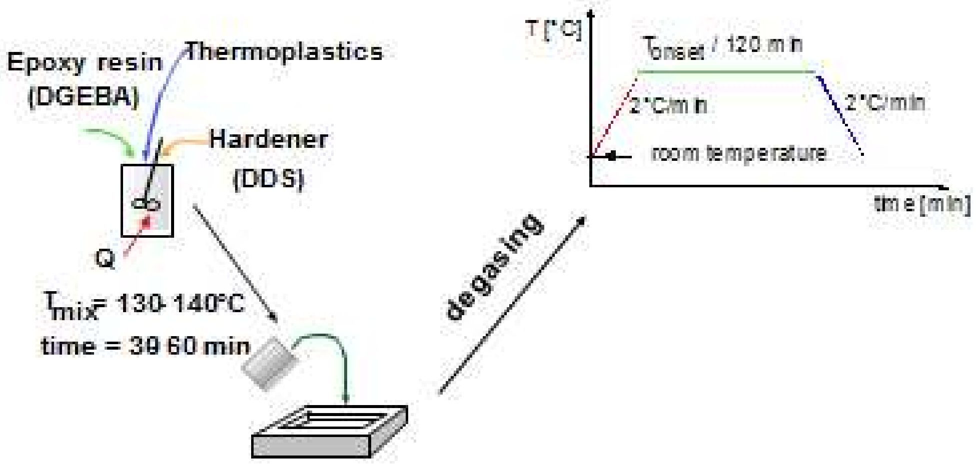


Figure 49: Epoxy-PAEPO composite preparation technique

4.3.1 Fire behavior

Figure 50 illustrates the combustion behavior as obtained with the cone calorimeter test on the epoxy composites. **Table 13** summarizes the most important results. This experiment was done in collaboration with IMDEA Materials, Getafe, Spain. After ignition the investigated material burns homogeneously with a stable flame zone above the surface. The combustion process of all the materials was reflected in the strong peak of HRR and a subsequent shoulder in the HRR. The HRR did not return to zero after flame-out, due to the after glowing of the samples. Upon addition of 10 wt % of PAEPO's (P1, P2, P3, P4 and P9) the change in the characteristic value of pHRR and EHC was thoroughly investigated.

Table 13: Averaged cone calorimeter and UL-94 test data

Sample	**pHRR (kW/m^2)**	**Mean EHC (MJ/kg)**	**T_d (°C)**	**LOI**	**UL-94 Test**
(EPC-DDS) **Reference**	**1080**	**22.0**	**385**	**22.0**	**-**
(EPC-DDS-P1 (10 wt %)) **MEPC-P1**	**849**	**21.8**	**387**	**29.2**	**-**
(EPC-DDS-P2 (10 wt %)) **MEPC-P2**	**674**	**20.2**	**395**	**30.0**	**-**
(EPC-DDS-P3 (10 wt %)) **MEPC-P3**	**641**	**20.6**	**377**	**29.8**	**-**
(EPC-DDS-P4 (10 wt %)) **MEPC-P4**	**884**	**22.3**	**393**	**29.8**	**-**
(EPC-DDS-P9 (10 wt %)) **MEPC-P9**	**685**	**19.2**	**377**	**32.5**	**V-0**

For analysis of the combustion behavior only the combustion process was considered; hence all the characteristic data are based on the main combustion process (after glowing was not taken into account). The peak of HRR of EPC-P1 and EPC-P4 was reduced about 20 % compared to the reference. In case of EPC-P2, EPC-P3 and EPC-P9 the reduction of peak of HRR were about 40 %. EPC-P2, EPC-P3 and EPC-P9 showed a clearly enhanced char formation resulting in an improved fire behavior, as it was intended by the chemical variation of the intumescent flame retardant (IFR) additive or PAEPO's back bone.

We can't ignore the fact, that the loading of intumescent flame retardant additives (P1, P2, P3, P4 and P9) was only 10 wt% for all the systems under study.

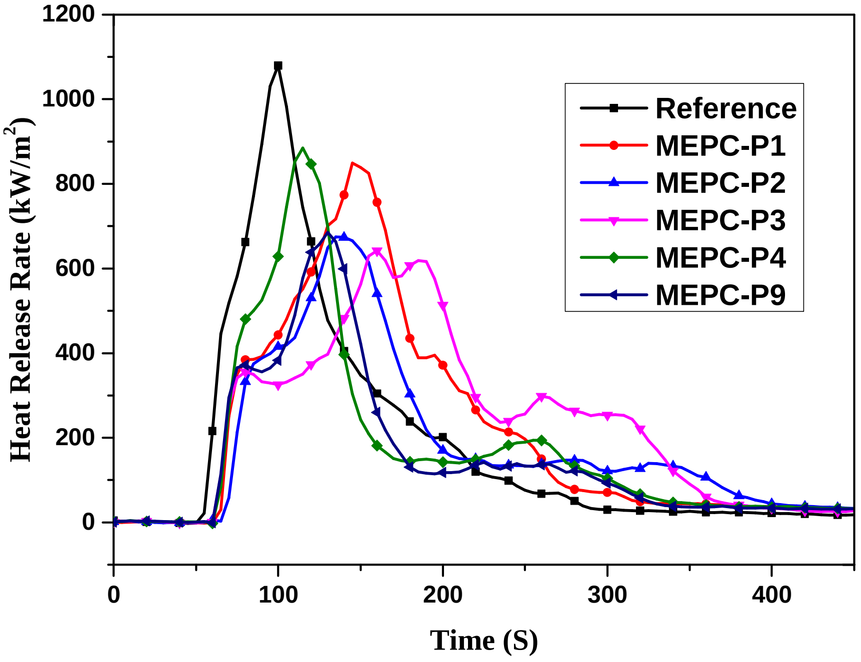


Figure 50: HRR plots of all epoxy composites including reference

The effective heat of combustion in the cone calorimeter (THE/TML) was hardly reduced for the EPC-P1 system compared to reference EPC. That revealed that 10 wt % of P1 (synthesized PSU) did not significantly change the combustion process. No significant fuel dilution occurred due to the increased sulfur content in this material. But when 10 wt% (additive loading) of P2 or P3 or P9 was added to the EPC, the effective heat of combustion was significantly reduced by 8-13 %.

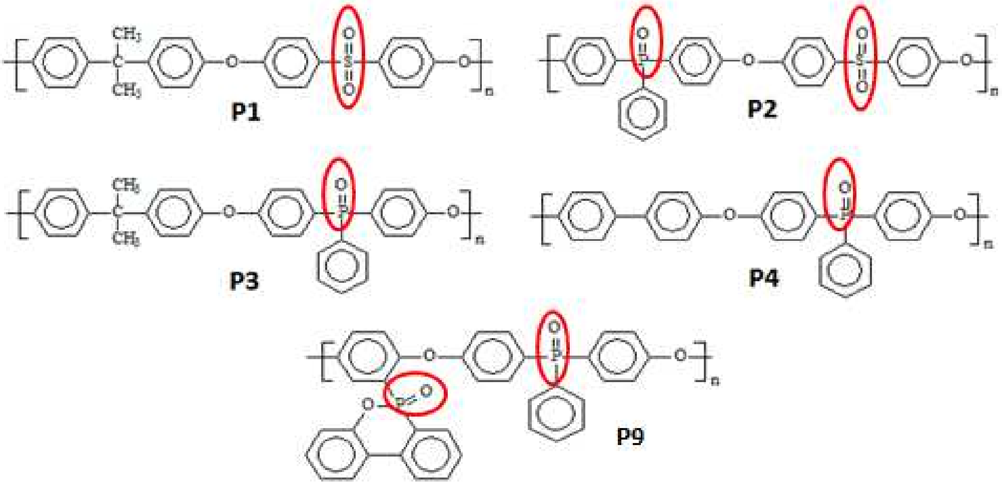


Figure 51: Groups, responsible for the reduction of pHRR and EHC

In case of P2 the reduction was due to the corresponding fuel dilution. Not only sulfur but phosphine oxide moiety in the polymer backbone can be hold responsible. The moderate reduction was caused by flame inhibition and increased charring. In spite of having phosphine oxide in the polymer backbone P4 proved to be less effective intumescence flame retardant additive compared to others but the reason behind that was not well understood. In the whole set of IFR additive P9 was proved to be the most effective one. Higher phosphorus content compared to the other PAEPO's leaded towards flame inhibition and further increased charring. P9 containing EPC composite showed V-0 rating in UL-94 test.

4.3.2 Decomposition of blends with EP:

The decomposition behavior of epoxy resin composites was described as determined by means of thermogravimetry (**Figure 52** & **Table 13**). For the reference DGEBA-DDS EP the main mass loss of around 87 % was found between 385 and 450 $^{\circ}$C at a heating rate of 10 K min^{-1}. The maximum mass loss was observed at 420 $^{\circ}$C. This factor fully depends on the DGEBA: DDS ratio resulting the crosslink density. The lower value of the temperature of maximum mass loss was due to DGEBA rich network with lower cross link density and due to the chemical structure.

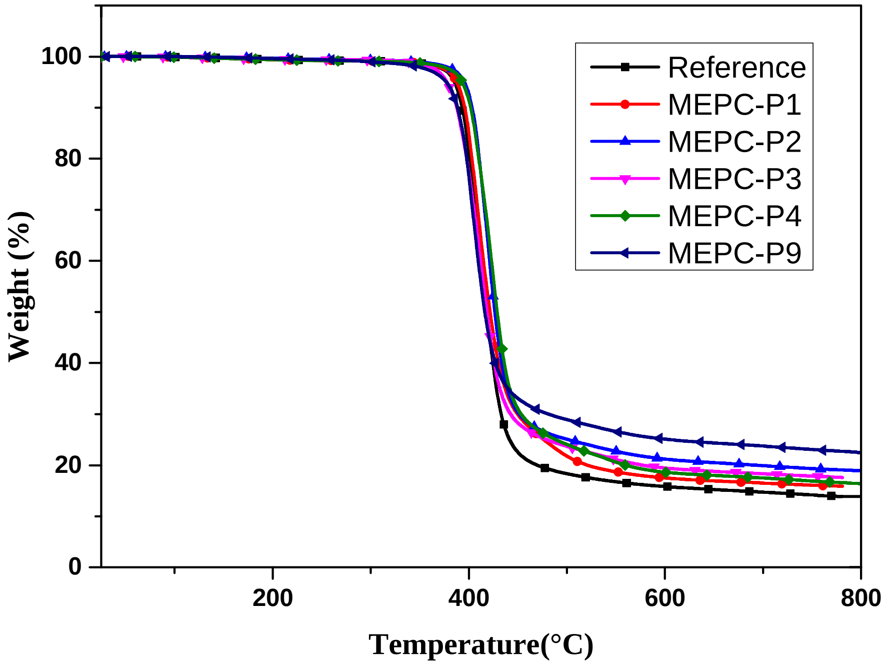


Figure 52: TGA analysis of all the epoxy composites

When intumescence flame retardants (PAEPOs i.e. P1, P2, P3, P4, and P9) were added into the reference system, different decompositions were identified. Main mass losses of around 72-77 % were found between 377 and 465°C. With loading of only 10 wt% of IFR's (i.e. P1, P2, P3, P4, and P9 respectively) decomposition temperature as well as the amount of char varies. The reason for this behavior is that different chemical backbones with different kinetically and thermodynamically controlled processes are competing with each other. Polymer P2 (having sulfur and phosphorus both in the polymer backbone) was proved to be the best among all five polymers. In spite of giving the best flame retardant composite polymer P9 decomposed a little bit early as compared to the reference.

4.3.3 Dynamic mechanical analysis:

Besides the flame retardancy of the polymers, the overall mechanical performance also plays an important role with respect to the material application. One important application of DMA is the measurement of the glass transition temperature of polymers. Above glass transition temperature, stiffness of the material drops dramatically with an increase in viscosity. At the glass transition, the storage modulus decreases dramatically and the loss modulus reaches maximum. Additive P1, P3, P4 were flexible polymers but the other two (P2 and P9) were brittle in nature. But P2 and P9 additives were proved to be better flame retardant. Addition of higher amount of IFR (higher loading) can increase the flame retardancy but at the same time can decrease the material properties if the IFR itself is brittle in nature. That's why it was necessary to keep balance between them. From DMA measurement the change in glass transition temperature (T_g) compared to the reference can be identified. In every case with 10 wt% additive loading, improvements in T_g (25-28 $^{\circ}$C) were observed. The results were a real proof of improvement of material properties using proper IFR additive.

Table 14: DMA data of EPC and its composites

Sample	Storage modulus (MPa)	T_g (°C)	Loss modulus (MPa)
EPC	**2185.5**	**185.2**	**173.4**
MEPC-P1	**1941.2**	**212.4**	**203.7**
MEPC-P2	**1912.4**	**213.0**	**204.3**
MEPC-P3	**2235.0**	**211.0**	**201.6**
MEPC-P4	**2204.0**	**210.2**	**204.8**
MEPC-P9	**1939.2**	**212.5`**	**201.2**

4.4 Phosphorus chemistry

Phosphorus forms many types of compounds, viz. trivalent (lone pair present, pyramidal), tetravalent (sp^3, tetrahedral), pentavalent (sp^3d, trigonal bipyramidal) and hexavalent (sp^3d^2, octahedral) compounds.

As discussed earlier, in the case of phosphorus from 3s level to 3d level promotional energy is small enough to allow the vacant d orbitals to participate in chemical bonding. The ready availability of 3d atomic orbitals of phosphorus accounts for its different chemical nature. Higher energy d-orbitals contribute to reduce electronegativity and greater polarizability of phosphorus compared to other group elements. In general phosphorus compounds prefer to react by pair mechanisms, using the nucleophilic reactivity of the lone pair electrons in the case of trivalent compounds and the electrophilicity of the phosphorus atom in pentavalent derivatives. As nucleophilic reagents, trivalent phosphorus compounds can rapidly react with both electron deficient centers and also with electronically saturated carbon centers.

