ABSTRACT


The most common flame retardant systems for rendering textiles flame retardant are halogen containing compounds. Halogen-based compounds are not environmentally friendly because they generate toxic gases, which are endocrine disruptive. Recently, phosphorus-nitrogen-based flame retardant systems have attracted more attention in the academia and industry because of their good thermal stability, low toxicity, and superior performance owing to the synergistic effect of nitrogen and phosphorous. Two of the widely used phosphorus-based flame retardants are Tetrakis(hydroxy methyl phosphonium chloride (THPC) and Pyrovatex. However, THPC requires a very special ammonia-based application method and equipment where Pyrovatex does not have good wash fastness properties. Hence, flame retardants that are durable to washing, halogen-free, efficient in performance, easy to apply and benign to the environment are in high demand. The main thrust of this work was two-fold: 1- the synthesis of novel bifunctional phosphorous-nitrogen containing monomers, and 2-their graft polymerization on cotton thermally in presence of the thermal initiator $K_2S_2O_8$. Three novel phosphorous-nitrogen flame retardant monomers were synthesized in our laboratory and characterized using Attenuated Total Reflectance/Fourier Transform-Infra Red (ATR/FT-IR) and Electron Spray Ionization Mass Spectrometry (ESI-MS). The monomers were applied separately and graft polymerized on cotton in presence of $K_2S_2O_8$. The performance of each monomer was evaluated using Thermal Gravimetric Analysis (TGA), % grafting, and flame test. It was shown that the performance of the monomers as
flame retardants finishes for cotton was in the following order: monomer 3 > monomer 1 > monomer 2. The molecular structures for monomers 1-3 are shown below.

The superior performance of monomer 3 was attributed to the presence of more nitrogen atoms compared to monomers 1 and 2, which increased the synergistic effect of the P-N system. Padding methods showed more promising results than exhaust methods.
Synthesis, Characterization and Evaluation of Novel Halogen Free Bi-Functional Flame Retardant Monomers

by
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A thesis submitted to the Graduate Faculty of North Carolina State University in partial fulfillment of the requirements for the degree of Master of Science in Textile Chemistry

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Hammad Arshad Cheema was born on July 20, 1983 in city called Sialkot, in the province of Punjab, Pakistan. He stayed with his parents by the completion of his higher secondary school education. Then he was admitted to National Textile University, Faisalabad the only prestigious school for textile education of its type in Pakistan. After completing his Bachelor of Engineering with major in Textile Chemistry he joined Nishat Dyeing and Finishing Mills, Ltd. Lahore, Pakistan. At this facility he worked at the position of shift supervisor in the department of textile printing. He was in charge of 16-color rotary printing m/c, and worked practically while playing with color matching in pigment, reactive, and vat-disperse printing. He was also fully involved in the process and product development for controlled IR reflecting fabrics for army, which is used as camouflage against night vision cameras. After that he managed to win a Fulbright Scholarship which resulted in his admission at North Carolina State University for Master of Science in Textile Chemistry degree.
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TABLE OF CONTENTS

LIST OF FIGURES........................................................................................................... vii

LIST OF TABLES ........................................................................................................... viii

1. INTRODUCTION ........................................................................................................ 1

2. LITERATURE REVIEW ............................................................................................. 3

   2.1 History of Flame Retardants for Textiles: .............................................................. 3

   2.2 Flammability of Textiles: ..................................................................................... 4

       2.2.1 Rate of Heat release ....................................................................................... 6

       2.2.2 Smoke ........................................................................................................... 7

       2.2.3 Chemical Nature of Fibers ........................................................................... 7

       2.2.4 Physical Structure of Yarn and Fabric ......................................................... 9

   2.3 Approaches to Obstruct Combustion Cycle: ....................................................... 9

       2.3.1 Coating Theory ............................................................................................ 9

       2.3.2 Thermal Theory .......................................................................................... 9

       2.3.3 Gas Theory ................................................................................................... 9

       2.3.4 Dehydration Theory .................................................................................... 10

   2.4 Mechanism of Flame Retardants .......................................................................... 10

       2.4.1 Gas or Vapor- phase Mechanism .................................................................. 11

           2.4.1.1 Comparison among different Halogen Derivatives ................................. 13

       2.4.2 Condensed Phase Mechanism ...................................................................... 14

           2.4.2.1 Effect of Dehydration on Char Formation ............................................. 14

           2.4.2.2 Effect of Cross-linking on Char Formation ........................................... 15

           2.4.2.3 Effect of Structural Parameters on Char Formation ............................ 16

       2.4.3 Intumescent Systems .................................................................................... 17

       2.4.4 Physical Approach, Insulation and Heat Sink .............................................. 19

   2.5 Classification of Flame Retardants ....................................................................... 21

       2.5.1 Inorganic Salts ............................................................................................. 21

       2.5.2 Phosphorus Containing Flame Retardants (PCFR). ...................................... 22

           2.5.2.1 PCFR and Condensed Phase Mechanism .............................................. 22
2.5.2.1.1 PCFR and Nitrogen Synergism ................................................................. 24
2.5.2.1.2 PCFR and Coating modes of action ...................................................... 24
2.5.2.1.3 PCFR’s effect on melt viscosity .............................................................. 25
2.5.2.2 PCFR and Vapor Phase Mechanism ......................................................... 25
   2.5.2.2.1 PCFR and Physical Modes of Action .................................................. 26
2.5.2.3 Interaction of PCFR with other Flame Retardants .................................... 26
   2.5.2.3.1 Synergism of the mixture of halogen-phosphorus additives ................ 26
   2.5.2.3.2 Phosphorus and antimony ............................................................... 27
   2.5.2.3.3 Phosphorus and Mineral Fillers ...................................................... 27
2.5.3 Halogen Containing Flame Retardants (HCFR) ......................................... 27
   2.5.3.1 Halogen- Antimony Synergism ............................................................. 28
   2.5.3.2 Ammonium Bromide as Flame Retardant .............................................. 29
   2.5.3.3 Environmental Concerns of HCFR .................................................... 29
2.5.4 Nano-clay based flame retardant systems .................................................. 31
2.6 Future Trends in Textile Flame Retardants: .................................................. 33
2.7 Environmental Concerns ............................................................................. 37
2.8 Evaluation of Flame Retardants ................................................................ 39
3 EXPERIMENTAL ......................................................................................... 41
  3.1 Materials ..................................................................................................... 41
  3.2 Glassware Outline ..................................................................................... 41
  3.3 Synthesis .................................................................................................... 42
     3.3.1 Synthesis of Monomer-1 (EDAEP) ......................................................... 48
     3.3.2 Synthesis of Monomer-2 (MDAEP) ....................................................... 49
     3.3.3 Synthesis of Monomer-3 (DMDAEP) ..................................................... 51
  3.4 Characterization ....................................................................................... 52
  3.5 Application of Monomers ........................................................................ 53
     3.5.1 Fabric ................................................................................................... 53
     3.5.2 Thermal Initiation Method ................................................................... 53
        3.5.2.1 Application of Monomers ............................................................... 53
3.6.1 SEM (Scanning Electron Microscopy) ................................................................. 55  
3.6.2 Grafting Percentage ....................................................................................... 55  
3.6.3 TGA (Thermal Gravimetric Analysis) ............................................................... 55  
3.6.4 Burning Test .................................................................................................. 56  
4 RESULTS AND DISCUSSION ............................................................................. 57  
4.1 Synthesis: ......................................................................................................... 57  
4.2 Characterization of Intermediates ..................................................................... 59  
4.2.1 Characterization of Intermediate 1 ................................................................. 59  
4.2.2 Characterization of Intermediate 2 ................................................................. 62  
4.2.2 Characterization of Intermediate 3 ................................................................. 62  
4.3 Characterization of Monomers ......................................................................... 64  
4.3.1 Molecular Structure Characterization of Monomer 1 .................................... 65  
4.3.2 Molecular Structure Characterization of Monomer-2 .................................... 67  
4.3.3 Molecular Structure Characterization of Monomer 3 .................................... 69  
4.3.4 P=O Absorption Frequency and Flame Retardancy ..................................... 71  
4.4 Application of Monomers ................................................................................. 72  
4.5 Evaluation of Fabrics ....................................................................................... 73  
4.5.1 Scanning Electron Spectroscopy (SEM) ......................................................... 73  
4.5.2 Grafting Percentage (graft. %). .................................................................. 75  
4.5.3 Thermogravimetric Analysis ....................................................................... 75  
4.5.4 Burning Test ................................................................................................ 78  
4.5.4.1 Surface Morphology of Char ................................................................. 82  
5 CONCLUSIONS ................................................................................................ 85  
6 FUTURE WORK .................................................................................................. 86  
7 REFERENCES ..................................................................................................... 87
# LIST OF FIGURES

<table>
<thead>
<tr>
<th>Figure</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>Figure 2.1</td>
<td>Steps in combustion cycle of textiles.</td>
<td>5</td>
</tr>
<tr>
<td>Figure 2.2</td>
<td>Monomers synthesized by Tsafack and Levalois-Grützmacher.</td>
<td>36</td>
</tr>
<tr>
<td>Figure 3.1</td>
<td>Reaction setup a) argon inlet b) bubbler c) addition funnel d) ice bat.</td>
<td>42</td>
</tr>
<tr>
<td>Figure 3.2</td>
<td>Vertical flame test schematic.</td>
<td>56</td>
</tr>
<tr>
<td>Figure 4.1</td>
<td>FT-IR spectrum of Intermediate 1.</td>
<td>60</td>
</tr>
<tr>
<td>Figure 4.2</td>
<td>Mass spectrums for Intermediate 1.</td>
<td>61</td>
</tr>
<tr>
<td>Figure 4.3</td>
<td>FT-IR spectrum of Intermediate 2.</td>
<td>62</td>
</tr>
<tr>
<td>Figure 4.4</td>
<td>FT-IR spectrum of Intermediate 3.</td>
<td>63</td>
</tr>
<tr>
<td>Figure 4.5</td>
<td>FT-IR Spectrum of Monomer-1</td>
<td>65</td>
</tr>
<tr>
<td>Figure 4.6</td>
<td>Mass spectrum of Monomer-1</td>
<td>66</td>
</tr>
<tr>
<td>Figure 4.7</td>
<td>FT-IR spectrum for Monomer 2</td>
<td>67</td>
</tr>
<tr>
<td>Figure 4.8</td>
<td>Mass spectrum of monomer 2</td>
<td>69</td>
</tr>
<tr>
<td>Figure 4.9</td>
<td>FT-IR spectrum for Monomer-3</td>
<td>70</td>
</tr>
<tr>
<td>Figure 4.10</td>
<td>Showing SEM images A) &amp; B)</td>
<td>74</td>
</tr>
<tr>
<td>Figure 4.11</td>
<td>TGA graph for cotton control and thermally initiated sample.</td>
<td>77</td>
</tr>
<tr>
<td>Figure 4.12</td>
<td>Showing char residue for A) untreated B)monomer-1 C)monomer-2 D)monomer-3</td>
<td>80</td>
</tr>
<tr>
<td>Figure 4.13</td>
<td>Showing char residue for A) untreated and E, F) monomer 1 G,H) monomer 3 (padding method) treated unwashed and washed cotton</td>
<td>80</td>
</tr>
<tr>
<td>Figure 4.14</td>
<td>SEM images of char (A, A1), (B, B1) and (C, C1) cotton treated with monomer-1, monomer-2, and monomer-3 at 500x and 2000x magnification respectively.</td>
<td>83</td>
</tr>
</tbody>
</table>
LIST OF TABLES

Table 2.1  Summary of thermal transitions for different fiber.................................8
Table 2.2  Test methods for testing flame retardancy.............................................39
Table 3.1  Summary of trials and conditions for each monomer...............................43
Table 4.1  Absorption peaks summary for Intermediate-1......................................61
Table 4.2  Absorption peaks summary for Intermediate-3......................................63
Table 4.3  Absorption peaks summary for Monomer-1..........................................65
Table 4.4  Absorption peaks summary for Monomer-2..........................................67
Table 4.5  Absorption peaks summary for Monomer-3..........................................70
Table 4.6  Table 4.6 % grafting for monomers 1-3.................................................75
Table 4.7  Table 4.7 Burning time for treated and untreated cotton based on the vertical flame test.................................................................78
1. INTRODUCTION
Fire has been a useful tool throughout human history, but a careful handling is required. If not handled carefully fire can easily result in a disaster resulting in loss of life, and property. In United Sates only fire has killed more people than all natural disasters combined. In the year 2009, according to National Fire Protection Association (NFPA) statistics [1] of fires in USA, 1.35 million fires resulted in 3010 deaths, 17,050 injuries and $12.53 billion value loss of property. Due to the organic nature of widely used materials such as plastics, home furniture, floor, wall coverings, and electrical instruments, these materials are easily flammable. However, these materials can be rendered resistant to flame by the use of chemicals or additives known as flame retardants. By the use of an appropriate flame retardant, the escape time for victims can be increased and flammability of the substrate can be decreased reasonably thus resulting in more chances to save life and valuable assets.

According to NFPA statistics for 2009 [1] for fires in USA, 28% of the total fires happened in residential structures. These fires resulted in 86% of total deaths, 77% of total injuries and 62% of total value for property loss. In the view of these statistics, it becomes critical to sort out important items in residential structures to control the aforementioned losses. A study [2] was carried out in 2005 that evaluated the role of combustible products that are commonly found in homes as initial fuel for fires. In addition to this, the study focused on mattresses and bedding materials, apparel, curtains and drapes, upholstered furniture, interior wall, floor, and ceiling coverings. This study excluded non-home product items such as trash, building materials, combustible liquids and gases. It showed that most of the deaths were a
result of fires involving upholstered furniture while most of the injuries and property damage were caused by mattresses and bedding materials. In that regard, the death toll caused by mattresses and bedding materials is very close to the first responding fuels (e.g. combustible liquids, gases, electrical cables, and building materials) in residential structures. Hence, it becomes crucial to render upholstery, mattresses and bedding material related textiles flame retardant, so that the danger caused by these items can be minimized.

The aim of this work is to synthesize novel, bi-functional, halogen-free, and phosphorus-nitrogen-based flame retardant monomers, that can be graft polymerized on cotton with good durability, owing to the covalent bonding of the polymer to the substrate, and better performance due to the synergistic effect of the phosphorous-nitrogen system. For this purpose, a two-step route was adopted for the synthesis of three novel phosphorous-nitrogen containing monomers 1-3. The monomers were characterized by using ATR/FT-IR and ESI-MS. Monomers 1-3 were molecularly designed to have two active sites (two vinyls), so that then have better chance of covalently bonding with the substrates and possibly crosslinking with themselves, which should furnish better durable finishes on the substrate, compared to one active site. The second objective of this work was to perform graft polymerization thermally in presence of a thermal initiator.
2. LITERATURE REVIEW
The purpose of this literature review is to thoroughly cover the work done in the field of flame retardancy for textiles. A brief historical introduction was given following the current technology. In addition, emphasis was placed on phosphorus and halogen-free flame retardants. In the view of environmental concerns, a brief summary was also added on the environmental impact of flame retardants.

