

ABSTRACT

EDWARDS, BRIAN TYNDALL. Synthesis, Characterization, and Evaluation of Novel Flame Retardant Monomers for Plasma-Induced Graft Polymerization. (Under the direction of Dr. Ahmed El-Shafei.)

Flame retardant fabrics serve a critical role in our world. To achieve flame resistant textiles, it is often necessary to use chemicals that are designed to aid in flame suppression. Typically, these flame retardants are applied through traditional wet processing techniques. However, wet processing may negatively alter the bulk properties of the substrate. Recently, the use of plasma for textile finishing has emerged as an exciting possible replacement or enhancement to existing wet processing methods. Plasma modification can be used to alter the surface of a textile without changing the material's bulk properties. In this way, a substrate can be selected for its bulk properties and its surface can be tailored to meet specific needs. This technology has been employed to impart a variety of different properties to textiles. Some examples include hydrophilic, hydrophobic, flame retardant, and antimicrobial textiles.

This research sought to produce novel flame retardant monomers that could be graft polymerized onto a cotton fabric using plasma. In this work, the synthetic route used to produce two novel flame retardant monomers is described. The outlined synthetic route was shown to be simple and to yield an acceptable amount of the target monomers. Additionally, some preliminary attempts were made at applying the monomers to cotton through the use of a

thermal initiator and through plasma exposure. Neither application produced an auto-extinguishing fabric, but both monomers showed that they were effective char promoters. The necessity for obtaining a very high degree of polymerization and grafting with monomers such as these is explained and some recommendations for achieving higher polymerization and grafting yields with these monomers in future research are provided.

Synthesis, Characterization, and Evaluation of Novel Flame Retardant
Monomers for Plasma-Induced Graft Polymerization

by
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BIOGRAPHY

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1 INTRODUCTION

Between the years of 1999 and 2008, there was an average of just over 1.6 million fires per year in the United States. As a result of these fires, an average of 3,625 Americans lost their lives and another 18,765 were injured annually. During this same time span, it is suggested that upwards of \$11.6 billion were lost annually as a direct result of fires [1]. The data for each individual year, which is provided by the National Fire Protection Association (NFPA), is summarized in Table 1-1. In 2008, 83% of all civilian fire fatalities occurred in the home and fire killed more Americans than all of the natural disasters that occurred during that year combined [2]. With these statistics in mind, it is apparent that fire continues to be a problem of enormous importance.

Table 1-1. Summary of fire statistics by year (excludes the events of September 11, 2001).

Year	Fires	Deaths	Injuries	Direct Dollar Loss (Millions)
1999	1,823,000	3,570	21,875	\$10,024
2000	1,708,000	4,045	22,350	\$11,207
2001	1,734,500	3,745	20,300	\$10,583
2002	1,687,500	3,380	18,425	\$10,337
2003	1,584,500	3,925	18,125	\$12,307
2004	1,550,500	3,900	17,875	\$9,794
2005	1,602,000	3,675	17,925	\$10,672
2006	1,642,500	3,245	16,400	\$11,307
2007	1,557,500	3,430	17,675	\$14,639
2008	1,451,500	3,320	16,705	\$15,478

In 2005, a study was published that evaluated the roles of combustible products that are commonly found in homes as initial fuels for fires [3]. This report excluded items that are not considered “home products,” such as trash, building materials, combustible gases or liquids, and others. Instead, the study focused on mattresses and bedding materials, apparel, curtains and drapes, upholstered furniture, interior wall coverings, floor coverings, ceiling coverings, and other items. It was found that upholstered furniture fires resulted in the most deaths involving home products while mattresses and bedding material fires resulted in the highest number of injuries and the highest amount of property damage. It is important to note that combustible liquids and gases, building materials, and electrical components were observed to be the most common initial fuels for home fires. However, if the number of home fire deaths that these initial fuels were responsible for are combined, the death toll is only slightly higher than that of the fifth leading initial fuel – mattresses and bedding materials. Upholstered furniture was the leading item, home product or not, involved in home fire deaths even though it was the tenth leading initial fuel for home fires [3]. All of this information suggests that textiles are a significant initial fuel for home fires and that textile-fueled home fires are associated with a high percentage of home fire deaths.

Since textiles play a significant role in fire fatalities, injuries, and property damage, it is critical that they be designed and/or modified in a manner that

increases their fire retardancy. There are several factors that affect the flammability of a textile. These factors include the chemical and crystal structure of the polymer (or blend of polymers) that composes the fibers, the construction of the fabric, the combustion environment of the textile, and the presence and chemistry of a flame retardant finish [4]. The application of a flame retardant finish to a textile is intended to increase the amount of fire protection offered by the textile, and consequently decrease the frequency and severity of injury and property loss that may result from the combustion of that textile. In addition to increasing the amount of fire protection offered by the textile, an ideal flame retardant finish would have no adverse effects on the textile's physical properties, would not alter the aesthetic properties of the textile, would be easy and inexpensive to produce and apply, and would be durable to cleaning processes [5]. Chemical flame retardant finishes find applications in apparel, protective clothing and equipment for emergency personnel, floor coverings, upholstery, draperies, military apparel and equipment, and the aerospace and aviation industries [6].

The method used to apply a flame retardant finish to a textile is dependent upon the type of fabric involved, the type of chemicals being used, and the availability of machinery and equipment. Chemicals with strong affinities for fiber surfaces may be applied by exhaustion using dyeing equipment in a batch process. Chemicals that lack affinity for fiber surfaces are applied to the textile in

a continuous process by immersion in the chemical or by some other mechanical means. A typical continuous process is the pad-dry-cure method, which is depicted in Figure 1-1. This method involves padding the chemical onto the fabric and then drying the fabric. The chemical is then fixed onto the fabric surface by an additional heating step, known as curing [6]. The textile industry is constantly seeking new technologies to lower costs, enhance productivity, and decrease environmental impact. Recently, the textile industry has begun to embrace plasma treatment of textiles as a potential replacement for many wet-processing methods such as those commonly used to apply flame retardant finishes.

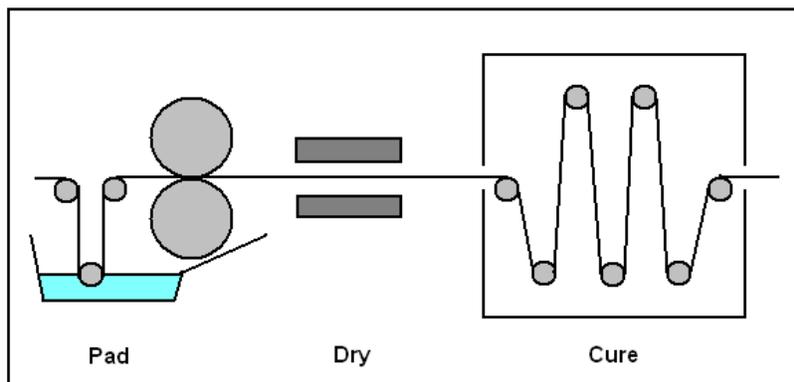


Figure 1-1. Schematic of conventional pad-dry-cure process. [6]

With these thoughts in mind, the aim of this research was to molecularly design, synthesize, and characterize novel halogen-free phosphorus-based flame retardant monomers that can be applied using plasma treatment. A

comprehensive review of available literature pertaining to flame retardant and plasma technologies as they relate to textiles is provided. The goal in developing these novel halogen-free flame retardant monomers is to provide the textile industry with safe and effective alternatives to current flame retardant finishing technologies that use the water-free plasma process.

2 LITERATURE REVIEW

The purpose of this review of literature is to provide a thorough explanation of available flame retardant and plasma technologies as they relate to textiles. The review is divided into two components. First, flame retardant finishing of textiles is examined. Topics such as history and legislation of flame retardant finishing, combustion of textiles, mechanisms for impeding the combustion cycle, and chemical classes of flame retardant finishes are explored. Second, plasma treatment of textiles is discussed. An introduction to plasma is included, as well as a description of plasma generating devices, plasma interactions with polymers, and modification of textiles by plasma.

2.1 Flame Retardant Finishing

2.1.1 History and Legislation

For many centuries, the hazards associated with flammable fabrics have been appreciated. One of the first recorded attempts to cope with these hazards was made by Jonathan Wyld of England in 1735, who patented a flame retardant composed of a mixture of alum, ferrous sulfate, and borax. In 1821, Joseph Louis Gay-Lussac worked with a flame retardant finish for jute and linen that was composed of borax, ammonium phosphate, and chloride. William Henry Perkin, Jr. achieved a durable flame retardant fabric in 1912 by precipitating stannic

oxide within the fiber. In addition to these attempts, the military strived to develop and introduce flame retardant treatments throughout the World Wars in an effort to reduce battlefield fire hazards. [5]

Despite the demonstrated need for flame retardant fabrics, it took a number of deaths from garment fires in 1952 to cause the hazards associated with flammable fabrics to be perceived for the first time as a consumer problem. As a result of this new perception, the Flammable Fabric Act was passed in 1953. Its purpose was to regulate the manufacture of flammable textiles that were available directly to consumers, such as apparel and interior furnishings for the home, office, or any other gathering place. Further progress led to a revision in 1967, which yielded the Amended Flammable Fabric Act. The modifications gave the United States Government, through the Secretary of Commerce, the capacity to “set mandatory flammability standards as needed to protect the people against unreasonable risk.” The amendments also allowed for the investigation of deaths and for the research and development of test methods and devices. In order to accommodate consumers and all of the various subdivisions of the industry, the Act declared that any standards that are developed should be “reasonable and practicable.” This meant that a compromise would need to be found between the effectiveness of the flame retardant treatment and its cost. [5]

The year 1970 saw new Federal Standards introduced by the Department of Commerce regarding the surface flammability of carpets. While these standards did not call for the addition of flame retardant chemicals to carpet, they undoubtedly brought about an increase in awareness for consumers and industry to the need for testing. In 1972, the Consumer Product Safety Act was passed and the Consumer Product Safety Commission was launched. This authorized the government to enact standards protecting the public from excessive hazards posed by flammable fabrics without prior communication with industry. That same year, 0-6X Children Sleepwear Standard DOC FF-3-71 was ratified. When it went into effect in 1973, an enforcement plan accompanied it. This plan consisted of fabric production acceptance testing, government prototype qualifications, and garment production acceptance testing. A very similar standard, 7-12 Children Sleepwear Standard DOC PFF-5-13, went into effect in 1975. This standard merely covered a different age range. The introduction of these standards compelled industry to meet stringent requirements such as vertical strip testing of flammability, durability to 50 washing and drying cycles, and low residual flame durations on fabrics and garments. [5]

To meet the requirements imposed on the children's sleepwear industry, manufacturers began using 100% nylon fabric that was treated with tris(2,3-dibromopropyl) phosphate (TBPP) [5]. However, in 1976, Ames testing showed that TBPP caused mutagenic changes in *Salmonella typhimurium*. Ames testing

is a quick biological assay that estimates the carcinogenic potential of a compound. The bacteria's genes which are responsible for histidine synthesis are modified so that the bacteria can only grow in an environment where histidine is provided. These mutated bacteria are plated with the suspect compound and a small amount of histidine to support their growth for an initial period of time. If the suspect compound is mutagenic, the bacteria will revert back to being able to grow on a histidine-free medium. Once the histidine supply is consumed, the plates are incubated for an additional 48 hours. The number of colonies that were able to grow and survive after the histidine was eliminated is proportional to the mutagenicity of the compound. As a result of its suspected carcinogenicity, production of TBPP was halted by January 1977 and the sale of garments containing TBPP was banned by April of the same year. [5]

Since 1983, it has been possible to produce flame retardant textiles that meet the requirements previously outlined in this thesis. Humanity has undoubtedly benefited from the safer environment that these materials have yielded. Given that effective flame retardant textiles have been manufactured since 1983, it is understandable that development in this field has been sluggish and advances have been relatively minor and specialized. However, over the last 2.5 decades a greater understanding of the chemistry of flame retardants has been achieved [6].

2.1.2 The Flammability of Textiles

2.1.2.1 Understanding Ignition, Pyrolysis, and Combustion

To better understand the mechanisms by which flame retardants work, it is first necessary to understand how textile materials burn. The process begins with ignition. Ignition may be spontaneous (autoignition) or may occur due to the application of an external source, such as a flame. Factors affecting the ignition of a textile material include the availability of oxygen, the temperature, and the physical and chemical properties of the polymer [7].

When heat is applied to a textile, the fiber's temperature increases until it's pyrolysis temperature, T_p , is reached. Once this temperature is reached, the fiber undergoes irreversible chemical decomposition. This irreversible chemical decomposition leads to the production of non-combustible gases such as carbon dioxide, water vapor, and the higher oxides of nitrogen and sulfur. Other products formed by this irreversible chemical decomposition include carbonaceous char, tars, and combustible gases. Examples of the combustible gases that may be formed are carbon monoxide, hydrogen, and numerous oxidizable organic molecules. Upon further heating, any tars that have formed will also pyrolyse to form more combustible gases, non-combustible gases, and carbonaceous char. [6]

Ultimately, the combustion temperature, T_c , is reached. When this happens, the volatile gases that are released by pyrolysis mix with oxygen. This

process, known as combustion, is a series of gas phase free radical reactions which are extremely exothermic and generate a great deal of energy in the form of heat and light. The thermal energy that is produced by this combustion process is sufficient to catalyze further pyrolysis of the fibers. This means that more volatile gases are created to supply the combustion process. Because the combustion cycle of textiles is self-perpetuating in this way, it is often thought of as a cycle [6]. The current model of the combustion of textile fibers is depicted in Figure 2-1.

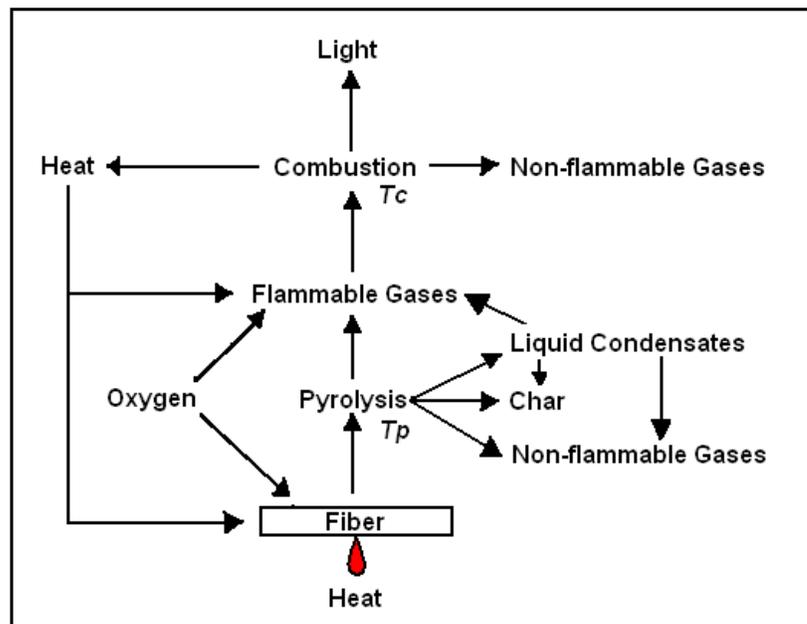


Figure 2-1. The combustion cycle of textile fibers. [6]

2.1.2.2 Flame Propagation and Rate of Heat Release

As depicted by the combustion cycle in Figure 2-1, the burning process of a fiber/fabric prolongs the polymer pyrolysis process. As the fiber is further pyrolysed, the flame is supplied with more fuel. This cyclic sequence of events allows the flame to spread across the polymeric substrate. Figure 2-2 shows a schematic of the propagation of a flame on a polymer surface. In this diagram, heat is being applied to the polymer surface. As a result of the heat application, pyrolysis products are released and engulfed as the diffusion flame advances over the decomposing polymer surface. Oxygen is available to facilitate the burning process and other non-combustible gases are emitted. [7]

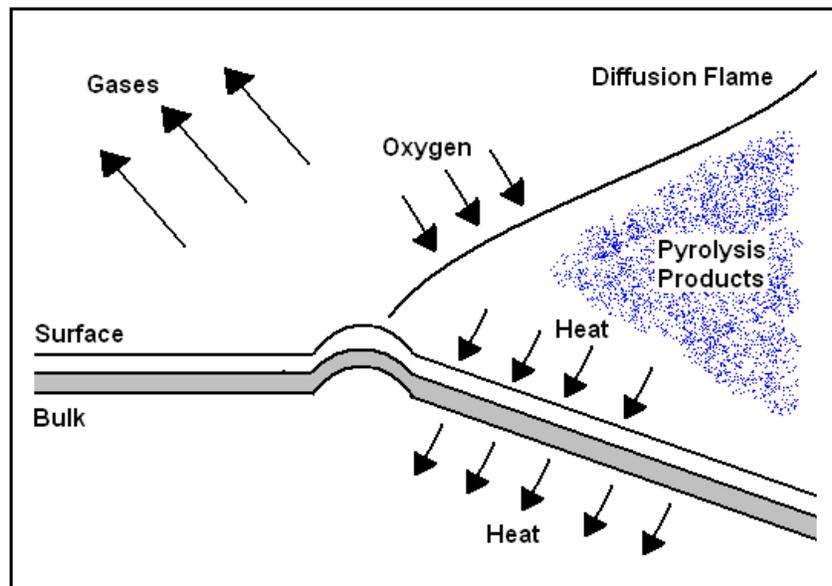


Figure 2-2. Illustration of flame propagation. [7]

It is generally acknowledged that under real-world fire conditions, the burning hazard associated with a fiber is determined by its rate of heat release. In fact, the rate of heat release has been described as the most critical parameter in determining the fire hazard of a material [10]. There is little difference between the heats of combustion, ΔH_c , for most fibers. However, it is the pace at which this heat is emitted by the fiber that determines the rate of flame propagation and, ultimately, the severity of burn injuries [7]. Flames that propagate slowly present potential victims with a greater window of time to escape danger. Cone calorimetry is often used to measure the rate of heat release of plastics, but experimental difficulties arise with textiles because textile materials are generally thin and consistent sample preparation is tricky [10]. Currently, there is very little published data pertaining to the rate of heat release of fibers, but the rate of heat release is becoming a more important consideration in regards to textile fire hazard assessment [7].

2.1.2.3 Visible Smoke and Combustion Gases

Smoke is generally classified as “a cloud of particles, individually invisible, which is opaque as a result of light scattering and/or absorption of visible light” [7]. However, when discussing the smoke formed by the burning of textiles, it is important to recognize the difference between combustion gases and visible

smoke. Combustion gases and visible smoke have different effects on victims and each has a unique significance during fires.