4.4.1 Synthesis of the monomer bis(4-fluorophenyl) phenylphosphine

Normally trivalent phosphorus is very unstable towards air, moisture and any kind of acid-base reaction medium. Trivalent phosphorus containing monomer was synthesized using Grignard reaction from dichlorophenyl phosphine and 4-bromo fluorobenzene. The product could not be obtained from the expected work up procedure. That was the reason when a new technique of synthesizing monomer from Grignard reaction was adopted. The product was collected from the quenched reaction mixture, using a small filtration technique using PTFE membrane filter. The solvents were removed via rotary evaporation followed by vacuum. An amber colored, highly viscous oily liquid was obtained.

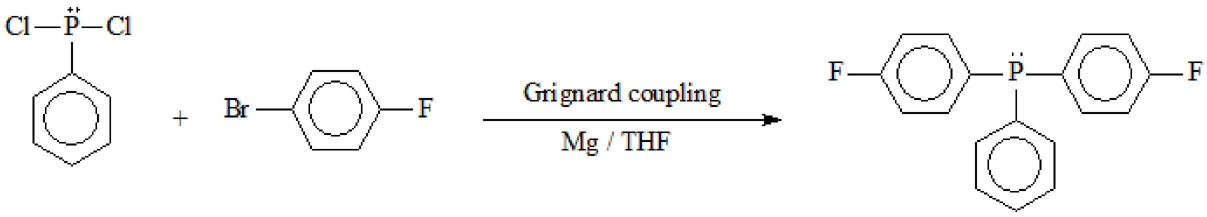


Figure 53: Synthesis route of trivalent phosphorus containing monomer

4.4.2 Synthesis of the polymers:

There were two general procedures that had been adopted to polymerize the trivalent phosphorus monomer with bisphenol-A. One was solution polymerization technique and another was solvent free bulk or melt polymerization technique. During polymerization it was difficult to control the phosphine oxide formation of the synthesized trivalent phosphorus containing monomer. So basically a random copolymer was prepared with separate phosphine and phosphine oxide unit. The goal was to prepare a polymer with trivalent phosphorus containing unit as high as possible. Phosphine oxide and phosphine containing units ratios were determined by ^{31}P NMR spectroscopy.

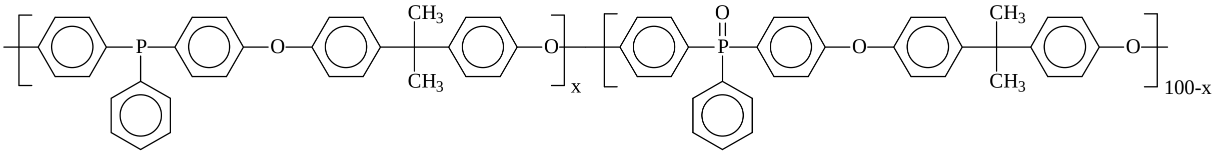


Figure 54: Basic structure of the random copolymer

4.4.2.1 Solution polymerization

Stoichiometric amount of trivalent phosphorus containing monomer and bisphenol-A was taken in a reaction flask under inert atmosphere with NMP and toluene as solvent. K_2CO_3 was used as base to form phenoxide and to initiate the polymerization reaction. The structure of the polymer **P11** is given in the following **Figure 55**

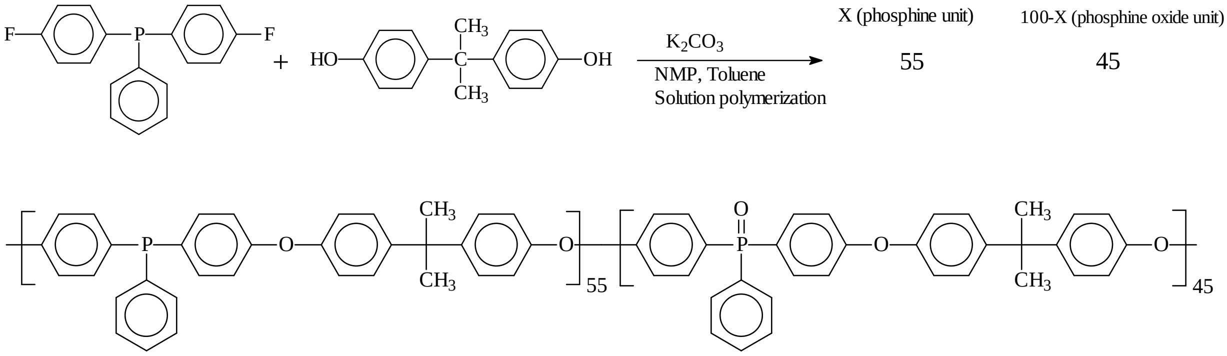


Figure 55: Reaction performed for solution polymerization and the synthesized random co polymer **P11**

4.4.2.2 Preparation of phosphine borane complex:

Clearly during solution polymerization trivalent phosphorus monomer is getting oxidized (45% in oxidized form) even in inert atmosphere. Highly reactive trivalent phosphorus containing monomer can easily get oxidised in presence of any mild base which is basically a common reactant during A_2 + B_2 polycondensation reaction (B_2 = diphenols). So the research was concentrated to find out a useful way of synthesizing linear trivalent phosphorus containing polymer. The idea of protecting the free electron of phosphorus was introduced. The easiest way was to do that by preparing a phosphine borane adduct. And after the polymerization reaction it was necessary to do one deprotection reaction.

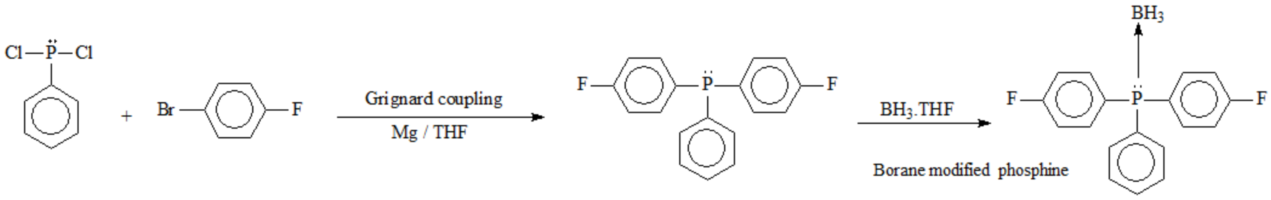


Figure 56: Synthesis of phosphine borane complex

Bis(4-fluorophenyl)phenylphosphine was treated with BH_3.THF (as received from Sigma Aldrich) to prepare borane protected bis(4-fluorophenyl)phenylphosphine. The prepared product was characterized using ^{1}H NMR. 1.23 ppm. Characteristic signal of BH_3 appeared at 1.23 ppm ($CdCl_3$, 3H, m, -BH_3). The signal of trivalent phosphorus at -7.49 pm was vanished and a new characteristic signal of P $\rightarrow BH_3$ at 19.66 ppm was appeared [^{31}P NMR ($CDCl_3$): 19.66 ppm (P $\rightarrow BH_3$)]. Detail ^{1}NMR individual signals are described in next chapter.

4.4.2.3 Solution polymerization using phosphine borane complex:

This borane protected bis(4-fluorophenyl)phenylphosphine with bisphenol-A were used further for polymerization. The method used for polymerization was A_2 + B_2 polycondensation reaction As usual dry NMP and toluene were used as solvents and K_2CO_3 was used as base. The structure of the polymer **P12** is given in the following Figure 51

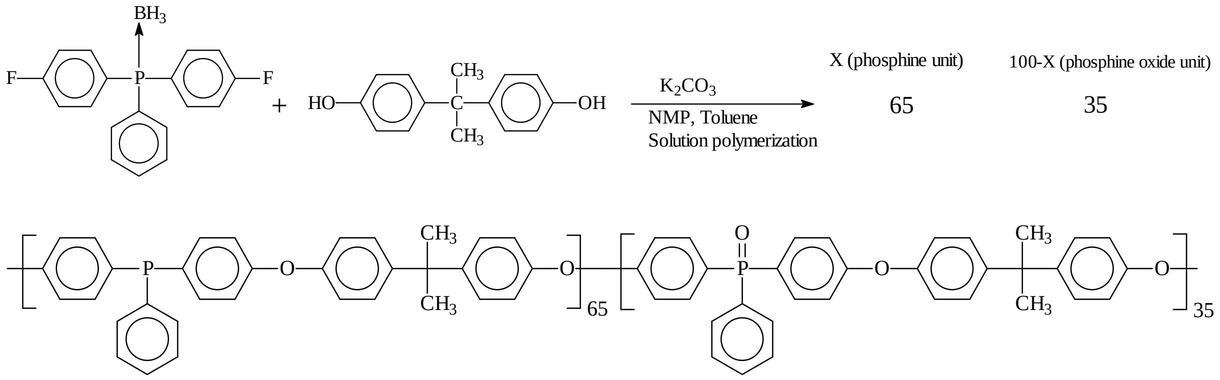


Figure 57: Polymerization reaction performed with borane complex and the synthesized random copolymer **P12**

Above observation led to the conclusion that even the phosphine borane adduct was not good enough to yield polymer with maximum trivalent phosphorus block although yield of phosphine unit was improved compared to the polymerization without protection. Phosphorus borane bond was getting broken when the polymer was precipitated in methanol and the exposed trivalent phosphorus was getting oxidized. So solution polymerization technique was not the best way to polymerize our monomer. Melt or bulk polymerization could be a way but it was not suitable for borane protected bis(4-fluorophenyl) phenylphosphine. The temperature required for bulk polymerization was around 340°C and that could break the phosphorus borane co-ordinate bond during reaction and could lead towards a polymer with higher phosphine oxide containing block.

4.4.2.4 Melt or bulk polymerization

This approach basically opens the possibility of synthesizing a broad number of aromatic polyethers in a one pot procedure. Condensation reaction occurs at high temperature (around 350°C). But with proper activation i.e. by activation using siloxy group polycondensation can result at somewhat lower temperature. There are several advantages of using silylated monomers instead of the protonated precursors. Firstly, polycondensation of silylated monomers with halogen containing electrophiles avoids the liberation of free hydrochloride or hydrofluoric acid, and thus, acid catalysed side reactions. Secondly, the liberated trimethylsilyl derivatives, such as fluoro or chloromethylsilane, trimethylsilylacetate, or hexamethyldisiloxane are highly volatile and easy to remove from the reaction mixture. Thirdly, silylation improves the solubility of the monomers and also reduces the melting point.

4.4.2.5 Synthesis of silylated bisphenol-A

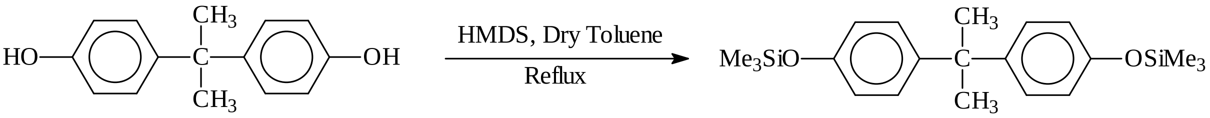


Figure 58: Synthesis of silylated bisphenol-A

Bisphenol-A along with hexamethyldisilazane and dry toluene were taken in a two neck reaction flux fitted with a condenser. Another neck was used to vent the NH_3, produced during the course of the reaction. The whole system heated in an oil bath to reflux. The reaction continued until the whole NH_3 was removed. Prepared product was characterized using ^{1}H NMR. Detail ^{1}H NMR signals are described in the next chapter.

4.4.2.6 Melt or bulk polymerization using silylated bisphenol-A:

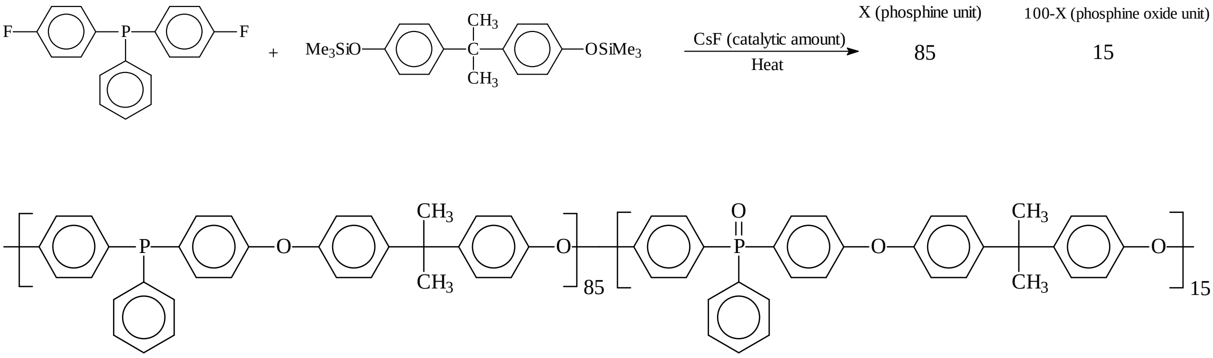


Figure 59: Polymerization reaction performed in melt using CsF and the synthesized random copolymer **P13**

Bulk polymerization reaction was performed using silylated bisphenol and activated difluoro phosphine without any kind of base or solvent. Reaction procedure involved only CsF and heat.

Reaction byproduct was volatile Me_3SiF which could be easily removed under vacuum only by heat.

Table 15: Formulation of melt polymerization

Monomer	Formula weight	Wt. taken (g)	Mole
Silylated BPA	372.65	1.5	0.004025
Phosphine monomer	298.27	1.2006	0.004025
CsF	151.9	0.04891	0.00032200
		0.091714	0.00060378
		0.15284	0.00100625

The formulation of the entire process is listed in **Table 15**. Below in **Figure 60** is the discussion of the ^{31}P NMR spectra of the polymers prepared using different techniques. The relative intensities of signals appearing for trivalent phosphorus and its oxide form were compared. In normal solution polymerization technique we were getting a polymer where 55% of the phosphorus was in trivalent stage (signals appeared at -7.9 ppm) and 45% was in oxide stage (signal appeared at 26.4 ppm). Even in case of phosphine borane complex using solution polymerization technique trivalent phosphorus content of the polymer could only be incresed by 10% (from 55% to 65%). Oxide formation of the polymer may be due to the presense of mild base (K_2CO_3) present in the reation mixture or due to the temperature that was required for polymerization. Using melt polymerization technique a polymer with maximum trivalent phosphorus content (intensity arround 85%) could be produced. From ^{31}P NMR spectra a conclusion could be drawn that the bulk polymerization or melt polymerization technique using silylated diphenol was the best possible way to polymerize trivalent phosphorus monomer with highest phosphine unit.