2.1 History of Flame Retardants for Textiles:
The treatment of wood with vinegar to impart fire resistant\(^*\) effect dates back to the first century BC. However the history of officially documented patents starts from British Pat. 551(1735). This patent reported the treatment of cellulose with a mixture of alum, iron sulphate and borax to render it flame retardant. The first systematic study on the flame proofing was carried out in 1821 by Gay-Lussac [3]. He used water solutions of ammonium chloride and ammonium phosphate to treat linen. Gay-Lussac was also the first one to suggest the reason for flame proofing by salts. According to him, effectiveness of salts is due to the low melting points, ultimately giving off nonflammable vapors or due to covering the fiber surface with a glassy layer.

In spite of some success in the field of flame retardancy, 1921 was the year when the first laundering fast process was developed [4]. Though the fabric was flame resistant, the afterglow was still a problem. In the following years, the introduction of binary systems

\(^*\) The terms fire and flame resistant mean same thing, a textile that does not continue to burn after the source of ignition has been removed. The term flame retardant refers to the chemical treatment applied in order to render textile flame resistant.
really proved a breakthrough. This finish proved invaluable during World War Two for outdoor cotton, which reported the use of chlorinated paraffins and antimony oxide [5]. In the history of flame retardants, the period from 1950 to 1970, resulted in the development of most of the current state of the art flame retardant finishes for cotton. It will be beneficial to first understand the burning behavior of textiles, and how this burning cycle can be impeded, in order to discuss the chemistry of flame retardants.

2.2 Flammability of Textiles:
Textiles are formed from fibers which are polymeric in nature. Hence, the flammability of textiles is based on the burning behavior of the pertinent polymers. In general, a flame is a gas-phase combustion process and is generated as the result of complete combustion. Combustion is the sequence of catalytic exothermic reactions, continuously provided by internally created free radicals and heat. The flammability of the textile depend on the chemical nature of fiber, the amount of heat and oxygen available, fabric weight and the construction pattern. Textiles result in diffused flames, because they need a continuous supply of oxygen diffused from the surroundings to the reaction zone. The typical model that depicts different steps toward textile combustion is shown in Figure 2.1, the Combustion Cycle: the Feedback Mechanism.

Continuous heating of textiles, results in a pyrolysis temperature $T_p$. At $T_p$, irreversible chemical changes take place which result in non-flammable gases, carbonaceous char, liquid condensates and flammable gases (carbon monoxide, hydrogen and other oxidizable molecules). The non-flammable gases released, mostly carbon dioxide, water vapor and
higher oxides of nitrogen and sulfur, depend on the chemical nature of the fiber. If the temperature of the substrate continues to rise, it results in combustion temperature $T_c$. At $T_c$, flammable gases in the presence of oxygen give immense amount of heat and light, which gives clue for the free radical nature of the combustion process.

Figure 2.1 Steps in combustion cycle of textiles [6]

The heat released from combustion is transferred back to the substrate resulting in continuation of the pyrolysis and the supply of flammable gases to the perpetuating combustion. Because of this heat transfer, the rate of the heat released is considered more important than the amount of heat from combustion [7]. Some of the free radical reactions that take place during the combustion can be summarized as shown in reaction scheme 2.1 [8].
The pyrolysis products which contain hydrogen radical are capable of reacting with atmospheric oxygen, to propagate the free radical reactions. The third reaction shown above is considered the most exothermic one, hence provides most of the energy required by the flame [7].

Other important features that should be kept in mind while studying the flammability of textiles are explained in the next sections.

**2.2.1 Rate of Heat release**

It was described that the rate of heat release was the most crucial parameter in determining the fire hazard of a textile substrate [9] because flame propagation is determined by the amount of heat evolved and not by the heat of combustion, and Cone Calorimetry was used for determining the rate of heat released. For textile materials, sufficient data are not available so far because of the difficulty of sample preparation and thinness of textile substrate.
2.2.2 Smoke
Smoke has an opaque cloud type body because of the absorption or scattering of light from individual particles [7]. Carbon monoxide is the most crucial combustion gas along with hydrogen cyanide, hydrogen chloride, sulfur oxide and other toxic organic molecules. In addition to this, smoke can impair visibility thus minimizing the chances of escape from fire area before the increase in temperature or collection of dangerous gases. Thus, there is a desperate need for smoke suppressants. Detailed reviews on flame, smoke and intermediates formed in flame were published somewhere else [7, 10, and 11].

The amount of smoke generated by a polymer depends on the chemical structure. Usually polymers with aliphatic back bones having oxygenated structures tend to form less smoke. On the contrary, polymers which have pendant aromatic groups or polyenic nature give smoky flames [7]. Also the presence of halogens decreases the amount of smoke, however, the halogen containing flame retardants give toxic and corrosive halogenated gases, which are endocrine disruptive in nature [12, 13].

2.2.3 Chemical Nature of Fibers
Like most of other properties, thermal behavior and decomposition of polymeric fibers also changes with chemical nature. The important measurements related to fire behavior of fiber forming polymers have been summarized in Table 2.1 [14].

According to the information given in Table 2.1, natural fibers are more prone to fire than synthetics. T_g, T_m, T_p and T_c are glass transition, melting, pyrolysis, and combustion temperatures, respectively. LOI is the Limiting Oxygen Index, an important measurement
that provides crucial information about the inherent burning behavior of a fiber. It shows that fibers with LOI values less than 21 % ignite easily and burn rapidly in air as compared to fibers with LOIs higher than 21% which burn slowly. In addition to this, fibers with LOIs above 26-28% are considered inherently flame retardant.

Table 2.1 Summary of Thermal Transitions for different fibers [14]

<table>
<thead>
<tr>
<th>Fiber</th>
<th>( T_g, ^\circ C )</th>
<th>( T_m, ^\circ C )</th>
<th>( T_p, ^\circ C )</th>
<th>( T_c, ^\circ C )</th>
<th>LOI, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wool</td>
<td>-</td>
<td>-</td>
<td>245</td>
<td>600</td>
<td>25</td>
</tr>
<tr>
<td>Cotton</td>
<td>-</td>
<td>-</td>
<td>350</td>
<td>350</td>
<td>18.4</td>
</tr>
<tr>
<td>Viscose</td>
<td>-</td>
<td>-</td>
<td>350</td>
<td>420</td>
<td>18.9</td>
</tr>
<tr>
<td>Nylon 6</td>
<td>50</td>
<td>215</td>
<td>431</td>
<td>450</td>
<td>20-21.5</td>
</tr>
<tr>
<td>Nylon 6.6</td>
<td>50</td>
<td>265</td>
<td>403</td>
<td>530</td>
<td>20-21.5</td>
</tr>
<tr>
<td>Polyester</td>
<td>80-90</td>
<td>255</td>
<td>420-447</td>
<td>480</td>
<td>20-21.5</td>
</tr>
<tr>
<td>Polypropylene</td>
<td>-20</td>
<td>165</td>
<td>470</td>
<td>550</td>
<td>18.6</td>
</tr>
<tr>
<td>Meta-aramid (Nomex)</td>
<td>275</td>
<td>375</td>
<td>410</td>
<td>&gt;500</td>
<td>29-30</td>
</tr>
<tr>
<td>Kevlar</td>
<td>340</td>
<td>560</td>
<td>&gt;590</td>
<td>&gt;550</td>
<td>29</td>
</tr>
</tbody>
</table>
2.2.4 Physical Structure of Yarn and Fabric
Structure of yarn and fabrics also influences the fire behavior to some extent for the given fiber. It was observed that low fabric area density and open structure intensify the burning rate compared to tightly woven and multi layered constructions [15].

2.3 Approaches to Obstruct Combustion Cycle:
In the view of the combustion cycle given in Figure 2.1, several obstruction theories were proposed, and a brief summary of these approaches have been given.

2.3.1 Coating Theory
According to this theory, the combustion cycle can be disrupted by the formation of a thin coating on the polymer surface. This coating can be formed either by chemical finishing or during the heating of a polymer. This layer excludes the air necessary for the combustion process and traps any tarry volatiles produced during polymer pyrolysis. This theory supports the working mechanism of easily fusible salts such as carbonates or borates.

2.3.2 Thermal Theory
This approach can hinder the substrate from combustion by removing the heat away from the substrate. This heat removal can be done either by dissipating the heat via an endothermic change in the flame retardant such as sublimation or by introducing a heat sink which takes away most of the heat.

2.3.3 Gas Theory
This theory supports either the formation of free radicals or non-flammable gases. As stated earlier, the combustion is a gas phase free radical process, in which the function of the flame retardant is to form radicals which trap the active radicals such as H, ‘OH and ‘OOH or to
replace these radicals with less active ones. This eventually results in termination of free radical chain propagation reactions. This approach dictates the decomposition of flame retardant to give non-combustible gases. These gases deplete the oxygen around the flame, ultimately resulting in flame retardancy. Examples of such gases are water vapor, CO₂, sulfur dioxide and hydrogen chloride.

2.3.4 Dehydration Theory
This approach advocates the catalytic dehydration of the substrate, which is cotton in most of the cases. The flame retardant causes changes in the decomposition of cotton thus resulting in less flammable tar and gases, and more char. Hence, flame retardant treated cotton decomposes at lower temperature than untreated cotton. Examples of such dehydrating agents are phosphoric and sulfuric acids [16, 17, and 18].

The dehydration approach was also proposed to work through acidic or basic mechanisms to eliminate the formation of levoglucosan, thus resulting in more char and less tar [19]. In this regard, usually a higher add-on of the flame retardant up to 10% is required. Also the basic mechanism favors the formation of dehydrocellulose followed by the formation of char [16, 17]

2.4 Mechanism of Flame Retardants
In the previous sections, basic information has been given about the nature of textile burning and its constituents. In this section, however, a detailed review will be given on the mechanistic chemistry of flame retardants. It was reported [20] that the most basic principles about the flame retardant’s mechanism for polymeric materials have been known since 1947.
Such as the effect of an additive on thermal degradation route, formation of barrier coating to exclude oxygen, dissipation of heat away from flame and inert gas evolution. Also the discovery of volatile halogen flame inhibiting effect led to the formulation of the radical trap gas phase mechanism [21]. In this section, emphasis will be placed on the mechanism of flame retardants for textile materials, i.e. the flame retardants which can be applied by coating, surface treatment or fiber incorporation.

2.4.1 Gas or Vapor-phase Mechanism
In this mechanism, the flame retardant moiety has to be volatile and reach the flame in gaseous form. In addition to this, flame retardants should also decompose and provide the flame with its active species. These active species from the flame retardant then replace or diminish the more active species from the flame through free radical mechanisms.

Fibrous polymers like other fuels react with atmospheric oxygen to give free radical-based chain reactions as shown below [8].

\[
\begin{align*}
H^+ + O_2 & \rightarrow \dot{OH} + O^+ \quad (2.1) \\
O^+ + H_2 & \rightarrow \dot{OH} + H^+ \\
\dot{OH} + CO & \rightarrow CO_2 + H^+ \quad (2.2)
\end{align*}
\]

Scheme 2.1 Free radical reactions during the combustion [8]
The reaction (2.2) is considered the most exothermic and the main energy providing step for the perpetual burning. In order to slow down or stop the combustion, it is imperative to hinder or stop these chain reactions.

The halogen derivatives have all the capacity and prerequisite to get involved in such kind of chain reactions. A halogen containing flame retardant initially takes part in the chain reaction by releasing a halogen (if it did not contain hydrogen) or halogen halide [7].

\[
\begin{align*}
MX & \rightarrow M' + X' \quad (2.3) \\
MX & \rightarrow M' + HX \quad (2.4)
\end{align*}
\]

Where \(X'\) denotes halogen radical and \(M'\) is the flame retardant molecule residue. The halogen radical further reacts with the substrate, to give hydrogen halide.

\[
\begin{align*}
RH + X' & \rightarrow HX + R' \quad (2.5)
\end{align*}
\]

Hydrogen halide is believed to be the actual flame inhibitor as it takes part in chain reactions as shown in reaction 2.6 and 2.7.

\[
\begin{align*}
H' + HX & \rightarrow H_2 + X' \quad (2.6) \\
OH' + HX & \rightarrow H_2O + X' \quad (2.7)
\end{align*}
\]

The rate of reaction denoted as (2.6) was found to be double that of the reaction denoted as (2.7). Moreover, the high ratio of \(H_2/OH\) in the flame front make the reaction denoted as
(2.6) as the main flame restraining reaction [22]. Also, the inhibiting effect is determined by the competition between reactions (2.1) and (2.6).

2.4.1.1 Comparison among different Halogen Derivatives
The flame retardant efficiency from different halogen derivatives is calculated on the bases of the rate of the reaction denoted as (2.6). The higher the rate constant \((K)\) for the reaction of hydrogen halide, the higher the flame retarding effect is. Also it was reported [24] that the rate constant readily decreases as the temperature increases, which is the reason why halogen flame retardants are not used in high temperature fires. According to Petrella’s [22] calculations, the forward reaction dominates in (2.6) between the temperature range of 500 to 1500K (Kelvin), and also \(K_{\text{HBr}}\) is much higher than \(K_{\text{HCl}}\). Also in another review, Larsen [25] showed that flame retardant potency of halogens is directly proportional to their atomic weight, such as shown by atomic weight ratios F: Cl: Br: I =1.0:1.9:4.2:6.7.

In addition to all of the above, the strength of carbon-halogen bond is also a determining factor. This is the reason why iodine and fluorine are not effective as flame retardants. The low bond strength of I-C bond results in low stability of iodine compounds. Also high stability of fluorine derivatives and high reactivity of fluorine atoms in reactions (2.6) and (2.7) render fluorine derivatives not useful as flame retardants. Accordingly, the higher potency of bromine derivatives is due to:

i. Lower bond strength and stability of aliphatic compounds

ii. Earlier and low temperature formation of HBr

iii. Higher volatility before decomposition
iv. Ease of dissociation

2.4.2 Condensed Phase Mechanism
Condensed phase mechanism suggests a chemical interaction between flame retardants and substrate. This results in the change of pyrolysis route or decomposition temperature. In this case, it gives less combustible gases, usually by favoring the formation of carbonaceous char and water [23]. Also, the heat released by combustion decreases as the amount of flame retardant increases, and, therefore, a higher amount of flame retardant is used by the condensed phase mechanism. Several modes of interaction for the condensed phase mechanism were suggested, the two most important ones were dehydration and crosslinking.