The primary combustion gas that causes concern is carbon monoxide, CO [11]. Carbon monoxide, as well as carbon dioxide and hydrogen cyanide, are asphyxiant gases that cause incapacitation and death in fires [12]. Organic irritants (such as acrolein, crotonaldehyde, formaldehyde, phenol, and styrene) and inorganic irritants (such as hydrogen halides, nitrogen oxides, sulfur oxides, and phosphates) are significant because they hinder escape attempts due to painful effects on the eyes and respiratory tract [7].

Visible heavy smoke is responsible for the striking reduction of visibility that is commonly associated with fires. By choking out the light in an enclosed space, visible smoke greatly impedes a victim's chance of escape. As the victim struggles to find an evacuation route, the concentration of toxic gases and the temperature of the enclosed space increase to grave levels.

In addition to determining its flammability properties, the chemical structure of the polymer determines smoke formation behaviors. Polymers that have aliphatic backbones, as well as those that are predominately aliphatic and oxygenated, tend to generate lesser amounts of smoke. On the other hand, polyenic polymers and polymers containing pendant aromatic groups have a tendency to produce smoky flames [7]. Polymers with low to intermediate levels of halogenation generally demonstrate an increased intensity of smoke

generation, while polymers with high levels of halogenation tend to show a reduction in smoke generation [7]. However, combustion of materials that are treated with halogenated flame retardants generates toxic and corrosive halogenated gases, which are endocrine disruptive [13,14]. Polymers with elevated thermal stability or which form small amounts of flammable pyrolyzates tend to produce less visible smoke [7]. One technique for minimizing the production of pyrolyzates, and thereby minimizing smoke generation, is to increase char formation [7].

2.1.2.4 Polymeric Composition of Fibers

Just as the chemical structure of individual polymers differ, so do their decomposition temperatures and behavior when exposed to a heat source. Table 2-1 summarizes the glass transition temperature (T_g), melting temperature (T_m), pyrolysis temperature (T_p), combustion temperature (T_c), and Limiting Oxygen Index (LOI) values of several common fibers. It is generally observed that as the combustion temperature, T_c , decreases and the temperature of the flame increases, the flammability of the fiber increases. Limiting Oxygen Index (LOI) values can also be used to make observations regarding the flammability of a fiber. A fiber with an LOI value of 21% or less is said to ignite easily and burn swiftly in air. Fibers having LOI values above 21% burn more gradually. When the LOI value of a fiber is greater than 26-28%, it may be considered to be flame

retardant and is capable of passing most small-scale ignition-resistance tests in the horizontal or vertical orientation. [7]

Table 2-1. Summary of thermal transitions for common fibers. [8]

Fiber	T_g, °C	T_m, °C	T_p, °C	T_c, °C	LOI, %
Wool	-	-	245	600	25
Cotton	-	-	350	350	18.4
Viscose	-	-	350	420	18.9
Nylon 6	50	215	431	450	20-21.5
Nylon 6.6	50	265	403	530	20-21.5
Polyester	80-90	255	420-447	480	20-21
Polypropylene	-20	165	470	550	18.6
Meta-aramid (Nomex)	275	375	410	>500	29-30
Para-aramid (Kevlar)	340	560	>590	>550	29

It is also important to make a distinction between the behaviors of natural fibers and synthetic fibers when they are exposed to a heat source. Natural fibers, such as cotton, have the tendency to ignite more willingly than synthetic fibers. In addition to being more resistant to ignition, synthetic fibers tend to shrink away from the heat source. This action is actually quite dangerous, because the resulting molten polymer can inflict very serious burn injuries as a result of the material melting or dripping on the user. [9]

2.1.2.5 Yarn and Fabric Structure

Another important consideration when examining the burning tendencies of a textile is the geometry of the yarns and the structure of the fabric. Very little research regarding the effect of yarn geometry on flammability has been

published, but data suggests that a more tightly spun yarn resists ignition better than a loosely spun yarn. Similarly, a tightly constructed fabric is more resistant to ignition than a loosely constructed fabric with an open structure. Increasing the density of a fabric or creating a layered fabric tends to increase a textiles resistance to ignition. [7]

2.1.3 Impeding the Combustion Cycle

As previously described, the combustion of textile fibers is a feedback mechanism. Flame retardant finishes function by interfering with the combustion of textiles at a particular stage during the cycle [15]. A flame retardant may diminish the amount of heat that is produced to a level below that which is required to sustain the combustion cycle. Altering the pyrolysis of the fiber to reduce the amount of flammable volatiles that are released and encourage the formation of carbonaceous char is also a possibility. In this case, the char will also serve as a barrier to keep the flame and polymer separated. The flame can be isolated from its oxygen supply and suffocated. Compounds that release halogens, like chlorine and bromine, when heated can be utilized to interfere with flame chemistry and serve as flame inhibitors. If the flow of heat back to the polymer can be prevented, the pyrolytic pathway can be halted. This is accomplished by using a heat sink or by creating a barrier, such as char or an intumescent coating, upon exposing the polymer to a flame. [7]

The two best known mechanisms by which flame retardants work are the condensed phase and the gas phase. In the condensed phase, the pyrolytic path of the substrate is changed and the availability of combustible gases is reduced by promoting the formation of carbonaceous char and water [16]. In the gas phase, the flame retardant decomposes and the active fraction of the molecule is supplied to the flame to stop the radical mechanism of combustion. As the flame dies down and its heat dwindles, so does the pyrolysis of the polymer. As a result, there is a significant decrease in the amount of combustible gases that are formed and the flame is suppressed [7].

2.1.3.1 Synergism

Synergism, when used in reference to flame retardants, describes a collective effect of two or more additives that is greater than the predicted effect of either of the additives acting individually [5]. More simply put, the combination of multiple chemicals provides more flame protection for the substrate than any of the individual components would alone. There are several examples of synergistic flame retardant systems. Halogen-antimony systems are widely used on a variety of polymers and work by both condensed phase and gas phase activities [7]. In some cases, bromine-chlorine systems are observed to be more effective with certain polymers than formulations containing only bromine [7]. Bromine-phosphorus synergism has been observed with a few polymers and phosphorus was even recommended to replace antimony as a halogen synergist

[7]. Finally, phosphorus-nitrogen synergism has been observed and will be explored more deeply in a later section [7].

2.1.3.2 The Condensed Phase Mechanism

The condensed phase mechanism is characterized by a chemical interaction between the polymer and the flame retardant compound at temperatures below that of the pyrolytic decomposition of the polymer. Instead of producing combustible gases via pyrolysis, non-combustible products like carbonaceous char, water, and carbon dioxide are produced [5,7]. Char serves as an inert insulating barrier, reducing gas, heat, and mass flow. In addition, the carbon is stabilized and averted from converting to combustible gases [7].

Within the condensed phase mechanism, there are two primary modes by which flame retardants function: cross-linking and dehydration. Cross-linking facilitates the stabilization of the polymer structure by supplying additional covalent bonds between the chains. These covalent bonds must be broken before the polymer chains can be degraded during pyrolysis. However, if a low degree of cross-linking is observed, the thermal stability of the polymer can decrease because the distance between the individual chains is too great to allow hydrogen bonding [7]. It is also suggested that cross-linking serves to increase the viscosity of a molten polymer, thereby slowing the rate of transport of volatile pyrolysis products to the flame [17].

2.1.3.2.1 Char Formation

As previously described, the formation of char impedes the combustion cycle by protecting the polymer surface from degradation and preventing the evolution of combustible gases [5,7]. In order for the char to be effective, it must form more quickly than the combustible gases that are produced by pyrolysis [7]. Figure 2-3 demonstrates how a phosphorus-based flame retardant may form a crosslink between two polymer chains. The phosphoric acid depicted in the schematic is formed upon the thermal decomposition of the flame retardant molecule. It is important to note that in order for the crosslink to develop, water must be released. This dehydration assists by diluting the combustible vapors.

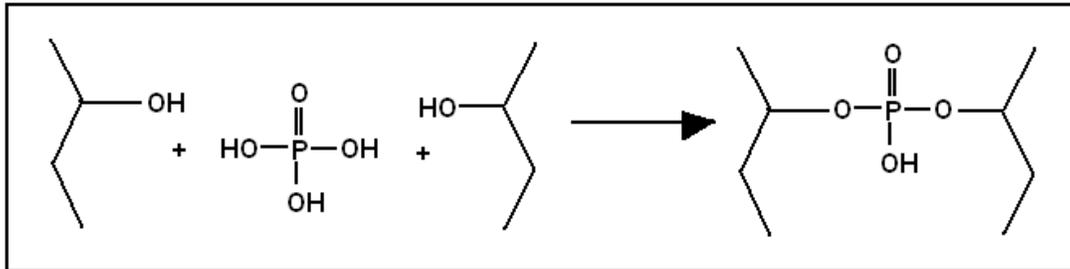


Figure 2-3. Crosslinking of polymer chains by phosphoric acid. [4]

In addition to the quantity of char that is formed, the degree of protection it offers is dependent upon the physical and chemical nature of the char. Figure 2-4 illustrates an ideal and a poor char structure. An ideal char structure consists of an intact structure of closed cells that contain pockets of gas. This occurs

when any gases that are emitted are encapsulated in the growing polymer melt. When this structure forms, a barrier is produced that prevents combustible liquids and gases from reaching the flame. This barrier also acts as an insulating layer to keep the polymer below its degradation temperature. Non-ideal char contains channels through which combustible pyrolysis products or molten polymer can escape. Any heat insulating effects of non-ideal char are eliminated because the molten polymer can be drawn through these fissures by capillary action and degraded in regions of elevated temperature. [7]

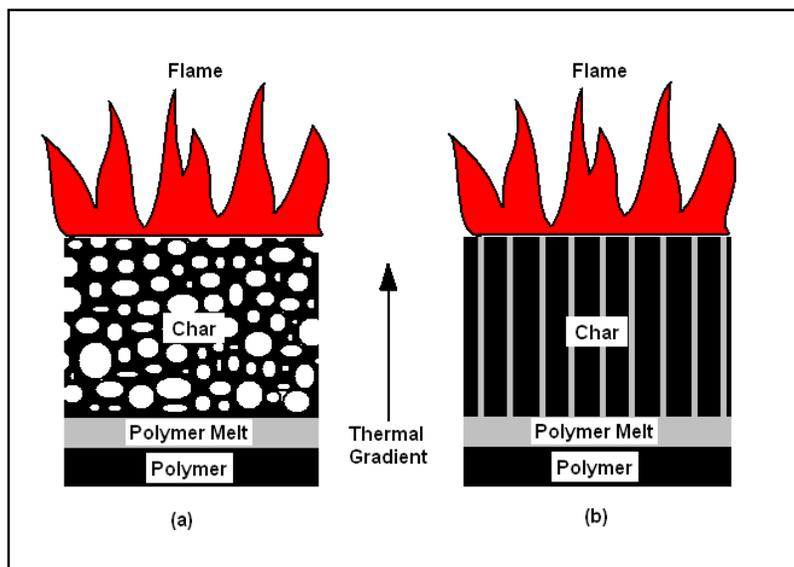


Figure 2-4. Illustration of (a) ideal char formation and (b) non-ideal char formation. [7]

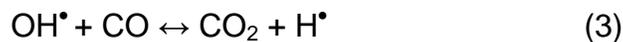
2.1.3.3 The Gas Phase Mechanism

The gas phase mechanism is typified by an interference in the combustion process within the flame. The pyrolytic processes are unchanged by the presence of the flame retardant. However, the amount of fuel consumed in the flame and the amount of heat that is produced decreases as the quantity of flame retardant increases. In addition, the amount of heat that is transmitted to the polymer surface decreases as the flame's heat diminishes, thereby slowing or halting the pyrolysis of the substrate. In order to be effective, the active fraction of the flame retardant molecule must be released into the flame upon thermal degradation. [5]

As a polymer undergoes pyrolysis, it produces species that are capable of reacting with atmospheric oxygen and advancing the combustion of available fuels by the branching reactions [5]:



The main exothermic reaction, which supplies the majority of the energy that is responsible for maintaining combustion, is:



To slow combustion, it is vital that the chain branching reactions (1) and (2) be slowed. Halogen derivatives, usually chlorine or bromine, function via the

gas phase. They release either a halogen atom (if the flame retardant does not contain hydrogen) or a hydrogen halide



where M' is representative of the residue of the flame retardant molecule having lost X^{\bullet} or HX . Halogen radicals react with available fuel to generate hydrogen halide:



The hydrogen halide is thought to be the flame inhibitor by altering the chain branching according to the following two reactions:



In reaction (7), hydrogen halide reacts with a hydrogen radical to produce hydrogen gas and a halide radical. In this way, reaction (1) is slowed and a halide radical is made available for reaction (6) so that more hydrogen halide can be produced. In reaction (8), hydrogen halide reacts with a hydroxyl radical to produce water and a halide radical. This impedes reaction (3) and, as with reaction (7), a halide radical is produced which can be used to generate additional hydrogen halide by reaction (6).

2.1.3.4 Physical Effects

Flame retardant properties can be given by physical effects, which may occur in the condensed phase as well as in the gas phase. Inorganic flame retardant chemicals are the main variety that function by physical effects. These chemicals are applied as “fillers” to textile substrates in large quantities, sometimes exceeding 60% of the weight of the final product. [5]

One common physical effect involves the dilution of the organic part of the structure and division of the structure into insulated regions. This is achieved by filling the pores and the amorphous regions of the polymer. Pyrolysis of the polymer is made difficult because additional heat is needed to reach the pyrolysis temperature. Therefore, fewer combustible gases and less heat are generated. As a result of this reduction in heat, pyrolysis of the polymer cannot be sustained and the fire is starved of fuel. This is often referred to as the “heat sink” effect, and is enhanced by a higher specific heat and a lower thermal conductivity of the filler. Examples of common fillers include alumina, mica, feldspar, clay, talc, pumice, and zinc oxide. An alternative heat sink effect can be observed in alumina trihydrate, which endothermally decomposes to release three moles of water into the gaseous phase while consuming 1170 J^{-1} . Similarly, calcium carbonate decomposes under heat to release carbon dioxide. Decompositions such as these serve to decrease the temperature of the pyrolyzing polymer, thereby contributing to the flame retardance of the substrate. Moreover, the

gases that are released by these decompositions dilute the combustible gases and the oxygen in the flame to further enhance the flame retardant effect. [5]

The coating and insulation effect is characterized by the formation of a shielding layer of glass or char that separates the polymer from the flame. This barrier obstructs the passage of combustible pyrolysis products to the flame while impeding the transfer of heat from the flame to the polymer. Gay-Lussac observed this type of effect in 1821 for boric acid on cotton [5]. Boric acid and its hydrated salts have low melting points and dehydrate in stages as shown below [5].



Sodium pentaborate, $\text{Na}_2\text{B}_{10}\text{O}_{16} \cdot 10\text{H}_2\text{O}$, is a useful flame retardant for cellulose. It is water-soluble and generates a clear, glassy layer that adheres uniformly to cellulose upon heating. It also is effective at promoting the formation of char. [5]

2.1.4 Classifications of Flame Retardants

Flame retardant finishing chemicals can be classified in a number of ways. Generally, they are grouped based on their chemical family or by the mechanism through which they impart flame retardant properties. Occasionally, flame

retardant chemicals may be classified based on the polymers that they are commonly used in association with.

The dominant classifications (based on chemical family) of flame retardant finishes are halogenated flame retardants and phosphorus-based flame retardants. In addition to these two classes, nitrogen-based and inorganic flame retardant chemicals are also used. However, these two classes normally perform poorly when used alone. For this reason, they are frequently used as synergists and can appreciably increase the flame retardancy of a polymer when used in this capacity.

2.1.4.1 Halogenated Flame Retardants

Halogenated flame retardants are generally believed to function via the gas phase mechanism as described in Section 2.1.3.3. A halogen atom is released into the flame, where it reacts with available fuels to form hydrogen halide. This hydrogen halide is responsible for imparting flame retardant properties by inhibiting the combustion reactions. [5]

2.1.4.1.1 Synergism Between Halogen and Antimony

Halogenated flame retardants have been used extensively in collaboration with antimony. When used in tandem, their synergism is apparently dependent upon action in both the condensed phase and the gas phase. During pyrolysis, some hydrogen halides are released, which react with Sb_2O_3 to produce either

SbX_3 or SbOX . SbX_3 is volatile and is released into the gas phase. Meanwhile, SbOX , which is a strong Lewis acid, may operate in the condensed phase to aid in the dissociation of carbon-halogen bonds. [7]

While some activity of Sb_2O_3 in the condensed phase is known, its core activity takes place in the gas phase. Antimony halides that are evolved into the gas phase react with atomic hydrogen to generate HX , SbX , SbX_2 , and Sb . Antimony combines with atomic oxygen, water, and hydroxyl radicals to yield SbOH and SbO , which scavenge hydrogen radicals. SbX_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^\bullet . It is also thought that antimony halides delay the escape of halogen from the flame, effectively increasing its concentration while simultaneously diluting the flame. Antimony halides may also “blanket” the polymer and prevent oxygen from reaching it as it pyrolyzes. [7]

2.1.4.1.2 Rising Health and Environmental Concerns

While there is some discrepancy regarding the percentage of the global flame retardant market that brominated compounds account for, it is common knowledge that brominated flame retardants are used extensively throughout the world to increase the fire resistance of materials. However, as the demand for brominated flame retardants increases, so does the concern that they may be toxic to people and the environment. This concern is rooted in the idea that while

brominated flame retardants provide valuable fire protection for materials, they may leach into the environment or release toxic combustion products upon burning. As a result of these growing concerns, many nations have established regulations that restrict the use of certain brominated flame retardants.

The intensification of concern regarding the toxicological and environmental impacts of brominated flame retardants is not without justification. Polybrominated diphenyl ethers (PBDEs) have become one of the main focuses. This is due to their structural resemblance to another variation of flame retardants, polybrominated biphenyls (PBBs), which were banned from production in the United States in 1976 and have been demonstrated to cause liver cancer in laboratory rats and mice [18]. The Department of Health and Human Services (DHHS) has determined that PBBs may reasonably be anticipated to be carcinogens, while the International Agency for Research on Cancer (IARC) has suggested that PBBs may be carcinogenic to humans [16]. Figures 2-5 and 2-6 show the structural similarities that exist between PBBs and PBDEs.

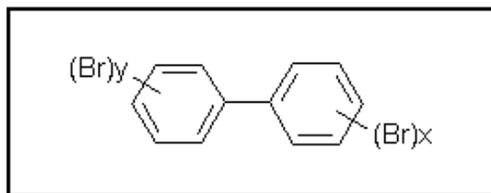


Figure 2-5. Polybrominated biphenyl (PBB).

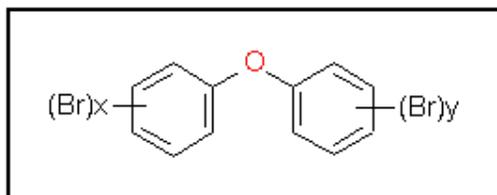


Figure 2-6. Polybrominated diphenyl ether (PBDE).