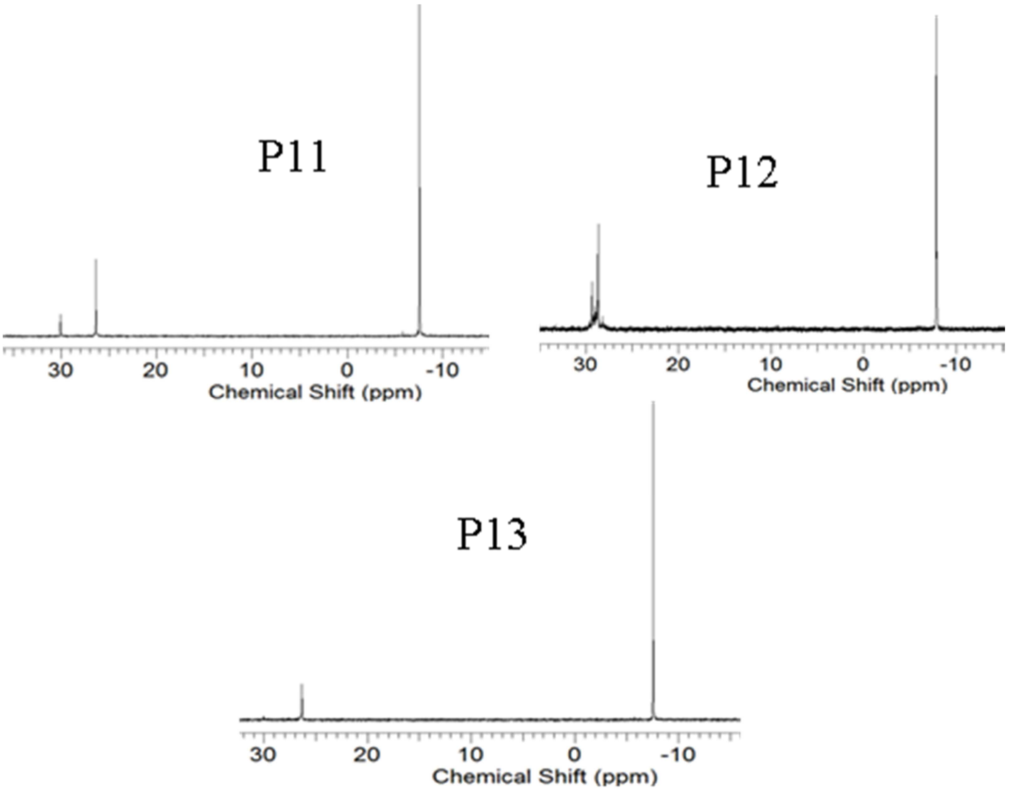


Figure 60: ^{31}P NMR spectra of (P11) copolymer prepared by solution polymerization (P12) copolymer by solution polymerization with phosphine borane complex and (P13) copolymer by melt polymerization with silylated di-phenol and CsF

After the success of the melt polymerization using CsF (as observed from the ^{31}P NMR spectra) interesting results were observed varying CsF molar concentration. After trial and error method P13 was obtained using 8% (molar concentration) CsF. Two other polymers P14 and P15 were synthesized using 15% and 25% CsF molar concentration. Molar masses of the synthesized polymers were determined by SEC with MALLS detection. Interestingly polymer obtained with higher CsF molar concentration (P15) was insoluble in THF or in DMAc. Hence determination of molar mass of P15 was not possible.

Table 16: Molar masses of the trivalent P containing polymers

Polymer	**M_w ^{a} (g/mol)**	**Đ^b (M_w/M_n)**
P13	42800	1.59
P14	37500	1.48
P15	-	-

a. *Weight-averaged molar mass detected by SEC; PolarGel-M column (PL); DMAc + 3g/l LiCl ;Agilent Technologies; Knauer-RI - detector K2301; MiniDAWN -LS - detector from Wyatt Technology; Flow rate 1.0 ml/min.*
b. *Đ; Dispersity M_w/M_n*

All these three polymers were characterized by ^{1}H NMR. Here below in **Figure 61** represents the comparative ^{1}H NMR spectra of P13, P 14 and P15.

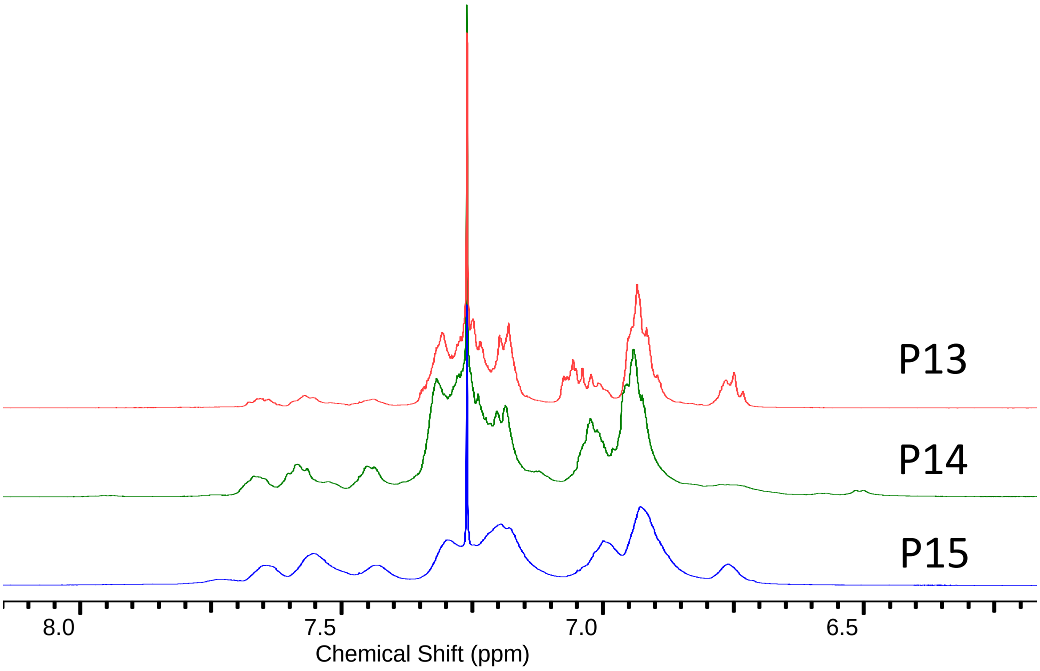


Figure 61: ^{1}H NMR spectra of random copolymer P13, P14 and P15

The ^{1}H NMR spectra were characterized by significant broadening of the polymer backbone signals. Although the reason was not clear for P15 but one can suppose that the formation of a cyclic structure could cause the line broadening because similar poly(arylene ethers), with or without fluorine substitution show narrower signals. Analyzing the ^{1}H spectra one has to consider the scalar couplings to ^{19}F and ^{31}P nuclei (J_{X-F}; J_{X-P}; X = H, C) which result in a significant signal splitting for ^{1}H NMR up to three bonds away. The directly bonded phosphorous resulted a large doublet splitting. The ^{31}P NMR spectra proved the presence of phosphine and phosphine oxide structure. Almost full conversion of 4-fluorine in the polycondensation reaction was proved by ^{19}F NMR spectroscopy.

4.4.3 Novel application of linear trivalent phosphorus polymer in Mitsunobu reaction:

There are a number of ways to get rid of the separation problem occurring during Mitsunobu reaction. In some approaches some additional reactions were required after the Mitsunobu reaction itself only to effect separation process. Fluorous approach was attractive among them because of comparatively easier separation technique involved. Reactive trivalent phosphorus containing copolymers (P13, P14) were tested as polymeric reagent in organic synthesis, more precisely in Mitsunobu reaction. A known semifluorinated alcohol was successfully prepared using perfluorodecyliodide, dec-9-ene-1-ol, azobisisobutyronitrile (AIBN) and tri-n-butyl tinhydride. **Figure 62** shows the synthesis scheme of this long chain semi fluorinated alcohol. A description of the synthetic process is in the experimental chapter.

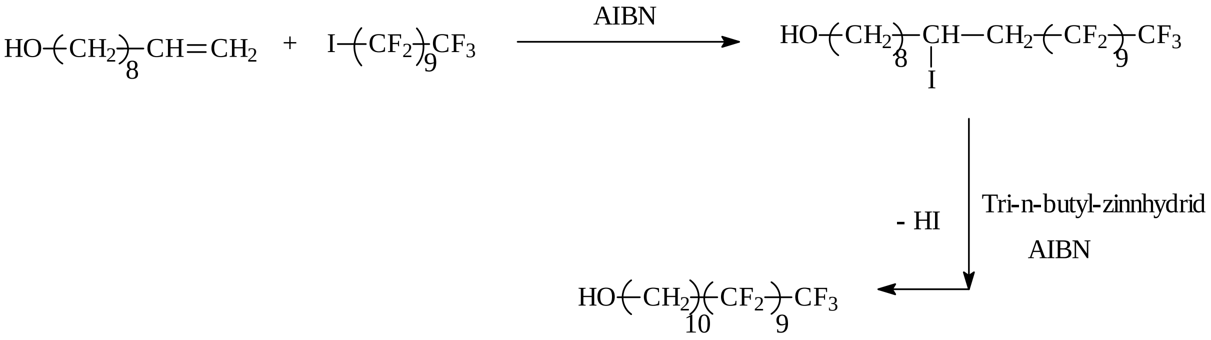


Figure 62: Synthetic scheme of semi fluorinated alcohol [197]

Structure of the semifluorinated alcohol was confirmed by ^{1}H NMR spectra given in the **Figure 63** below. The individual signal details of the ^{1}H NMR spectra are in the experimental chapter.

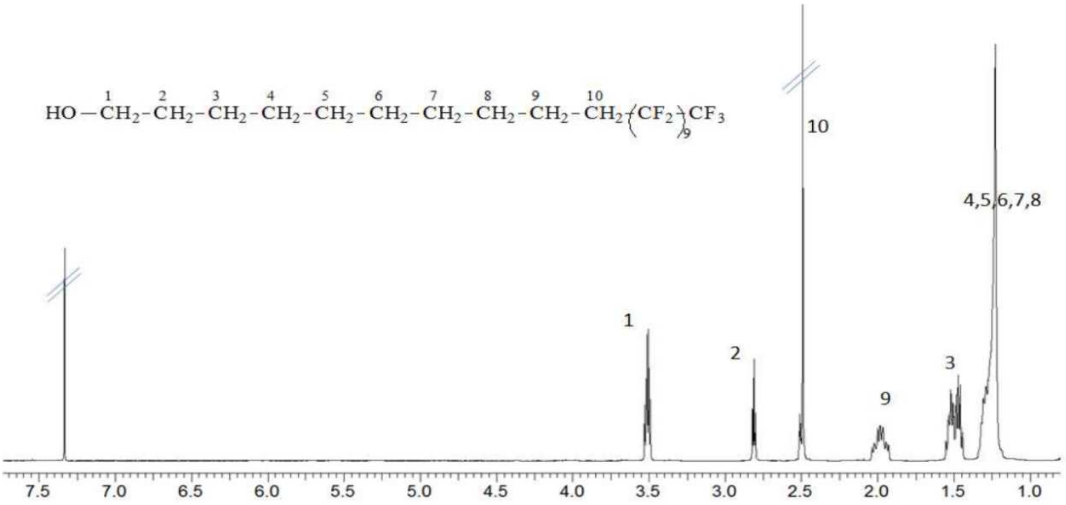


Figure 63: ^{1}H NMR of the semifluorinated alcohol

A model reaction (standard Mitsunobu reaction) was successfully performed using dimethyl ester of 5-hydroxy isopthalic acid with a long chain semi fluorinated alcohol in presence of triphenyl phosphine (TPP) and diethyl-aza-dicarboxylate (DEAD). Expected Mitsunobu adduct (ether derivative of 5-hydroxy isophthalic acid) was confirmed by ^{1}H NMR spectra. **Figure 64** shows the model Mitsunobu reaction performed. Synthetic database is given in the experimental chapter.

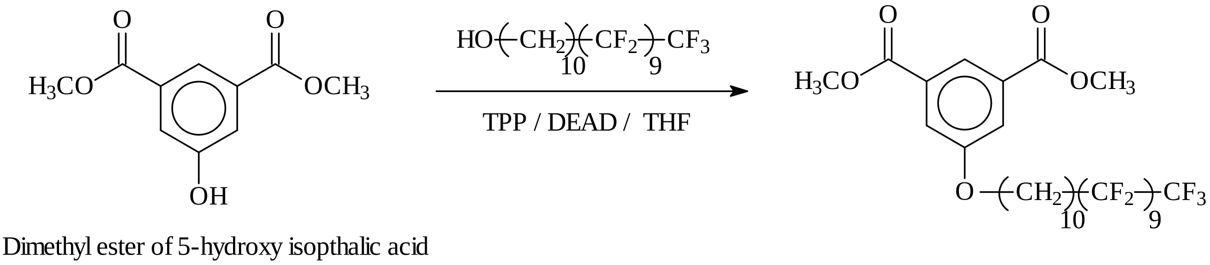


Figure 64: Model Mitsunobu reaction

After the success of the model Mitsunobu reaction (**Figure 64**) the aim was to replace the triphenyl phosphine with reactive trivalent phosphorus containing copolymers. **Figure 65** represents the actual work done. Basically the whole system of the model Mitsunobu reaction scheme was kept intact except the TPP part. Below in Table 17, represents the synthetic database of the reaction performed with trivalent phosphorus polymer.