2.4.2.1 Effect of Dehydration on Char Formation
Phosphorus-based flame retardants favor dehydration and char formation in oxygen containing polymers. It was reported that 2% of phosphorus was enough to make cellulose flame retardant, as compared to 5-15% phosphorus for polyolefins [26]. The reason for this has been given as the polymers which have less oxygen or hydroxyls interact slowly with phosphorus and have to proceed through oxidation. In which case, 50-99% of phosphorus is lost by evaporation, in the form of oxides formed during the pyrolysis of phosphorus derivatives [27].

In the case of the condensed phase in cellulose, two alternative routes, A and B, were proposed. In the case of route A, in presence of an acid, dehydration takes place [28]. In the case of route B, however, the dehydration is accompanied by a carbonium ion formation.

\[(A) \text{R}_2\text{CH-CHR’OH} + \text{ZOH (acid)} \rightarrow \text{R}_2\text{CH-CHR’OZ} + \text{H}_2\text{O} \rightarrow \text{R}_2\text{C=CHR’} + \text{ZOH}\]
Scheme 2.2 Two alternate routes for condensed based mechanism in cellulose

Scheme (A) was verified as the flame retardant route for cellulose, by Differential Thermal Analysis (DTA) and Oxygen Index (OI). This mechanism greatly depends on structure of the polymer, as amorphous regions decompose before the complete decomposition of phosphorus ester, which results in loss of flame retardancy. This can be overcome by increasing the amount of flame retardant. Scheme (B) shows the dehydration of cellulose by carbonium ion based mechanism. In this case, strong acid activity is observed by the active flame retardant derivative which decrystallizes the crystalline regions rapidly. Thus, making the flame retardant efficiency not greatly dependant on the microstructure of the polymer [28].

2.4.2.2 Effect of Cross-linking on Char Formation

It is being long known that cross-linking enhances the char formation in the pyrolysis of cellulose [29]. As the result of cross-linking, covalent bonds form between different chains which are stronger than hydrogen bonding. These bonds are required to be broken before the polymer pyrolysis decomposition takes place. On the other hand, in case of fewer cross-links, the distance between the chains increases. Ultimately decreasing the stability and hydrogen bonding which makes the polymer more prone to decomposition.
Char formation in cellulose was confirmed by the initial auto cross-linking, via the formation of ether linkage between hydroxyl groups. This auto cross-linking is being supported by the initial weight loss due to the loss of water molecule at about 251°C, and is linearly related to the amount of char. On the contrary, cross-linking of rayon interferes with auto cross-linking thus decreasing the initial weight loss and char formation [30].

2.4.2.3 Effect of Structural Parameters on Char Formation
The char forming tendency (CFT) is defined as the amount of residue at 850°C per structural unit, divided by 12 [7]. Linear correlations between CFT and char residue (CR) by Van Krevelen [25] are well known. These equations hold only for non-treated and substrates treated with condensed phase flame retardants, but they do not hold in presence of halogen [25].

It was observed that pyrolysis and combustion are closely related to the chain rigidity, aromaticity, crystallinity, and resonance stability of the polymer structure. In addition, crystallinity and the degree of polymerization determine the amount of energy required to melt and degrade the polymer. It was reported that vacuum pyrolysis for purified cellulose increases with the increase in orientation and less ordered regions (LOR), and is inversely proportional to the square root of the degree of polymerization [31, 32]. Also char increases with increases in the LOR, and the extent of auto cross-linking was also reported as proportional to the percentage of char formation. The energy of activation for crystalline and LOR is also different [32].
A different approach was noticed for blends such as cotton and wool [33]. The amount of char in this case increases more than the char from individual polymers. This effect was reported owing to the decrystallization of ordered regions in cotton by the swelling of the amino derivatives formed in the pyrolysis of wool. Since levoglucosan forms due to the rearrangement of crystalline regions, which were lowered by blending with wool, eventually resulting in more char from amorphous regions. In addition to this, the decrease in the activation energy for cellulose (blend with 18% wool) from 220.1 to 103.4 kJ/mol was also attributed to the increase in the LOR. Cotton-polyester blend gave the same kind of results, along with evolution of more flammable gases such as ethylene [34].

A review on polymer structure and flammability relationship was given by Pearce [35, 36]. Also, an interesting attempt was reported by Lyon [37], to develop a kinetic model for the polymer pyrolysis.

### 2.4.3 Intumescent Systems

Intumescent systems can be described as flame retardant technology, which causes flammable material to foam, on exposure to heat, forming an insulating barrier which keeps the heat away from the substrate [38]. Intumescent systems offer physical and thermal barrier to block the flow of high temperatures and rapid fire spread. In doing so, temperature within the body of such a material increases, which causes melting of thermoplastic matrix. At a certain temperature, an endothermic gas producing chemical reaction takes place. This gas traps in small bubbles and solidifies. The solidified multicellular thick char provides an insulating layer which prevents the flow of heat to the substrate, thus resulting in flame
retardancy [39]. Several models were proposed explaining the mechanism by which intumescent systems work, but there are still questions that need to be answered such as, what is the effect of the material properties on performance of intumescent systems, and a description of the complicated sequence of physical, thermal, and chemical events which characterize these systems. A comprehensive review on that topic was given by Horrocks [40].

The fire resistant efficiency of an intumescent material depends on the ratio of C, N, and P atoms in the compound [41]. The first fire intumescent coating material was patented in 1938 [42]. Since then intumescent systems received substantial attention because of their minimal fire hazard. Horrocks et al. [43] recently patented a range of intumescent treated textiles. These textiles were reported as having higher than expected oxidation barrier. These systems require the intumescent to be in intimate contact with the surface of char forming, and flame retardant fibers. When both intumescent and fiber are exposed to heat and form char at the same time, a char bonded structure is formed. This combined char, shows superior flame retardancy when exposed to temperatures above 500°C-1200°C, with significantly reduced heat release rate.

Another research group [44] showed that ammonium and melamine phosphate containing intumescent show fire barrier properties for flame retarded viscose and cotton equivalent to high performance fibers such as aramids.
Though intumescent coatings are capable of exhibiting good fire resistance for substrates, they have some disadvantages as well such as water solubility, brushing problem and high cost [38].

The intumescent systems which work in combination of polymer charring and foam are characterized by low environmental impacts [38]. In the view of this property, a good number of such systems were developed.

2.4.4 Physical Approach, Insulation and Heat Sink
Most of the added inorganic salts work according to this approach. It is known as the physical approach because the added salt stays in the polymer physically, introducing insulating domains in fiber pores and amorphous regions. Also on heating, the added salts decompose exothermally, thus removing the heat away from the body of the flame. The added salts might be alumina trihydrate, mica, clay, talc, zinc oxide, pumice and other materials e.g. alumina trihydrate releases three moles of water and consumes 1170 J⁻¹ as heat of dehydration [45].

\[
\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O} \xrightarrow{\triangle} \text{Al}_2\text{O}_3 + 3\text{H}_2\text{O}
\]

Scheme 2.3 Water from Alumina Trihydrate

A similar effect was reported for CaCO₃.
The salts are usually added in large amounts, as fillers ranging from 40-60%. In this way, these salts not only deplete the organic portion of the polymer but also form insulated areas in the pores and amorphous regions of the polymer. Hence, the pyrolysis temperature of the polymer increases and the amount of combustible gases that evolve decreases, eventually resulting in less heat evolved. Also, less heat will be available for continuous pyrolysis that adds greatly to the fire retardant nature of the substrate. The gases given off during these decompositions dilute the combustion gases and oxygen in the flame. The evolving gases from salts can also react endothermically with the flame gases, thus resulting in an additional heat sink.

Coating and insulation are other physical approaches for flame retardancy. The flame retardant forms a glassy foam or char that hinders the passage of flammable gasses from the pyrolyzed polymer to the flame front. At the same time, this layer serves as an insulation to obstruct the flow of heat to the polymer surface. Boron derivatives had been identified since 1821 to work by this physical approach. One such example is that of boric acid and its hydrated salts which have low melting points and release water in stages as shown below.

\[
\begin{align*}
\text{CaCO}_3 & \xrightarrow{\triangle} \text{CaO} + \text{CO}_2 \\
\text{H}_3\text{BO}_3 & \xrightarrow{130-200^\circ\text{C}/-2\text{H}_2\text{O}} \text{HBO}_2 & \xrightarrow{-\text{H}_2\text{O}} \text{B}_2\text{O}_3
\end{align*}
\]
It was reported that highly soluble mixtures of boric acid salts can be produced due to the formation of polyions [46]. A mixture of 7:3 for borax and boric acid can work as an effective flame retardant when it has an add-on of 5%, but up to 20% is required to decrease the glow resistance [47].

### 2.5 Classification of Flame Retardants

Flame retardants can be classified in number of ways. The classification can be based on the mechanism type e.g. gas phase or condensed phase flame retardants as given in 2.4. Also the chemical class they belong to, can be determined in their type as phosphorus, halogen or halogen-free flame retardants. Flame retardants can also be classified on the basis of their properties as permanent or non-permanent, and based on the type of substrate e.g. flame retardants for cotton, polyester, and nylon etc. In this review, chemical nature based classification will be considered, and the following classes will be discussed:

1. **Inorganic Salts**
2. **Phosphorus Containing Flame Retardants**
3. **Halogen-based Flame Retardants**
4. **Halogen-free Flame Retardants**

### 2.5.1 Inorganic Salts

This is a broad category which might contain any salt of inorganic nature. It contains fillers, which are used to promote “heat sink effect” as discussed in section 2.4.4. This list might include alumina, mica, feldspar, clay, talc, pumice, and zinc oxide etc.
Boron derivatives form insulated coatings as discussed in section 2.4.4. It might include boric acid and its hydrated salts, which have low melting points.

2.5.2 Phosphorus Containing Flame Retardants (PCFR)
The chemistry of flame retardants mainly is centered on six elements including phosphorus, antimony, chlorine, bromine, boron and nitrogen. In this section, phosphorus-based flame retardants will be covered from the applied point of view, more basic chemistry about phosphorus, different oxidation states and its compounds can be found in the text book by Lyons [48]. Several other reviews [7, 49] also cover the topic very well. A review by Granzow [50] in 1978 has information which is difficult to get from other sources. Most of the reviews over this period, suggest both condensed phase and gas phase mechanisms for phosphorus-based flame retardants. It was recognized that the mode of action depends on polymer systems and fire exposure conditions [7], and quite likely the existence of both mechanisms at the same time.

2.5.2.1 PCFR and Condensed Phase Mechanism
PCFR promote char formation especially in oxygen containing polymers such as cellulose.

Char formation means:

- Less material actually burnt
- Accompanied water vapors deplete the combustible vapors
- Protection of underlying polymer
- Usage of heat for char formation
The route of cellulose burning is very well documented [7, 51]. It is well known that when cellulose reaches its pyrolysis temperature, it depolymerizes to tarry carbohydrate products normally levoglucosan, which further decomposes to organic combustible fragments such as alcohols, aldehydes, ketones and hydrocarbons. However in the presence of PCFR, cellulose is phosphorylated by the phosphoric acid, formed by thermal decomposition of PCFR. Phosphoric acid is very efficient for catalytic phosphorylation because of its low volatility. The phosphorylated cellulose then decomposes endothermically to char and water vapor [7, 52]. Hence, the formed char and water vapor serve the above mentioned roles. The flame retardant effect of PCFR increases more if it inhibits the oxidation of char as well. The presence of PCFR was reported to inhibit at least the oxidation of carbon to carbon dioxide, resulting in decrease of heat evolution. Also, the nitrogen containing PCFR was reported to stay longer in char by the formation of polyphosphoramidic or polyphosphorimidic acids [53].

In poly (ethylene terephthalate), PCFR were reported to decrease the amount of combustible volatiles and increase the nonvolatile char [52]. Recent studies showed that char quality is also very important along with the quantity and rate of char formation. Char quality plays an important role as a barrier to mass and heat transfer [7]. In porous char, dominance of closed cells over open cells, and absence of cracks and channels are important.

In the polymers which do not char easily such as oxygen free hydrocarbons, PCFR are usually not very effective unless supplemented by other char forming additives. A
comprehensive review along with very useful references of char forming additives is given by Horrocks [7].

2.5.2.1.1 PCFR and Nitrogen Synergism
It is well known that the presence of nitrogen containing compounds along with PCFR increases the fire retardant effect. This enhancement in flame retardant effect depends on the nitrogen containing compound and polymer nature. The effect was attributed to the formation of P-N containing compounds which are better phosphorylating agents than phosphoric acid [54]. In this regard, it can be inferred that only the nitrogen-phosphorus will act in synergism. Another theory postulates that the presence of nitrogen delays the evaporation of phosphorus from condensed phase [55]. Another study [56] which was conducted on polyester-cotton blends has reported that nitrogen containing resin application enhances the condensed phase activity of PCFR. A further study on thermoplastic polymers shows that red phosphorus with nitrogen containing compounds such as melamine enhances the oxidation of phosphorus and give off inert gases including ammonia. Also ammonia was reported [57] to enhance flame retardancy because of its inert nature without taking part in chemical reactions.

2.5.2.1.2 PCFR and Coating modes of action
Surface chemistry of charring was supported by a number of researchers especially for oxygen containing polymers. This is being further supported by the smoldering inhibition tendency of PCFR. The mode of action for smoldering (also known as glowing combustion of char) inhibition was reported as some sort of polyphosphoric acid coating, possibly a physical barrier. Also this coating can cause the deactivation of oxidation active sites on
carbon [58, 59]. As shown in the studies [58, 59], even 0.1% of phosphorus can inhibit the oxidation of free carbon. It was reported that it is caused by the bonding of P=O and hydrophilic phosphoric acid groups to the sites prone to oxidation. This research was carried out at Alma-Ata (Kazakhstan), which also shows that PCFR reduce the permeability of char [60].

2.5.2.1.3 PCFR’s effect on melt viscosity
It is well known that even the presence of 0.15% of phosphorus in PET fabric can make the fabric pass the vertical flame test, possibly because of the melting or dripping away of the polymer from flame. This dripping is caused by the catalyzed thermal breakdown of polymer caused by PCFR. However, this effect is greatly decreased by the presence of any non-melting solid such as cotton fibers. Same effect has been observed for the fabrics which have been printed by infusible pigments [61]. One relatively less focused area of research is the dispersion of solid flame retardants such as alumina trihydrate with the help of phosphorus containing alkyl acid surfactants in polymer melt as filler.