Polybrominated diphenyl ethers are additive flame retardants. Since they are not chemically bound to the substrate, they have a tendency to leach out into the environment [19]. Like PBBs, PBDEs are very stable in the environment and emerging evidence suggests that they bioaccumulate [19]. Some recent research demonstrates that the concentration of PBDEs in mother's milk from the Faroe Islands and serum samples from Norway and the United States increased between the late 1970s and the early 2000s [20, 21, 22]. While more recent data seems to suggest that the concentration of PCBEs in human milk has leveled off [23, 24], their persistence is a cause for alarm because there is some indication that PCBEs may cause liver toxicity, thyroid toxicity, and neurodevelopmental toxicity [19].

While there is still much to learn about the potential toxicological effects of PCBE exposure, several nations have proposed legislation banning their use until more facts become available. In light of escalating concerns surrounding the toxicity of brominated flame retardants, traditional halogen-based flame retardant suppliers are venturing into the non-halogenated flame retardant

market [9]. One example is the Great Lake Chemical Corporation, which was the only U.S. producer of penta-PBDEs. In 2003, Great Lake Chemical Corp. agreed to phase out the production of penta- and octa- PBDEs by December of 2004 [19]. This voluntary action was taken following discussions with the Environmental Protection Agency (EPA), who decided to put a stop to new uses for these two brominated flame retardants.

2.1.4.2 Phosphorus-Based Flame Retardants

Despite the very significant role of halogenated flame retardants, the recent increase in concern over their use has stimulated strong interest in phosphorus-based flame retardants. While phosphorus-based flame retardants have been produced commercially for a long time, their applications have been limited to specific polymers. This is because their mechanism of action, which is generally linked with the condensed phase and char formation, requires them to react with the polymer during decomposition. As the phosphorus-containing molecule undergoes thermal decomposition, it produces phosphoric acid. In polymers containing hydroxyl groups, particularly cellulose, the phosphoric acid that is generated forms cross-links with the polymer chains in a dehydration reaction as depicted earlier in Figure 2-3. The presence of these cross-links modifies the pyrolysis process, leading to a reduction in the production of flammable pyrolysis products [6]. A table that compares phosphorus-based

flame retardants to other flame retardant systems, especially those containing halogens, is provided and labeled Table 2-2.

Table 2-2. Advantages and disadvantages of phosphorus-based flame retardants. [23]

Advantages	Disadvantages
<ul style="list-style-type: none"> · Lower density compared with halogen types · No need for antimony oxide synergist · Less persistence and bioaccumulation · Effective char formation in charable polymers · Better photostability · Less likely to intensify smoke obscuration · Less acid gas evolution upon burning · No halodioxin formation · Increased biodegradability · Avoid negative public image 	<ul style="list-style-type: none"> · Difficulty in making high %P compounds · No good general synergist · Tendency to be hydrophilic; promote moisture uptake · May hydrolyze to form acids that damage substrate · May be less thermally stable; limits processing temperatures · Thermal and hydrolytic stability may impede recycling · Some toxicity questions related to reactivity · Increased cost

There are many types of phosphorus-based flame retardants that are used on a wide array of substrates. Ammonium phosphates, melamine phosphates, and related phosphorus acid amine salts are useful with polyolefins. Elemental red phosphorus, having been properly stabilized and coated, is a very effective fire retardant when used in association with molded nylons, epoxies, or certain other plastics. Phosphoric acid esters are an expansive group of flame retardant compounds and are used in conjunction with several polymers. Metal

salts, particularly those incorporating aluminum, of organic phosphonic and phosphinic acids are useful as flame retarding additives with polyamides and polyesters. Phosphonic acid esters can be built in to polyester fibers, while certain phosphinic acid esters are used for post-treatment of polyester fabric. The dominant durable flame retardant finish for cotton is based on the reaction of tetrakis(hydroxymethyl)phosphonium salts with urea and ammonia. [25]

2.1.4.2.1 Synergism Between Phosphorus and Nitrogen

It has been known for some time that certain nitrogen compounds will synergize the action of phosphorus in cellulose. This synergistic effect is dependent upon the nitrogen compound that is used [26] as well as the polymer to which it is applied. One theory to explain this observed synergism attributes the effect to the creation of P-N bonded intermediates that are superior phosphorylating agents when compared to the phosphorus compounds acting unaccompanied [27]. Another study suggests that the nitrogen compounds delay the volatility loss of phosphorus from the condensed phase [28]. The opposite is proposed by a study [29] that examines urea-formaldehyde-diammonium phosphate on cotton-polyester blend fabric. This research suggests that the nitrogen resin enhances the gas phase action of the phosphorus by some means. Yet another study [30] investigates red phosphorus with melamine and other nitrogen compounds in a number of thermoplastic polymers. This research proposes that nitrogen compounds enhance the oxidation of phosphorus and

give off inert gases, such as ammonia, that can have a considerable impact on the fuel value of the evolved combustible gases. Finally, it is thought that organic nitrogen may aid in controlling the pH during the crosslinking reactions of phosphoric acid. A pH that is too acidic will cause cellulose to undergo acid hydrolysis, while a pH that is too high will prevent acid-catalyzed crosslinking from taking place all together. Since the nitrogen can be protonated, it can reduce the quantity of available acid [6].

2.1.5 Evaluating Flame Retardants

In a world of increasing regulations, it is important to develop standard test methods that allow a flame retardant fabric to be evaluated for the amount of protection it offers. Often, a specific test is used to evaluate all fabrics that are designed for a particular end-use. Examples of specific end-uses that may be required to provide a certain level of fire protection include general apparel, children's sleepwear, protective apparel, upholstery, floor coverings, bed coverings, and military fabrics [4]. These test methods describe precisely how testing should be conducted to ensure that any results are repeatable and so that all fabrics are held to the same standard. Standard test methods control variables such as the type and size of the fabric sample, the duration of the fabric's exposure to the flame, and the angle at which the fabric is presented to the flame. Table 2-3 provides a list of some common test methods, their sponsoring organization, and a very brief description of how they work [4].

Table 2-3. Summary of common standard test methods for flame retardant fabrics. [4]

Test Method	Sponsoring Organization	Description
16 CFR 1610	Consumer Product Safety Commission (CPSC)	Fabric held at 45° to flame for 1 second; for general apparel
16 CFR 1615/1616	CPSC	Fabric held vertical to flame for 3 seconds; for children's sleepwear
NFPA 1971	National Fire Protection Association (NFPA)	Fabric held vertical to flame for 12 seconds; for protective clothing
NFPA 701	NFPA	Fabric held vertical to flame for 45 seconds to 2 minutes; for drapery
ASTM D-2863 Limiting Oxygen Index (LOI)	American Society for Testing and Materials (ASTM)	Fabric held vertical to flame in atmosphere of different oxygen levels and ignited from top; determines minimum oxygen level needed to allow combustion

2.2 Plasma Technologies

2.2.1 An Introduction to Plasmas

As with any industry, the textile industry constantly seeks new technologies that will enhance efficiency, boost productivity, and decrease expenses. Recently, the use of plasmas to impart physicochemical surface modifications to textile substrates has become an intriguing approach to replace

or enhance conventional wet-processing techniques. Plasmas are generally regarded as a distinct fourth state of matter, separate from solids, liquids, and gases. They are defined as gaseous states of matter that contain an energetic assortment of ions, free electrons, free radicals, and visible, ultraviolet, and infrared radiation [31].

Plasma was first identified by Sir William Crookes, who described it as “radiant matter” in an August 22, 1879 lecture to the British Association for the Advancement of Science [32]. In 1928, Irving Langmuir first used the term “plasma” to describe this matter [33]. Despite being the last discovered state of matter, most of the material in our visible universe exists as plasma [34].

Plasmas are often broadly categorized as being either natural or man-made. The sun, most stars, and a sizeable fraction of the gas that permeates interstellar space are some examples of natural plasmas that exist beyond the bounds of the Earth’s atmosphere. Within the Earth’s atmosphere, abnormal conditions are needed to promote the formation of plasmas because of the unfavorably low temperatures and high pressures that are commonly found. Perhaps the most frequently encountered example of natural plasma within the Earth’s atmosphere is lightning, which is formed when electrical currents in the lightning discharge ionize and heat atmospheric gases to extremely high temperatures. Observable at high altitudes, the aurora is an example of plasma that is generated as energetic electrons and ions strike the atmosphere at 80 to

100 km above the Earth's surface. At even higher altitudes, the Earth is encircled by dense plasma known as the ionosphere, which is formed by ultraviolet radiation from the sun. At altitudes surpassing the ionosphere, the Earth is encapsulated by magnetized plasma that is termed the magnetosphere.

[34]

In addition to the natural occurrence of plasmas, there are numerous instances where plasmas are found in man-made devices. Through a great deal of research, it is now possible for man to control plasmas and utilize them in a variety of applications. One of the most significant applications of man-made plasma is the endeavor to accomplish controlled thermonuclear fusion [34]. Some more familiar applications of man-made plasma include neon and fluorescent lighting, electric arc welders, and plasma etching machines, which are used daily around the world [34]. The electronics industry has benefited from the swift expansion of plasma technologies, with advancements being made in the processing of microchips and semiconductors [31]. Now, much exploration into the use of plasmas for surface modification of textile substrates is underway. Although only a handful of companies have begun using plasma technologies commercially for this purpose, it is clear that the textile industry has embraced plasma treatments as a potential solution to many of the downfalls of traditional wet processing.

2.2.1.1 Defining Plasma

As previously described, plasmas are defined as an ionized gas containing an energetic assortment of charged particles, electrons, free radicals, and molecular fragments. Plasmas form upon the ionization of a sizeable quantity of gas. Some plasmas, such as those that occur in the sun and stars, are completely ionized. On the other hand, the plasmas that are used in industrial and research settings are usually only partially ionized.

Plasmas may differ in the way they are generated or by the properties they possess once they are formed. However, all plasmas share certain similarities. To be classified as plasma, a volume of ionized gas must meet three criteria. The first criterion relates to the charge of the plasma. Since plasmas are generated from the ionization of neutral gases, it follows that the concentration of negatively charged ions and electrons is equivalent to the number of positively charged ions. While there may be localized regions that possess a charge, the net charge for the entire bulk of the plasma is zero and the plasma is said to be quasineutral. The second criterion speaks to the degree of ionization of the gas. All gas contains negligible quantities of ionized species. This ionization may be the result of one of several factors, including ultraviolet radiation or electric fields. However, to be considered plasma, the degree of ionization within the gaseous body must be sufficient for it to be conductive and for it to be strongly responsive to electric or magnetic fields. The third criterion

describes the collective behavior that plasma must demonstrate. This means that particles within plasma are influenced by regions of particles that are a considerable distance away. As a charged particle moves through plasma, it produces electric and magnetic fields. These disturbances manipulate the behavior of other distant charged particles. Simply put, plasma is capable of the processes that generate electric and magnetic fields to which the remainder of the plasma then reacts. [35,36]

2.2.1.2 Properties of Plasma

There are a variety of ways to generate and control plasma for commercial or academic use. Regardless of the system being used, all plasmas can be classified based on their plasma temperature, plasma density, and plasma frequency. Each of these internal qualities affects the plasma and the result of any treatment that is carried out in the presence of the plasma. Plasma temperature does not refer to the temperature of the bulk plasma, but instead is a measure of the thermal kinetic energy of the individual electrons and ions within the plasma. When fully ionized, each of the ions or electrons in the plasma will possess a high kinetic energy, resulting in the average temperature of the bulk of the plasma being very high. In these “thermal” plasmas, the ions and electrons are said to be at local thermodynamic equilibrium. However, since there is a significant difference between the mass of electrons and the mass of ions or neutral atoms, electrons come into thermal equilibrium with themselves much

more quickly than they come into thermal equilibrium with the larger ions and neutral atoms. Given that electrons are much lighter than ions, they can be accelerated much more quickly to much higher velocities, even in very weak electric fields. This instance is typical of plasmas in which only a small fraction of the gas is ionized. In these “non-thermal” plasmas, the temperature of the electrons is still very high, while the bulk of the plasma remains near ambient temperature. The temperature of the bulk of the plasma is a very important consideration because hot plasmas operate at temperatures that will degrade textile substrates. Therefore, non-thermal plasmas are necessary for the treatment of textiles and polymeric materials.

Plasma density refers to the number of active species per unit volume. Plasma density can be calculated through the Boltzmann relation (9), which correlates electron density, n , with plasma potential, Φ .

$$n = n_0 e^{(e\Phi/KT)} \quad (9)$$

In this relation, n_0 is the particle density of the gas that is used to create the plasma. The charge on a single particle is e . The term K is Boltzmann’s constant and T is plasma temperature. [37]

Finally, plasma frequency is the frequency at which oscillations in the plasma occur. In order to understand plasma frequency, it is useful to think of

the negatively charged electrons within the plasma as one mass and the positively charged ions as another mass. If the negatively charged mass is withdrawn from the positively charged mass such that their charges no longer cancel, an electric field will be established. This electric field then accelerates the negatively charged electrons back towards the positively charged ions to cancel their charge. At the moment of cancellation, the momentum of the electrons is at a maximum. This allows them to recreate the charge separation in the opposite phase. In this way, a simple harmonic motion is established with the plasma oscillating at a characteristic frequency. Figure 2-7 depicts this motion. [38]

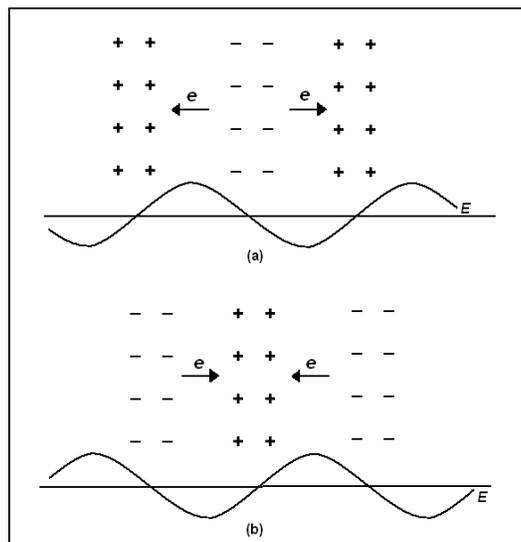


Figure 2-7. Oscillations in plasma. (a) Displaced electrons give rise to a restoring force and acceleration. (b) Following half a cycle, the charges are interchanged.

[38]

2.2.2 Generating Plasma: A Look at Plasma Systems

In order to generate and sustain plasma, a source of energy is needed that is capable of causing dissociation and ionization of the gas that is being used. For this purpose, direct current (DC) or alternating current (AC) power supplies may be utilized [39]. With direct current, the flow of electrons is unidirectional and continuous. Dissimilarly, alternating current is characterized by the periodic reversal of the direction in which the electrons are flowing. With AC, the flow of electrons is oscillatory and follows a sinusoidal pattern. In radio frequency (RF) power supplies, such as the one used for the purposes of this research, the frequency of these oscillations is 13.56 MHz.

With some systems, the material that is being treated must be placed directly into the plasma discharge. This type of system is referred to as an *in-situ* device. These types of configurations are known for consuming less feed gas and power. Other systems may allow materials to remain just outside of the plasma discharge. Since the active species of the plasma are directed downstream of the discharge to the material being treated, these configurations are referred to as downstream devices. Because the material does not have to be placed in a plasma chamber, it is possible to treat complex shapes. A reduction in monomer fragmentation and electrode/chamber coating is also observed. [40]

Plasmas may be produced with an inductively coupled system or a capacitively coupled system. They may also be produced in a low-pressure vacuum setting or at atmospheric pressure. Subsequent sections will discuss each of these categories in more detail.

2.2.2.1 Inductively Coupled Systems

In an inductively coupled system, an inductive circuit element is placed adjacent to a discharge region. Through this inductive circuit element, energy from a radio frequency power source is coupled with an ionized gas. In a system that utilizes a planar configuration, the inductive circuit element is generally a coil-shaped conductor. Figure 2-8 depicts a cross-sectional view of this type of configuration, where the RF coil resides above the discharge region. Alternatively, in a system that utilizes a cylindrical configuration, the inductive circuit element assumes the shape of a helix that surrounds the discharge region. This type of configuration is depicted in Figure 2-9. With large radio frequency currents flowing through this inductive circuit element, a radio frequency magnetic flux is generated. This magnetic flux penetrates into the discharge region, where a solenoidal radio frequency electric field is established. This electric field is responsible for accelerating the electrons in the discharge and maintaining the plasma. [41]

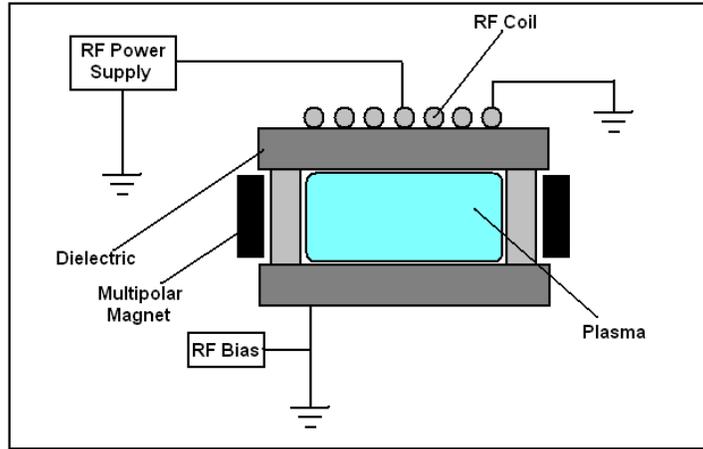


Figure 2-8. Planar inductively coupled plasma device.

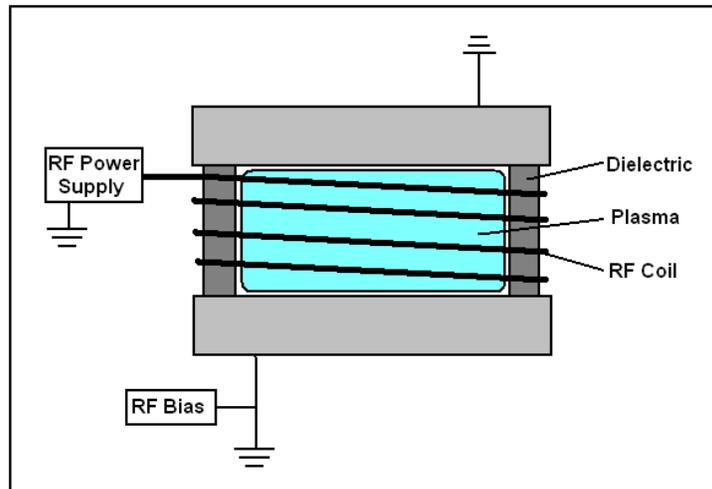


Figure 2-9. Cylindrical inductively coupled plasma device.