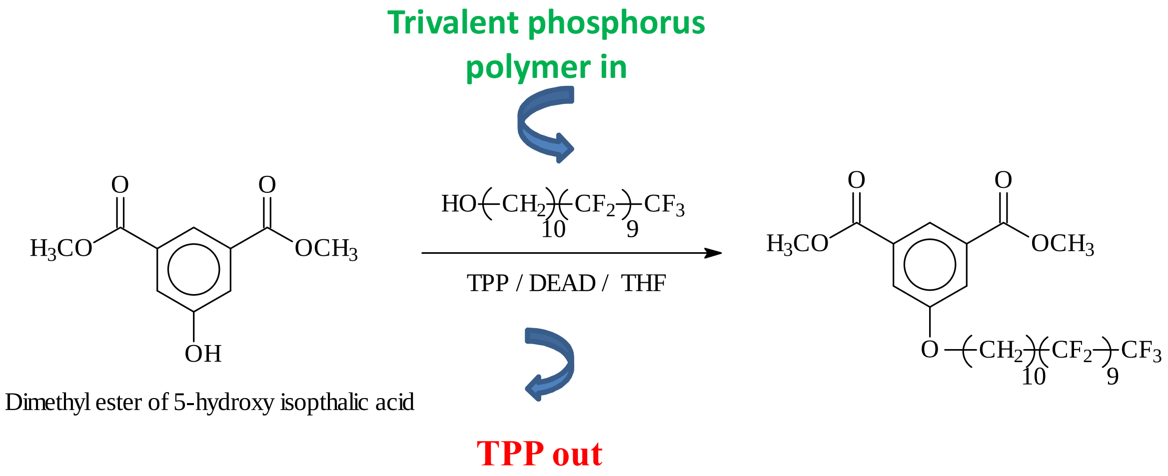


Figure 65: The synthesis performed using polymer P13 and P14

Table 17: Reaction formulation for Mitsunobu reaction using polymer P13 and P14

Ingrediants	Formula weight	Wt. taken (g)	Mole
5-hydroxy di-isophthalate	210	0.045	0.0002188
Semifluorinated alcohol	676.35	0.148	0.0002188
Trivalent phosphine polymer	486.54 (one repeating unit)	0.127	0.0002625
DEAD	174.16	0.057	0.0003282

Structure of the Mitsunobu adduct was confirmed by ^{1}H NMR spectra given in the **Figure 66** below.

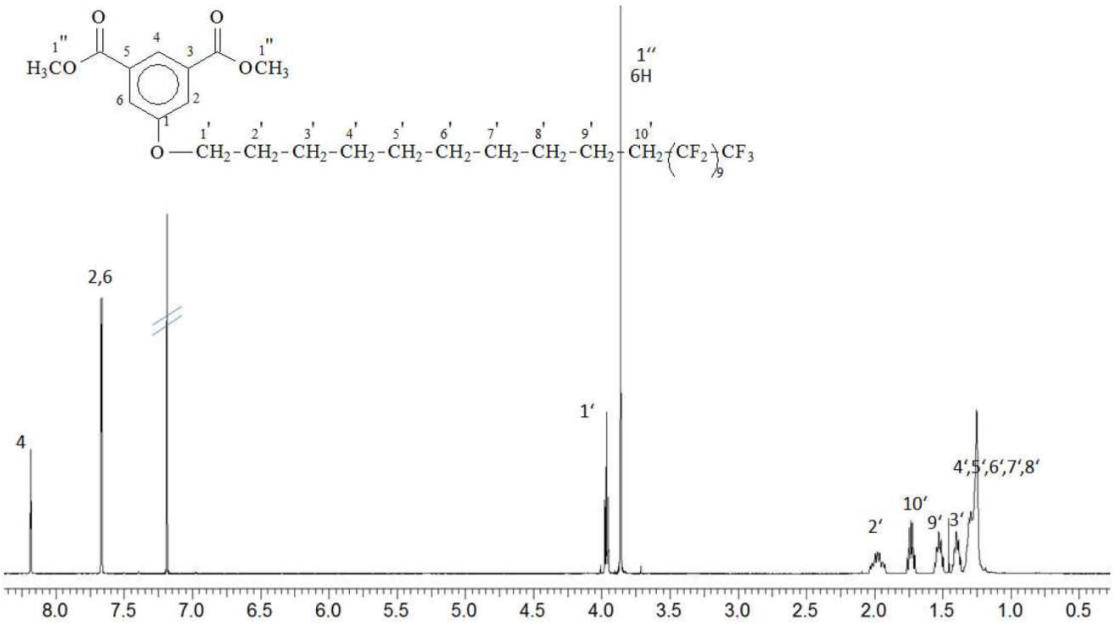


Figure 66: ^{1}H NMR of the Mitsunobu adduct

Due to scalar coupling with the oxygen and fluorine atoms splitting of the ^{1}H NMR signal occured. Excepet the protons at C-2, C-4, C-6 and C-1' positions, all other proton got splitted. The spectra did not show any signal corresponding to terminal –OH of the starting material at 10.2 ppm and showed new signals at 3.96 ppm due to formation of ether linkage. That reflects the complete conversion of the 5-hydroxyl group. The individual signal details of the ^{1}H NMR spectra are in the experimental chapter.

Table 18 represents the relative yield between the model Mitsunobu reaction (where TPP used as a reactant) and the reaction where trivalent phosphorus polymers [P13 (M_w : 42800 g/mol) and P14 (37500g/mol)] were used replacing TPP. The model Mitsunobu reaction was performed using the semifluorinated alcohol. The idea from the previous studies revealed that higher fluorine content of the reactants affected the separation process of Mitsunobu reaction. But like other standard Mitsunobu reaction methods all the remaining reagents or the byproducts had to be separate either by silica column chromatography or by fluorous filtration procedure.

Table 18: Respective yield of Mitsunobu reaction

Reactant	(%) yield
TPP	~ 33
Trivalent phosphorus polymer	
P13	~ 55
P14	~ 50
P15	-

During the course of the research the technique of silica column chromatography was adopted for purification. Because of these complicated separation methods the reaction yield was only around 33 % in case of TPP. But better results were obtained when TPP was replaced with higher phosphine unit containing polymers such as P13 and P14. Using polymer P15 the Mitsunobu reaction was not successful as polymer P15 was getting dissolved in reaction medium. The reason for that can be explained from the NMR spectra of the polymer itself. The broad ^{1}H NMR spectra of polymer P15 compared to P13 and P14 was suggesting a tendency of formation of a cyclic polymer.

At the end of the Mitsunobu reaction the phosphine copolymers are generally transformed into poly(arylene ether phosphine oxide). Poly(arylene ether phosphine oxides) are insoluble in diethyl ether whereas the Mitsunobu adducts are fully soluble in diethyl ether. So the product was isolated from the reaction medium by adding diethyl ether into it. Then the soluble fraction with desired product was collected and was evaporated under vacuum.

The purification step with silica column chromatography technique was not required. Only a wash with hexane and recrystallization from ethyl acetate led to a pure product. The reaction yield was also increased up to 50 % in case of using polymer P14 and 55% in case of polymer P13.

So using trivalent phosphorus polymer compared to triphenyl phosphine, not only reaction yield was increased but preparation and purification step (which was not so easy in case of model Mitsunobu reaction) of the final product became also easier.

Chapter 5

Conclusion and outlook

5 Conclusion and outlook

5.1 Conclusion

The first motivation of the work was to synthesize new class of phosphine oxide containing poly(arylene ethers) and improvement of the properties of the polymers by proper selection of the monomers. Those polymers should have high processability and high T_g. Their thermal stability should be high enough for further application. To execute that plan, the aim of the work was concentrated to synthesize three different phosphine oxide containing monomers which were structurally different. The polymers were planned to synthesize using A_2+ B_2 solution polymerization technique through S_NAr mechanism. The knowledge on high performance poly(arylene ether phosphine oxides) with higher phosphorus content was planned to be expanded and the effect of phosphorus on flame retardancy was extensively studied. To execute that plan previously synthesized halogen free phosphine oxide monomer was aimed to polymerize with 10-(2, 5-Dihydroxypheny), 10-H-9-Oxa-10-Phosphaphenanthrenelo-oxide (DOPO-HQ).

Next goal of the work was to use the synthesized poly(arylene ether phosphine oxides) as an intumescent flame retardant (IFR) in epoxy resins. Bisphenol A based epoxy resin and Bis(4-aminophenyl) sulfone (DDS) was selected as the matrix and hardener respectively. In the present study PSU control (BPA based polysulfone) with four different PAEPOs (P2, P3, P4, P9) and their corresponding blends with epoxy resin were planned to investigate. The pyrolysis and the fire retardancy mechanisms of blends with epoxy resin were tackled by means of a comprehensive thermal analysis (thermogravimetry (TG)) and the fire tests [limiting oxygen index (LOI), cone calorimeter, UL 94].

The last plan was to prepare highly unstable bis(4-fluorophenyl) phenylphosphine and then to develop a technique to polymerize it. Always there was a possibility to have a phosphine oxide polymer. So the basic goal was to prepare a polymer with higher trivalent phosphorus content. After preparing the polymer the next aim was to utilize it in organic synthesis such as in Mitsunobu reaction. Idea behind that was to solve the separation problem during the course of Mitsunobu reaction. For that purpose a model reaction using triphenyl phosphine was performed and then the same reaction was repeated replacing triphenyl phosphine with the phosphine polymer of higher molar mass.

5.1.1 Synthesis and characterization of poly(arylene ether phosphine oxides)

All poly(arylene ether phosphine oxides) were synthesized by nucleophilic aromatic polycondensation. The synthetic strategy led to a series of PAEPOs allowing for the first time a direct comparison of the effect of phosphine oxide, trifluoromethyl- and methylether groups. The polymers obtained covered a wide range of weight average molar masses (8,000 – 125,000 g/mol) as determined by size exclusion chromatography with multi-angle light scattering detection (MALLS). FTIR, NMR spectroscopy and MALDI-TOF revealed formation of the desired polymer structure of the linear poly (arylene ethers). All polymers were easily soluble in common organic solvents, thus enabling processing from solution. Flexible films casted from the polymer solutions showed good tensile strength and Young's modulus.

The thermal decomposition and combustion behavior and the burning behavior of selected samples were extensively studied. The T_g's of all PAEPOs are higher than the BPA-PSU control without P=O units. The glass transition temperatures of BPA-containing PAEPOs with PO units range up to 200 °C while biphenylene-containing PAEPOs showed T_g's about 20-30 °C higher (rise from 200 °C to 225 °C). This indicates the higher stiffness of the biphenylene-containing aromatic polyethers (compare P2 vs P4, P5 vs P6 and P7 vs P8). Methoxy substituents on the phenylene ring do not have a significant effect on T_g. All samples exhibited excellent thermal stability in nitrogen atmosphere. In all cases, degradation started above the onset of degradation for PSU. The decomposition of all polymers started well above 400 °C. An early mass losses at about 200 °C are caused by residues of solvents, for instance in sample P4and in all cases, well above the PSU control. The non-substituted sample P4 showed the highest thermal stability, while the introduction of $–CF_3$ and $-OCH_3$ substituents reduces the onset of decomposition. The char yields at 750 °C (at a heating rate of 10 K/min) were higher than 25 wt. %, except in samples where isopropylidene groups were introduced (P3, P7, P8). In this case, also additional biphenylene units do not support higher char formation. TGA-FTIR measurements assessed the chemical structure of evolved pyrolysis products. FTIR spectra of the char showed the presence of phosphorus as expected. From the thermal analysis it was understandable that all materials were char forming and phosphorus mainly locked in the residue. Based on the characterization results, decomposition mechanisms were derived in order to select a proper structure suitable to improve the physical and flame retardant properties of high performance polymers.

Additionally, pyrolysis combustion flow calorimetric measurements were performed which revealed differences in the heat release behavior for different polymers. Phosphine oxide moieties have a significant influence on flame retardancy. Polymer P2 with both phosphine oxide and sulfone units has a drastically reduced pHHR and HRC than regular PSU. Comparing pHRR and THR values from PCFC data indicated that in polymers P5, P6, P7 and P8 improvement occurs in the direction of strongly reduced combustion. Thus, a high impact for flame retardancy can be foreseen.

5.1.2 Synthesis and characterization of higher phosphorus containing PAEPOs and their application as flame retardant additive in epoxy resin matrix

In the next segment, synthesis of poly(arylene ether phosphine oxides) with higher phosphorus content was reported. The polymers were not characterizable using NMR spectroscopy due to the presence of DOPO-HQ in the polymer backbone. The weak P-O bond was getting opened in presence of base in the reaction mixture. So in the reaction medium closed and open both structures were present simultaneously. MALDI-TOF was used to determine the formation of the polymers. Peak to peak distances came in good agreement with the molar mass of the polymer repeating units.

Newly synthesized P9 along with other four polymers from first segment (P1, P2, P3, P4) were introduced in epoxy resin composite as flame retardant additives. The pyrolysis and fire retardancy of the epoxy resin composites were tackled by thermogravimetry and fire tests (cone calorimeter, limiting oxygen index and UL-94). Comparing the results (pHRR and EHC) obtained from cone calorimetry it was clearly visible that the inclusion of phosphine oxide into the sulfur containing backbone made the MEPC-P2 composite better flame retardant compared to MEPC-P1, MEPC-P3 and MEPC-P4. Loading of only 10wt % led to a decrease of around 40 % of pHRR values which is quite good compared to previous observations. The amount of smoke release also decreased in case of the MEPC-P2 and MEPC-P9 polymer composites. Dripping during burning considered being an important fire hazard. For MEPC-P2 and MEPC-P9 composites the dripping behavior was significantly reduced.

Figure 67: V-0 rating composites (MEPC-P9) in UL-94 test

In UL-94 test with the whole series of polymer composites the best result was obtained with MEPC-P9 composite which was prepared using newly synthesized higher phosphorus containing PAEPO. With 10 wt % loading MEPC-P9 composite showed V-0 rating in UL-94 test. From the above observation a conclusion can be drawn that the chemical structure of the intumescent flame retardant (IFR) additives can highly influence the fire behavior of the composite. From the DMA analysis it was obtained that after addition of polymer additives, T_g values were increased by 25-30°C compared to reference epoxy resin composite.

5.1.3 Trivalent phosphorus chemistry and application in Mitsunobu reaction

At the last segment the discussion was about the synthesis of trivalent phosphorus containing monomers and polymers and their use in organic synthesis. First aim of this part was to synthesize pure bis(4-fluorophenyl)phosphine. The product could not be obtained from the expected work up procedure. During work up due to the presence of base, freshly prepared proactive bis(4-fluorophenyl)phosphine could transform into phosphine oxide. That was the reason when a new technique of synthesizing monomer from Grignard reaction was used. The product was collected from the quenched reaction mixture using a small filtration technique using PTFE membrane filter.