2.5.2.2 PCFR and Vapor Phase Mechanism
In general, the chemical mode of action is mainly followed by the formation of high thermally stable compounds such as phosphine oxide and trialkylphosphate oxides, which make these compounds volatile only under high temperatures as in presence of a flame. The breakdown of triphenyl phosphine oxide and triphenyl phosphate to smaller fragments such as P₂, PO, PO₂, and HPO₂ were shown in mass spectroscopy results by Hastie [62, 63]. These
fragments scavenge the hydrogen atoms from the flame just like halogens as discussed earlier, thus reducing the concentration of high energy hydrogen radicals.

Phosphonium oxide compounds were reported to follow the vapor phase route, caused by their stability near the condensed phase condition. This inference was further supported by studying the effect of volatile phosphonium oxide compounds on wool and wool-polyester blends, the higher the volatility of phosphonium oxide higher the flame retardant effect [64]. However, the efficiency of PCFR mainly depends on the nature of the substrate, i.e. the ability of the substrate to release volatile fuel and to form a char.

2.5.2.2.1 PCFR and Physical Modes of Action
Physical modes of action are based on the study of heat capacity, heat of vaporization and possibly the endothermic heat of dissociation in the vapor phase. This is considered a type of vapor phase mechanism. It was reported [65] that PCFR also contribute to flame retardancy by their heat capacity and heat of vaporization to some extent. These inferences are mainly verified by studies on non-fibrous polymers such as poly (methyl methacrylate) (PMMA) and urethane foam [65, 66].

2.5.2.3 Interaction of PCFR with other Flame Retardants

2.5.2.3.1 Synergism of the mixture of halogen-phosphorus additives
It was reported that [67] the synergism between phosphorus and halogens (bromine especially) is not a general phenomenon but additively was observed. In one study [68], bromine was reported to work as a blowing agent and increase the char volume. A similar behavior was reported for polyurethane foams [69] containing bromine and phosphorus.
Different ratios of bromine to phosphorus were reported to be effective, but the most effective one was the Br:P of 3:1, in red phosphorus-decabromodiphenyl system [70].

2.5.2.3.2 Phosphorus and antimony
There are some studies which show favorable results but an antagonistic approach is generally considered for phosphorus and antimony. The main reason probably is due to the formation of antimony phosphate which is inert as a flame retardant.

2.5.2.3.3 Phosphorus and Mineral Fillers
A study by Schraf [71], for comparison of TiO$_2$ and SnO$_2$ on char formation of ammonium polyphosphate system, shows that TiO$_2$ results in stronger and continuous char as compared to more porous and flakier char in the case of SnO$_2$. TiO$_2$ enhances the char quality by a physical bridging effect. Several protective routes were suggested for synergism between phosphorus and mineral fillers, but the confirmation of results requires more research.

2.5.3 Halogen Containing Flame Retardants (HCFR)
HCFR follow the vapor phase mechanism by forming hydrogen halide as discussed in section 2.4.1. Hence, HCFR scavenge active hydrogen radicals and give less active halogen radicals, such as bromine and chlorine. Usually the flame inhibiting activity of HCFR is enhanced by the addition of additives, such as antimony trioxide.

These additives are known as synergists. The efficiency and mode of action differ widely among different additives. These additives not only take part in free radical reactions but also act through the condensed phase mechanism, physical effect and intumescence. The potency of different synergists was compared by the synergistic effect (SE) and FR-effectiveness [7].
2.5.3.1 Halogen-Antimony Synergism
Halogenated flame retardants are widely used in combination with antimony. The synergism offered by antimony is dependent upon the action in both the condensed phase and the gas phase. In the presence of halogenated FR, hydrogen halide is released during the pyrolysis, and reacts with Sb\textsubscript{2}O\textsubscript{3} to produce either SbX\textsubscript{3} or SbOX. SbX\textsubscript{3} is volatile and is released into the gas phase as shown in scheme 2.6.

\[
\begin{align*}
\text{Sb}_2\text{O}_3 + 6\text{HX} & \rightarrow 2\text{SbX}_3 + 3\text{H}_2\text{O} \\
\text{SbX}_3 + 3\text{H}^- & \rightarrow \text{Sb} + 3\text{HX} \\
\text{SbX}_3 & \rightarrow \text{SbX}_2^- + \text{X}^- \\
\text{RH} + \text{X}^- & \rightarrow \text{R}^- + \text{HX} \\
\text{R}^- + \text{X}^- & \rightarrow \text{RX} (\text{not flammable})
\end{align*}
\]

Scheme 2.6 Reactions of Sb\textsubscript{2}O\textsubscript{3} during combustion

SbOX, is a strong Lewis acid, and may operate in the condensed phase to aid in the dissociation of carbon-halogen bonds [7].

Some activity of Sb\textsubscript{2}O\textsubscript{3} in the condensed phase was reported, however, its core activity takes place in the gas phase. In the condensed phase, the added Sb\textsubscript{2}O\textsubscript{3} lowers the charring temperature for cellulosic materials. In addition, antimony halides that are evolved into the gas phase react with atomic hydrogen to generate HX, SbX, SbX\textsubscript{2}, and Sb. Antimony combines with atomic oxygen, water, and hydroxyl radicals to yield SbOH and SbO, which scavenge hydrogen radicals. SbX\textsubscript{3} reacts with water to produce SbOH and HX. SbO and Sb are also finely dispersed throughout the flame and catalyze the association of H\textsuperscript{\cdot}. Also antimony halides delay the escape of halogen from the flame, effectively increasing its
concentration while simultaneously diluting the flame. “Blanketing effect” of hindering the penetration of oxygen to the pyrolyzed polymer was also reported [72].

### 2.5.3.2 Ammonium Bromide as Flame Retardant

The higher flame retardant efficiency of NH$_4$Br was reported to be caused by the low dissociation energy of NH$_4$Br to HBr and NH$_3$ as compared to C-halogen bond.

\[
\text{NH}_4\text{Br} \rightarrow \text{HBr} + \text{NH}_3
\]

The radical trap activity and physical effects of HBr and NH$_3$ operate simultaneously. The synergism between HBr and NH$_3$ can exist if both are present in the flame at same time [7]. However, little is known about the role of ammonia in the presence of free radicals. NH$_4$Br is used as a non-permanent FR on cellulosic materials but can also be used as an FR for PP.

### 2.5.3.3 Environmental Concerns of HCFR

Halogens are well known for their flame retardancy for a long time especially brominated and chlorinated compounds. In addition to their effectiveness for inhibiting flame, some classes of halogen containing compounds are also considered toxic to human health because they have been reported to form dioxins and furans on combustion and many can be bioaccumulative, such as polybrominated diphenyl ethers (PBDEs).
Several USA states such as California, Maine and Washington have already banned the use of brominated and chlorinated flame retardants based on diphenyl ethers. All this happened because there is growing evidence that PBDEs persist in the environment and accumulate in living organisms, as well as toxicological testing indicates that these chemicals may cause liver toxicity, thyroid toxicity, and neurodevelopmental toxicity. PBDEs are additive flame retardants which can leach to environment and bioaccumulate due to their stable nature. Environmental monitoring programs in Europe, Asia, North America, and the Arctic found traces of several PBDEs in human breast milk, fish, aquatic birds, and elsewhere in the environment. Particular congeners, tetra- to hexabrominated diphenyl ethers, are the forms most frequently detected in wildlife and humans. The mechanisms or pathways through which PBDEs get into the environment and humans are not known yet, but could include releases from manufacturing or processing of the chemicals into products like plastics or textiles, aging and wear of the end consumer products, and direct exposure during use (e.g., from furniture) [73]. Another class of compounds which was banned in 1976 is polybrominated biphenyls (PBBs).

![Polybrominated biphenyl](image)
It was demonstrated PBBs cause liver cancer in laboratory rats and mice [74]. The Department of Health and Human Services (DHHS) and the International Agency for Research on Cancer (IARC) suggested that PBBs may be carcinogenic to human health. Because of the aforementioned reasons and other publicity issues with halogen containing flame retardants, suppliers of these chemicals are venturing into non-halogenated options. Further detail about the development of non-halogenated flame suppressants can be found in section 2.6.

2.5.4 Nano-clay based flame retardant systems
The flame retardant systems discussed so far have some disadvantages. For example, boron-based systems are non-durable, halogen containing flame retardants are toxic, and exhibit environmental and publicity issues. The phosphorus containing flame retardants which are crosslinked on fabric surface are the most successful commercial option. However, these have adverse effects on the fabric handle.

The most recent and novel route to render cotton flame retardant is the nano-clay layer by layer (LbL) assembly method [75]. Clay/polymer LbL assemblies can be applied on wood and paper fibers [76]. Also montmorillonite (MMT) coated wood fibers shows increased thermal stability relative to unmodified fibers tested by thermogravimetric analysis. This motivation leads to the recent research on application of LbL assemblies on cotton fibers [75, 77].

In a recent study [75], the growth, structure, and mechanical behavior of LbL thin films, composed of the weak polyelectrolyte polyethylenimine and Laponite clay, were studied.
This study showed that these thin layers of nanoclay can be an interesting alternative to present flame suppressants for fibers and fabrics. Such thin film coating systems can be useful for protective layers e.g. flame retardant or hard coating. These layers coat the surface of cotton fibers in three dimensions and provide substantial thermal stability.

It was reported that clay delays the degradation of cotton fibers by forming a sheath-like ceramic barrier [75, 77]. This layer is formed by the reassembly of finely dispersed clay particles and it causes 70 to 80 % reduction in heat release for nanocomposites. It is usually achieved at clay loadings of 2 to 5%.

Layer by layer (LbL) assemblies have been well studied since 1990, and it is a relatively simple technique for fabricating multifunctional thin layers. These layers are achieved by dipping the substrate in dilute solution of polymer or particles, thus resulting in deposition of multiple positive/negative pair of layers also known as bilayers (BL). These multilayers were reported to assemble via electrostatic interactions, hydrogen bonding, donor acceptor interactions, and covalent bonds. The thickness of BL which is usually 1-100nm depends on the chemistry of the layered components, counter ions, molecular weight, ionic strength, pH, and the temperature of dipping solution [77].

A recent nano-clay-based study by the same group of Grunlan et al. [77] focused on producing flame retardant system for cotton fibers using branched polyethylenimine (BPEI) and montmorillonite (MMT) thin layer assemblies. Coating results only 1 to 4% increase in fabric weight where 13% residue was left over from coated fabric after heat treatment at 500 °C under an air atmosphere, whereas the control fabric completely combusted. A reduction in
the afterglow and retention of fabric structure were also observed after complete burning of the sample. SEM results of the burnt samples also support sheath-like coating mechanism. In addition to this, microcalorimeter results support the generation of fewer combustible volatiles. Also, there is very slight difference in the feel and appearance of coated and uncoated samples which shows that layer-by-layer assembly does not alter the physical properties of the fabric. According to Grunlan et al. [77], other flame retardant particles and polymers can also be used in these coatings and further research in his group is underway.

2.6 Future Trends in Textile Flame Retardants:

Along with the development in conventional FR systems containing phosphorus and halogens, there are some recent examples where researchers have tried different compounds and approaches to obtain flame retardant textile fibers. In this section, several examples of newer novel systems will be presented after discussing general consideration for future trends in flame retardant development.

Though the dispute on halogen containing flame retardants is old, the scientific justification is not clear cut so far. The suppliers are looking for green alternatives in order to hedge against the development of halogen containing flame retardants in order to cope with publicity issues. To come up with halogen-free flame retardant alternatives, phosphorus-based flame retardants are of particular importance. Phosphorus based systems have lower density than halogen-based systems, less likely to bioaccumulate and persist in environment, better photostability, act as a char enhancers, can react with fibers and are free of negative public image. However, the challenges in developing efficient phosphorus-based systems are
to get high phosphorus percentages on the fabric, problem of moisture uptake, thermal stability, cost, and achieve less damage to polymer properties.

One study [78] has focused on phosphorus/silicone-based finishes to achieve flame retardancy on cotton fibers. This research described the synthesis and application of a new phosphorus/silicon flame retardant finish. The chemical structure of the finish was confirmed by IR-spectroscopy. Also the application conditions for this finish were studied and optimized. An optimized procedure was determined by evaluating the various finishing conditions, such as flame-retardant, cross-linking agent, catalyst dosage, pH value of the finishing liquor, curing temperature, curing time, and the influence of additives on the effect of flame-retardant. Phosphorus-based chemistry is under study once again due to its high thermal stability and low toxicity. As compared to other durable phosphorus finishes such as tetrakis (hydroxymethyl) phosphonium chloride (THPC) and N-hydroxymethyl (3-dimethoxylphosphono) propionamide (Pyrovatex CP), the new finish [78] has the advantages of good durability and formaldehyde-free application.

Another similar study [79] used a very interesting environmentally friendly technique to produce regenerated flame retardant cellulose-silicate fibers. Enzymatically modified wood pulp which can be directly dissolved in aqueous sodium hydroxide solution containing zinc compounds was used as a cellulose source. Fibers were spun from the solution by coagulation in an alkaline spinning bath containing silicon compounds. This method has the advantage of not giving any hazardous emissions such as formaldehyde. The fibers obtained by this process shows LOI of up to 45% which is quite high and favorable for flame
retardancy. The fiber nature was inspected by SEM, and it was found that the fibers had skin/core geometry with zinc silicate mostly distributed on skin and cellulose as the core. It was shown that the fibers formed were also fast to multiple washing cycles and also had antibacterial activity.

Similarly, another novel approach to render cotton flame retardant in a benign way was reported in 2007 by Tahlawy et al. [80]. The researchers have tried to develop an alternate flame retardant system based on sodium stannate/phosphorus and chitosan for cellulosic textiles. This system offers not only good flame retardancy, but also it is biodegradable, non-toxic, non-dermatitis and non-mutagenic to humans. Chitosan was added as the source of nitrogen and to facilitate the phosphorylation stage. It was found that the addition of 1% of chitosan decreases the requirement of sodium stannate by one third as used conventionally. This provides aesthetic and handle features to the textile. Also thermogravimetric analysis showed an increase in the residual percent of the fabric and decrease in both thermal degradation onset point (TDOP) and maximum degradation rate point as a function of stannate concentration. Also the effect of curing temperature and time, chitosan concentration, and the sequence of treatment was studied in detail.