In the planar configuration, multipolar magnets may be added around the circumference of the discharge region to maximize the radial uniformity of the plasma. To attain the same effect in a cylindrically configured device, the coil

can be wrapped asymmetrically around the discharge region [42]. Fewer turns in the inductive circuit element of a cylindrically configured device results in reduced energy loss, meaning that a single turn would be preferred.

2.2.2.2 Capacitively Coupled Systems

Capacitively coupled systems are a popular choice for materials processing applications. A depiction of this type of system is provided and labeled Figure 2-10. In this type of configuration, one of two parallel electrodes is connected to a power supply. The other electrode is grounded. With a sufficient voltage applied across the electrodes, the ionization of atoms occurs and electrons are freed. In this way, plasma is generated and sustained in the discharge region between the electrodes.

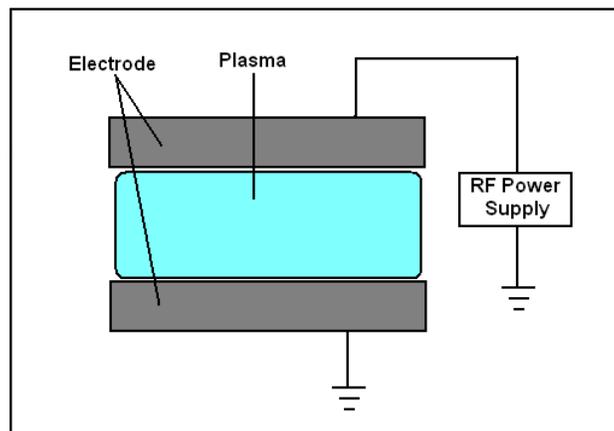


Figure 2-10. Capacitively coupled plasma device.

Capacitively coupled systems may be operated in a low-pressure vacuum or at atmospheric pressure. To enhance the efficiency of the power transfer, the power source must be driven through a matching network [43]. The temperature of the bulk of the plasma is low enough to prevent any degradation of the substrate. However, the electrons contained within are energetic enough to create surface modifications.

2.2.2.3 Vacuum Plasma Devices

Vacuum plasma devices have a proven record of effective modification of textile substrates. When research pertaining to plasma treatment of textiles is conducted, it is most commonly done under vacuum. In a vacuum plasma device, the discharge region is located in a chamber with a controlled environment. Pressures within this chamber are typically below 10 Torr [44].

One disadvantage of operating a plasma device under vacuum is that expensive vacuum equipment must be used. This vacuum equipment must be maintained as well, which may lead to additional costs or downtime for the device. Another disadvantage is that the device operates in a vacuum chamber, which is a closed environment, making it difficult to design a continuous process. Typically, the substrate is placed in the chamber, a vacuum is applied to the chamber, the plasma is generated, the substrate is treated, the vacuum is removed, and the chamber is opened so that the substrate can be collected. In order for a continuous process to work, the substrate must pass through a series

of chambers of gradually decreasing pressure until it finally reaches the main vacuum chamber. Once there, it is treated with the plasma before it exits the device again through a series of chambers of gradually increasing pressure. In this way, pressure is stepped down from atmospheric to the desired vacuum conditions as the substrate enters the device. Then, it is stepped back up from vacuum pressure to atmospheric pressure as it leaves the machine. Figure 2-11 shows a schematic of this type of device.

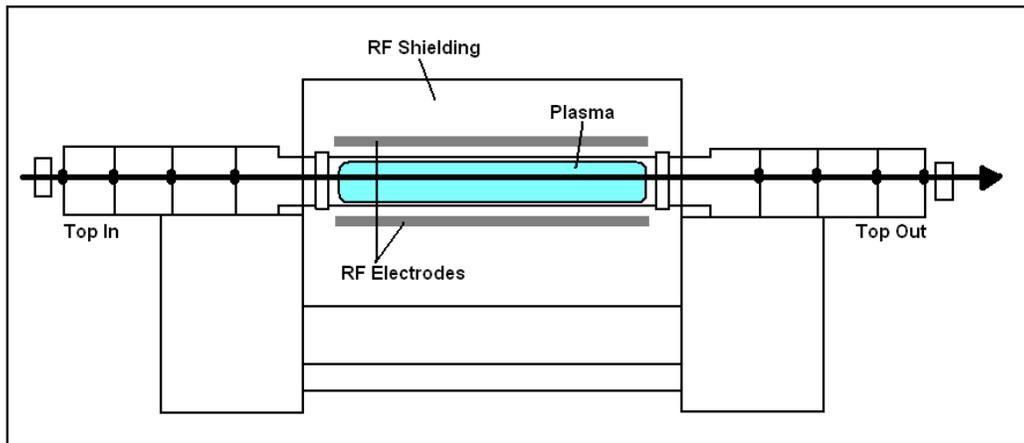


Figure 2-11. Schematic of continuous process plasma device. [45]

Despite these disadvantages, the main advantages of using a vacuum plasma device are very significant. Since the plasma is being generated in a closed system, the environment inside the vacuum chamber is more controllable and consistent than one operating at atmospheric pressure. Additionally, operating in a closed vacuum system means that operators have a reduced risk

of exposure to any chemicals or other hazardous materials that may be used or created within the chamber.

2.2.2.4 Atmospheric Pressure Plasma Devices

Atmospheric plasma devices, as their name suggests, operate without the confines of a vacuum chamber. In 1988, four requirements for producing a stable plasma at atmospheric pressure were outlined [46]. First, helium was used as a feed gas. This increases the period of the Townsend discharge, impeding the conversion of the plasma to an arc discharge. Second, a dielectric was needed on the lower electrode plate. This insulating barrier is selected based on the required level of heat resistance for the application and also aids in the prevention of arc formation. Third, a brush-style upper electrode produced the most consistent plasma. This electrode consisted of 25 fine wires made with tungsten or stainless steel. Lastly, a stable discharge was generated using high frequency sources in the kilohertz (kHz) or radio frequency (MHz) range. So long as these requirements were adhered to, a uniform plasma was created that resisted transformation to an arc discharge and compared favorably to radio frequency vacuum plasmas [47].

To overcome the batch processing limitations and elevated expenses of vacuum plasma devices, the trend of developing sources that can operate at atmospheric pressure is growing steadily. Atmospheric pressure plasmas have demonstrated their ability to modify textile substrates. With an open-perimeter

device, these textile substrates can be fed through the plasma in a continuous process. In addition, atmospheric pressure plasmas can operate at temperatures that do not degrade the polymers that are used in the construction of fabrics. These facts combine to support atmospheric pressure plasma treatment as an exciting possibility for the textile industry. Research into the potential applications of modifying textile substrates with an atmospheric pressure plasma source is ongoing. It is probable that the growth in atmospheric pressure plasma devices will continue until all plasma-processing applications are conducted at atmospheric pressure or until it is clear that operation under a vacuum is inevitable [44].

2.2.2.4.1 Corona Discharge Plasmas

A typical corona discharge plasma system consists of two opposing electrically conductive electrodes that are separated by a gap and are connected to a high voltage power source. The geometry of the electrodes is asymmetric, with one electrode being constructed of pointed needle or thin wires and the other electrode taking the shape of a flat plate or large diameter cylinder. Figure 2-12 depicts this configuration. Continuous or pulsed AC or DC sources may be used to power these systems. The electric field that is created around the pointed needle or thin wire ionizes surrounding gases. In this way, plasma is generated that discharges in a conically shaped spray from the needle or wire. [48]

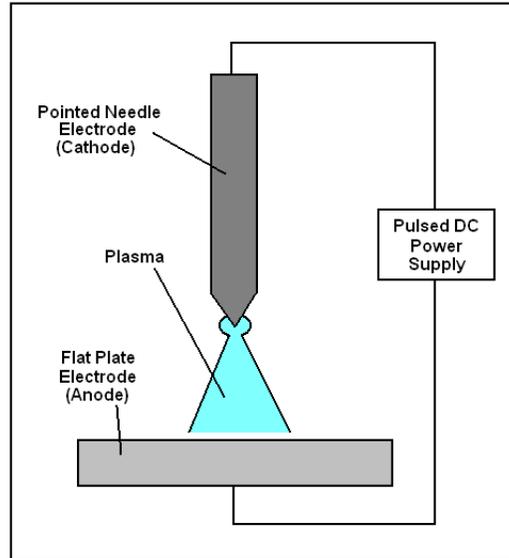


Figure 2-12. Schematic of corona discharge plasma system.

Corona discharges are weakly ionized, with electron density decreasing significantly with distance from the point of generation. With this in mind, it is difficult to design a device that is capable of processing large surface areas. In order to do so, the needles or wires of the electrode would have to be spaced further apart. To compensate for this, the upper electrode would need to be spaced very closely to the lower electrode. Even then, the total exposure time of the substrate would likely be too low to justify treatment. Additionally, the level of power that can be used in a corona discharge system is restricted by the ability of the needle or wire to dissipate heat as well as its cross-sectional capacity. Despite being well established, these disadvantages make corona discharge systems flawed for textile applications. [48]

2.2.2.4.2 Dielectric Barrier Discharge (DBD) Plasmas

Dielectric barrier discharge (DBD) systems are characterized by two parallel conducting plate electrodes that are separated by a gap of approximately 10 millimeters. When a voltage is applied, the gas between the plates is ionized and the plasma discharge is generated. Figure 2-13 provides a schematic of this type of device. Usually, this plasma occurs in the form of a narrow thermal arc that jumps between the electrodes. This would be useless for textile processing. To prevent the transition of the plasma into an arc, one or both of the electrodes is concealed by a dielectric. In order for the plasma to endure this type of configuration, it is forced to spread over the full surface area of the electrodes to carry the necessary current. Therefore, the plasma can occupy a large volume and is uniform. [48]

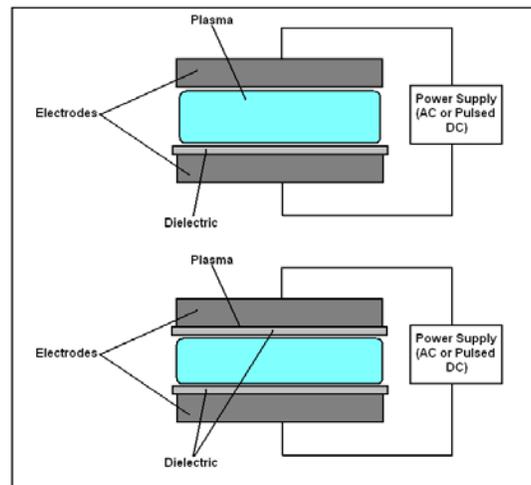


Figure 2-13. DBD plasma systems with one dielectric (top) or two dielectrics (bottom).

The discharges from this type of system can take two forms. Filamentary discharges consist of microdischarges that are approximately 100 micrometers in diameter. These discharges are channels of current that run between the two electrodes and have lifetimes on the nanosecond scale. Theoretically, the spatial distribution of these microdischarges should be random such that, over a short period of time, all of the volume between the electrodes experiences a discharge. This would create a visually uniform plasma. In practice, imperfections or residual charges on the electrodes and dielectrics create preferred striking points for the plasma. An observer peering into the discharge region would see bright vertical columns within the plasma, some that are stationary and some that move about. [48]

The second form of discharge is referred to as homogeneous. By controlling gas composition, electrode spacing, and the frequency of the power source, a continuous and uniform discharge is created. This type of discharge is preferred for textile processing because of this spatial uniformity. In contrast to homogeneous discharges, processing speeds with filamentary discharges must be slower to allow enough time for the microdischarges to contact as much of the substrate as possible. [48]

2.2.2.4.3 Atmospheric Pressure Glow Discharge (APGD) Plasmas

Similarly to DBD systems, atmospheric pressure glow discharge (APGD) systems consist of two parallel planar or curved electrodes that are separated by

a distance of a few millimeters. A schematic of an APGD device is provided and labeled Figure 2-14. Upon the application of a relatively low voltage (around 200 V) at a high frequency (up to 60 MHz), a uniform glow discharge plasma is generated between the electrodes. The distinguishing feature between APGD systems and DBD systems is the absence of dielectrics from APGD devices. Instead, bare metal is exposed, allowing for sizably higher power densities to be coupled into the discharge. Additionally, APGD plasmas are denser than DBD plasmas. [48]

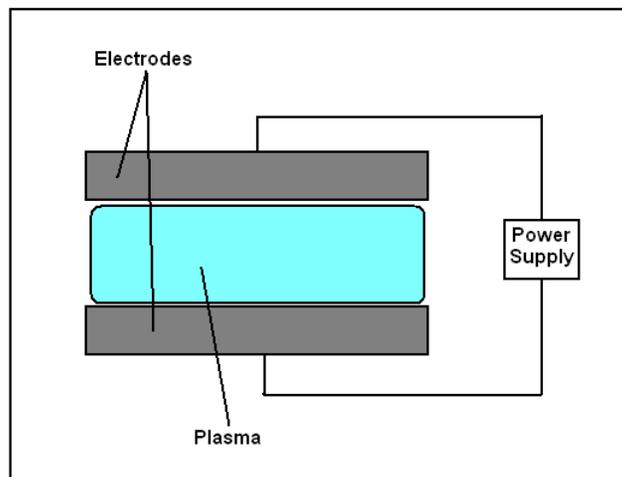


Figure 2-14. Schematic of atmospheric pressure glow discharge (APGD) device.

Generally, the result of applying a voltage across two bare metal plates would be a thermal arc. However, the dense non-thermal plasmas that can be generated in APGD devices are credited to the use of helium gas and the careful

control of the distance between the electrodes as well as the frequency of the driving voltage. APGD plasmas are an abounding source of the reactive species that are needed for textile treatments. [48]

2.2.2.5 Gas Selection

The active species within the plasma bulk impact the type of modification that will be performed on the substrate. As such, the variety and concentration of gases that are fed into the plasma discharge can be adjusted to achieve certain results. Some common gases that are incorporated into plasmas include helium, oxygen, argon, nitrogen, ammonia, and others. A number of the surface modifications that are achieved by plasmas containing these gases are discussed in later sections.

As previously stated, the generation of an atmospheric plasma is generally dependent upon the use of helium as a seed gas. Helium has an ionization energy of around 24.6 electron volts, the highest of any atom on the periodic table. This means that a great deal of energy should be necessary to remove one of its electrons. However, since helium lacks the assortment of energy levels that more complex gases have, it has few options for dealing with incoming energy other than ionization. Helium, as with other noble gases, has high-energy metastable states that allow it to remain ionized for extended intervals of time. This makes helium an excellent choice for combination with other gases because it aids in their collision-induced ionization. [48]

Helium is a finite resource and is becoming ever more expensive. This presents a dilemma, as some plasma sources use large quantities of helium in high concentrations for operation. To counteract this drawback, a helium recycling system can be integrated into a plasma devices design. This can be done because helium is not consumed in the process of plasma generation. [48]

2.2.3 Interactions Between Plasma and Substrates

The action of the plasma rarely penetrates beyond the outer layers (no more than a few micrometers deep) of a polymeric material [49]. This makes plasma treatment of textiles ideal for physicochemical surface modifications, leaving the bulk chemical and mechanical properties of the substrate intact. Some effects that have been achieved by plasmas on textile substrates include etching and redeposition, functionalization, plasma polymerization, radical formation, and grafting. Each of these modifications is dependent upon the polymer being used as well as parameters such as gas, pressure, power, exposure time, and frequency.

2.2.3.1 Etching, Redeposition, and Backscattering

Plasma etching is a technique that is used to remove material from the surface of a substrate. In contrast to many traditional chemical wet processing techniques, plasma etching can be selective and even anisotropic. This means

that particulate removal only occurs along one axis. Four basic plasma etching processes are observed. Figure 2-15 demonstrates each of these categories.

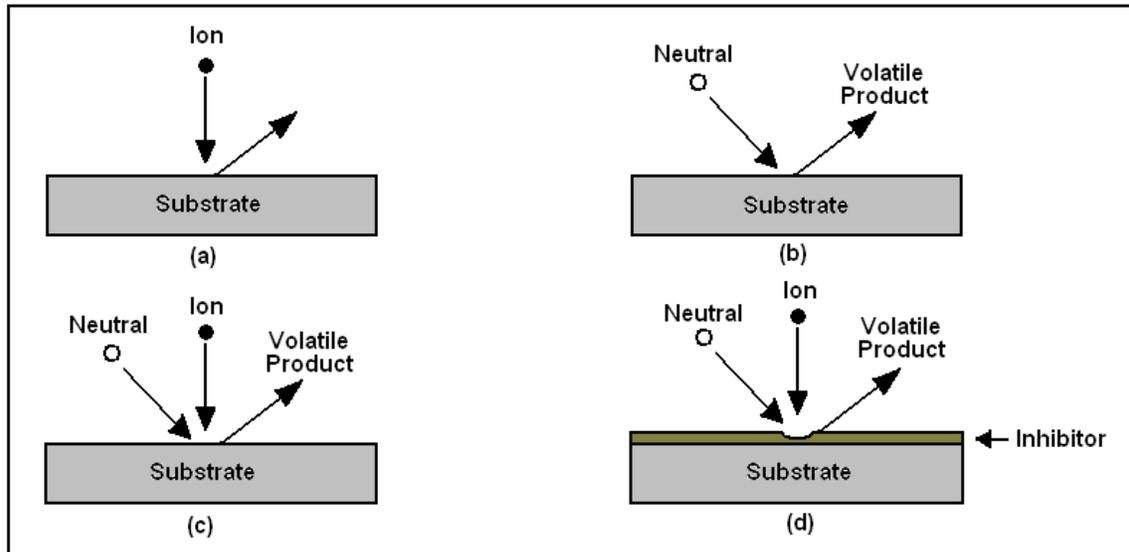


Figure 2-15. Etching mechanisms: (a) sputtering; (b) pure chemical etching; (c) ion energy-driven etching; (d) ion-enhanced inhibitor etching. [48]

In sputtering, which is strictly a physical and unselective process, ions are accelerated toward and collide with the surface of the substrate, ejecting surface atoms. Yields are typically low for sputtering, on the order of one ejected atom per incident ion. Sputtering can be an anisotropic process since it is dependent upon the angle of the incident ion. [43]

With pure chemical etching, free electrons in the plasma bulk collide with gas atoms or molecules, causing their dissociation to form reactive etchants. These etchants then react chemically with the surface of the substrate to

generate volatile products, which then leave the substrate's surface. Since this type of process relies on the chemical reactions between the etchants and the target species that exist on the surface of the substrate, it is decidedly selective and isotropic. [43]

A mixture of sputtering and chemical etching typifies ion energy-driven etching. Initially, active species that are generated in the plasma bulk collide with the surface of the substrate to produce reactive sites. Then, a chemical reaction between these sites and the neutral gas creates volatile products that are released. The combination of these processes enhances the yield of etched products to levels beyond what either process could achieve by itself. Due to this processes reliance on chemical and physical effects, it is both selective and anisotropic. [43]

The final category of etching, termed ion-enhanced inhibitor etching, shares many similarities with ion energy-driven etching. The distinguishing feature is the use of an inhibitor. This inhibitor is deposited uniformly over the surface of the substrate. A vertical barrage of ions prevents the inhibitor from accumulating on horizontal faces. Meanwhile vertical faces, which are not subjected to the ion impacts, are coated. The uninhibited regions then become the focus of a chemical attack, which produces volatile products that leave the substrate. This process is anisotropic and results in vertical sidewalls. [43]

It is important to consider that material that has been ejected from the surface of the substrate may ultimately return to the substrate in one of two ways. If the substrate is textured, ejected particles have a tendency to accumulate on its vertical faces in a process known as redeposition. If the substrate is very smooth, ejected particles will enter the plasma bulk. There, they collide with gaseous species before falling back to the surface of the substrate in a process known as backscattering. [43]

2.2.3.2 Radical Formation and Reaction

Radicals are formed upon the collision of active species from the plasma bulk with the surface of the substrate. If the energy that is carried by the impacting active species is sufficient to dissociate the bond that it collides with, a radical will be produced. Therefore, the ability to generate surface radicals is dependent upon both gas composition and the chemical construction of the substrate. Once formed, surface radicals are unstable. Inevitably, they will react with other molecules or the atmosphere. If some control is exerted over the species that are made available for reaction with these radicals, some very useful surface modifications can be realized.