After that the research goal was oriented to synthesize a poly(arylene ether) from the bis-(4-fluorophenyl) phosphine. But the polymer should have phosphine moiety instead of phosphine oxide for further application. To execute that plan at first the phosphorus lone pair of phosphine was blocked using borane. But after the polymerization reaction it was observed that the copolymer was consisting of 35 % of phosphine oxide unit. The reasons for that might be either the temperature of polymerization reaction or the polymer precipitation step using methanol/HCl. During the course of the polymerization reaction the phosphine borane bond was raptured. At that point, the technique of melt polymerization using silylated diphenol and CsF was introduced. Due to presence of silylated monomer the polymerization reaction temperature was reduced and the volatile byproducts were easily removed from the system. From the ^{31}P NMR spectra it was also proved that the melt polymerization or bulk polymerization technique using CsF was the best out of three different technique of polymerization of phosphine monomer (solution polymerization, solution polymerization using phosphine borane complex, melt polymerization using silylated diphenol and CsF).

Next aim was to use the trivalent phosphorus containing polymer in Mitsunobu reaction replacing TPP. The model Mitsunobu reaction was performed using a semifluorinated alcohol. From the previous studies the idea was that the higher fluorine content of the reactants could led to an improved separation process for Mitsunobu reaction. But like other standard Mitsunobu reaction methods all the remaining reagents or the byproducts had to be separated either by silica column chromatography or by fluorous silica gel filtration procedure. Because of these complicated separation methods the reaction yield was only around 33 % using triphenyl phosphine (TPP). But better results were obtained when the TPP was replaced with higher phosphine unit containing polymers. In case of polymers the purification step with column chromatography technique was not required. Only a wash with hexane and recrystallization from ethyl acetate led to a pure yield. The reaction yield was also increased up to 55%. So from the above observation it can be concluded that triphenyl phosphine containing polymers were more efficient compared to triphenyl phosphine in case of the separation of the Mitsunobu adduct was concerned.

5.2 Outlook

The synthetic strategy led to the preparation of a series of poly(arylene ether phosphine oxides) and allowed a detail structure property relationship study. The effect of phosphine oxide, trifluoromethyl group and methoxy group came in direct comparison. From the results obtained from the thermal degradation, combustion and burning behaviour of all the PAEPO's it was observed that all the polymers were char forming and phosphorus stayed normally in the condensed phase during combustion (locked in the char). Decomposition mechanisms were derived in order to select a proper structure which can be used to improve the physical and flame retardant properties of high performance polymers. The presence of CF_3-groups gave excellent results in this juncture. These products may be used as highly efficient flame retardants in special applications (for instance, as combined toughness and fire retardants in high performance composites) where the presence of halogen is not critical.

Higher phosphorus content has high influence on flame retardancy. Higher phosphorus content makes a polymer more flame retardant. In case of composites the same logic can be applicable. Higher loading of intumescent flame retardant additive can lead to a better flame retardant composite. But increasing the loading of flame retardant can deteriorate the material properties of polymer composites. Sticking onto the aim of using IFR loading as minimum as possible satisfactory results were obtained in the sense of flame retardancy and glass transition temperature. Loading of only 10wt % led to a decrease of around 40 % of pHRR values which is quite good compared to previous observations. From the previous results it was obtained that the reduction of pHRR by 40 % could only happened when the loading was 20 wt % or more.

The idea of higher phosphorus content flame retardant additive can be expanded and there can be a possibility of introducing hyperbranched poly(arylene ether phosphine oxides) into the composite system. Because of the highly branched structure hyperbranched polymer will have certainly more phosphorus content that the linear polymers. The process can be initiated to synthesize hyperbranched polymer from some known monomers using A_2+ AB_2 or A_2+B_3 preparation technique. Bis(4-fluorophenyl) phenyl phosphine oxide can act as a A_2 monomer.

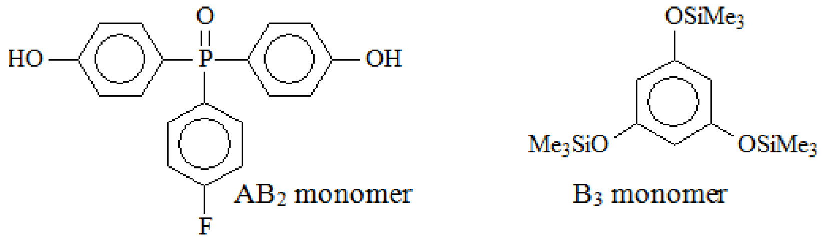


Figure 68: AB_2 and B_3 monomers for hyperbranched polymer synthesis

On the basis of the obtained results the use of trivalent phosphorus containing polymer instead of TPP in Mitsunobu reaction is highly recommendable. It was not achieve a 100 % trivalent phosphorus unit containing polymer during the polymerization of bis(4-fluorophenyl)phosphine. But it would be wonderful to achieve. These separation friendly polymeric Mitsunobu reagents will widen the application of Mitsunobu reaction in synthetic chemistry since the major deterrence for conducting parallel Mitsunobu reactions is often the inefficient product isolation encountered with traditional reagents.

Chapter 6

Experimental part

6 Experimental part

6.1 Materials and characterization technique

6.1.1 Solvents

- Dichoromethane (Acros, Germany);
- N-Methyl-2-pyrrolidone (NMP) (Merck, Germany); NMP was purified by stirring with NaOH and distilled from P_2O_5
- Dimethyl acetamide (Acros, Germany);
- Diethyl ether (Acros, Germany);
- Dimethyl sulfoxide (Acros, Germany);
- d-Dimethyl sulfoxide (Acros, Germany);
- Chloroform (Acros, Germany);
- d-Chloroform (Acros, Germany);
- Dimethyl formamide (Acros, Germany);
- Dry toluene (Aldrich, Germany);
- Methanol (Acros, Germany);
- Dry tetrahydrofuran (THF) (Aldrich, Germany);
- Glacial acetic acid (Merck, Germany);
- Acetone (Merck, Germany);
- Ethyl acetate (Aldrich, Germany);
- Hexane (Aldrich, Germany);

The solvents were purified and dried following the usual procedure [201] [202] .

6.1.2 Chemicals

- 4-Methoxyphenylphosphonic dichloride (TCI, Europe);
- Phenylphosphonic dichloride (Aldrich, Germany);
- Dichlorophenyl phosphine (Aldrich,Germany);
- 5-Bromo-2-fluoro benzotrifluoride (Flurochem, UK);

- 4-Bromo fluorobenzene (Aldrich,Germany);
- Magnesium turnings (Merck, Germany);
- Boron tri bromide (BBr_3) (Fluka, Germany);
- Hydrobromic acid (HBr) (Acros, Germany);
- 4,4′-Isopropylidenediphenol (BPA) (Aldrich, Germany);
- 4,4′-Dihydroxy biphenyl (DHB) (Aldrich, Germany);
- 4,4′-Sulfonyldiphenol (SDP) (Aldrich, Germany);
- DOPO-Hydroquinone (China);
- Hexamethyldisilazane (Aldrich, Germany);
- Bisphenol A diglycidyl ether (Spain);
- 4,4’ diaminophenyl sulfone (Aldrich, Germany);
- Dimethyl ester of 5-hydroxy isopthalic acid (Aldrich, Germany);
- Cesium fluoride (CsF) (Aldrich, Germany);
- Chlorosilane (Aldrich, Germany);
- Diethyl azadicarboxylate (DEAD) (Aldrich, Germany);
- Triphenyl phosphine (TPP) (Aldrich, Germany);
- Perfluorodecyliodid (Aldrich, Germany);
- Dec-9-ene-1-ol (Aldrich, Germany);
- Azo bis isobutylonitrile (AIBN) (Aldrich, Germany);
- Tri-n-butyl-zinnhydrid (Aldrich, Germany);
- Hydrochloric acid (Acros, Germany);
- Concentrated sulphuric acid (Acros, Germany);

The chemicals were used as received unless otherwise noted.

6.2 Characterization and testing methods

6.2.1 Elemental analysis

Carbon and hydrogen content of the compounds were analyzed by pyrolysis method using a Vario EL (Elementar, Germany) elemental analyzer

6.2.2 Fourier transforms infrared spectroscopy (FTIR)

FTIR spectroscopy was used to examine the structure of the monomers and polymers. IR spectra of the polymer films were recorded with a Vertex 80V FTIR spectrophotometer instrument (Germany) with KBr pellets, for the monomers. FTIR spectra of polymers were taken directly from thin films (10- 15µm). The characteristic infrared absorption bands of arylene ether and related compounds are given in **Table 19**

Table 19: Table of characteristic IR absorption

Frequency, cm^{-1}	Bond	Functional Groups
3640–3610 (s, sh)*	O–H stretch, free hydroxyl	alcohols, phenols
3500–3200 (s,b)*	O–H stretch, H–bonded	alcohols, phenols
3100–3000 (s)*	C–H stretch	Aromatics
3100–3000 (m)*	=C–H stretch	Alkenes
3000–2850 (m)*	C–H stretch	Alkanes
1715 (s)*	C=O stretch	ketones, saturated aliphatic
1710–1665 (s)*	C=O stretch	unsaturated aldehydes, ketones
1680–1640 (m)*	–C=C– stretch	Alkenes
1500–1400 (m)*	C–C stretch (in–ring)	Aromatics

1470–1450 (m)*	C–H bend	Alkanes
1320–1000 (s)*	C–O stretch	alcohols, carboxylic acids, esters, ethers
1250-1100(s)*	=C-F Stretch	Aryl fluoride
1350-1120(s)*	-CF_3, -CF_2-	Aryl fluoride
1400-730(s)*	C-F Stretch	Aryl fluoride

* m=medium, s=strong, n=narrow, b=broad, sh=sharp

6.2.3 Nuclear magnetic resonance (NMR) spectroscopy

^{1}H, ^{13}C, ^{19}F, ^{31}P NMR- spectra [202] [203] were referred to tetramethylsilane (TMS) at zero ppm. ^{1}H-NMR (500 MHz), ^{13}C-NMR (100 MHz) were recorded on a Bruker DRX 500 MHz instrument [reference zero ppm with TMS (^{1}H and ^{13}C-NMR)]. Solvents used for ^{1}H-NMR / ^{13}C-NMR/ ^{19}F-NMR/ ^{31}P-NMR were $CDCl_3$ and DMSO-d^6 depending on the solubility of the polymers in the particular solvent and internal standard ($CDCl_3$: $\delta(^1H) = 7.26$ ppm; $\delta(^{13}C) = 77.0$ ppm; DMSO-d$_6$: $\delta(^1H) = 2.5$ ppm; $\delta(^{13}C) = 39.6$ ppm). The ^{19}F NMR spectra were referenced on external C_6F_6 (δ (^{19}F) = -162.9 ppm) and the ^{31}P NMR spectra were referenced on external H_3PO_4 ($\delta(^{31}P) = 0$ ppm).

6.2.4 MALDI-TOF MS (matrix assisted laser desorption ionization time-of-flight mass spectrometry)

Mass spectra were acquired on an Autoflex Speed TOF/TOF system (Bruker Daltonics GmbH) in reflector mode. The measurements were carried out in linear mode and positive polarity by pulsed smartbeam laser (modified Nd:YAG laser). An ion acceleration voltage of 20kV was used. The calibration of the measurements was performed by using of external PMMA standards. For the sample preparation, the polymer P(F)6 was mixed with 2-(4-hydroxy-phenylazo) benzoic acid (HABA) and the polymer P(F)7 with dithranol as matrices dissolved in THF.

For measuring the samples were dissolved first in $CHCl_3$ and then mixed with 2-(4-hydroxyphenylazo) benzoic acid (HABA) as matrix dissolved in THF. 1 µl-portion was superimposed on the target. After solvent removal, the samples were exposed to desorption or ionization process induced by pulsed smart beam laser. The ionized molecules were accelerated and reflected by electric fields and projected on a mass sensitive detector. Accumulation of 200 single-laser-spot spectra represents each mass spectrum.

6.2.5 Solubility study

The solubilities of the polymers were investigated in different organic solvents such as NMP, DMF, THF, DMSO, DMAc, chloroform, dichloromethane and acetone by dissolving small amounts of each polymer in a test-tube and dissolving it in a minimum amount of particular solvent. It was attempted to obtain 10% (w/v) solution of all polymers in different solvents.

6.2.6 Gel permeation chromatography (GPC)

Determination of the molar masses was performed by size exclusion chromatography (SEC) equipped with HPLC pump (Serie 1200 from Agilent Technologies) coupled with differential refractive index (RI) detector (ETA 2020,WGE Dr. Bures, Germany) and a multiangle laser light scattering detector (MALLS) DawnEOS (Wyatt Technologies, USA). For the polymers soluble in THF, PL Mixed C chromatography column (Polymer Laboratories Ltd., UK) was used with THF as a solvent with a flow rate of 1 mL/min. Polar Gel-M chromatography columns (Polymer Laboratories Ltd., UK) were used with *N*,*N*-dimethylacetamide/ LiCl (3 g/L) as eluent with a flow rate of 1 mL/min. The evaluations were made with the software ASTRA 4.9 (Wyatt Technology Corp. USA). Molar mass distributions were evaluated with fit of the molar mass/eV dependence and extrapolating over the whole RI signal.

6.2.7 Preparation of films

For the preparation of free-standing films, a weighed quantity of polymer was dissolved in a measured amount of dichloromethane (polymer concentration: 15 wt.-%) and was poured in flat bottom Petri dishes to obtain polymer films. The Petri dishes were covered and the solvent was allowed to evaporate at a controlled rate at 30°C overnight. The Petri dishes were then kept in a vacuum oven and the temperature of the oven was slowly raised to 120°C and kept under continuous vacuum for 5–6 h to remove any trace of solvent. Finally, the Petri dishes were placed in boiling water to remove the films and then films were dried again at 100°C under vacuum. Flexible films were obtained for each polymer.

6.2.8 Thermal characterization

6.2.8.1 Differential scanning calorimetry (DSC)

DSC measurements were made on a DSC Q 1000 of TA Instruments at a scan rate of 20 K/min under nitrogen [203]. Pieces of polymer film samples were kept in sealed aluminum pans and glass transition temperature (T_g) was taken at the middle of the step transition in the second heating run. DSC is a dominant technique for the thermal analytical investigation. It measures the difference in energy inputs into a substance and reference materials as they are subjected to a control temperature programme.