Tsafack et al. [81, 82, and 83] in 2005-2006 published a series of papers in which they showed the synthesis and application of novel phosphorus-nitrogen based systems. Most importantly, these monomers were applied by using plasma. It was proved that simple nucleophilic substitution reactions based on a two step process can be used successfully to produce durable flame retardant finishes. Also these finishes can be successfully grafted and
polymerized by using a microwave argon-based plasma system. This method offered the advantage of using an eco-friendly plasma technique instead of a conventional pad-dry-cure method. The synergism between nitrogen and phosphorus was also discussed and the results proved that the synergism exists. This research shows the potential of a whole new range of phosphorus-based halogen-free flame retardant systems, which can be applied by using plasma. The monomers synthesized by Tsafack’s group are shown in Figure 2.2

![Monomers synthesized by Tsafack and Levalois-Grützmacher](image)

Figure 2.2 Monomers synthesized by Tsafack and Levalois-Grützmacher [81]

An extension of Tsafack’s work was done by El-Shafei et al. [84], at North Carolina State University. In this study, an increase in the char up to 20% after heating the cotton sample up
to 950°C was demonstrated. An exhaustive research is in progress on such reactive phosphorus-based systems by the same group. The future work is also the modification of Tsafack’s [81] work in order to synthesize novel bifunctional, reactive, and halogen-free phosphorus-nitrogen-based flame retardant finish, which are expected to be durable and can be graft polymerized on substrates via atmospheric pressure plasma.

2.7 Environmental Concerns
In the view of extended use for textile flame retardants on different consumer products there are some environmental concerns as well. In order to meet the mandatory and voluntary standards developed by national and state governments, industry groups and standard setting organizations, consumer products such as home textiles are required to pass these tests.

The route to render the textile product flame retardant is complex. The selection of the chemical and how to apply depends on cost, performance, and consumer expectations. Hence, the task is to have a balance among the hazard of death, injury and property loss from fire with risk to human health and environment because of flame retardant chemicals.

Health and environmental issues related to halogen containing flame retardants were reported in section 2.5.3.3. Other particular problems associated with flame retardant application are [7]

- Release of formaldehyde to the atmosphere
- Emissions of volatile organic compounds (VOC)
- Use and emission of ammonia
• Discharge of unfixed flame retardant from washing-off effluent

The above given considerations are crucial because the most widely used systems are formaldehyde-based such as Pyrovatex, and are applied in the presence of ammonia. Formaldehyde and VOC emissions can be minimized by using scrubbers, where liquid effluents can be neutralized and washed before release. There are economical benefits as well in recycling and reusing liquid effluents. However, it needs further research to come up with a reasonable system. A study conducted in UK [85] shows that the application of chemometrics to flame retardant finishing chemistry reduces formaldehyde emissions by up to 75% and improves the performance of phosphorus by improving fixation.

It can be stated that as chemists work hard toward gaining better understanding of the chemistry and mechanism of flame retardancy, the world will better understand the chemistry of FRs, strive for process optimization, and recycling of water and the environmental footprint will be reduced. Hence, further research is needed on:

• Development of less expensive, durable, non-toxic chemicals that are easy to apply
• Introduction of new non-toxic and efficient systems
• Development of efficient application technologies (e.g. plasma)
• Environmentally friendly finishes (formaldehyde free)
2.8 Evaluation of Flame Retardants
The flammability of a material depends on many factors including the fiber type, fabric weight, and construction, method of ignition, extent of heat and material exchange, and the presence or absence of flame retardants. That is why a test to evaluate a flame retardant textile is greatly dependent on the end-use and very specific tests were developed over the years in the view of end uses. Particular end uses, which require flame retardancy, and testing include general apparel, children’s sleepwear, protective apparel, upholstery, floor coverings, bed coverings, and military fabrics [6]. Hence, the variety in usage of textiles has led to the variety of different tests; a list of some of the most important tests is shown in Table 2.2 [6].

Table 2.2. Test methods for testing flame retardancy

<table>
<thead>
<tr>
<th>Test method</th>
<th>Sponsoring organization</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>16 CFR 1610</td>
<td>Consumer Product Safety Commission (CPSC)</td>
<td>Fabric held at 45° to flame for 1 second; for general apparel</td>
</tr>
<tr>
<td>16 CFR 1615/1616</td>
<td>CPSC</td>
<td>Fabric held vertical to flame for 3 s. For children’s sleepwear.</td>
</tr>
<tr>
<td>NFPA 1971</td>
<td>National Firefighters Fabric Protection Association (NFPA)</td>
<td>Fabric held vertical to the flame for 12 s, for protective clothing</td>
</tr>
<tr>
<td>NFPA 701</td>
<td>NFPA</td>
<td>Fabric held vertical to flame for 45 s to 2 min. For drapery.</td>
</tr>
<tr>
<td>Standard</td>
<td>Organization</td>
<td>Description</td>
</tr>
<tr>
<td>-------------------</td>
<td>--------------------------------</td>
<td>--------------------------------------------------------------------------------------------------------------------------------------------</td>
</tr>
<tr>
<td>ASTM D-2863</td>
<td>ASTM</td>
<td>Fabric is held vertical in different oxygen/nitrogen ratios and ignited from top. Determines minimum level of oxygen needed for combustion.</td>
</tr>
<tr>
<td>ISO 6940/6941</td>
<td>International standards</td>
<td>Vertically held specimens, determination of the ease of ignition and the flame spread properties.</td>
</tr>
<tr>
<td>DIN 54333 T1</td>
<td>Detaches Institute fur</td>
<td>Horizontally held specimens, because of the heat distribution less severe than vertical tests.</td>
</tr>
<tr>
<td></td>
<td>Normung</td>
<td></td>
</tr>
</tbody>
</table>
3 EXPERIMENTAL
The objective of this research is the synthesis, characterization and evaluation of novel bifunctional halogen-free flame retardant monomers (1-3). Synthesis, characterization and application of the novel phosphorus-based monomers (1-3) have been reported in this research. Organophosphorus- based chemistry is well known for its effectiveness in flame retardancy. Acrylate containing phosphorus-based monomers were reported by M.J. Tsafack and J. Levalois-Grützmacher [81, 82, and 83]. They successfully reported the synthesis and flame retardant effectiveness of those monomers. In addition to this, monomers synthesized by the Tsafack’s group were also durable. However, crosslinking agent (20%) and photoinitiator (5%) were used in excess, which not only increases the cost but also affects the fabric handle. The purpose of this research is to synthesize novel bifunctional monomers with good durability without adversely affecting the fabric handle.

3.1 Materials
Ethyl dichlorophosphate, methyl dichlorophosphate, N, N dimethylphosphoramic dichloride, triethyl amine, ethanol amine, acryloyl chloride, dichloro methane, potassium persulphate, and Mohr’s salt were purchased from Sigma Aldrich, USA and used as received. The other reagents were of laboratory grade and used as received.

3.2 Glassware Outline
A three-neck round bottom flask was used as the main reaction vessel. The configuration of the apparatus is shown in Figure 3.1 [84].
The reaction was carried out under argon using a three-neck flask with a stir bar. One of the side necks was used as the inlet for argon. In the middle neck, a condenser was used, and to the top of condenser an oil bubbler was attached to monitor the argon flow properly. In the third neck, an addition funnel was used in order to add the chemicals dropwise while running the reaction under argon. The initial phase of the reaction was performed in an ice bath, and the second phase was conducted at room temperature with continuous stirring.

3.3 Synthesis
The synthesis of each monomer was completed in two steps. In the first step the intermediate was synthesized and in the second step, acryloyl chloride was reacted to the intermediate to form the final product. In this research, ethyl di(acryloyloxyethyl)phosphoramidate (EDAEP)
monomer 1, methyl di(acryloyloxyethyl)phosphoramidate (MDAEP) monomer 2 and N, N-dimethyl di(acryloyloxyethyl)phosphoramic (DMDAEP) monomer 3 were synthesized. For simplicity, these monomers have given the names such as monomers 1, 2 and 3, respectively. Intermediate of monomer 1 has been given the name intermediate 1, similarly intermediate 2 and intermediate 3 for monomers 2 and 3, respectively. Table 3.1 shows the different conditions tried to synthesize the required product.

Table 3.1 Summary of trials and conditions for each monomer

<table>
<thead>
<tr>
<th>Trial</th>
<th>Recipe</th>
<th>Conditions (Temp. and Time)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Step-1</td>
<td>Step-2</td>
</tr>
<tr>
<td>1.</td>
<td>CH₂Cl₂ 100ml</td>
<td>Et₃-N 15.1g</td>
</tr>
<tr>
<td></td>
<td>Et-NH₂ 6.1g</td>
<td>CH₂Cl₂ 100ml</td>
</tr>
<tr>
<td></td>
<td>Et₃-N 15.1g</td>
<td>Ar.Cl 9.05g</td>
</tr>
<tr>
<td></td>
<td>EDCP 8.15g</td>
<td></td>
</tr>
<tr>
<td>2.</td>
<td>CH₂Cl₂ 50ml</td>
<td>Et₃-N 7.5g</td>
</tr>
<tr>
<td></td>
<td>Et-NH₂ 3.0g</td>
<td>CH₂Cl₂ 50ml</td>
</tr>
<tr>
<td></td>
<td>Et₃-N 7.5g</td>
<td>Ar.Cl 4.50g</td>
</tr>
<tr>
<td></td>
<td>EDCP 4.75g</td>
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Table Continued

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<th>Step-1</th>
<th>Step-2</th>
<th>Step-1</th>
<th>Step-2</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.</td>
<td>CH(_2)Cl(_2) 10ml</td>
<td>Et(_3)-N 1g</td>
<td>0°C 1hr</td>
<td>0°C 3hr</td>
</tr>
<tr>
<td></td>
<td>Et-NH(_2) 0.30g</td>
<td>CH(_2)Cl(_2) 10ml</td>
<td>Room 1hr</td>
<td>Room 0hr</td>
</tr>
<tr>
<td></td>
<td>Et(_3)-N 1g</td>
<td>CH(_2)Cl(_2) 10ml</td>
<td>Room 1hr</td>
<td>Room 0hr</td>
</tr>
<tr>
<td></td>
<td>EDCP 0.47g</td>
<td>Ar.Cl 0.45g</td>
<td>Room 1hr</td>
<td>Room 0hr</td>
</tr>
<tr>
<td>4.</td>
<td>CH(_2)Cl(_2) 10ml</td>
<td>Et(_3)-N 1g</td>
<td>0°C 1hr</td>
<td>0°C 3hr</td>
</tr>
<tr>
<td></td>
<td>Et-NH(_2) 0.30g</td>
<td>CH(_2)Cl(_2) 10ml</td>
<td>Room 2hr</td>
<td>Room 0hr</td>
</tr>
<tr>
<td></td>
<td>Et(_3)-N 1g</td>
<td>CH(_2)Cl(_2) 10ml</td>
<td>Room 2hr</td>
<td>Room 0hr</td>
</tr>
<tr>
<td></td>
<td>EDCP 0.47g</td>
<td>Ar.Cl 0.45g</td>
<td>Room 2hr</td>
<td>Room 0hr</td>
</tr>
<tr>
<td>5.</td>
<td>CH(_2)Cl(_2) 20ml</td>
<td>Et(_3)-N 1.5g</td>
<td>0°C 1hr</td>
<td>0°C 3hr</td>
</tr>
<tr>
<td></td>
<td>Et-NH(_2) 0.60g</td>
<td>CH(_2)Cl(_2) 20ml</td>
<td>Room 2hr</td>
<td>Room 0hr</td>
</tr>
<tr>
<td></td>
<td>Et(_3)-N 1.5g</td>
<td>CH(_2)Cl(_2) 20ml</td>
<td>Room 2hr</td>
<td>Room 0hr</td>
</tr>
<tr>
<td></td>
<td>EDCP 0.81g</td>
<td>Ar.Cl 0.9g</td>
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<td>Room 0hr</td>
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<tr>
<td>6.</td>
<td>CH(_2)Cl(_2) 50ml</td>
<td>Et(_3)-N 15g</td>
<td>0°C 1hr</td>
<td>0°C 3hr</td>
</tr>
<tr>
<td></td>
<td>Et-NH(_2) 6.1g</td>
<td>CH(_2)Cl(_2) 50ml</td>
<td>Room 2hr</td>
<td>Room 0hr</td>
</tr>
<tr>
<td></td>
<td>Et(_3)-N 15g</td>
<td>CH(_2)Cl(_2) 50ml</td>
<td>Room 2hr</td>
<td>Room 0hr</td>
</tr>
<tr>
<td></td>
<td>EDCP 8.15g</td>
<td>Ar.Cl 6.79g</td>
<td>Room 2hr</td>
<td>Room 0hr</td>
</tr>
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</table>
### Trials with Methylidichlorophosphate (MDCP)

<table>
<thead>
<tr>
<th>Trial#</th>
<th>Recipe</th>
<th>Conditions (Temp. and Time)</th>
</tr>
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<tbody>
<tr>
<td>7.</td>
<td><strong>Step-1</strong></td>
<td><strong>Step-2</strong></td>
</tr>
<tr>
<td></td>
<td>CH₂Cl₂ 10ml</td>
<td>Et₃-N 1g</td>
</tr>
<tr>
<td></td>
<td>Et-NH₂ 0.30g</td>
<td>CH₂Cl₂ 10ml</td>
</tr>
<tr>
<td></td>
<td>Et₃-N 1g</td>
<td>Ar.Cl 0.45g</td>
</tr>
<tr>
<td></td>
<td>MDCP 0.37g</td>
<td>Room 2hr</td>
</tr>
<tr>
<td>8.</td>
<td><strong>Step-1</strong></td>
<td><strong>Step-2</strong></td>
</tr>
<tr>
<td></td>
<td>CH₂Cl₂ 10ml</td>
<td>Et₃-N 1g</td>
</tr>
<tr>
<td></td>
<td>Et-NH₂ 0.30g</td>
<td>CH₂Cl₂ 10ml</td>
</tr>
<tr>
<td></td>
<td>Et₃-N 1g</td>
<td>Ar.Cl 0.45g</td>
</tr>
<tr>
<td></td>
<td>MDCP 0.37g</td>
<td>Room 2hr</td>
</tr>
<tr>
<td>9.</td>
<td><strong>Step-1</strong></td>
<td><strong>Step-2</strong></td>
</tr>
<tr>
<td></td>
<td>CH₂Cl₂ 10ml</td>
<td>Et₃-N 1g</td>
</tr>
<tr>
<td></td>
<td>Et-NH₂ 0.30g</td>
<td>CH₂Cl₂ 10ml</td>
</tr>
<tr>
<td></td>
<td>Et₃-N 1g</td>
<td>Ar.Cl 0.45g</td>
</tr>
<tr>
<td></td>
<td>MDCP 0.37g</td>
<td>Room 2hr</td>
</tr>
<tr>
<td>10.</td>
<td><strong>Step-1</strong></td>
<td><strong>Step-2</strong></td>
</tr>
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</table>
Table Continued