2.2.3.2.1 Surface Functionalization

When a substrate is exposed to plasma, radicals that are created on its surface may undergo chemical reactions with the gaseous species that exist in

the plasma bulk. This process, sometimes referred to as surface functionalization, is dependent upon the type of gases that are being fed into the plasma. If some fraction of the plasmas feed gas consists of oxygen (O_2), it is likely that surface analysis of the treated substrate will reveal an increase in oxygen-containing functional groups such as hydroxyls, carboxyls, epoxides, and carbonyls. The result of such a treatment is an increase in surface energy and hydrophilicity. Dissimilarly, an increase in hydrophobicity can be achieved through the use of carbon tetrafluoride (CF_4) in the feed gas. Surface fluorination causes a decrease in surface tension. If nitrogen or ammonia gas is used to generate the plasma, an increase in the ratio of nitrogen atoms to carbon atoms should be observed. Some functional groups that may be added in this process include amines, nitriles, and amides. Figure 2-16 depicts some groups that may be commonly added using oxygen or nitrogen gas. [51]

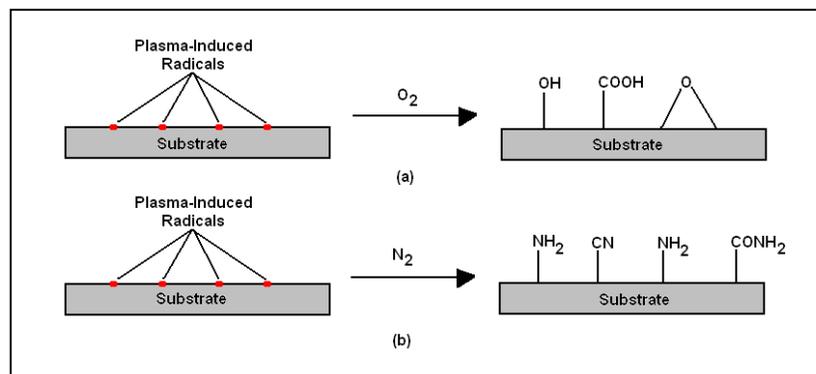


Figure 2-16. Illustration of surface functionalization using (a) oxygen and (b) nitrogen.

2.2.3.2.2 Plasma Polymerization

Plasma polymerization occurs when a thin film is deposited onto the surface of the substrate. Growth of the polymer chains occurs with the assistance of the plasma's reactive species. Radicals that form in the plasma bulk and on the surface of the substrate initiate the polymerization. Then, in the propagation stage, monomer molecules are continuously added as the chain grows and the active site relocates. This may occur on the surface of the substrate or in the plasma bulk as monomers encounter growing polymer chains. Finally, the growth of each polymer chain is terminated when the active site reacts with another radical. A pair of monomer radicals may react together or a monomer radical may react with radicals that are attached to the surface of the substrate. Similarly, two radicals that are attached to the substrate may form a union. Figure 2-17 provides an illustration of some of the reactions that may occur in plasma polymerization. While plasma polymerization shares many similarities with conventional polymerization techniques, it should be emphasized that there are differences. In particular, if a polymer film is created using plasma polymerization, its properties may differ from those of a conventionally created polymer film that uses the same monomers. [52]

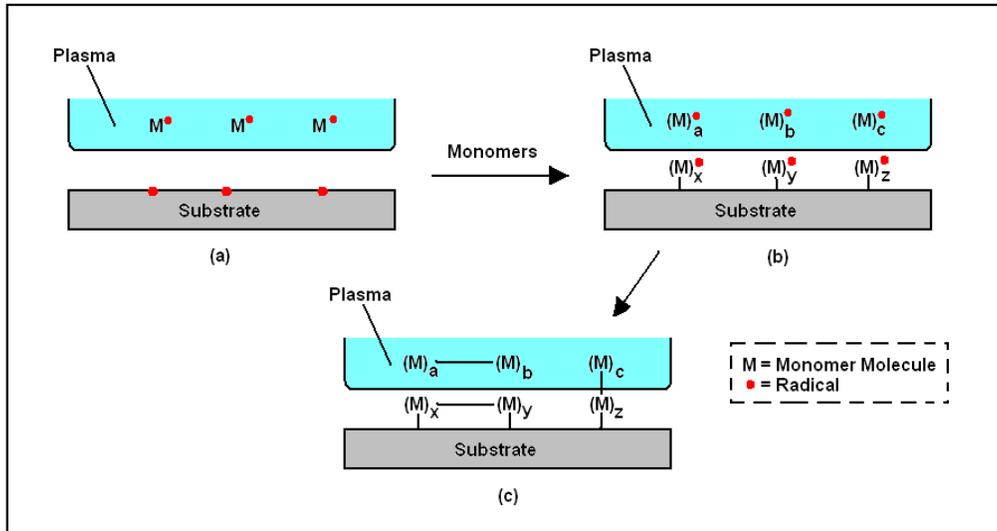


Figure 2-17. Illustration of (a) initiation, (b) propagation, and (c) termination in plasma polymerization.

2.2.3.2.3 Plasma-Induced Grafting

Plasma-induced graft polymerization is characterized by use of plasma to encourage covalent bond formation between a substrate and monomers. In this process, the active species in the plasma are used to create radicals on the surface of the substrate. Then, monomers are exposed to the radicals and graft to the substrate's surface. This process is shown in Figure 2-18. Monomers may be applied outside of the plasma discharge or may be incorporated into the feed gas of the plasma. Typically, monomer molecules have a vinyl group at one end that reacts easily with surface radicals. This technique can be used to bestow a wide array of surface properties to substrates while leaving their bulk properties intact.

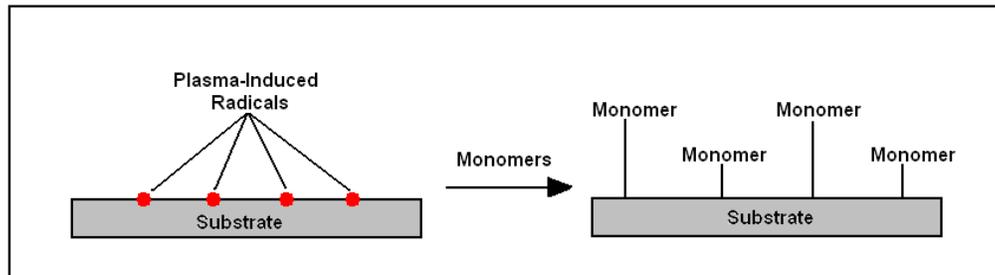


Figure 2-18. Illustration of plasma-induced grafting.

2.2.4 Plasma Applications for Textiles

Investigations into potential commercial applications for plasma treatment of textile substrates are ongoing. This section aims to introduce a few ways that plasma treatments have been employed to produce beneficial properties on textiles.

2.2.4.1 Hydrophobic and Hydrophilic Treatments

Research has demonstrated that plasma treatments can yield a water repellent surface. One way of achieving water repellency is through the incorporation of fluorocarbon gases into the plasma [53]. The aim of this process is to increase the ratio of fluorine to carbon on the surface of the substrate, especially through the addition of $-CF_3$ functionalities. The low surface tension that is exhibited by highly fluorinated compounds is a function of their weak intermolecular interactions [54]. Fluorocarbon monomers can be grafted and polymerized to an activated substrate to achieve the same effect [54].

On the other hand, plasma can also be used to make a fabric more hydrophilic. One common way to increase the wettability of an otherwise hydrophobic textile is to use oxygen gas in the plasma. As previously mentioned, the result of this is an increase in hydroxyls, carboxyls, epoxides, and carbonyls. These polar groups increase the surface energy of the substrate, making water more attracted to it. Alternatively, grafting of monomers such as acrylic acid [55], acrylamide [56], or methyl methacrylate [57] has also been used to increase the hydrophilicity of a polymeric substrate.

2.2.4.2 Desizing Treatments

The removal of warp sizes is a critical step in textile processing. Sizes are applied to yarns before weaving. Their purpose is to boost weaving efficiency by strengthening yarns and reducing the friction the yarns experience as they rub across one another at high speeds during weaving. These sizes must be removed prior to dyeing and finishing to ensure that these processes produce the intended effects. Traditionally, desizing is a very energy intensive process involving multiple hot water baths. These baths use large quantities of water and sizeable amounts of energy.

Plasma treatments have been used to assist the removal of warp sizes from textiles. One recent study examined the effects of helium and helium/oxygen plasmas for the removal of PVA warp sizes from cotton [58]. The results demonstrated that the effect of plasma treatment was two-fold. First,

plasma treatment removed some of the warp size by volatilizing it. Second, the warp size that remained on the substrate was more easily removed by washing in cold water, erasing the need for heating the wash baths. This observed effect is attributed to the chain scission of the warp size as well as its polar surface functionalization by oxygen plasma.

2.2.4.3 Improving Adhesion

Several fibers display highly desirable mechanical properties but are too chemically inert or smooth for use in composite applications. Traditional wet-processing techniques that can be utilized to overcome this issue may also negatively alter the fiber's bulk properties. Plasma treatments, on the other hand, can be used to etch the fiber's surface and add more reactive surface functionalities. The result of such treatment is improved adhesion of the fiber to the resin matrix. This is accomplished while maintaining the integrity of the fiber's bulk properties.

The research that has been conducted suggests four mechanisms through which adhesion of fibers to resin matrices is enhanced by plasma treatment. First, plasma etching removes contaminants from the surface of the fibers that may interfere with fiber-resin bonding. Second, the etching of plasma increases the amount of surface area on the fiber that is available for bonding with the resin. Third, plasma treatment can increase the strength of the fiber's surface layers through cross-linking. Finally, plasma-induced surface functionalization

can facilitate bond formation, whether ionic or covalent, between the fiber and the resin. [59]

2.2.4.4 Sterilization and Antimicrobial Treatments

In some cases, it is necessary to completely eliminate microorganisms from a textile substrate. Typically, this sterilization process is carried out through the use of high-pressure steam, heat, or chemicals. Unfortunately, these techniques may have undesired results on the substrate or consumers. For example, the heat that is required to destroy some microorganisms is unacceptable for polymers that melt at low temperatures. Furthermore, one dominant chemical used for the sterilization of polymeric substrates, ethylene oxide (EtO), is classified as a carcinogen. In consideration of these disadvantages, plasma sterilization has been investigated. Plasma sterilization relies on UV irradiation, photodesorption, and etching to rid the substrate of microbes. Photodesorption is defined as the light-catalyzed removal of a substance from an interface. As it relates to bacteria, photodesorption occurs when photons are used to break chemical bonds and volatilize atoms which are intrinsic to the microorganism. This alternative process has been shown to eliminate bacteria, viruses, fungi, and spores. [60]

If one wishes to prevent the growth of microorganisms on a textile substrate all together, an antimicrobial finish should be applied. Traditionally, this is accomplished through padding, or otherwise applying, an antimicrobial

chemical to the substrate. As with other wet-processing techniques, this approach may consume large amounts of energy and water, use harmful chemicals, or negatively modify the substrate. For these reasons, the use of plasma to accomplish an antimicrobial substrate has been investigated. The main way to employ plasma to increase the antimicrobial properties of a textile is through plasma-induced grafting of antimicrobial monomers.

2.2.4.5 Flame Retardant Treatments

Most relevant to this thesis is the use of plasma to assist in decreasing the flammability of a textile substrate. This is done through the plasma-induced grafting of flame retardant monomers onto the substrate. Some good examples of this technique can be taken from the work of M.J. Tsafack and J. Levalois-Grützmacher [61-63]. In this research, the authors synthesize novel phosphorus-based flame retardant monomers with an acrylic group at one end to provide a graftable functionality. These monomers are depicted in Figure 2-19. The substrates, which include cotton and PAN, are immersed in solutions containing the monomer, a photoinitiator, and a cross-linking agent. After being pressed to remove excess solution, the fabrics are subjected to argon plasma exposure in a vacuum plasma system. Then, they are washed to remove non-grafted polymer and unreacted monomer.

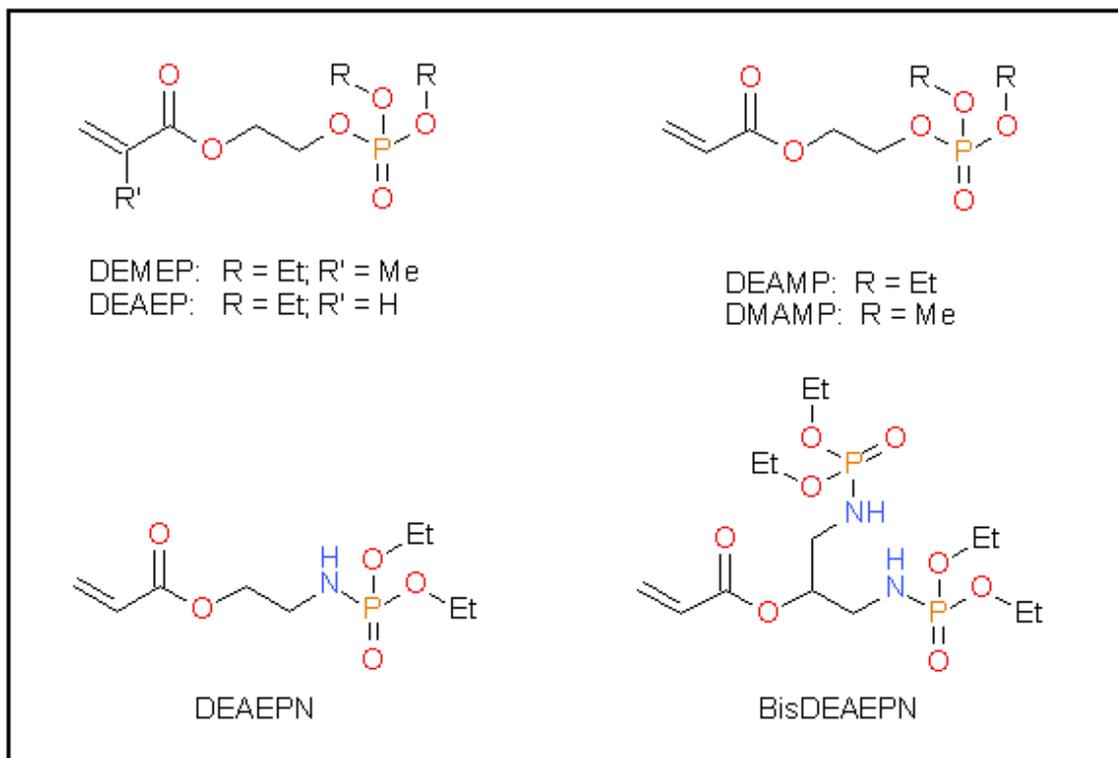


Figure 2-19. Flame retardant monomers synthesized by Tsafack and Levalois-Grützmaier. [61]

The results of this research were promising, with increases in LOI values being observed for all monomers. It was found, as one would expect, that the presence of nitrogen enhanced the flame retardant effect on cotton and that the degree of flame retardance offered by each monomer was a function of its chemical structure. The authors also demonstrated that the treatments were durable to washing at elevated temperatures, proving the establishment of covalent bonds between the monomers and the substrate.

3 METHODS

The objective of this research was to expand on the work done by M.J. Tsafack and J. Levalois-Grützmacher, which was presented in Section 2.2.4.5. The goals were to utilize the synthetic approach described in their studies to create other novel phosphorus-based flame retardant monomers and to investigate the graft polymerization of these monomers onto cotton using several techniques. This chapter will be divided into three sections. In the first section, the synthesis of two novel phosphorus-based flame retardant monomers will be described. The methods that were used for their characterization will also be provided. In the second section, the techniques that were used to apply these monomers to cotton will be explained. These techniques include an early attempt at thermally initiated grafting as well as an attempt at plasma-induced grafting. Finally, the third section will describe the testing methods that were used to evaluate the flame retardant properties of these treated cotton fabrics.

3.1 Synthesis and Characterization of Monomers

3.1.1 Chemicals

Dimethyl chlorophosphate, *N,N,N',N'*-tetramethylphosphorodiamidic chloride, ethanolamine, triethylamine, acryloyl chloride, and dichloromethane were all purchased from Sigma-Aldrich. These chemicals were used as

received. An argon gas cylinder was purchased from Machine & Welding Supply Company and used as received.

3.1.2 Glassware Configuration

The reactions described hereafter were conducted in a three-neck round bottom flask (RBF). To the right neck, a gas inlet was attached through which argon gas was continuously fed. Argon was needed to create a closed inert atmosphere for the reactions to take place in. To the center neck, a condenser was attached. Atop the condenser, an oil bubbler was fixed to allow for the monitoring of argon gas flow through the system. To the left neck, an addition funnel was used to introduce chemicals to the reaction. The addition funnel served two purposes. First, it was necessary because some of the chemicals used in these procedures degrade rather quickly upon exposure to air. Adding them to the reaction through an addition funnel helped to maintain the integrity of the closed argon environment. Second, the use of the addition funnel made the controlled dropwise addition of reagents much easier. When appropriate, the three-neck RBF was lowered into an ice bath. All glassware was thoroughly cleaned and dried before use. This configuration is shown in Figure 3-1.