6.2.8.2 Thermo gravimetric analysis (TGA)

Thermal decomposition behaviour of these polymers was investigated on a TGA Q 5000 of TA Instruments at a heating rate of 10 K/min under nitrogen or synthetic air. 8-10 mg sample was taken and decomposition temperature (T_d) of the polymer was studied under nitrogen and/or synthetic air depending on the purpose. Such analysis relies on a high degree of precision in three measurements: weight, temperature and temperature change. TGA is commonly employed in research and testing to determine characteristics of materials such as polymers, to determine degradation temperatures, absorbed moisture content of materials, the level of inorganic and organic components in materials, decomposition points of explosives and solvent residues.

6.2.9 Pyrolysis combustion flow calorimeter (PCFC)

The Microscale Combustion Calorimeter (MCC-1, Fire Testing Technology, UK), also called pyrolysis combustion flow calorimeter (PCFC) is a small-scale flammability testing technique to screen polymer flammability and it is regarded as one of the most effective methods for investigating the combustion properties of materials. The burning behavior of polymers was measured by MCC as follows: About 5 mg polymer samples were heated to 700 °C at a heating rate of 1 K s^{-1} in a stream of nitrogen flowing at 80 $cm^{3}\cdot min^{-1}$. The volatile, anaerobic thermal decomposition products in the nitrogen gas stream are mixed with a 20 $cm^{3}\cdot min^{-1}$ stream of 20 vol% oxygen and 80 vol% nitrogen prior to entering a 900 °C combustion furnace. The calculation of combustion-relevant data (heat release capacity (HRC), heat release rate (HR) heat of combustion (HOC) and residue was carried out according to refs. [204] [198] [200] [199]

6.2.10 Fire behaviour

The flammability of the materials (materials reaction when exposed to a small flame) was determined by UL-94 test according to IEC 60695-11-10 (specimen size 126mm × 12.7mm × 3.2mm) and limiting oxygen index (LOI) according to ISO 4589 (specimen size 126mm × 6.5mm × 3.2mm). A come calorimeter (Fire testing technology, East Grinstead, UK) according to ISO 5660 was used to evaluate the fire fire behavior under forced-flaming conditions. Square size specimen plates (100mm × 100mm × 4mm) were placed in aluminum trays and exposed to the irradiation (50 kW m^{-2}) of the cone heater. Each material was tested according to the reproducibility.

6.2.11 Mechanical characterization

6.2.11.1 Dynamic mechanical analysis (DMA)

Dynamic mechanical analysis was carried out on an Eplexor from GABO, Ahlden (Germany) at a heating rate of 5 K / min and a frequency of 10 Hz. The temperature dependence of storage modulus, loss modulus and loss tangent (tan δ) was measured from 40 °C to 250 °C. The maximum of the (tan δ) was used to determine the glass transition temperature of the polymer film sample.

6.2.11.2 Mechanical testing

The stress–strain behavior of the linear poly(arylene ether) films was measured at room temperature using a Zwick/Roell UPM 1456 instrument (Germany) at a measuring speed of 10 mm/min of the specimen length.

6.3 Monomer synthesis

6.3.1 Synthesis of the monomer bis(4-fluorophenyl)phenylphosphine oxide

The procedure that we followed in some of our previous work was [146] applied for synthesizing the monomer bis(4-fluorophenyl) phenylphosphine oxide (chemical structure see **Figure 69**).

In a 250-mL three-necked round-bottom flask equipped with a condenser, nitrogen inlet, and stir bar a solution of 4-bromo fluorobenzene (19.45 g, 110 mmol) in THF was added slowly to magnesium turnings (3.7 g, 152 mmol). The reaction was initiated by addition of a trace of iodine. The resulting mixture was stirred at 25°C for 4–5 h, until consumption of almost all magnesium turnings. After complete addition of the bromide the resulting brown solution was heated to reflux for 2.5 h. After that the reaction mixture was cooled to 0°C with an ice bath. Subsequently, a solution of 10.0 g (50 mmol) of phenylphosphonic acid dichloride in 35 mL of THF was added over a period of 30 min. The reaction mixture was allowed to warm to room temperature and kept for overnight under stirring. Finally, the excess Grignard reagent was quenched with 50 mL saturated ammonium chloride solution. The organic material was extracted into ether; washed with water, 5% NaOH, and water; followed by drying over magnesium sulfate. The solvents were removed via rotary evaporation followed by vacuum.

An amber colored, highly viscous oily liquid was obtained which was purified by column chromatography using dichloromethane/methanol as eluent. The separated fractions were dried to yield 10.8 g (67.03%) of a white solid.

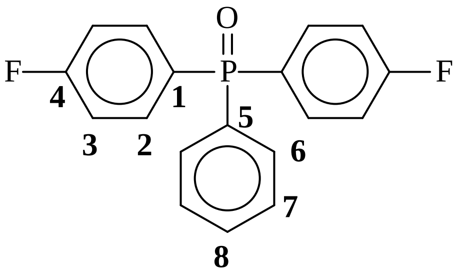


Figure 69: Chemical structure of bis(4-fluorophenyl) phenylphosphine oxide with assignment of NMR signals

Yield: 10.8 g (67.03%). Melting point: 124 °C.

Elemental analysis: Calcd. for $C_{18}H_{13}F_2OP$ (314.27 g /mol): C: 68.79%; H: 4.17%; found: C: 68.29%; H: 4.10%.

FTIR (KBr) ῡ: 3025, 1611, 1498, 1325, 1055, 875, 845, 645 cm^{-1}.

^{1}H NMR ($CDCl_3$) δ: 7.66 (4H, m, H-2), 7.64 (2H, m, H-6), 7.57 (1H, m, H-8), 7.48 (2H, m, H-7), 7.16 (4H, m, H-3) ppm.

^{13}C NMR ($CDCl_3$) δ:165.08 (d, C-4), 134.46 (dd, C-2), 132.17 (d, C-8), 132.09 (d, C-5), 131.84 (d, C-6), 128.61 (d, C-7), 128.35 (dd, C-1), 115.93 (dd, C-3) ppm.

^{19}F NMR ($CDCl_3$) δ: -107.40 (s) ppm.

^{31}P NMR ($CDCl_3$) δ: 28.19 (s) ppm.

6.3.2 Synthesis of bis(4-fluoro-3-trifluoromethyl phenyl)phenylphosphine oxide

The monomer (see **Figure 70**) was synthesized according to the early stated procedure. Here in place of 4-bromo fluorobenzene, 5-bromo-2-fluoro benzotrifluoride (27.01 gm, 110 mmol) was being used for 10gm of phenyl phosphonic acid dichloride. A slightly yellowish colored, highly viscous oily liquid was obtained which was purified by column chromatography using dichloromethane/methanol as eluent. After drying the fractions, 13.5 g (73.09%) of a pale yellow solid was obtained.

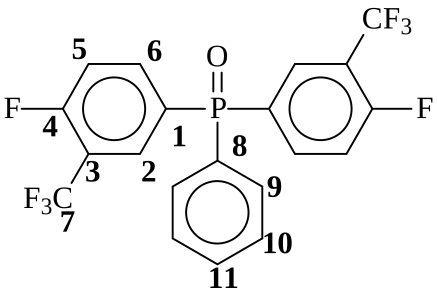


Figure 70: Chemical structure of bis (4-fluoro-3-trifluoromethyl phenyl) phenylphosphine oxide with assignment of NMR signals

Yield: 13.5 g (73.09%). Melting point: 92-94 °C.

Elemental analysis: Calcd.for $C_{20}H_{11}F_8OP$ (450.26 g /mol): C: 53.35%; H: 2.46%; Found: C: 53.85%; H: 2.73%.

FTIR (KBr) ῡ: 3035, 1612, 1323, 1057, 865, 843, 645 cm^{-1}

^1H NMR ($CDCl_3$) δ: 7.98 (m, H-2), 7.82 (m, H-6), 7.64 (m, H-9), 7.63 (m, H-11), 7.54 (m, H-10) 7.35 (m, H-5) ppm.

^{13}C NMR ($CDCl_3$) δ:162.20 (d, C-4), 137.81 (dd, C-6), 133.07 (C-11), 131.73 (d, C-9), 131.35 (m, C-2), 130.22 (d, C-8), 129.11 (d, C-10), 128.71 (d, C-1), 121.83 (q, C-7), 119.50 (dq, C-3), 117.77 (dd, C-5) ppm.

^{19}F NMR ($CDCl_3$) δ: -61.62 (d, F-7), -106.87 (q, F-4) ppm.

^{31}P NMR ($CDCl_3$) δ: 25.98 (s) ppm.

6.3.3 Synthesis of the monomer bis(4–fluoro-3-trifluoromethyl phenyl)-4′-methoxyphenyl phosphine oxide

The monomer (see **Figure 71**) was prepared according to earlier procedure. 5-Bromo-2-fluoro benzotrifluoride (23.4 g, 100 mmol) was being used along with Mg turning (3.2 g, 131 mmol) for 10 g of 4-methoxy phenylphosphonic acid dichloride. A reddish-yellow, highly viscous oily liquid was obtained which was purified by column chromatography using dichloromethane/methanol as eluent. The dried fractions yielded 12.1 g (63.2%) of a pale yellow solid.

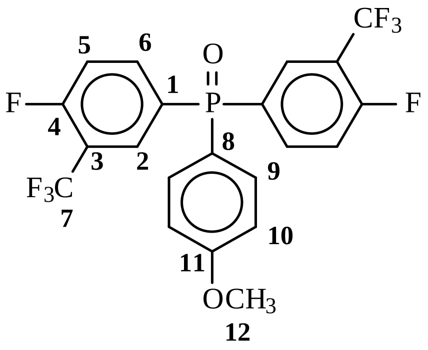


Figure 71: Chemical structure of bis(4–fluoro-3-trifluoromethyl phenyl)-4′-methoxyphenylphosphineoxide with assignment of NMR signals

Yield: 12.1 g (79 %). Melting point: 105 – 108 ^{0}C.

Anal. Calcd for $C_{21}H_{13}O_2F_8P$ (480.293 g/mol): C, 52.52; H, 2.73. Found: C, 52.73; H, 2.86.

IR (KBr): 3005, 2943, 1615, 1497, 1325, 1029, 900, 834, 657 cm^{-1}.

^{1}H NMR ($CDCl_3$): 7.97 (dd, H-2), 7.91 (m, H-6), 7.54 (dd, H-9), 7.34 (m, H-5), 7.03 (dd, H-10), 3.88 ppm (s, H-12).

^{13}C NMR ($CDCl_3$): 163.39 (C-11), 162.16 (d, C-4), 137.81 (dd, C-6),133.79 (d, C-9), 131.34 (m, C-2), 129.21 (d, C-1), 121.90 (q, C-7), 121.05 (d, C-8), 119.50 (m, C-3), 117.75 (dd, C-5), 114.78 (d, C-10), 55.47 ppm (C-12).

^{19}F NMR ($CDCl_3$): -62.64 (d, F-7), -108.26 ppm (q, F-4).

^{31}P NMR ($CDCl_3$): 25.81 ppm.

6.3.4 Synthesis of the monomer bis(4-fluorophenyl)phenylphosphine

In a 250-mL three-necked round-bottom flask equipped with a condenser, nitrogen inlet, and stir bar a solution of 4-bromo fluorobenzene (21.2 g, 120 mmol) in perfectly dried THF was added slowly to magnesium turnings (3.7 g, 152 mmol). The reaction was initiated by addition of a trace of iodine. The resulting mixture was stirred at 25°C for 4–5 h, until consumption of almost all magnesium turnings. After complete addition of the bromide the resulting brown solution was heated to reflux for 2.5 h. After that the reaction mixture was cooled to 0 °C with an ice bath. Subsequently, a solution of 10.0 g (60 mmol) of dichloro phenylphosphine in 35 mL of dry THF was added over a period of 30 min.

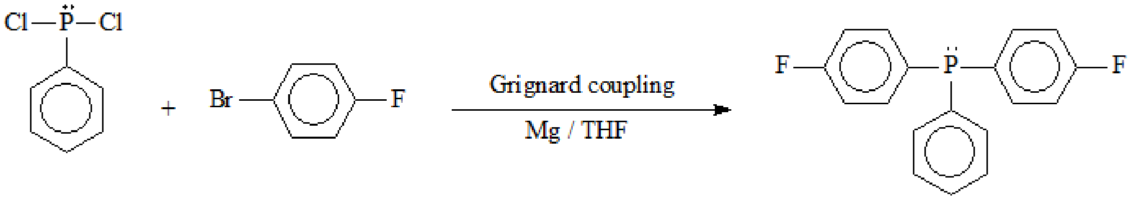


Figure 72: Synthesis of trivalent phosphorus containing monomer

The reaction mixture was allowed to warm to room temperature and was kept for overnight under stirring maintaining perfect inert atmosphere. From reaction mixture pure product was collected using filtration column technique under vacuum. The solvents were removed via rotary evaporation followed by vacuum. An amber colored, highly viscous oily liquid was obtained.

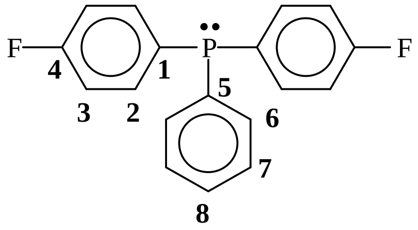


Figure 73: Chemical structure of bis(4-fluorophenyl) phenylphosphine with assignment of NMR signals

Yield: 12.8 gm (77.01 %)

Anal. Calcd for $C_{18}H_{13}F_2P$ (298.27 g/mol): C, 72.48; H, 4.39.

^{1}H NMR ($CDCl_3$) δ: 7.56 (4H, m, H-2), 7.46 (2H, m, H-6), 7.35 (1H, m, H-8), 7.27 (2H, m, H-7), 7.15 (4H, m, H-3) ppm.

^{31}P NMR ($CDCl_3$): -7.8 ppm.

6.3.5 Synthesis of silylated bisphenol A

Bisphenol-A (0.2 mol) and hexamethyldisilazane (0.3 mol) were refluxed in dry toluene (150 ml) until the evolution of NH_3 had almost ceased. The evolution of NH_3 was controlled using litmus paper. The reaction mixture was then concentrated in vacuum and the product was isolated by distillation over a short path apparatus in a vacuum of 10^{-2} bar.