<table>
<thead>
<tr>
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<th>Step</th>
<th>Step</th>
<th>Step</th>
</tr>
</thead>
<tbody>
<tr>
<td>11.</td>
<td>1.</td>
<td>Step</td>
<td>1.</td>
</tr>
<tr>
<td>CH₂Cl₂</td>
<td>10ml</td>
<td>Et₃-N</td>
<td>1g</td>
</tr>
<tr>
<td>Et-NH₂</td>
<td>0.30g</td>
<td>CH₂Cl₂</td>
<td>10ml</td>
</tr>
<tr>
<td>Et₃-N</td>
<td>1g</td>
<td>Ar.Cl</td>
<td>0.45g</td>
</tr>
<tr>
<td>MDCP</td>
<td>0.37g</td>
<td>12.</td>
<td>Step</td>
</tr>
<tr>
<td>CH₂Cl₂</td>
<td>20ml</td>
<td>Et₃-N</td>
<td>1.3g</td>
</tr>
<tr>
<td>Et-NH₂</td>
<td>0.60g</td>
<td>CH₂Cl₂</td>
<td>20ml</td>
</tr>
<tr>
<td>Et₃-N</td>
<td>1.3g</td>
<td>Ar.Cl</td>
<td>0.9g</td>
</tr>
<tr>
<td>MDCP</td>
<td>0.745g</td>
<td>13.</td>
<td>Step</td>
</tr>
<tr>
<td>CH₂Cl₂</td>
<td>50ml</td>
<td>Et₃-N</td>
<td>10g</td>
</tr>
<tr>
<td>Et-NH₂</td>
<td>6.1g</td>
<td>CH₂Cl₂</td>
<td>50ml</td>
</tr>
<tr>
<td>Et₃-N</td>
<td>15g</td>
<td>Ar.Cl</td>
<td>6.79g</td>
</tr>
<tr>
<td>MDCP</td>
<td>7.45g</td>
<td>Trials with N,N diphosphoramic dichloride (DMPDC)</td>
<td></td>
</tr>
</tbody>
</table>

**Trials with N,N diphosphoramic dichloride (DMPDC)**

<table>
<thead>
<tr>
<th>Trial#</th>
<th>Recipe</th>
<th>Conditions (Temp. and Time)</th>
</tr>
</thead>
<tbody>
<tr>
<td>13.</td>
<td>Step-1</td>
<td>Step-2</td>
</tr>
<tr>
<td>CH₂Cl₂</td>
<td>10ml</td>
<td>Et₃-N</td>
</tr>
<tr>
<td>Et-NH₂</td>
<td>0.30g</td>
<td>CH₂Cl₂</td>
</tr>
<tr>
<td>Et₃-N</td>
<td>1g</td>
<td>Ar.Cl</td>
</tr>
<tr>
<td>DMPDC</td>
<td>0.41g</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Step-1</td>
<td>Step-2</td>
</tr>
<tr>
<td>---</td>
<td>--------</td>
<td>--------</td>
</tr>
<tr>
<td>14.</td>
<td>CH₂Cl₂ 10ml</td>
<td>Et₃-N 1g</td>
</tr>
<tr>
<td></td>
<td>Et-NH₂ 0.30g</td>
<td>CH₂Cl₂ 10ml</td>
</tr>
<tr>
<td></td>
<td>Et₃-N 1g</td>
<td>Ar.Cl 0.45g</td>
</tr>
<tr>
<td></td>
<td>DMPDC 0.41g</td>
<td></td>
</tr>
<tr>
<td>15.</td>
<td>CH₂Cl₂ 10ml</td>
<td>Et₃-N 1g</td>
</tr>
<tr>
<td></td>
<td>Et-NH₂ 0.30g</td>
<td>CH₂Cl₂ 10ml</td>
</tr>
<tr>
<td></td>
<td>Et₃-N 1g</td>
<td>Ar.Cl 0.45g</td>
</tr>
<tr>
<td></td>
<td>DMPDC 0.41g</td>
<td></td>
</tr>
<tr>
<td>16.</td>
<td>CH₂Cl₂ 20ml</td>
<td>Et₃-N 1.3g</td>
</tr>
<tr>
<td></td>
<td>Et-NH₂ 0.60g</td>
<td>CH₂Cl₂ 20ml</td>
</tr>
<tr>
<td></td>
<td>Et₃-N 1.3g</td>
<td>Ar.Cl 0.9g</td>
</tr>
<tr>
<td></td>
<td>DMPDC 0.82g</td>
<td></td>
</tr>
<tr>
<td>17.</td>
<td>CH₂Cl₂ 50ml</td>
<td>Et₃-N 15g</td>
</tr>
<tr>
<td></td>
<td>Et-NH₂ 6.1g</td>
<td>CH₂Cl₂ 50ml</td>
</tr>
<tr>
<td></td>
<td>Et₃-N 15g</td>
<td>Ar.Cl 6.79g</td>
</tr>
<tr>
<td></td>
<td>DMPDC 8.2g</td>
<td></td>
</tr>
</tbody>
</table>

Key: Et-NH₂ = ethanolamine, Et₃-N = triethylamine, Ar.Cl = acryloyl chloride, Temp. = temperature

For monomer 1, monomer 2 and monomer 3, trial numbers 6, 12 and 17 (in blue color) show the final conditions and recipe used to synthesize these monomers, respectively.
3.3.1 Synthesis of Monomer-1 (EDAEP)
Dichloro methane (50mL) was added into a 250ml three neck round bottom flask containing a stir bar. Then, ethanol amine (6.1g, 0.1mol) and triethylamine (15g, 0.15mol) were added into the flask, and the reaction was allowed to stay in an ice bath for 15 minutes before ethyl dichloro phosphate (8.15g, 0.05mol) was added dropwise under argon. Because the reaction was exothermic, ethyl dichloro phosphate was diluted by dissolving in CH₂Cl₂ (1:20). The reaction mixture was allowed to run at 0°C for 1 hour and at room temperature for 2 hours. The reaction showing the synthesis of the intermediate for EDAEP is shown in scheme 3.1.

After giving 3 hours in total for intermediate 1 synthesis, the precipitated triethylamine hydrochloride salt was removed by vacuum filtration, and the filtrate was then used for the next step.

The filtrate from step 1 was transferred into a clean three-neck round bottom flask. To the filtrate, triethylamine (15g, 0.15mol) was added, and the three-neck flask was then connected to an inlet for argon gas, a condenser and an addition funnel and cooled to 0°C as shown in Figure 3.1. The reaction mixture was allowed to stay at 0°C for 20 minutes. To the reaction mixture, acryloyl chloride (6.79g, 0.07mol) dissolved in CH₂Cl₂ (20ml) was added dropwise, and the reaction mixture was allowed to stay at 0°C for 3hrs. Then, the reaction

Scheme 3.1, Synthesis of intermediate-1
mixture was filtered by vacuum filtration to remove triethylamine hydrochloride precipitate. The filtrate was washed with 10% Na$_2$CO$_3$ aqueous solution several times, and anhydrous MgSO$_4$ was added to the filtrate to remove any residual water, and the mixture was filtered again, and the solvent was removed by rotary evaporator leaving the monomer (EDAEP) in brownish yellow in 76% yield. The monomer was dissolved in methanol and stored in an air-tight jar wrapped in aluminum foil and kept in the dark.

The reaction for the synthesis of monomer 1 (EDAEP) from intermediate 1 is shown in scheme 3.2.

![Scheme 3.2, Synthesis of monomer-1](image)

### 3.3.2 Synthesis of Monomer-2 (MDAEP)

The synthesis of monomer 2 was carried out using the same procedure adopted for monomer 1. Intermediate 2 was first prepared by the reaction of methyl dichlorophosphate (7.45g, 0.05mol) with ethanolamine (6.1g, 0.1mol) in the presence of triethylamine (15g, 0.15mol) and dichloromethane (50ml) under argon at 0°C. The reaction mixture was kept at 0°C for 1 hour while stirring and then allowed to warm to room temperature. Then, the reaction was allowed to continue at room temperature for 2 hours. The reaction mixture was filtered by
vacuum filtration to remove triethylamine hydrochloride precipitate leaving the filtrate containing intermediate 2 only (Scheme 3.3).

Intermediate 2 was transferred into a clean three-neck round bottom flask which was connected to an argon line, a condenser with a bubbler and an addition funnel as shown in Figure 3.1. The flask was lowered into an ice bath and triethylamine (15g, 0.15mol) was added into the flask. Then, the reaction mixture was allowed to continue at 0°C for 20 minutes. At this stage, acryloyl chloride (6.79g, 0.07mol) dissolved in dichloro methane (100ml) was added dropwise into the reaction mixture, and the reaction was allowed to continue at 0°C for 3 hours. Monomer 2 (brownish yellow) was isolated in 67% yield using the same procedure adopted for monomer 1. Scheme 3.3 shows the synthesis for monomer 2.

Scheme 3.3 Synthesis of monomer-2 (MDAEP)
3.3.3 Synthesis of Monomer-3 (DMDAEP)
Monomer 3, N, N dimethyl di(acryloyloxyethyl)phosphoramic (DMDAEP) was synthesized in two steps. In the first step, N, N-dimethyl phosphoramic dichloride (8.2g, 0.05mol) dissolved in CH₂Cl₂ was added to a mixture containing ethanolamine (6.1g, 0.1mol) and triethylamine (15g, 0.15mol) dissolved in CH₂Cl₂ (50ml). The reaction mixture was allowed to stay for 1 hour at 0°C and 2 hours at room temperature. The reaction mixture was filtered by vacuum filtration to remove triethylamine hydrochloride precipitate leaving the filtrate containing intermediate 3.

In the second step, intermediate 3 was transferred into a clean three-neck round bottom flask fitted with the same connections described before, shown in Figure 3.1. The flask was lowered into an ice bath and triethylamine (15g, 0.15mol) was added, and the reaction mixture was allowed to stay at 0°C for 20 minutes. Then, acryloyl chloride (6.79g, 0.07mol) dissolved in CH₂Cl₂ (20ml) was added to the reaction mixture dropwise using a dropping funnel, and the reaction mixture was allowed to continue at 0°C for 3 hours. Monomer 3 was isolated in 73% yield using the same procedure adopted for monomer 2. Scheme 3.4 summarized the synthesis for monomer 3.
Scheme 3.4 Synthesis of monomer-3 (DMDAEP)

3.4 Characterization
Monomers 1-3 and their intermediates were characterized using attenuated total reflectance/Fourier transform infra red (ATR/FT-IR) and Electron Spray Ionization Mass Spectrometry (ESI-MS). ATR/FT-IR spectrum was recorded on a Nicolet Nexus 470 spectrophotometer. For each sample, a drop of the monomer under investigation was placed directly onto the germanium crystal of the Avatar OMNI-Sampler, and a background spectrum was collected prior to each sample. The instrument was set to collect the spectra at a resolution of 4 cm⁻¹ and a total of 32 scans.
Mass spectrum was carried out at the Mass Spectrometry Facility, Department of Chemistry, North Carolina State University. High resolution exact mass measurements were collected for the sodiated or protonated molecular ions of the samples. This was accomplished using an Agilent Technologies 6210 LC-TOF mass spectrometer. Samples were diluted in methanol and analyzed using 1 \( \mu \)L flow injection at 300 \( \mu \)L/min using an eluent of water:methanol mixture (25:75 v/v) containing 0.1% formic acid. The instrument was operated in the positive-ion mode with a capillary voltage of 4 kV, nebulizer pressure of 30 psig, and a drying gas flow rate of 10 L/min at 350°C. The fragmenter voltage was set at 110 V, and the skimmer voltage was 60 V. Reference ions of purine at \( m/z \) 121.0509 and HP-0921 at \( m/z \) 922.0098 were used as internal standards, and were simultaneously introduced through the use of a second orthogonal sprayer.

3.5 Application of Monomers

3.5.1 Fabric
Fabric used for this research was Test Fabric # 400, with gsm of 102 gm/m². It has construction of 78x76 plain weave and come in bleached desized form.

3.5.2 Thermal Initiation Method
The thermal initiator used for this study was potassium persulphate (KPS) (K\(_2\)S\(_2\)O\(_8\)) 5% along with Mohr’s salt 1% for preventing homopolymerization and promoting free radical graft polymerization of the monomer on the substrate.

3.5.2.1 Application of Monomers
For each monomer, the application recipe includes monomer, thermal initiator (KPS) and Mohr’s salt. Each monomer was evaluated at concentration of 300g/l prepared by dissolving
the monomer in CH$_3$OH. However, thermal initiator (5%) and Mohr’s salt (1%) were dissolved in distilled water separately. Then these two solutions were pad applied separately on the cotton sample.

A 140x220 mm swatch of cotton fabric was first padded with solution containing initiator and Mohar’s salt at pick up of 85 to 90%. Then the sample was dried and padded with a monomer solution. The cotton sample was allowed to dry. At the end, treated sample was cured at 120°C for 3.5mints.

Monomers were also applied by exhaust method to compare results with padding method. For exhaust method each monomer was evaluated at concentration of 50% o.w.f. Solution was prepared by dissolving the monomer in distilled water. However, thermal initiator (5% o.w.f) and Mohr’s salt (1% o.w.f) were dissolved in distilled water separately and mixed together.

A 140x220 mm swatch of cotton fabric was immersed in a monomer solution and agitated for 3 minutes. After that, the cotton sample was taken out of the monomer solution and allowed to dry and then cured at 120°C for 3.5mints.

Washing durability for up to 25 accelerated washes was checked by slightly modifying McSherry et al [86] method. The only modification was that the samples were washed for 2 hours and supposed that it will be equal to 25 accelerated washes instead of 4 hours washing equivalent to 50 accelerated washes according to McSherry et al method.
3.6 Evaluation of Fabrics

To determine the effectiveness of the monomers used for flame retardancy, the finished fabrics were first Soxhlet extracted with different solvents such as methanol and acetone. Then the fabrics was characterized and evaluated using scanning electron microscopy (SEM), thermal gravimetric analysis (TGA), burning test, and % grafting.

3.6.1 SEM (Scanning Electron Microscopy)
The surface morphology of the treated and untreated samples was analyzed by SEM. The images were recorded on PHENOM FEI model number 800-03103-02 under vacuum. The fabric samples were first sputter coated with sputter coater EMITECH SC7620. The sputtering was done to make the samples conductive. Char from treated and untreated samples was scanned to see the difference in surface morphology.