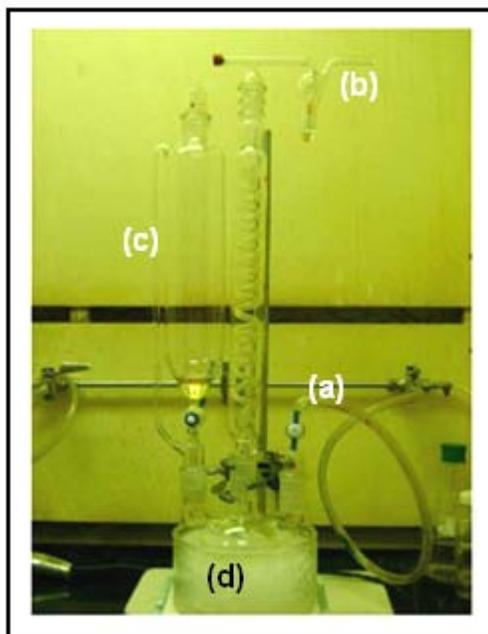


Figure 3-1. Closed argon-atmosphere reaction setup showing (a) argon inlet, (b) argon outlet, (c) addition funnel with equalizer, and (d) 3-neck RBF in ice bath.

3.1.3 Synthesis of Compound 1

The glassware was configured as described in Section 3.1.2 and the three-neck RBF was lowered into an ice bath. The regulator on the gas cylinder was opened so that argon gas flowed slowly through the system. The addition funnel was removed temporarily so that 200 mL of dichloromethane and a magnetic stirrer could be added. As the solvent was stirred at 0°C, 12.3 mL of triethylamine (8.90 g; 88 mmol) was added. Next, 4.8 mL of ethanolamine (4.89 g; 80 mmol) was introduced to the stirring solution. At this point, the addition funnel was reattached to the left neck. To the addition funnel, 8.6 mL of dimethyl

chlorophosphate (11.56 g; 80 mmol) was added. The stopcock of the addition funnel was opened so that the dimethyl chlorophosphate was added dropwise to the solution as it was stirred at 0°C. Once the addition was complete, the reaction was allowed to warm to room temperature gradually as the ice melted. After stirring for a total of 8 hours, the triethylamine hydrochloride precipitate was removed by vacuum filtration. A small amount of the filtrate was collected for characterization. Figure 3-2 shows the reaction scheme for the preparation of this intermediate.

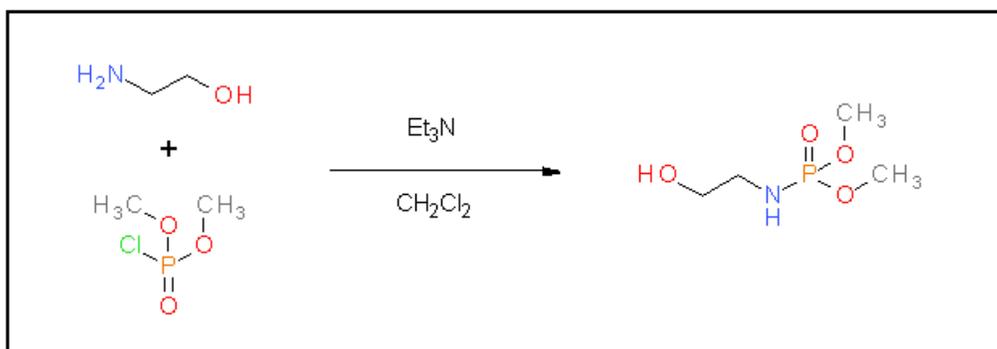


Figure 3-2. Reaction scheme for the formation of Intermediate 1.

The filtrate from the previous step and a magnetic stirrer were added to a three-neck RBF that was then configured as described in Section 3.1.2. The three-neck RBF was lowered into an ice bath so that the filtrate could be cooled. As the filtrate stirred at 0°C, the regulator on the gas cylinder was opened so that

argon gas flowed slowly through the system. The addition funnel was temporarily displaced so that 12.3 mL of triethylamine (8.90 g; 88 mmol) could be added. Once this addition was complete, the addition funnel was reattached to the left neck of the RBF. Into the addition funnel, a mixture of 6.47 mL of acryloyl chloride (7.24 g; 80 mmol) and 25 mL of dichloromethane was added. The addition funnel's stopcock was opened to allow for the dropwise introduction of this mixture to the chilled and stirring filtrate/triethylamine solution. Once the addition was complete, the reaction was allowed to warm to room temperature gradually as the ice melted. After stirring overnight at room temperature, the triethylamine hydrochloride precipitate was removed by vacuum filtration. The filtrate was then washed twice in a separation funnel with equal volumes of a saturated solution of sodium carbonate (Na_2CO_3). The organic layer was collected and the solvent was evaporated in vacuo to yield the product. A small amount of this product was collected for characterization. The remainder of the product was stored under argon. Figure 3-3 shows the reaction scheme for the generation of Compound 1 from Intermediate 1.

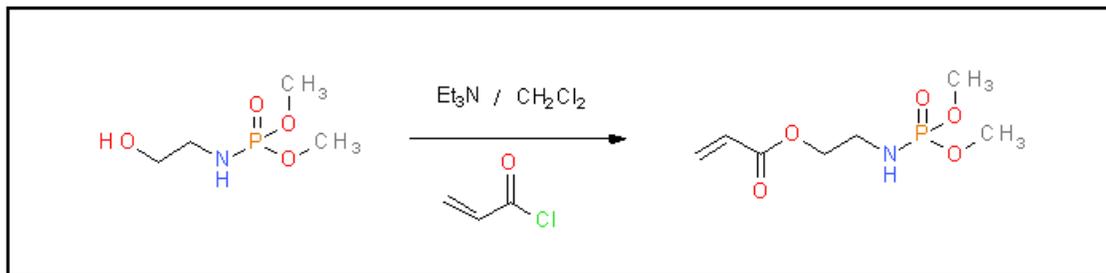


Figure 3-3. Reaction scheme for the formation of Compound 1.

3.1.4 Synthesis of Compound 2

The glassware was configured as described in Section 3.1.2. The regulator on the gas cylinder was opened to allow argon gas to flow slowly through the apparatus. After the RBF was lowered into an ice bath, the addition funnel was temporarily removed so that 200 mL of dichloromethane and a magnetic stirrer could be added. While the addition funnel remained displaced, 12.3 mL of triethylamine (8.90 g; 88 mmol) was added to the solvent as it stirred at 0°C. To this solution, 4.8 mL of ethanolamine (4.89 g; 80 mmol) was added. The addition funnel was reattached to the left neck and to it was added 11.6 mL of *N,N,N',N'*-tetramethylphosphorodiamidic chloride (13.65 g; 80 mmol). The stopcock of the addition funnel was opened so that this reactant could be introduced dropwise to the chilled and stirring solution. Following the completion of this addition, the reaction was kept at 0°C for an additional 5 hours. It was then allowed to stir overnight at room temperature before the triethylamine hydrochloride precipitate was removed by vacuum filtration. A small amount of

the filtrate was collected for characterization. Figure 3-4 shows the reaction scheme for the formation of this intermediate.

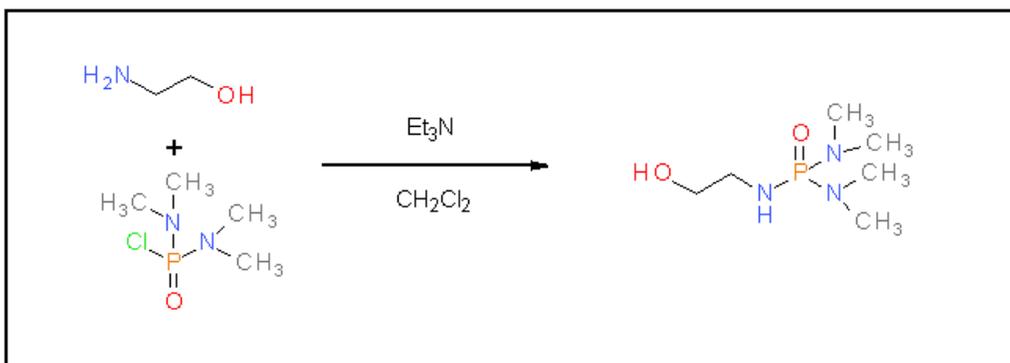


Figure 3-4. Reaction scheme for the formation of Intermediate 2.

The filtrate from the previous step and a magnetic stirrer were added to a three-neck RBF that was then outfitted as described in Section 3.1.2. The RBF was lowered into an ice bath so that the filtrate could cool to 0°C . The regulator on the gas cylinder was then opened to allow argon to flow slowly through the system. As the filtrate stirred, the addition funnel was temporarily removed so that 12.3 mL of triethylamine (8.90 g; 88 mmol) could be added. Once replaced, a mixture of 6.47 mL of acryloyl chloride (7.24 g; 80 mmol) and 25 mL of dichloromethane was added to the addition funnel. The stopcock of the addition funnel was opened to allow for the dropwise introduction of this mixture to the chilled and stirring filtrate/triethylamine solution. Once the addition was

complete, the reaction was kept at 0°C for 3 additional hours before being allowed to stir overnight at room temperature. The triethylamine hydrochloride precipitate was removed by vacuum filtration and the filtrate was washed twice in a separation funnel with equal volumes of a saturated solution of sodium carbonate (Na₂CO₃). The organic layer was collected and the solvent was evaporated in vacuo to yield the product. A small amount of this product was collected for characterization and the remainder was stored under argon. Figure 3-5 shows the reaction scheme for the generation of Compound 2 from Intermediate 2.

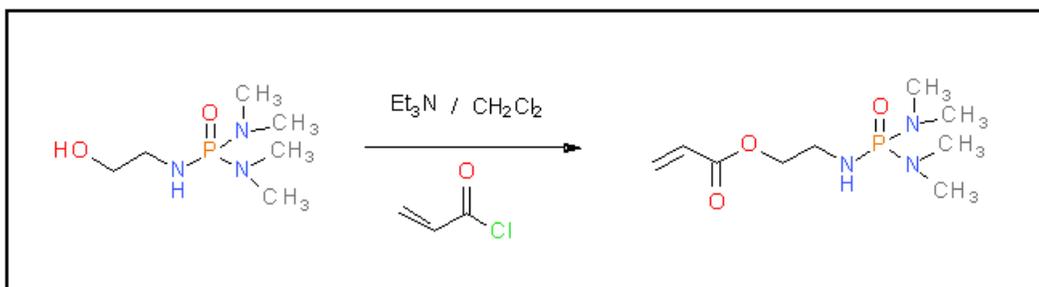


Figure 3-5. Reaction scheme for formation of Compound 2.

3.1.5 Characterization

The products that formed as a result of these reactions were characterized by two techniques. First, mass spectra were obtained at the North Carolina State University Department of Chemistry Mass Spectrometry Facility. High resolution exact mass measurements were gathered of the sodiated (Intermediate 1 and

Compound 1) or protonated (Intermediate 2 and Compound 2) molecular ions of the samples. This was accomplished using Electrospray Ionization (⁺ESI) on an Agilent Technologies 6210 LC-TOF mass spectrometer. Samples were diluted in methanol and analyzed by means of a 1 μL flow injection at 300 μL/min in a water:methanol mixture (25:75 v/v) with 0.1% formic acid. The instrument was operated in 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 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, which were used as internal standards, were simultaneously introduced through the use of a second orthogonal sprayer.

Second, Fourier transform infrared (FT-IR) spectra of the reaction products were collected. This analysis was performed in the TECS Analytical Instrumentation and Service Lab at North Carolina State University's College of Textiles. A Nicolet Nexus 470 spectrophotometer equipped with an Avatar OMNI-Sampler accessory was used to obtain the spectra. The instrument is pictured in Figure 3-6. This configuration utilizes the attenuated total reflectance (ATR) sampling technique. The source of infrared radiation within the instrument was a Globar with an air-cooled ceramic base. The instrument employed a deuterated triglycine sulfate (DTGS) detector. For each sample, a drop was placed directly onto the germanium crystal of the Avatar OMNI-Sampler. The

pressure tower was then lowered and the spectrum was collected. A background spectrum was collected prior to each sample. The instrument was set to collect absorbance spectra at a resolution of 4 cm^{-1} . A total of 64 scans were averaged to produce each spectrum.



Figure 3-6. Photograph of Nicolet Nexus 470 spectrophotometer showing (a) Avatar OMNI-Sampler, (b) pressure tower, and (c) germanium crystal.

Finally, to obtain a profile of how the monomers behaved when heated, thermogravimetric analysis was performed. A Perkin Elmer Pyris 1 TGA (serial number 537N9071908), which is pictured in Figure 3-7, was used. 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 950°C at a rate of $20^{\circ}\text{C}/\text{min}$.



Figure 3-7. Photograph of Perkin Elmer Pyris 1 TGA.

3.2 Application of Monomers

3.2.1 Chemicals

Several chemicals were used in addition to water and the newly synthesized monomers. Potassium persulfate, methanol, and sodium hydroxide remained in the lab from recent studies and were used as they were found. The potassium persulfate originated from Fisher Scientific. Methanol was supplied by Sigma-Aldrich. Ethylene glycol dimethacrylate (EGDMA) was obtained from Tokyo Chemical Industry (TCI) and contained 100 ppm of hydroquinone inhibitor. The hydroquinone was removed by extracting the EDGMA solution twice with equal volumes of 5% (w/v) sodium hydroxide (Acros Organics) solution. This

extraction was easily monitored because the sodium salt of hydroquinone is intensely colored. The sodium hydroxide extractions could be stopped when the brownish-red color was no longer present. Then, traces of sodium hydroxide were removed from the monomer by washing with distilled water until the pH of the water layer returned to neutral.

3.2.2 Selection of Fabric

For the purposes of this research, cotton fabric was selected to receive treatment. This selection was based on the well-documented use of phosphorus based flame retardants with cellulose. Their mode of action has been discussed in previous sections. The cotton fabric was desized, scoured, and bleached before it was procured. It weighed roughly 110.2 g/m^2 and had approximately 26 ends/cm and 29 picks/cm. The fabric was constructed using a plain weave.

3.2.3 Thermally Initiated Grafting of Monomers

The initial application of the novel monomers to cotton attempted to utilize thermally initiated grafting. Past research has shown that monomers with an acryloyl group, such as those that were synthesized during the first portion of this research, can be grafted to cotton fabrics using a thermal initiator. When a thermal initiator is heated above its decomposition temperature, initiator radicals are produced which are expected to abstract hydrogen atoms from cellulose. Once this occurs, the vinyl groups of the monomers can undergo graft

polymerization at these active sites. Potassium persulfate was selected as the thermal initiator for this study. Since the primary goal of this research was plasma-induced graft polymerization, this work with a thermal initiator served only to obtain preliminary information regarding the monomer's ability to promote char formation.

Solutions were prepared by dissolving the monomer and potassium persulfate in distilled water at different ratios. Monomer concentrations that were evaluated were 100 (10%), 200 (20%), and 300 (30%) g/L. Potassium persulfate concentration was maintained at a constant 50 (5 %) g/L. This means that 3 solutions were prepared for each monomer (for a total of 6 baths). A 150 mm by 200 mm swatch of cotton fabric was immersed into each bath for 4 minutes with agitation. The fabrics were then removed from the bath and dried in an oven for 20 minutes at 60°C. Next, the treated fabrics were cured in an oven at 120°C for 5 minutes. After being removed from the oven, a 70 mm by 200 mm strip was cut from each swatch. This strip was subjected to burn testing, which will be described in a later section.

These treatment conditions were based on a study [64] that examined the thermally initiated grafting of acrylamide onto cotton fabrics. In this research, the authors used potassium persulfate. Their data suggests that an initiator concentration of around 5% provided the best balance of cost and grafting yield. Beyond 5%, the grafting yield increased only a very small and insignificant

amount. The data reported in this paper also explained that 5 minutes at 120°C was sufficient to degrade 97% of the initiator.

3.2.4 Plasma-Induced Grafting of Monomers

3.2.4.1 Atmospheric Pressure Plasma Lab Configuration

The plasma source that was used for this research was an APJeT Atmospheric Pressure Plasma Reactor (APPR) IV (serial number 0007m). The technology used in this device was developed as part of a collaborative effort between the University of California – Los Angeles and Los Alamos National Laboratory. The device, pictured in Figure 3-6, is currently housed at North Carolina State University's College of Textiles on Centennial Campus. This plasma source generates a non-thermal atmospheric pressure glow discharge through a capacitively coupled system. The electrodes are fashioned in a coaxial configuration and the device may be operated in *in-situ* or downstream mode. For this work, the device was operated in *in-situ* mode.

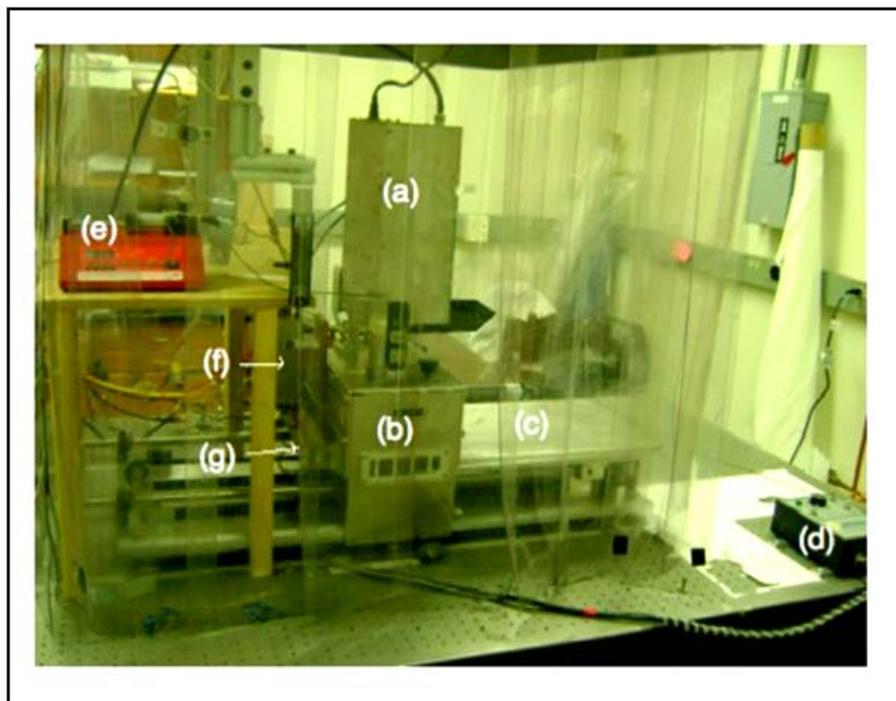


Figure 3-8. Photograph of APJeT APPR IV showing (a) matching network, (b) discharge chamber, (c) stage, (d) stage speed controller, (e) monomer syringe pump, (f) evaporator, and (g) applicator.