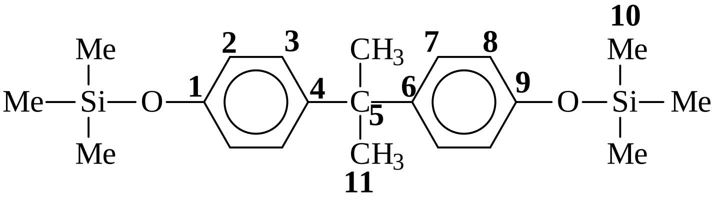


Figure 74: Chemical structure of silylated bisphenol-A

Yield: 12.5 gm (76.59 %)

^{1}H NMR ($CDCl_3$) δ: 7.34 (4H, dd, H-3,3'; H-7,7'), 7.05 (4H, dd, H-2,2'; H-8,8'), 1.5 (6H, s, H-11,11'), 0.005 (18H , s, H-10) ppm.

6.3.6 Synthesis of bis(4-fluorophenyl) phenylphosphine-borane complex

The synthetic route of choice for the borane protection of bis(4-fluorophenyl) phenylphosphine was the use of BH_3.THF in THF as solvent due to its ease of handling. BH_3.THF (4 equiv.) was added to a THF solution of the bis(4-fluorophenyl) phenylphosphine at 0°C and was allowed to stir overnight at room temperature to give the corresponding phosphine-borane adduct.

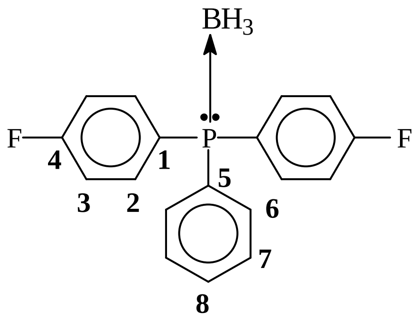


Figure 75: Chemical structure of bis(4-fluorophenyl) phenylphosphine-borane complex with assignment of NMR signals

^{1}H NMR ($CDCl_3$) δ: 7.56 (4H, m, H-2), 7.46 (2H, m, H-6), 7.35 (1H, m, H-8), 7.27 (2H, m, H-7), 7.15 (4H, m, H-3) ppm, 1.23 (3H, m, -BH_3) ppm.

^{31}P NMR ($CDCl_3$): 19.66 ppm ($P \rightarrow BH_3$)

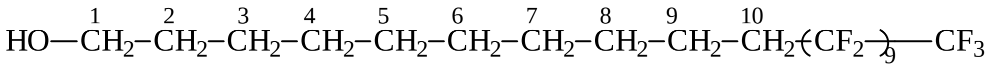
6.3.7 Synthesis of semifluorinated alcohol

Firstly in three neck reaction flask 5.0006 g (5.71 ml) dec-9-ene-1-ol was taken. In a separate vial 20.671 gm perfluorodecyliodide was weighed and then poured into the main reaction flask. Closing the system with septum the system was kept in vacuum and then flashed with N_2. Vacuum and flashing with N_2 then continued for three more time. In an oil bath the system fitted with a condenser and a magnet was heated up to 75°C on top of a magnetic stirrer.

Table 20: Materials required synthesizing semi fluorinated alcohol

	Perfluorodecyliodide	**Dec-9-ene-1-ol**	**AIBN**	**Tri-n-butyl-tinhydride**
Formula weight (g/mol)	645	156.27	164	291.05
Mole	0.032	0.032	0.00047 0.0003	0.064

Portion wise first 77.08 mg AIBN was added into the system and then it was heated at 80°C for 5 hrs. 30 ml of dry toluene was added into the system with another portion of 49.2 mg AIBN. Keeping N_2 on through one inlet, 16.934 ml of tri-n-butyl tinhydride was added through another inlet using syringe. Keeping temperature fixed at 80°C the reaction was run for another 18 hr. After removing from heat the reaction was cooled down for 30-45 mins and then poured into a beaker containing 500 ml of methanol. Then the beaker was left for 1-2 days. By that time the excess tin hydride was fully removed from the product and came into methanol. Then it was filtered and the filtered product was washed three-four times using fully cold toluene. After removal of initial solvent the product was put into the vacuum drier for overnight at 50°C. Perfectly white powder was obtained. Then it was characterized using ^{1}H NMR.



$$HO-\overset{1}{CH_2}-\overset{2}{CH_2}-\overset{3}{CH_2}-\overset{4}{CH_2}-\overset{5}{CH_2}-\overset{6}{CH_2}-\overset{7}{CH_2}-\overset{8}{CH_2}-\overset{9}{CH_2}-\overset{10}{CH_2}-(CF_2)_9-CF_3$$

Figure 76: Chemical structure of semifluorinated alcohol with assignment of NMR signals

Yield: 20.5 gm (61 %)

^{1}H NMR ($CDCl_3$ and drop of DMSO-d^6) δ: 3.51 (2H, t, H-1), 2.78 (2H, tt, H-2), 2.5 (2H, tt, H-10), 1.98 (2H, ddt, H-9), 1.51 (2H, tt, H-3) ppm, 1.23-1.30 (10H, tt, H-4,5,6,7,8) ppm.

6.3.8 Synthesis of Mitsunobu adduct

10 mmol of 5-Me-IPA, 10 mmol of HO-H_nF_n and 12 mmol of TPP were taken in a round bottom flask and then the flask mouth was closed with septum immediately. After that using a pipe attached with a needle the reaction container was kept simultaneously under vacuum and nitrogen. The process was repeated for 3-4 times. Then the round bottom flask was put under ice bath and slowly and steadily DEAD was added into the reaction. Around 25 ml of dry THF was added into the reaction. The whole system (with ice bath) was kept on a magnetic stirrer for 25 mins. After that slowly the ice bath was removed and the reaction system was left under stirring for another 24 hrs keeping temperature at around 50°C.

After 24 hrs of reaction, round bottom flask was removed from stirring/ heating and the THF was evaporated using a rotary evaporator. Di-ethyl ether was added into the system and kept stirring for another sometime. Then the product was filtered and purified using column chromatography. Perfect white coloured product was obtained.

When we replaced TPP with our reactive polymer the same procedure was followed but the purification step was a lot easier. There was no need for column chromatography for purification. Only a hexane wash was required to remove the slight yellowish colour.

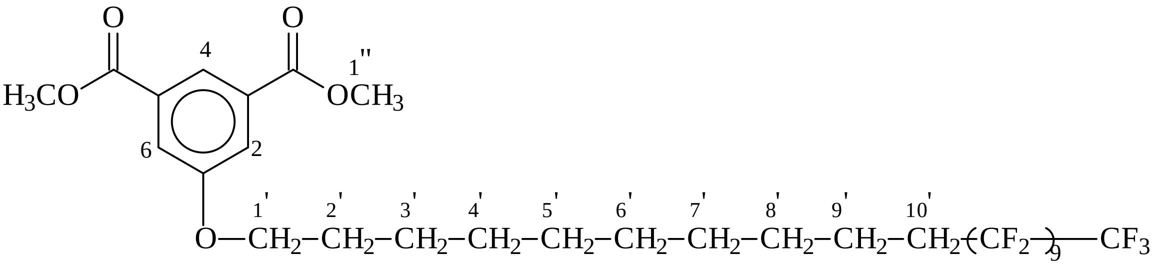


Figure 77: Chemical structure of Mitsunobu adduct with assignment of NMR signals

Yield: Using TPP (33 %)
Using polymers (50-55 %)

^{1}H NMR ($CDCl_3$) δ: 8.23 (1H, s, H-4), 7.70 (2H, s, H-2 and H-6), 3.96 (2H, dt, H-1'), 3.82 (6H, s, H- 1"), 2.01 (2H, tt, H-2'), 1.75 (2H, tt, H-10'), 1.52 (2H, ddt, H-9'), 1.42 (2H, tt, H-3') ppm, 1.23-1.30 (10H, tt, H-4,5,6,7,8) ppm

6.4 Synthesis of polymers

Polymerization reactions for the synthesis of PAEPOs were carried out with stoichiometric amounts of the respective bisfluorophosphine oxide monomer and the bisphenol in presence of an excess of K_2CO_3 in NMP and toluene as solvent.

The reaction components according to **Table 21** were weighted into a pre-dried three-necked flask equipped with nitrogen inlet, mechanical stirrer and condenser with Dean-Stark trap. The reaction was carried out under nitrogen and mechanical stirring. The reaction mixture was heated at 140 °C for the first four hours. The water that formed due to deprotonation of the diphenols was removed azeotropically with toluene by means of a Dean-Stark trap. After completion of the bisphenoxide formation the temperature was raised up to 180 °C and maintained for further four hours. After that time, the effective nucleophilic displacement reaction happened. The resulting viscous polymer solution in NMP was precipitated in the tenfold excess of methanol containing a few drops of conc. HCl for better removal of the excess base present in the system. The isolated fibrous polymers were washed several times with hot water to remove inorganic impurities. The obtained polymers were dried under reduced pressure in a vacuum oven for 12 hours at 65 °C. The fibrous product was dried again at 120 °C for 5 h under vacuum and used for further analysis.

Table 21: Batch size for synthesis of poly(arylene ether phosphine oxide)s

Polymer	Diol (mol) (g)	Bisfluoro compound (mol) (g)	NMP (mL)	K_2CO_3 (g)	Toluene (mL)
P2	0.00289 0.725	0.00289 0.910	16.3	0.960	32.7
P3	0.00219 0.500	0.00219 0.688	11.88	0.726	23.7

P4	0.00201	0.00201	10	0.668	20.1
	0.375	0.632			
P5	0.00141	0.00141	9.63	0.470	19.2
	0.324	0.639			
P6	0.00150	0.00150	9.57	0.498	19.1
	0.28	0.677			
P7	0.00164	0.00164	11.6	0.578	23.2
	0.375	0.790			
P8	0.00174	0.00174	11.6	0.578	23.2
	0.325	0.840			

6.4.1 Poly(arylene ether phosphine oxide) [PAEPO] P2

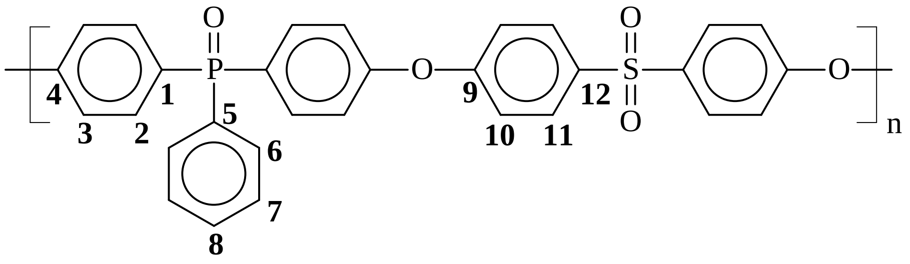


Figure 78: Chemical structure of PAEPO P2 with assignment of NMR signals

Elemental analysis: Calcd. for $C_{30}H_{21}O_5PS$ (524.52) $_n$: C: 68.7%; H: 4.04%. Found C: 69.01%; H: 4.05%.

FTIR (KBr) ῡ: 3068 (aromatic C-H stretch), 1598 (aromatic C=C stretch), 1485 (P-Ar stretch), 1322 (C-O-C asymmetric stretch), 1056 (C-O-C symmetric stretch) cm^{-1}.

^{1}H NMR ($CDCl_3$) δ: 7.83 (d, H-2), 7.78c (d, H-11), 7.61 (dd, H-6); 7.49 (t, H-8), 7.4 (t, H-7), 6.82 (d, H-10) ppm.

^{13}C NMR ($CDCl_3$) δ: 162.10 (C-9), 159.99 (C-4), 158.08 (C-12), 136.12 (d, C-3), 133.92 (C-8), 131.4 (d, C-6), 130.85 (m, C-2), 128.78 (d, C-5), 119.88 (C-10), 119.62 (d, C-7), 119.29 (C-11), 116.10 (d, C-1) ppm.

^{31}P NMR ($CDCl_3$) δ: 28.7 (s) ppm.

6.4.2 Poly(arylene ether phosphine oxide) [PAEPO] P3

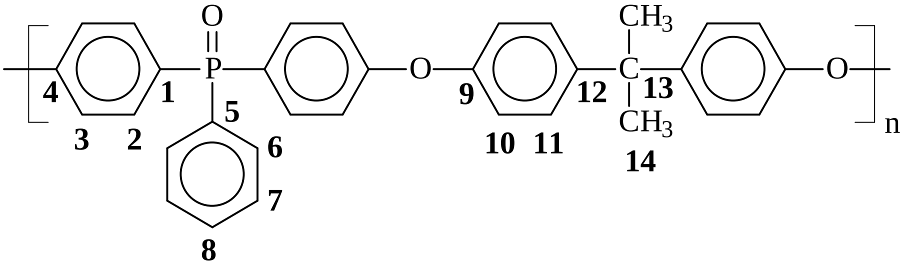


Figure 79: Chemical structure of PAEPO P3 with assignment of NMR signals

Elemental analysis: Calcd. for $C_{33}H_{27}O_3P$ $(502.54)_n$: C: 78.87%; H: 5.42% ; Found: C: 78.95%; H: 5.44%.

FTIR (KBr) ῡ: 3058 (aromatic C-H stretch), 1601 (aromatic C=C stretch), 1486 (P-Ar stretch), 1324 (C-O-C asymmetric stretch), 1054 (C-O-C symmetric stretch) cm^{-1}.

^{1}H NMR ($CDCl_3$) δ: 7.66 (m, H-6), 7.58 (H-2), 7.52 (t, H-8), 7.44 (m, H-7), 7.22 (d, H-11), 7.01 (d, H-3), 6.94 (d, H-10), 1.68 (s, H-14) ppm.

^{13}C NMR ($CDCl_3$) δ: 161.1 (C-4), 153.3 (C-9), 146.7 (C-12), 134.0 (d, C-2), 132.9 (d, C-5), 132.0 (d, C-6), 131.8 (C-8), 128.4 (d, C-7), 128.3 (C-11), 126.1 (d, C-1), 119.5 (C-10), 117.5 (d, C-3), 42.3 (C-13), 31.0 (C-14) ppm.

^{31}P NMR ($CDCl_3$) δ: 29.0 (s) ppm.