3.6.2 Grafting Percentage
Grafting percentage (graft. %) was calculated using the following formula.

\[
\text{graft.\%} = \frac{(W_g - W_o)}{W_o} \times 100
\]

Where \( W_g \) = weight of sample after grafting, \( W_o \) = weight of sample before grafting

3.6.3 TGA (Thermal Gravimetric Analysis)
The thermal decomposition profile of treated and untreated samples was assessed by TGA. Perkin Elmer Pyris 1 TGA (serial number 537N9071908), was used for this analysis. Nitrogen gas was used to purge the balance head and furnace at a flow rate of 20 mL/min. The furnace was programmed to heat from 25°C to 800°C at a rate of 20°C/min.
3.6.4 Burning Test
The burning test according to ASTM D 6413-08 was used to compare the flammability of treated and untreated samples. A fabric sample of size 63x204mm was mounted in the sample holder as shown in Figure 3.3. The flame from a Terrill burner was placed at the distance of 0.75 inches from the bottom of sample as shown in Figure 3.3.

![Figure 3.2 Vertical flame test schematic](image)

The flame was introduced to the sample for 3 seconds. After the flame was removed, the sample was observed for burning time, afterglow and char length for both treated and untreated cotton.
4 RESULTS AND DISCUSSION

4.1 Synthesis:
The main objective of this research was to synthesize the aforementioned three novel monomers (monomers 1-3). Synthesis of analogous monofunctional monomers was reported by Tsafack, MJ et al. [81] and Brian [84].

The monomers synthesized in the present work were called bifunctional because they possess two vinyl groups per molecule, to enhance the % degree of grafting and hence the durability. The synthesis of these monomers was achieved in two steps as shown before in schemes 3.1, 3.2, 3.3, and 3.4.

The reaction scheme illustrating the synthesis of monomers 1-3 is shown in Scheme 3.5.

Scheme 3.5 Schematic diagram showing the synthesis of monomers 1-3.
In step 1, the reaction was performed in the presence of triethylamine (Et$_3$N) as acid scavenger and dichloro methane (CH$_2$Cl$_2$), an S$_N$2 type addition reaction. Triethylamine was used in excess in order to speed up the reaction by readily scavenging the acid formed during the reaction. The addition of the phosphorous containing compound was conducted carefully because of its air sensitive nature. The phosphorous containing compound was first dissolved in excess of CH$_2$Cl$_2$ and then added dropwise to the reaction medium. In step 1, nucleophilic attack took place via the nitrogen not the oxygen due to the strong nucleophilic nature of NH$_2$ group compared to the OH group in ethanolamine [87]. The first substitution takes place readily but the second substitution was slow due to the reduction in the electropositive nature of phosphorus. That is why it takes more time (3-4hrs) in the intermediate synthesis of these bifunctional monomers as compared to monofunctional monomers (2hrs) [81]. The addition of phosphorous containing compound was done very carefully in order to hinder the oxidation of phosphate [88]. After the completion of the first step, the precipitates were separated by vacuum filtration and the filtrate was stored in an air tight jar wrapped in aluminum foil under dark.

In the second step, acryloyl chloride pre-dissolved in excess of CH$_2$Cl$_2$ was added to a mixture of the filtrate (from the first step) and triethylamine. This reaction proceeds via the nucleophilic attack of the OH in the intermediate on the electrophilic carbonyl carbon of acryloyl chloride, to substitute the chloride in the acid chloride. It was shown that the addition of acryloyl chloride was the most important step in the whole reaction. Dissolving acryloyl chloride in excess of CH$_2$Cl$_2$ and then adding this mixture to the reaction vessel
(three-neck round bottom flask containing intermediate and triethylamine) dropwise controls the rate of reaction. Before calculating the molar ratio’s of the reactants for step 2, it is important to calculate the yield of step 1. It was observed that excess of acryloyl chloride hinders the synthesis of final product. Special precautions should be taken for eyes, breath and skin as acryloyl chloride has nasty smell with lachrymose nature. The esterification reaction (step 2) was optimized in terms of reaction time. Too longer reaction time for step 2 can lead to unwanted products and shorter reaction time can result in insufficient reaction yield. Step 2 for bifunctional monomers took less time (3hrs at 0°C) than monofunctional monomers step 2, which requires overnight stirring at room temperature [81, 84].

4.2 Characterization of Intermediates
The molecular structures of intermediates were confirmed by using FT-IR and ESI-MS for intermediates 1, however intermediate 2 and 3 were confirmed only by FT-IR.

4.2.1 Characterization of Intermediate 1
Figure 4.1 shows the FT-IR spectrum for intermediate 1.
Table 4.1 shows the assignment of peaks which were found in the spectrum for intermediate 1. According to Thomas et al. [89] the presence of organophosphorus compounds can be confirmed by the presence of P=O in such compounds, in the range of 1156 cm\(^{-1}\) to 1287 cm\(^{-1}\). For intermediate 1, the P=O peak appears at 1177.4 cm\(^{-1}\), which confirms the presence of intermediate 1. Also very strong peak at 1040 cm\(^{-1}\) was observed, which is the characteristic peak for P-O-C. Medium peak at 1642.0 cm\(^{-1}\) can be assigned to NH\(_2\) deformation but for primary amine there should be two peaks in the region of 3460 cm\(^{-1}\) to 3280 cm\(^{-1}\) which are not found in the spectrum. Hence, the peak at 3292.7 cm\(^{-1}\) corresponds to the –OH groups.
Table 4.1 Infra-red peaks summary for intermediate 1

<table>
<thead>
<tr>
<th>Wavenumber (cm⁻¹)</th>
<th>Assignments</th>
</tr>
</thead>
<tbody>
<tr>
<td>3292.7</td>
<td>O-H stretch</td>
</tr>
<tr>
<td>2980</td>
<td>SP³ carbons</td>
</tr>
<tr>
<td>1642.0</td>
<td>N-H deformation</td>
</tr>
<tr>
<td>1445.3</td>
<td>C-H deformations</td>
</tr>
<tr>
<td>1177.4</td>
<td>P=O stretch</td>
</tr>
<tr>
<td>1040 &amp; 949.4</td>
<td>P-O-C antisymmetric stretch</td>
</tr>
</tbody>
</table>

The structure of intermediate 1 was also confirmed by +ESI-MS. The theoretical mass for the intermediate 1 was 212.0926 and for the protonated ion is 213.0926. The peak at 213.0995 confirms the presence of desired product, (M+H)⁺, shown in Figure 4.2.

Figure 4.2 +ESI-MS for intermediate 1
4.2.2 Characterization of Intermediate 2

Figure 4.3 show the FT-IR spectrum for intermediate 2.

The FT-IR spectrum for intermediate 2 can also be explained similarly to intermediate 1, due to resemblance in structure. FT-IR spectrum in Figure 4.3 shows all the necessary peaks that confirms the structure of intermediate 2. The peak for P=O, can be seen at 1176.4 cm⁻¹. Similarly, characteristic peaks for P-O-C appeared at 1037.5 cm⁻¹. The peak at 2960.6 cm⁻¹ corresponds to C-H stretching for an sp³ carbon. The peak at 1398 cm⁻¹ can be assigned to C-H deformations. Intermediate 2 and intermediate 3 were only analyzed using FT-IR.

4.2.2 Characterization of Intermediate 3

Figure 4.4 show the FT-IR spectrum for intermediate 3.
Figure 4.4 FT-IR spectrum of intermediate 3.

Peaks observed in the FT-IR spectrum for intermediate 3 are summarized in Table 4.2.

<table>
<thead>
<tr>
<th>Wavenumber (cm(^{-1}))</th>
<th>Assignments</th>
</tr>
</thead>
<tbody>
<tr>
<td>3392.7</td>
<td>N-H stretch</td>
</tr>
<tr>
<td>2980</td>
<td>(sp^3) carbons</td>
</tr>
<tr>
<td>1646.1</td>
<td>N-H deformation</td>
</tr>
<tr>
<td>1477.4</td>
<td>N-CH(_2) (C-H deformations)</td>
</tr>
</tbody>
</table>
From Table 4.2, it can be seen that the spectrum for intermediate 3 has some additional peaks corresponding to P-N (CH₃)₂ vibrations [91], in addition to peaks for –NH, P=O, and P-O-C. The presence of additional peaks confirms the structural differences of intermediate 3 from intermediate 1 and intermediate 2 as can be seen at the top middle of Figures 4.4, 4.3 and 4.1. According to the study by Thomas et al. [91], P-N (CH₃)₂ containing compounds show four characteristic weak peaks in the regions of 1261-1321 cm⁻¹, 1155-1205 cm⁻¹, 1058-1075 cm⁻¹, and a strong peak appears between 935-1008 cm⁻¹. All the four characteristic peaks were observed for intermediate 3 and were assigned in the Table 4.2. It was reported that [91] a weaker peak appears for some P-N (CH₃)₂ containing compounds around 750 cm⁻¹, and for intermediate 3 this peak appeared at 735 cm⁻¹, which is acceptable.

4.3 Characterization of Monomers
Molecular structures of monomers 1-3 were confirmed FT-IR and +ESI-MS.

<table>
<thead>
<tr>
<th>Table Continued</th>
<th>1302.7</th>
<th>P-N (CH₃)₂ vibration</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1200.9</td>
<td>P=O stretch</td>
</tr>
<tr>
<td></td>
<td>1071.6</td>
<td>P-N (CH₃)₂ vibration</td>
</tr>
<tr>
<td></td>
<td>1005</td>
<td>P-N (CH₃)₂ vibration</td>
</tr>
<tr>
<td></td>
<td>735</td>
<td>P-N (CH₃)₂ vibration</td>
</tr>
</tbody>
</table>
4.3.1 Molecular Structure Characterization of Monomer 1

The FT-IR spectrum for monomer 1 is shown in Figure 4.5 and Table 4.3 gives the summary of the functional groups observed in the FT-IR spectrum for monomer 1.

![Figure 4.5 FT-IR Spectrum of monomer 1](image)

<table>
<thead>
<tr>
<th>Wavenumber (cm(^{-1}))</th>
<th>Assignments</th>
</tr>
</thead>
<tbody>
<tr>
<td>3393.8</td>
<td>N-H Stretch</td>
</tr>
<tr>
<td>2981.6</td>
<td>sp(^3) carbons</td>
</tr>
<tr>
<td>2605.2</td>
<td>OH stretch</td>
</tr>
<tr>
<td>1720.0</td>
<td>C=O stretch</td>
</tr>
<tr>
<td>1664.3</td>
<td>CH=CH stretch</td>
</tr>
</tbody>
</table>
The peak at 3393.8 corresponds to the secondary amine (NH). The two most important peaks are for carbonyl carbon (C=O) and P=O. The peak at 1720 cm$^{-1}$ corresponds to the carbonyl of an ester. The peak at 1199.7 cm$^{-1}$ corresponds to the P=O, which confirms the molecular structure of monomer 1.

ESI-MS results for monomer 1 are shown in Figure 4.6. The theoretical mass for the compound was 320.1029, hence the mass for sodiated molecular ion should be 343.1029. The peak at 343.1033 confirms the presence of the sodiated ion of monomer 1.

Scan 315-390 m/z

Figure 4.6 Mass spectrum of monomer 1
4.3.2 Molecular Structure Characterization of Monomer-2

Monomer 2 was also confirmed by using FT-IR and ESI-MS. FT-IR spectrum of monomer 2 is shown in Figure 4.7, and Table 4.4 shows a summary of the characteristic peaks for monomer 2.

Table 4.4 Absorption peaks summary for monomer 2

<table>
<thead>
<tr>
<th>Wavenumber (cm(^{-1}))</th>
<th>Assignments</th>
</tr>
</thead>
<tbody>
<tr>
<td>3391.3</td>
<td>N-H stretch</td>
</tr>
<tr>
<td>2981.1, 2950.1</td>
<td>sp(^3) carbons</td>
</tr>
<tr>
<td>2605.0</td>
<td>OH stretch</td>
</tr>
</tbody>
</table>
The peak at 3391.3 cm\(^{-1}\) corresponds to NH groups. The strong peak at 1719.1 cm\(^{-1}\) corresponds to the carbonyl of the ester group in the structure. The peak at 1198.7 cm\(^{-1}\) corresponds to P=O. Additionally, the peak at 1030 cm\(^{-1}\) corresponds to P-O-C, and the peak at 1635.4 cm\(^{-1}\) corresponds to the CH stretch of the vinyl group.

The \(^{+}\)ESI-MS for monomer 2 is shown in Figure 4.4. The calculated mass for the compound was 306.0873, thus the mass for sodiated molecular ion should be 329.0873. Hence, the peak at 329.0764 confirms the molecular structure for monomer 2.
4.3.3 Molecular Structure Characterization of Monomer 3

The molecular structure for monomer 3 was confirmed through FT-IR. Figure 4.8 shows the FT-IR spectrum for monomer 3, and Table 4.5 shows a summary of the characteristics peaks found in FT-IR spectrum for monomer 3.
Figure 4.9 FT-IR spectrum for monomer 3

Table 4.5 Absorption peaks summary for monomer 3

<table>
<thead>
<tr>
<th>Wavenumber (cm(^{-1}))</th>
<th>Assignments</th>
</tr>
</thead>
<tbody>
<tr>
<td>3469.5</td>
<td>N-H stretch</td>
</tr>
<tr>
<td>2947.2</td>
<td>sp(^3) carbons</td>
</tr>
<tr>
<td>1721.1</td>
<td>C=O stretch</td>
</tr>
<tr>
<td>1674.9</td>
<td>C=O in secondary or tertiary amides</td>
</tr>
<tr>
<td>1621.2</td>
<td>CH=CH stretch</td>
</tr>
<tr>
<td>1410.8</td>
<td>C-H deformations</td>
</tr>
</tbody>
</table>
FT-IR shows a weak peak at 1721.1 cm$^{-1}$, which corresponds to the carbonyl of the ester group as in monomer 1 and 2. It showed all the required peaks confirming the presence of P-N (CH$_3$)$_2$ vibration at 1322.6 cm$^{-1}$, 1004.6 cm$^{-1}$, and 742.1 cm$^{-1}$. However, the FT-IR spectrum showed a strong peak at 1674.9 cm$^{-1}$, which indicated that the acylation step did not exclusively took place on the OH to form the corresponding ester and some acylation took place at the NH. In contrast to the molecular structures of monomers 1-2, the attachment of –N(CH$_3$)$_2$ , instead of –OCH$_3$ or –OC$_2$H$_5$, to the phosphorous atom in monomers 3 increases the nucleophilic character of the NH group and makes it a stronger nucleophile than that of the –OH, which explains the reason for the presence of the two different carbonyls, one for the ester and the other for the amide. However, monomer 3 can still act as a potential flame retardant because it has two active vinyl groups. Confirmation of molecular structure for monomer 3 by ESI-MS has not been attempted so far.