The plasma device is powered by an ENI[®] RF power generator (model number ENI OEM-12A-21041-51) that is capable of generating 1250 W at 13.56 MHz. Figure 3-7 shows this solid-state power generator. The power is delivered through a matching network and to the electrodes, which are housed in the discharge chamber. The fabric is mounted flat atop the stage and passed horizontally through the discharge chamber. Adjustments to the Leeson Speedmaster motor controller are used to vary the stage speed and, as a result, the fabric's dwell time within the discharge. A Neslab CFT-75 recirculating water

chiller is responsible for keeping the stage cool. The flow rates of gases are monitored and controlled using the flowmeters that are pictured on the left in Figure 3-7.

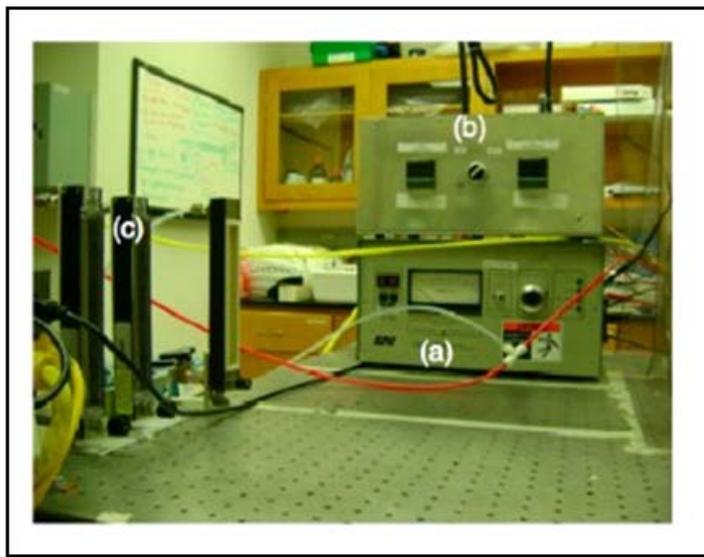


Figure 3-9. Photograph of (a) power generator, (b) evaporator and applicator temperature controller, and (c) gas flowmeters.

Finally, the device is equipped with a monomer deposition system that was not used for this work. The liquid monomers are loaded into the syringe pump that is shown in Figure 3-6. The pump forces the liquid through a line and into an evaporator. The evaporator is set at a temperature just above the boiling point of the monomer. Once the monomers enter the evaporator, they are vaporized. The vapor is then forced into an applicator, which is set at a

temperature that is slightly higher than the evaporator. Both the evaporator and applicator can be seen in Figure 3-6. The temperature control unit is included in Figure 3-7. From the applicator, the vapor is driven down to the substrate with argon gas. Since the substrate is attached to a cooled stage, the monomer vapor condenses on its surface.

3.2.4.2 Application of Monomers

70 mm by 200 mm strips of the previously described cotton fabric were attached to the stage of the plasma device with tape. The stage of the device was cooled to 14°C. The gap between the electrodes was set at 3 mm. The helium gas was turned on and set at a flow rate of 60 SLPM. After a count of ten seconds to ensure that the helium environment in the inter-electrode space was uniform, the RF power was turned on to initiate the plasma. For these preliminary studies, the power of the device was set to 600 W. The stage, and consequently the fabric, was then moved through the discharge region. The stage speed controller was employed to vary the exposure time of the fabric within the discharge. Once the fabric had completed its pass through the discharge region, the plasma and helium flow were stopped. The fabric was immediately flipped over and attached to the stage. The helium flow and plasma were restarted as before and the fabric was passed back through the discharge region. In this way, it was hoped that both sides of the fabric would be activated.

After the fabric emerged from the discharge region, the plasma and helium flow were halted.

Having been exposed to the plasma on both sides, the fabric was immediately taken from the stage and immersed in the monomer solution. This solution contained 20% (w/v) of monomer and 10% (w/v) of EGDMA in methanol. For 1 minute, the fabric was agitated in this solution. The fabric was then removed and laid flat for 30 minutes to allow for evaporation of the methanol. Once this time had elapsed, the fabric was transported back to the plasma lab where it was reattached to the stage. The helium gas flow was restarted and the power generator was turned on to establish the plasma. Again, 600 W was used. Once the plasma was stable and uniform, the fabric was passed through the discharge region. After it emerged, the power generator was turned off and the helium flow was stopped so that the fabric could be flipped over and reattached. The plasma was then reinitiated as before and the fabric was passed back through the discharge. After the plasma had been turned off, the fabric was removed from the stage and stored in a zippered storage bag until burn testing.

3.2.5 Washing Procedure

Treated samples also underwent a washing procedure that was intended to remove any ungrafted monomer or homopolymer from the substrate. A 70 mm by 200 mm strip of each treated fabric was immersed in 50 mL of methanol in a 250 mL Erlenmeyer flask. The flasks were sealed and placed in a

Boekel/Grant ORS-200 Reciprocating Water Bath (serial number 8R 05 34005). The device was set at a reciprocating speed of 165 shakes/min and a temperature of 50°C. After 30 minutes at these conditions, the fabrics were removed from the flasks and rinsed with clean methanol. The fabric samples were then laid flat to dry. Once dry, the samples were stored in a zippered storage bag until further testing.

3.3 Evaluation of Fabrics

3.3.1 Burn Test Procedure

Vertical flame tests were used to assess all treated samples. The procedure was similar to that of ASTM D 6413-08. Fabrics were mounted into a sample holder and suspended vertically in the flame cabinet. A schematic of this flame cabinet is shown in Figure 3-8. A Tirrill burner was connected to a methane gas source and lit. The flame was then placed 0.75 inches below the bottom center of the sample, where it remained for 3 seconds. After 3 seconds, the flame was removed from beneath the sample while a stopwatch was simultaneously started. The stopwatch was stopped once the flame was extinguished. Afterglow and melt drip can also be measured using this technique, but neither of these phenomena were observed during testing. Additionally, char length can be determined from this method and used to draw conclusions about the effectiveness of a flame retardant treatment. However,

since all tested fabrics burned entirely, there was no need to measure char length.

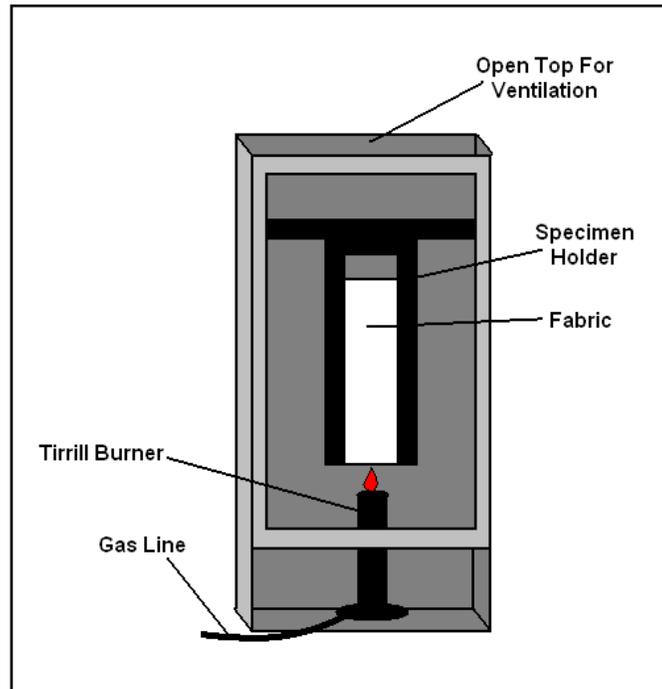


Figure 3-10. Schematic of flame cabinet.

3.3.2 Thermogravimetric Analysis

To further investigate the thermal decomposition of the unwashed treated fabrics, thermogravimetric analysis (TGA) was conducted. The Perkin Elmer Pyris 1 TGA that was described previously (Section 3.1.5) was used. 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 950°C at a rate of 20°C/min.

The resulting thermograms were then analyzed with the Pyris™ software to determine the temperature at onset of degradation, the temperature at the maximum rate of degradation, the temperature at the end of the degradation, and the amount of char residue that remained at 950°

4 RESULTS AND DISCUSSION

The intent of this chapter is to effectively communicate and explain the results that were obtained from the work outlined in the previous chapter. As with the previous chapter, this one will be divided into three sections. The first section will describe some observations that were made during each reaction and illustrate the mechanism by which each reaction proceeds. This section will also explain the mass spectrometry and FTIR spectroscopy results that were used to characterize these compounds. The second section will provide and explain the observations that were made as these monomers were applied to cotton fabric. Finally, the third section will explore the outcomes of burn testing that was done to evaluate the treated fabrics.

4.1 Synthesis and Characterization of Monomers

4.1.1 Mechanisms of Reactions

To synthesize the desired products, two reaction steps are necessary. The first step, which was used to form Intermediate 1 and Intermediate 2, follows an S_N2 mechanism [65-67]. Figure 4-1 illustrates the proposed mechanism for the production of these intermediates. The first stage of this reaction, or the addition stage, is characterized by the nucleophilic attack of phosphorus by the amine. The amine, which has an active lone pair, is attracted to the partial positive charge on the phosphorus. This partial positive charge is the result of

the electron withdrawing nature of the oxygen and chlorine atoms that are bonded to the phosphorus. The attack by the amine group of ethanolamine is preferred over the attack by the hydroxyl functionality because of the amine's stronger nucleophilic character. As the bond is formed between the nitrogen and the phosphorus, the phosphorus-oxygen double bond is converted to a single bond and the oxygen assumes a negative charge. Then, the elimination stage of the reaction occurs in two steps. First, the oxygen-phosphorus double bond reforms and a chloride ion is released. Then, the chloride ion extracts a single hydrogen from the positively charged nitrogen to form the desired intermediate and HCl. At this point, triethylamine is used as an acid scavenger to bind the HCl as it forms. Since triethylamine hydrochloride is not soluble in dichloromethane, it precipitates and can be easily removed by filtration.

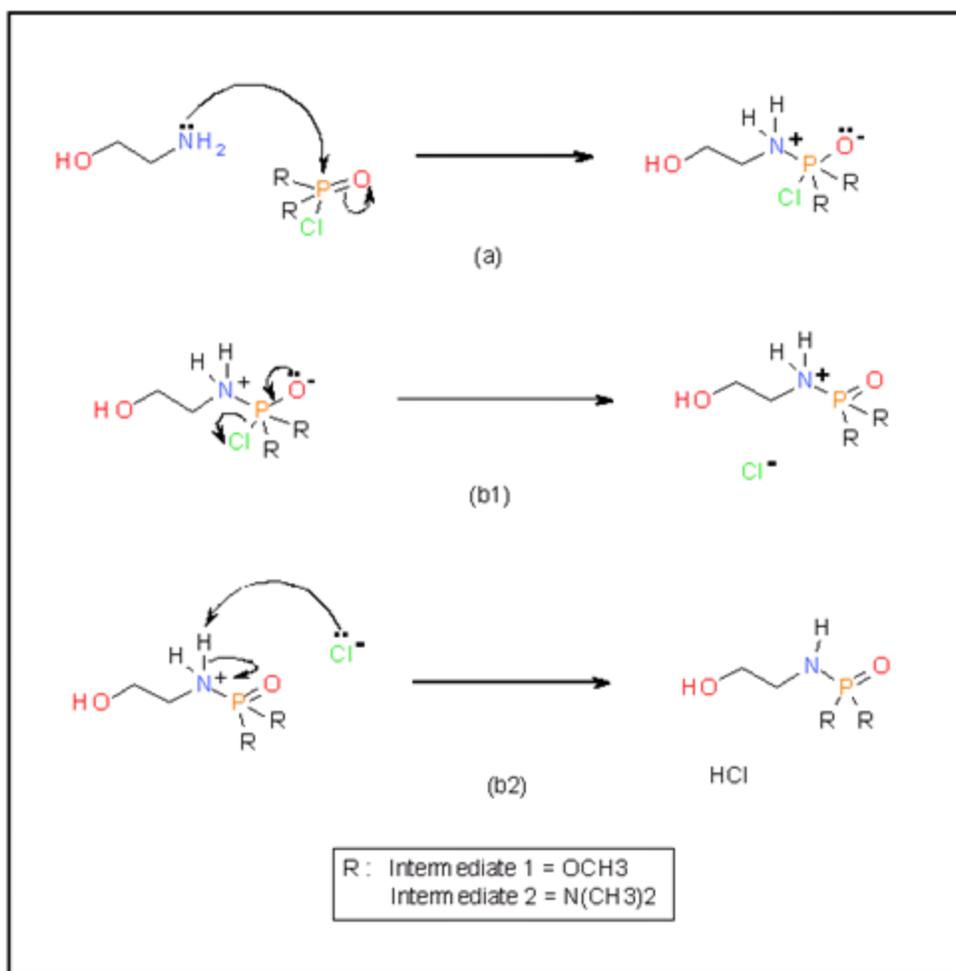


Figure 4-1. Reaction mechanism for formation of intermediates showing (a) addition stage and (b1 and b2) elimination stage.

The second step of the reaction, which was used to produce the desired final products, also follows an S_N2 mechanism. The proposed mechanism for this reaction is provided and labeled Figure 4-2. The carbon in acryloyl chloride that is bonded directly to oxygen and chlorine is partially positive and susceptible to nucleophilic attack. This attack is carried out by one of the lone pairs on the

oxygen of the intermediate's hydroxyl group. As this new carbon-oxygen bond is formed, the existing carbon-oxygen double bond is converted into a single bond. When the carbon-oxygen double bond reforms, a chloride ion is released. The chloride ion can then pull a hydrogen from the positively charged oxygen to form the desired final product and HCl. As with the first step, triethylamine binds the acid as it forms and the resulting triethylamine hydrochloride precipitates. Once precipitated, it is easily removed by filtration.

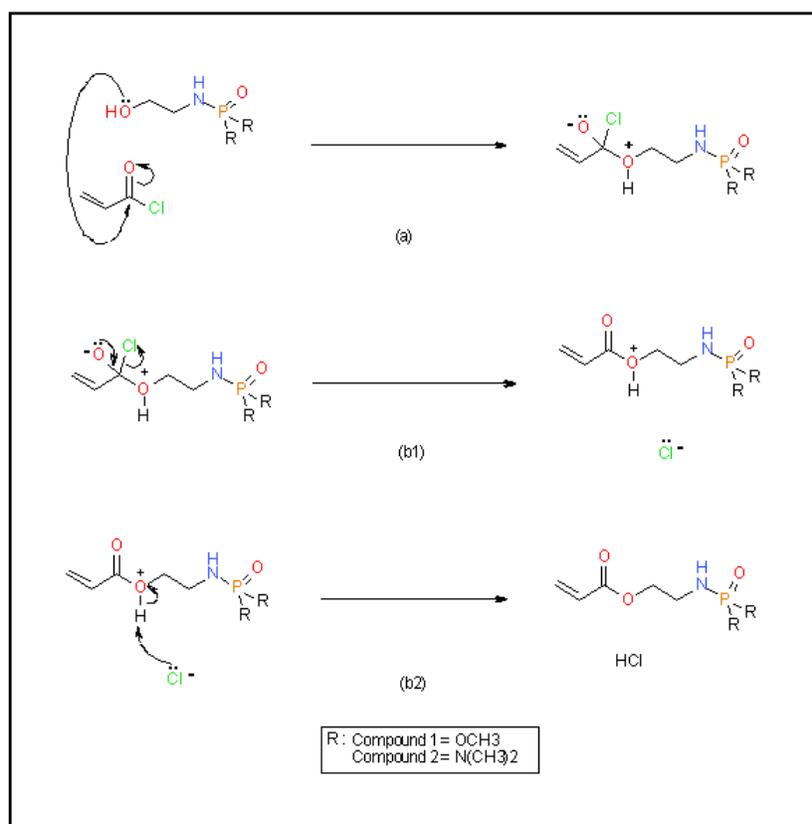


Figure 4-2. Reaction mechanism for final products showing (a) addition state and (b1 and b2) elimination stage.

4.1.2 The Need for Cooling

The necessity of cooling these reactions can be shown using Le Chatelier's principle. Le Chatelier's principle suggests that subtracting a species from one side of a reaction causes the reaction to favor the side from which the species was reduced. The reactions used in this research are exothermic, meaning that heat is emitted as a product of the reaction.



If the reaction mixture is placed on ice and heat is removed from the system, the equilibrium of the reaction will oppose this by shifting so that more heat, and consequently more product, is produced. In this way, cooling these reactions on ice increases the rate and yield of the reactions.

4.1.3 Synthesis of Compound 1

The most straightforward way to monitor these reactions is through the formation of the insoluble triethylamine hydrochloride salt. During the first step of this two-step synthesis, triethylamine hydrochloride salt began to precipitate immediately upon the dropwise addition of dimethyl chlorophosphate. This suggests that the reaction was fast. Following filtration, the solution of Intermediate 1 in dichloromethane was observed to be pale yellow.

Similarly, precipitate began to develop immediately when acryloyl chloride was added dropwise to the filtrate/triethylamine solution during the second step of this synthesis. This means that, like the reaction used to form the intermediate, this reaction was fast. After the salt was removed by filtration, the solution of Compound 1 in dichloromethane was observed to be pale yellow. This color darkened slightly as the solvent was removed and Compound 1 was concentrated. Once the solvent was completely removed, Compound 1 was determined to be a yellow, slightly viscous liquid and was produced at an acceptable yield of 76% (13.6 g).

4.1.3.1 Characterization of Intermediate 1

Figure 4-3 shows the mass spectrum that was obtained from the filtrate of the first step of the reaction. Since the calculated mass of Intermediate 1 was 169.0504, it follows that the calculated m/z of the sodiated molecular ion of Intermediate 1 was 192.0396. The peak at m/z 192.0390 proves the presence of the desired product. The strong signal that is seen below m/z 150 is most likely associated with unreacted triethylamine.