6.4.3 Poly(arylene ether phosphine oxide) [PAEPO] P4

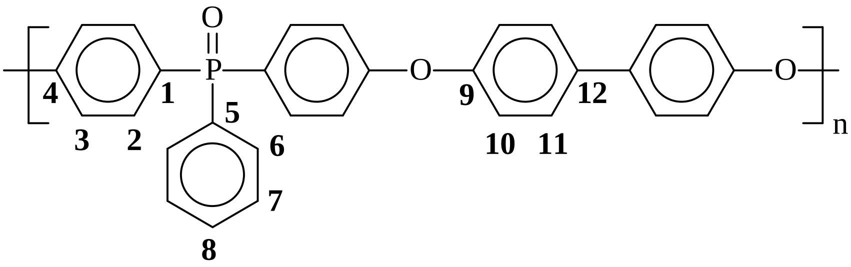


Figure 80: Chemical structure of PAEPO P4 with assignment of NMR signals

Elemental analysis: Calcd. for $C_{30}H_{21}O_3P$ $(460.46)_n$: C: 78.25%; H: 4.60%. Found: C: 78.28%; H: 4.63%.

FTIR (KBr) ῡ: 3038 (aromatic C-H stretch), 1599 (aromatic C=C stretch), 1484 (P-Ar stretch), 1325 (C-O-C asymmetric stretch), 1052 (C-O-C symmetric stretch) cm^{-1}.

^1H NMR ($CDCl_3$) δ: 7.69 (m, H-6), 7.64 (H-2), 7.22 (d, H-11), 7.54 (t, H-8), 7.47 (m, H-7), 7.12 (d, H-10), 7.08 (d, H-10) ppm.

^{13}C NMR ($CDCl_3$) δ: 160.9 (C-4), 155.0 (C-9), 136.7 (C-12), 134.1 (d, C-2), 132.8 (d, C-5), 132.0 (d, C-6), 131.9 (C-8), 128.5 (d, C-7), 128.5 (C-11), 126.4 (d, C-1), 120.4 (C-10), 117.8 (d, C-3) ppm.

^{31}P NMR ($CDCl_3$) δ: 28.9 (s) ppm.

6.4.4 Poly(arylene ether phosphine oxide) [PAEPO] P5

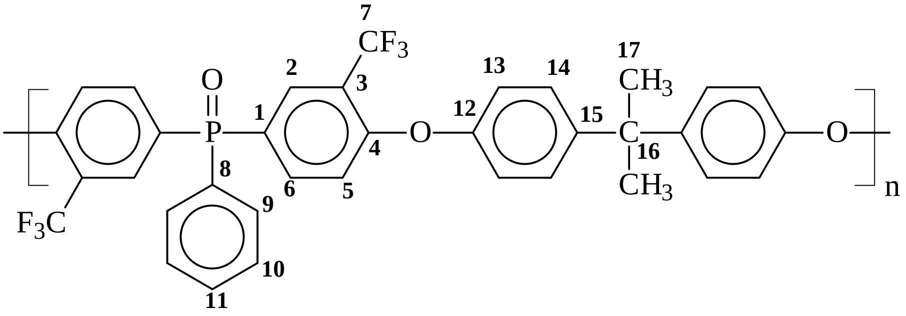


Figure 81: Chemical structure of PAEPO P5 with assignment of NMR signals

Elemental analysis: Calcd. for $C_{35}H_{25}O_3F_6P$ $(638.55)_n$: C: 65.83%; H: 3.95%. Found: C: 65.88%; H: 3.83%.

FTIR (KBr) ῡ: 3038 (aromatic C-H stretch), 1599 (aromatic C=C stretch), 1486 (P-Ar stretch), 1323 (C-O-C asymmetric stretch), 1052 (C-O-C symmetric stretch), 1258, 1136 (C-F stretching) cm^{-1}.

^1H NMR ($CDCl_3$) δ: 7.95 (d, H-2), 7.65 (dd, H-6, H-9), 7.58 (t, H-11), 7.49 (dt, H-10), 7.26 (d, H-14), 6.99 (d, H-13), 6.94 (d, H-5) ppm.

^{13}C NMR ($CDCl_3$) δ: 159.4 (C-4), 152.5 (C-12), 137.0 (C-6), 132.6 (C-11), 131.8 (d, c-9), 131.3 (m, C-2), 131.2 (d, C-8), 128.9 (d, C-10), 128.5 (C-14), 125.6 (d, C-1), 122.8 (q, C-7), 120.9 (dq, C-3), 120.1 (C-13), 117.3 (d, C-5), 42.5 (C-16), 30.9 (C-17) ppm.

19F NMR ($CDCl_3$) δ: -63.5 (s, F-7)

^{31}P NMR ($CDCl_3$) δ: 26.4 (s) ppm.

6.4.5 Poly(arylene ether phosphine oxide) [PAEPO] P6

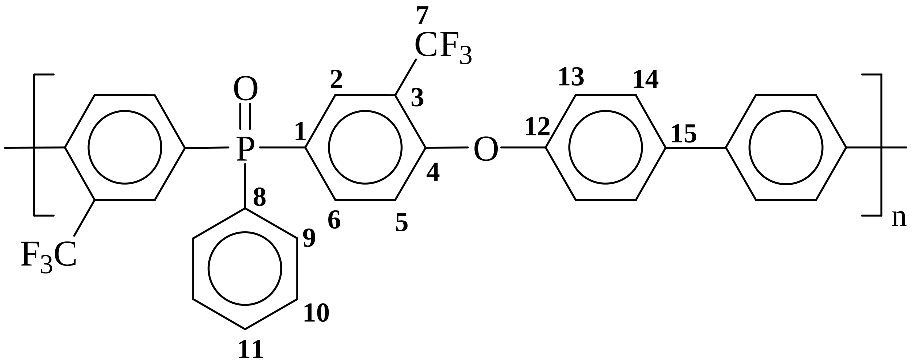


Figure 82: Chemical structure of PAEPO P6 with assignment of NMR signals

Elemental analysis: Calcd. for $C_{32}H_{19}O_3F_6P$ $(596.464)_n$: C: 64.44%; H: 3.21%. Found: C: 64.88%; H: 3.37%.

FTIR (KBr) ῡ: 3038 (aromatic C-H stretch), 1601 (aromatic C=C stretch), 1485 (P-Ar stretch), 1323 (C-O-C asymmetric stretch), 1055 (C-O-C symmetric stretch), 1258, 1136 (C-F stretching) cm^{-1}.

^1H NMR ($CDCl_3$) δ: 7.99 (d, H-2), 7.73 (dd, H-6), 7.67 (dd, H-9), 7.61 (H-11, H-14), 7.52 (t, H-10), 7.16 (H-13), 7.03 (d, H-5) ppm.

^{13}C NMR ($CDCl_3$) δ: 159.1 (C-4), 154.3 (C-12), 137.0 (C-6), 137.4 (C-15), 137.1 (d, c-6), 132.7 (C-11), 131.8 (d, C-9), 131.3 (m, C-2), 131.0 (d, C-8), 129.0 (d, C-10), 128.8 (C-14), 126.0 (d, C-1), 122.8 (q, C-7), 121.2 (dq, C-3), 120.8 (C-13), 117.8 (d, C-5) ppm.

19F NMR ($CDCl_3$) δ: -63.4 (s, F-7)

^{31}P NMR ($CDCl_3$) δ: 26.4 (s) ppm.

6.4.6 Poly(arylene ether phosphine oxide) [PAEPO] P7

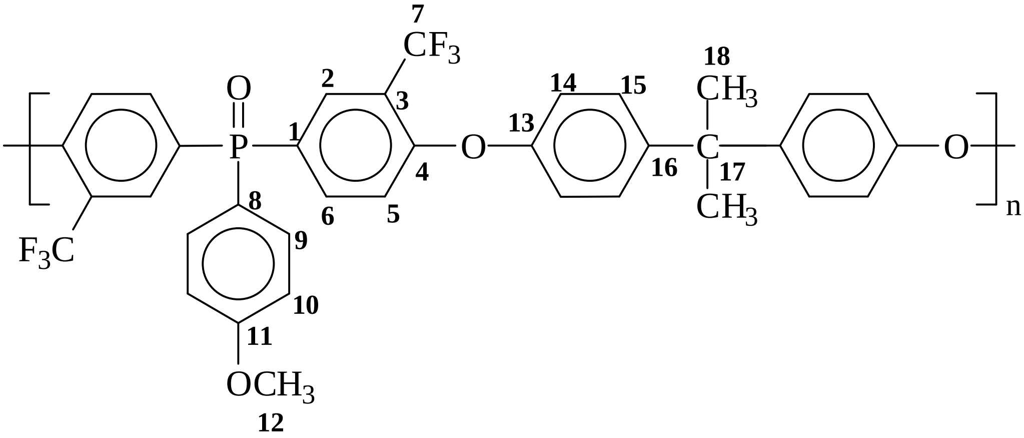


Figure 83: Chemical structure of PAEPO P7 with assignment of NMR signals

Elemental analysis: Calcd. for $C_{36}H_{27}O_4F_6P$ $(668.571)_n$: C: 64.67%; H: 3.60%. Found: C: 64.86%; H: 3.93%.

FTIR (KBr) ῡ: 3038 (aromatic C-H stretch), 1598 (aromatic C=C stretch), 1485 (P-Ar stretch), 1325 (C-O-C asymmetric stretch), 1057 (C-O-C symmetric stretch), 1261, 1137 (C-F stretching) cm^{-1}..

^{1}H NMR ($CDCl_3$) δ: 7.95 (d, H-2), 7.65 (dd, H-6), 7.55 (dd, H-9), 7.25 (d, H-15), 6.99 (H-10, H-14), 7.35 (d, H-5), 3.85 (H-12), 1.69 (H-18) ppm.

^{13}C NMR ($CDCl_3$) δ: 163.0 (C-11), 159.2 (C-4), 152.5 (C-13), 147.6 (C-16), 137.0 (d, C-6), 133.8 (d, C-9), 131.2 (m, C-2), 128.5 (C-15), 126.2 (d, C-1), 122.9 (q, C-7), 122.2 (d, C-8), 120.8 (m, C-3), 120.0 (C-14), 117.4 (d, C-5), 114.5 (d, C-10), 55.4 (C-12), 42.5 (C-17), 30.9 (C-18) ppm.

19F NMR ($CDCl_3$) δ: -63.4 (s, F-7)

^{31}P NMR ($CDCl_3$) δ: 26.8 (s) ppm.

6.4.7 Poly(arylene ether phosphine oxide) [PAEPO] P8

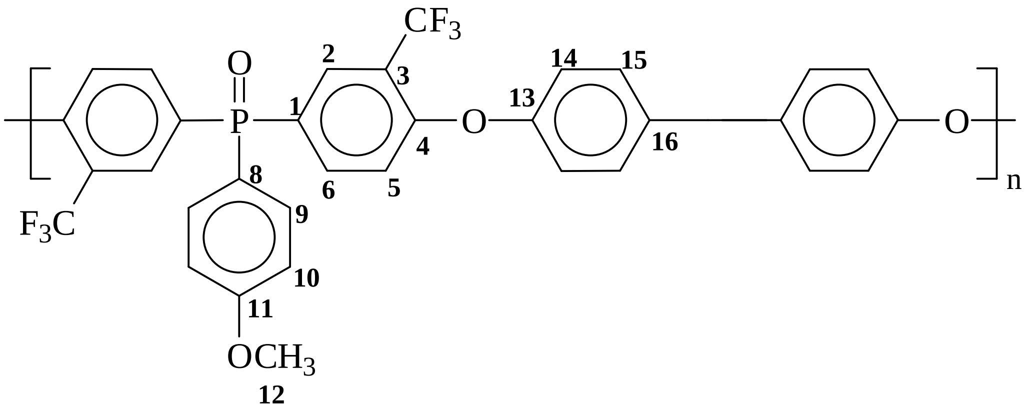


Figure 84: Chemical structure of PAEPO P8 with assignment of NMR signals

Elemental analysis: Calcd. for $C_{33}H_{21}O_4F_6P$ $(626.491)_n$: C: 63.27%; H: 3.38%. Found: C: 63.58%; H: 3.62%.

FTIR (KBr) ῡ: 3038 (aromatic C-H stretch), 1601 (aromatic C=C stretch), 1485 (P-Ar stretch), 1323 (C-O-C asymmetric stretch), 1053 (C-O-C symmetric stretch), 1258, 1130 (C-F stretching) cm^{-1}..

^{1}H NMR ($CDCl_3$) δ: 7.98 (d, H-2), 7.73 (dd, H-6), 7.58 (dd, H-9), 7.60 (d, H-15), 7.16 (d, H-14), 7.02 (H-5, H-10), 3.86 (H-12) ppm.

^{13}C NMR ($CDCl_3$) δ: 163.1 (C-11), 159.0 (C-4), 154.5 (C-13), 137.6 (C-16), 137.1 (d, C-6), 133.8 (d, C-9), 131.3 (m, C-2), 128.8 (C-15), 126.6 (d, C-1), 122.8 (q, C-7), 122.0 (d, C-8), 121.1 (m, C-3), 120.8 (C-14), 117.8 (d, C-5), 114.6 (d, C-10), 55.4 (C-12),

19F NMR ($CDCl_3$) δ: -63.3 (s, F-7)

^{31}P NMR ($CDCl_3$) δ: 26.7 (s) ppm.

Chapter 7

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7 References

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Chapter 8

Appendix

8 Appendix

8.1 List of figures

8.2 List of tables

Versicherung

Hiermit versichere ich, dass ich die vorliegende Arbeit ohne unzulässige Hilfe Dritter und ohne Benutzung anderer als der angegebenen Hilfsmittel angefertigt habe; die aus fremden Quellen direkt oder indirekt übernommenen Gedanken sind als solche kenntlich gemacht. Die Arbeit wurde bisher weder im Inland noch im Ausland in gleicher oder ähnlicher Form einer anderen Prüfungsbehörde vorgelegt.

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Frühere erfolglose Promotionsverfahren haben nicht stattgefunden.

Hiermit erkenne ich die Promotionsordnung der Fakultät Mathematik und Naturwissenschaften der Technischen Universität Dresden vom 23.02.2011 an.

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Dresden, 15.05.2015