### 4.3.4 P=O Absorption Frequency and Flame Retardancy

According to Kandola et al. [92], cotton treated with phosphorus-based flame retardants catalyzes the dehydration of cellulose at temperature lower than the decomposition
temperature of cellulose by the formation of phosphoric acid. That dehydration furnishes thermally stable double bonds in cellulose chains leading to much higher char yield. Further investigations into the chemical structure dependence of phosphorus compound on conjugated double bond formation were carried by Katsurra and Inagaki [93]. According to Katsurra and Inagaki [93], formation of conjugated double bonds in cellulose chains depend on the electron density of phosphoryl group. This was further supported by FT-IR analysis of the vibrational frequency of P=O, which was consistent with the experimental results. Hence, it was concluded that there is a strong relationship between the flame retardancy and the P=O stretching frequency. The higher the P=O vibrational frequency, the better the flame retardancy, due to the ease of double bond formation.

Similar results were observed in the present study as well. The P=O vibrational frequencies for monomers 1, 2, and 3 were 1198.7 cm\(^{-1}\), 1199.7 cm\(^{-1}\) and 1240.1 cm\(^{-1}\), respectively. In the case of monomer 3, phosphoryl group has higher electron density due to the electron donating nature of nitrogen compared to oxygen in monomers 1 and 2. Hence, it should be expected that monomer 3 would show better flame retardancy than monomers 1 or 2. Moreover, it was reported that the presence of electron withdrawing groups such as cyano and carboxyl on phosphoryl group did not show any flame retardancy [94].

4.4 Application of Monomers
To study the efficiency of the novel synthesized monomers 1-3 as flame retardants, monomers (1-3) were pad applied thermally in presence of potassium persulphate (KPS) as thermal initiator, by preparing 10 ml of 300g/l solution for each monomer. Each of the
monomers were also applied by exhaust method. Both methods were successful for monomers grafting as confirmed by Soxhlet extraction, SEM, grafting percentage, and burning test results for treated and untreated cotton.

The padding method showed much promising results compared to the exhaust method, in terms of even application, and grafting % as shown in Table 4.6. Monomer 2 showed inefficient results in exhaust method, and therefore it was not further studied using the padding method.

4.5 Evaluation of Fabrics
4.5.1 Scanning Electron Spectroscopy (SEM)
Surface morphology can provide useful information about the surface morphology for the substrates following any chemical changes on the surface. To address any surface changes following the monomer applications, SEM analysis was performed on both treated and untreated cotton samples. Moreover, SEM images of the charred samples were also analyzed to determine the efficiency of each monomer as a flame retardant.

The SEM images showed remarkable difference in the treated and un-treated cotton samples as shown in Figure 4.10, which clearly showed the presence of coating on treated samples which confirmed the graft polymerization of the monomers. These samples were not washed before SEM scanning to see whether the presence of monomer 1, 2 or 3 on cotton would perform as a flame retardant finish.
Figure 4.10 SEM monographs of un-treated cotton (A & B), and (C, D), (E, F), (G & H) cotton treated with monomer 1-3 (exhaust method), respectively, at 500x and 2000x magnification, respectively.
4.5.2 Grafting Percentage (graft. %)

Grafting percentage (graft. %) was calculated both for the exhaust and padding methods before and after washing. The following formula was used to calculate the grafting %

\[
\text{graft. } \% = \frac{W_g - W_o}{W_o} \times 100
\]

Where \( W_g \) = weight of sample after treatment, \( W_o \) = weight of sample before treatment.

Table 4.6 shows the grafting percentage obtained for each monomer.

Table 4.6 % grafting for monomer 1-3

<table>
<thead>
<tr>
<th>Monomer</th>
<th>Grafting % Exhaust Method (50% o.w.f) (Without Washing)</th>
<th>Grafting % Padding Method (300 g/l) (Without Washing)</th>
<th>Grafting % Padding Method (300 g/l) (After 25 accelerated washes)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Monomer 1</td>
<td>25%</td>
<td>46%</td>
<td>12%</td>
</tr>
<tr>
<td>Monomer 2</td>
<td>7%</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>Monomer 3</td>
<td>17%</td>
<td>43%</td>
<td>23%</td>
</tr>
</tbody>
</table>

4.5.3 Thermogravimetric Analysis

TGA results for treated and untreated cotton are shown in Figure 4.11. Figure 4.11A shows the thermogram for the control sample, Figure 4.11B, Figure 4.11C, and Figure 4.11D show
thermogram for cotton treated with monomers 1, 2, and 3, respectively. TGA was performed on samples before washing.

It was shown before [81,82] that cotton treated with phosphorus-based flame retardants starts decomposing at lower temperature than control cotton, due to phosphoric acid catalyzed hydrolysis, which eventually produces more char.

In the present work, the control sample degraded over the range 298°-399 °C with 80% weight loss with the maximum rate of decomposition beginning at 378 °C. The % weight left beyond 399°C was less than 20%, and the % weight left at 800°C was less than 8%. On the other hand, the cotton treated with monomer 1 (Figure 4.11B) and monomer 3 (Figure 4.11D) degraded in the range 230°-320°C with only 40% weight loss with the maximum rate of decomposition at 278°C. Also, the weight left at 800°C was up to 25% (Figure 4.11B) and (Figure 4.11D) , compared to less than 9% for the control sample (Figure 4.11A). Cotton treated with monomer 3 (Figure 4.11D) also showed similar results as cotton treated with monomer 1 (Figure 4.11B). However, monomer 2 (Figure 4.11C) treated cotton showed less efficiency compared to monomers 1 and 3, owing to the low % grafting. TGA graphs for monomers 1 and 3 were similar for the exhaust and padding methods.
Previous research [81, 82] showed that for a polymer to be effective as a flame retardant it should have a decomposition temperature close or lower than that of the substrate, in order to interfere with the burning process. Monomers 1-3 exhibited decomposition temperature lower than that of the untreated cotton. Furthermore, the weight loss for the untreated cotton in the decomposition range was due to the formation of flammable volatiles. However, in the case of cotton treated with monomer 1 and 3, the weight loss decreased by 40%, potentially due to the formation of less volatiles and more char. The char residue left at 800°C for treated cotton was 18% greater than untreated cotton for monomer 1 and 3. In the case of monomer 2, the weight left at 800°C is almost the same as untreated cotton, probably showing the inefficiency of monomer 2 at high temperature. Hence, it can be stated that the
treatment with monomers 1 and 3 rendered cotton remarkably thermally stable. On the other hand, monomer 2 did not show good flame retardancy perhaps due to the low % grafting on the substrate, which was measured as shown in Table 4.6.

4.5.4 Burning Test
63x204mm samples of cotton treated with monomer 1, monomer 2, and monomer 3 and the vertical flame test was performed on the three samples to evaluate the flammability of the treated samples compared to control cotton and untreated cotton samples. Table 4.7 show the results for time of burning for each of the treated and untreated samples.

Table 4.7 Burning time for treated and untreated cotton based on the vertical flame test

<table>
<thead>
<tr>
<th>Monomer</th>
<th>Burning Time (seconds)</th>
<th>Burning Time (seconds)</th>
<th>Burning Time (seconds)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Exhasut method</td>
<td>Padding method</td>
<td>Padding method</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(Without Washing)</td>
<td>(After Washing)</td>
</tr>
<tr>
<td>Untreated cotton</td>
<td>23.9</td>
<td>23.9</td>
<td>23.9</td>
</tr>
<tr>
<td>Monomer 1</td>
<td>13.4</td>
<td>3</td>
<td>21</td>
</tr>
<tr>
<td>Monomer 2</td>
<td>15.4</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>Monomer 3</td>
<td>8.5</td>
<td>4</td>
<td>15</td>
</tr>
</tbody>
</table>
It can be seen from Table 4.7 that the burning time decreases remarkably for treated samples both by the exhaust and padding methods. Burning time can be attributed to the performance of each monomer such that the less the burning time the more efficient the monomer in flame retardancy and char formation. Similar results were reported before [84, 95]. Again the padding method gave better results than the exhaust method. Thus burning test results were consistent with the % grafting obtained as shown in Table 4.6.

The underlying reason for such burning behavior was linked to the lower decomposition temperature for the treated sample. According to Hobart et al. [95], lower decomposition temperature for the treated cotton combined with less available fuel due to the presence of flame retardant causes the flame to propagate quickly in search of combustible fuel. This was actually observed during the burning test. For the treated cotton, the flame runs through the whole sample very quickly with no char left. However, the main difference among the treated and untreated cotton was the after glow. There was absolutely no after glow for the treated samples, where the untreated cotton fabric burns vigorously, with much stronger flame and high heat of combustion. However, for the treated samples, the flame was weak, with very little heat of combustion and significant charring. The increase in the char for the treated cotton was very high so that the burnt samples kept their structural integrity. The results of the burning tests are summarized in Figure 4.12 and 4.13 for visual assessment of the char left.
Figure 4.12 Showing char residue for A) untreated, B) monomer 1, C) monomer 2, D) monomer 3 (exhaust method) treated cotton.

Figure 4.13 Showing char residue for A) untreated, E, F) monomer 1, G, H) monomer 3 (padding method) treated unwashed and washed samples, respectively.
As shown in Figure 4.12, monomer 3 (D) has given the maximum char out of three monomers applied by the exhaust method. For monomers applied by the padding method, unwashed samples for monomer 1 (E) and 3 (G) furnish self-extinguishing cotton, showing better performance compared to the exhaust method results, which is consistent with the results obtained from % grafting and burning time. After washing, the flame retardancy was reduced significantly as shown by samples (F) and (H) due to decrease in % grafting, and increase in burning time (close to untreated cotton) and char residue. Hence, more work needs to be done to enhance the durability of the flame retardant finish on cotton, which is an active research paradigm in El-Shafei’s group.

The increase in char formation for the cotton samples treated with phosphorus-based flame retardant is consistent with the proposed condensed phase mechanism. The presence of phosphorus-based flame retardant alters the pyrolysis path of the substrate by lowering the decomposition temperature, eventually reducing the formation of gaseous combustibles and favors the formation of char, which was confirmed using the TGA results shown in Figure 4.11, and the flame test (Fig. 4.12, and 4.13) results. Franklin and Rowland [96] in a study for cotton treated with seven different commercially available flame retarding products concluded similar results. According to Franklin and Rowland, chemical processes occurring during the pyrolysis of untreated and treated cotton are similar. For flame retardants treated cotton, pyrolysis products were formed at lower temperatures. These observations were interpreted as an indicator that the presence of flame retardant finish enhances all the pyrolysis processes, dehydration, and char formation at the expense of processes leading to
the formation of combustible volatiles that lead to flamed combustion. This could be the underlying reason for shorter burning time and higher amount of char except Figure 4.13 (E) and (G) where there were enough applied monomers to make cotton self extinguishing.

4.5.4.1 Surface Morphology of Char
After the burning test, it was observed that all the treated samples formed chars as compared to no char left at all for untreated cotton. Char from samples treated with different monomers were different in appearance. The surface morphology of char is related to the performance of the relevant flame retardant. It was shown previously [97] that more effective flame retardants left a noticeable coating on the surface of char which not only serve as a barrier to heat but also keep the char firm and intact. The surface scans of the char left from samples treated with monomer 1, monomer 2 and monomer 3 by the exhaust method is shown in Figure 4.14 at 500x and 2000x magnification.

Char formed from cotton samples treated with monomers 1 and 3 shows a coating which is continuous and all over the surface of fibers (Figure 4.14, A and C). Char from monomer 3 Figure 4.14 (C) treated sample was more firm and intact as compared to char from monomer 1, Figure 4.14 (A) treated sample. However, monomer 2 Figure 4.14 (B) showed char which was thin and weak in strength. Due to the extra nitrogen attached to phosphorus in monomer 3 as compared to oxygen in monomer 1 and 2 which is less electron donating by mesomeric effect compared to nitrogen because of its higher electronegativity, the electron density of phosphorus in monomer 3 is much higher. Hence, it can be concluded that higher the electron density of phosphorylating group as in monomer 3, the higher its performance.
Figure 4.14 SEM images of chars (A, A1), (B, B1) and (C, C1) cotton treated with monomer 1, monomer 2, and monomer 3 (exhaust method) at 500x and 2000x magnification, respectively.
The performance of monomers 1-3 both for exhaust and padding method was evaluated as a flame retardant using TGA analysis, % grafting and flame test. The TGA results collected for monomer 1 and monomer 3 were very similar for the exhaust and padding methods. The burning test results for monomer 1 give less char length than monomer 3 in the case of padding method. However, the char formation after washing, firmness of char and presence of even coating in SEM images for monomer 3 make it superior than monomer 1 in performance. Monomer 3 demonstrated the shortest burning time and more char formation even at low % grafting compared to monomer 1 for exhaust method. The superior performance of monomer 3 can be attributed to the presence of one more nitrogen atom, which increases the P-N synergistic system, producing more thermally stable and highly crosslinked matrix residue [97], which holds the cellulose fragments in the condensed phase longer, thus furnishing more and integrated charring.
5 CONCLUSIONS
The main objective of this research was the synthesis, characterization and evaluation of three novel bi-functional halogen-free phosphorus-nitrogen-based flame retardant monomers 1-3. The monomers were successfully synthesized, characterized, and their performance as flame retardants was evaluated.

The molecular structures of monomers 1 and 2 were characterized using ATR/FT-IR and +ESI-MS, where monomer 3 was characterized by ATR/FT-IR only. Cotton samples treated with monomers using the padding method showed much better performance of flame retardancy than the ones treated by the exhaust method. SEM images and % grafting showed that these monomers can be grafted on cotton using potassium persulphate, a free radical thermal initiator. The results obtained from TGA, grafting % and flame tests demonstrated that monomers 1-3 were effective flame retardant finishes for cotton with monomer 3 achieving the best performance, followed by monomer 1, and monomer 2, respectively. The thermogravimetric analysis showed that the decomposition temperature of the treated samples was lower than that of the untreated cotton. Also, the char residue was much higher in the case of the treated samples than that of the control sample.

The superior performance of monomer 3 can be attributed to the presence of extra nitrogen which enhances the synergistic effect of phosphorus-nitrogen-based flame retardants.
6 FUTURE WORK
The author is interested in continuing this research to perform free-radical graft polymerization of monomers 1-3 on cotton using atmospheric plasma glow discharge and see the compatibility of monomers with other chemical finishes such as easy care, water repellent and antimicrobial finishes. Furthermore, he would like to study the effect of the finishes on the fabric color (yellowing) and handle.
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