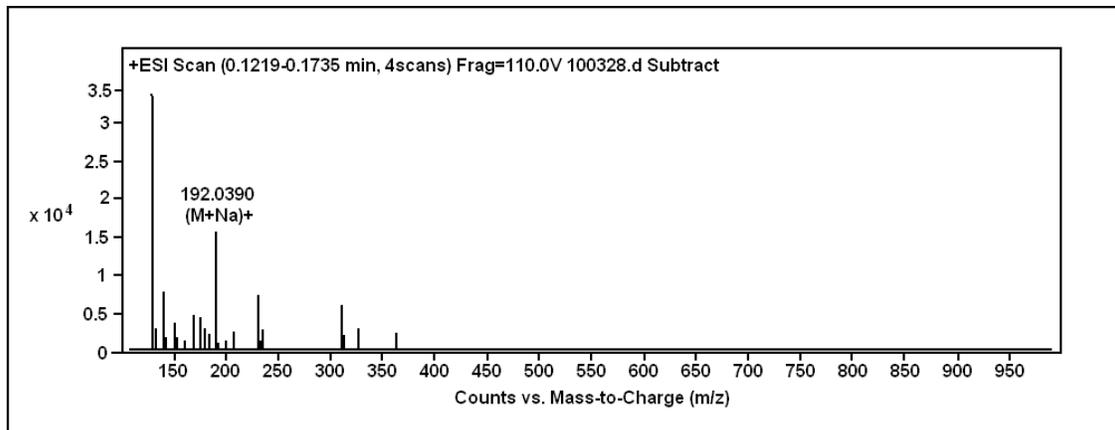


Figure 4-3. Mass spectrum of Intermediate 1.

Appendix A shows the FTIR spectrum that was obtained from Intermediate 1. A summary of relevant peaks from this spectrum can be found in Table 4-1. The spectrum certainly seems to contain the peaks that one would expect from a molecule with the chemical structure of Intermediate 1. The peak at 3379.4 cm^{-1} can be assigned to the O-H stretch of the primary alcohol and the N-H stretch of the secondary amine. The weak signal at 1652.3 cm^{-1} is most likely from the N-H deformation. The peaks at 1461.5 cm^{-1} and 1400.5 cm^{-1} can be assigned to C-H deformations. According to previous surveys [68,69], the P=O and P-O-CH₃ absorption bands of this molecule can aid in its characterization. In a molecule such as this intermediate, the frequency of the P=O vibration should occur between 1156 cm^{-1} and 1287 cm^{-1} [68]. The only signal that appears in this region is at 1182.8 cm^{-1} , so this peak is assigned to the P=O vibration of Intermediate 1. If dimethyl chlorophosphate remained

unreacted, the P=O absorption would occur between 1280-1299 cm^{-1} [68]. The absence of a peak in this area proves that the nucleophilic substitution has taken place. In addition, the P-O-CH₃ group of a quinquivalent organophosphorus compound, such as Intermediate 1, should have an absorption between 905-1060 cm^{-1} [69]. More specifically, this peak should be very near to 1036 cm^{-1} , which corresponds to a P-O-Et group [69]. Thus, the strong signal at 1040.6 cm^{-1} can be assigned to the P-O vibration of the P-O-CH₃ group.

Table 4-1. Summary of relevant peaks from FTIR spectrum of Intermediate 1.

Wavenumbers (cm^{-1})	Assignment
3379.4	O-H and N-H stretch
1652.3	N-H deformation
1461.5	C-H deformation
1400.5	N-CH ₂ (C-H deformation)
1182.8	P=O vibration
1040.6	P-O-C vibration

4.1.3.2 Characterization of Compound 1

Figure 4-4 shows the mass spectrum that was obtained from the analysis of Compound 1. The calculated mass of Compound 1 was 223.061. The sodiated molecular ion of Compound 1 would therefore have an m/z of 246.0502. The signal at m/z 246.0507 confirms the presence of the desired product. Moreover, it is clear that the peak from the intermediate, which was seen at m/z

192.0390, is completely gone in this spectrum. As with the spectrum of Intermediate 1, the strong peak below m/z 150 is the result of unreacted triethylamine.

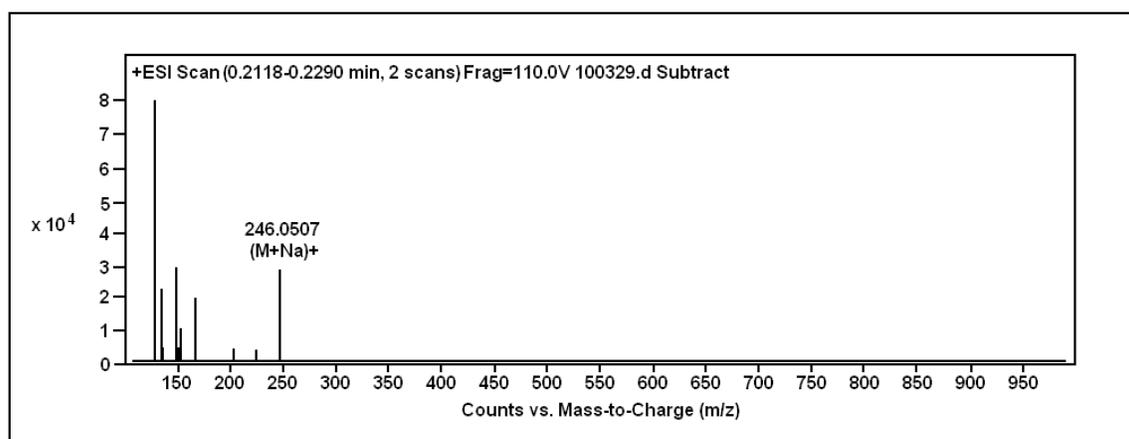


Figure 4-4. Mass spectrum of Compound 1.

The FTIR spectrum from Compound 1 is provided and labeled Appendix B. The relevant peaks from this spectrum are summarized in Table 4-2. The peaks at 3393.9 cm^{-1} and 3255.5 cm^{-1} can be assigned to O-H and N-H stretches. The strength of the O-H stretching signal is significantly decreased from the spectrum of Intermediate 1. Additionally, a relatively strong peak has emerged at 1721.4 cm^{-1} . This peak can be assigned to the C=O stretch of an ester. The peak at 1636.4 cm^{-1} is characteristic of a vinyl group. These pieces of evidence indicate that the hydroxyl functionality of Intermediate 1 has been replaced by an acryloyl group through the formation of an ester. The peaks

corresponding to the P=O vibration and P-O-CH₃ group shift only slightly when compared to Intermediate 1.

Table 4-2. Summary of relevant peaks from FTIR spectrum of Compound 1.

Wavenumbers (cm ⁻¹)	Assignment
3393.9	O-H stretch
3255.5	N-H stretch
1721.4	C=O stretch
1636.4	C=C stretch
1448.4	C-H deformation
1410.4	N-CH ₂ (C-H deformation)
1191.3	P=O vibration
1029.4	P-O-C vibration

Finally, the thermogram that was obtained from the thermogravimetric analysis of Compound 1 is provided as Appendix E. According to a previous study [61], the phosphate linkages of the polymerized forms of some very similar monomers began to decompose between 205°C - 215°C. In the thermogram for Compound 1, it can be seen that slightly more than 40% of the monomer has been lost to evaporation by the time this temperature is reached. This result indicates that if the monomers are applied and are not polymerized, a significant fraction of that which is added on will evaporate before the molecules can release their flame retarding fraction.

4.1.4 Synthesis of Compound 2

The synthesis of Compound 2 was a two-step process that mirrored the synthesis of Compound 1. In this case, *N,N,N',N'*-tetramethylphosphorodiamidic chloride was the phosphorus-containing compound that was used. The first step of this synthesis was slightly slower than the first step of the synthesis of Compound 1. Once the dropwise addition of *N,N,N',N'*-tetramethylphosphorodiamidic chloride began, it took several minutes for the precipitate to begin to form. As a result, the reaction was kept at 0°C for longer to ensure that it was driven to completion. This perceived decrease in rate of reaction could be explained in several ways. First, the phosphorus reaction center is slightly more shielded from attack than in dimethyl chlorophosphate. The $-\text{N}(\text{CH}_3)_2$ groups are more bulky than $-\text{OCH}_3$ groups, and this increased steric hindrance could be responsible for slowing the reaction. Second, the phosphorus reaction center in dimethyl chlorophosphate possesses a more positive partial charge, making it more susceptible to nucleophilic attack. This is because the $-\text{OCH}_3$ groups of dimethyl chlorophosphate are slightly less electron-donating than $-\text{N}(\text{CH}_3)_2$ groups. Even so, the reaction proceeded without difficulty once it began. Removal of the precipitated triethylamine hydrochloride yielded a pale yellow filtrate containing the target intermediate (Intermediate 2) in dichloromethane.

There was no delay in the formation of triethylamine hydrochloride salt during the second step of this synthesis. The reaction was quick and straightforward. However, the reaction was kept at 0°C for longer than the equivalent step in the synthesis of Compound 1 to be certain that it was completed. The filtrate that was given after the removal of the precipitate was pale yellow. As with Compound 1, the color darkened as the solvent was removed and the monomer was concentrated. Complete evaporation of the solvent yielded 15.7 g (78.8%) of Compound 2 as a yellow, slightly viscous liquid.

4.1.4.1 Characterization of Intermediate 2

Figure 4-5 shows the mass spectrum that was collected from the filtrate of the first step of the reaction. The calculated mass of Intermediate 2 was 179.1187. The protonated molecular ion of this molecule has a calculated m/z of 180.126. The spectrum shows a strong signal at m/z 180.1258, which corresponds to the target intermediate.

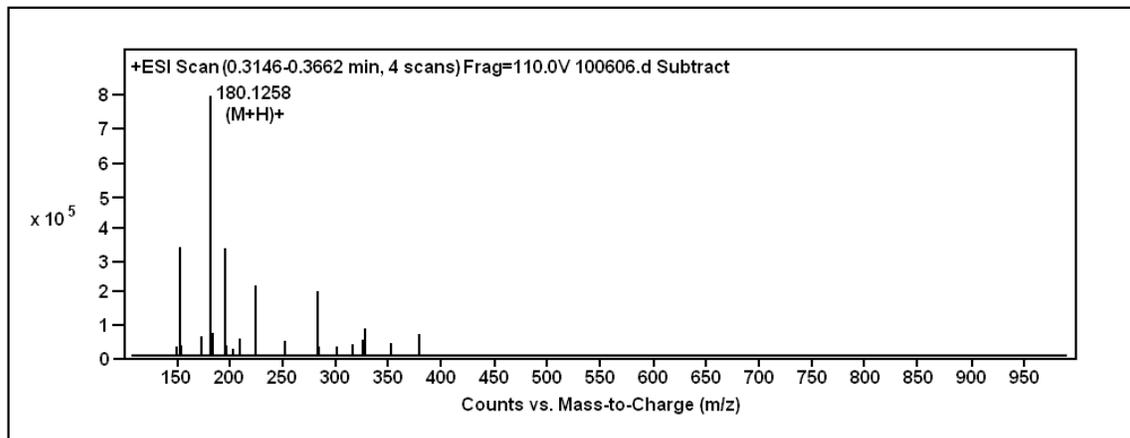


Figure 4-5. Mass spectrum of Intermediate 2.

The FTIR spectrum that was obtained from Intermediate 2 is provided as Appendix C. The relevant peaks from this spectrum are summarized in Table 4-3. The peaks at 3382.0 cm^{-1} and 1645.6 cm^{-1} indicate the N-H vibrations of the secondary amine. The peak at 1457.4 cm^{-1} signals a C-H deformation. The P=O absorption frequency occurs in the same location with this molecule as it did for Intermediate 1 and Compound 1. Previous studies [70] have shown that P-N-Me₂ compounds have four characteristic absorption bands. The first should be present in the region of $1261\text{-}1321\text{ cm}^{-1}$ [70]. This peak can be seen in the spectrum of Intermediate 2 at 1297.9 cm^{-1} . The second absorption occurs between 1155 cm^{-1} and 1205 cm^{-1} and is usually very near 1180 cm^{-1} [70]. Typically, this peak is obscured by the P=O band. In the spectrum of Intermediate 2, this band can be seen at 1159.5 cm^{-1} . As expected, this band is obscured by the P=O vibration. The third characteristic absorption occurs

between 1058 cm^{-1} and 1075 cm^{-1} and is generally close to 1065 cm^{-1} [70]. This signal is reportedly weak. This weak signal is observed at 1062.8 cm^{-1} in the spectrum of Intermediate 2. Finally, the last characteristic absorption band is typically seen between 935-1008 cm^{-1} [70]. This signal is strong and can usually be seen very near to 975 cm^{-1} . In the spectrum of Intermediate 2, this strong signal is seen at 984.8 cm^{-1} . Additionally, some P-N-Me₂ compounds show a peak near 750 cm^{-1} . This absorption is seen in the provided spectrum at 745.0 cm^{-1} .

Table 4-3. Summary of relevant peaks from FTIR spectrum of Intermediate 2.

Wavenumbers (cm^{-1})	Assignment
3382.0	N-H stretch
1645.6	N-H deformation
1457.4	N-CH ₂ (C-H deformation)
1297.9	P-N(Me) ₂ vibration
1192.8	P=O vibration
1159.5	P-N(Me) ₂ vibration
1062.8	P-N(Me) ₂ vibration
984.8	P-N(Me) ₂ vibration
745.0	P-N(Me) ₂ vibration

4.1.4.2 Characterization of Compound 2

The mass spectrum that was obtained from the analysis of Compound 2 is provided and labeled Figure 4-6. The calculated mass of Compound 2 was

249.1242 and the protonated molecular ion of this molecule has a calculated m/z of 250.1315. The peak at m/z 250.1317 is indicative of the presence of the target product. Not surprisingly, the peak at m/z 180.1260, which corresponds to Intermediate 2, is greatly reduced in this spectrum.

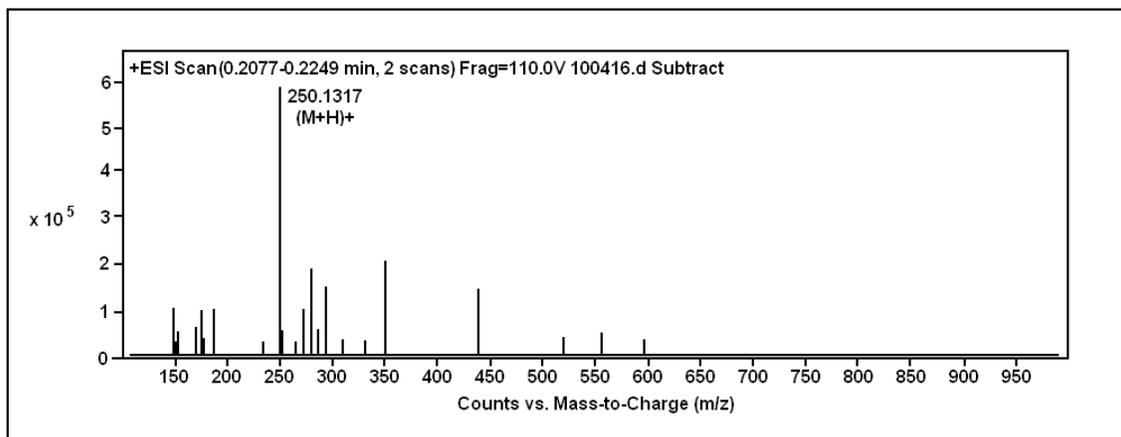


Figure 4-6. Mass spectrum of Compound 2.

The FTIR spectrum that was collected from Compound 2 is given as Appendix D. Table 4-4 provides a summary of the relevant peaks from this spectrum. The most critical peaks in this spectrum are found at 1719.9 cm^{-1} and 1642.2 cm^{-1} . These peaks are characteristic of the C=O stretch of an ester and the C=C stretch of a vinyl group, respectively. Their presence indicates that the hydroxyl group has been replaced by an ester and that the desired acryloyl functionality has been incorporated into the molecule. The peaks indicating P=O stretching and P-N-Me₂ groups in the spectrum of Intermediate 2 are still

observed in the spectrum of Compound 2 with one exception. Not unexpectedly, the peak that was seen at 1159.5 cm^{-1} is now completely hidden by the P=O vibration.

Table 4-4. Summary of relevant peaks from FTIR spectrum of Compound 2.

Wavenumbers (cm^{-1})	Assignment
3393.3	N-H stretch
1719.9	C=O stretch
1642.2	C=C stretch
1458.0	N-CH ₂ (C-H deformation)
1410.1	N-CH ₂ (C-H deformation)
1297.2	P-N(Me) ₂ vibration
1195.8	P=O vibration
1065.5	P-N(Me) ₂ vibration
985.0	P-N(Me) ₂ vibration
744.7	P-N(Me) ₂ vibration

The thermogram that was obtained from the thermogravimetric analysis of Compound 2 is provided and labeled as Appendix F. As previously mentioned, it is expected that the phosphate linkages of the monomer should degrade near the range of 205°C to 215°C. In the thermogram, it is clear that over 70% of the monomer has evaporated by the time this temperature is reached. This result shows that if the monomers are applied and are not polymerized, a majority of

that which is added on will have evaporated before its flame retarding fraction could be released.

4.2 Application of Monomers

4.2.1 Thermally Initiated Grafting of Monomers

When the monomers were applied with a thermal initiator, the most significant change that took place was a yellowing of the fabrics. Figure 4.7 shows an image that displays this color change for Compound 1. The concentration of monomer in the treatment bath increases from left to right. As shown in the photograph, the yellowness of the fabric after curing increased as the monomer concentration increased. The fabric's stiffness also increased as monomer concentration increased.



Figure 4-7. Photograph of thermally initiated treatments with Compound 1 (left to right: 100 g/L, 200 g/L, 300 g/L).

Regarding color change and stiffness, the trends associated with Compound 1 continued with Compound 2. Figure 4-8 shows a photograph of fabrics treated with Compound 2. With increasing monomer concentration, the yellowness and stiffness of the fabrics after curing also increased. When comparing Figure 4-8 with Figure 4-7, the most obvious difference is that Compound 2 gives far less yellowing when applied under these conditions.



Figure 4-8. Photograph of thermally initiated treatments with Compound 2 (left to right: 100 g/L, 200 g/L, 300 g/L).

4.2.2 Plasma-Induced Grafting of Monomers

Fabrics that were immersed in the monomer solutions and exposed to plasma showed no detectable changes in color or stiffness. In a previous study [61], the stiffness of fabrics after plasma-induced graft polymerization of phosphoroamidate monomers increased significantly as polymerization and grafting yields increased. Therefore, the absence of an increase in stiffness of

the fabrics treated in this research was taken as an early indication that only a low degree of grafting had occurred.

4.3 Evaluation of Fabrics

4.3.1 Burn Test Results

4.3.1.1 Thermally Initiated Samples

Table 4-5 summarizes the results that were obtained from the burn tests that were conducted on the thermally initiated samples. Char length is not reported because all samples burned over their entire length. The results show that the treated fabrics actually burned more quickly than untreated cotton. While this result may be alarming at first, it has been observed in many other studies [71-74]. These works, which represent only a fraction of those describing this phenomenon, report a significant increase in burn rate and flame propagation at low add-ons of phosphorus-based flame retardants. In these works, burning rates increase sharply at very low add-ons before reaching a maximum and beginning to decrease. The correlation between horizontal burning rate and phosphorus-based flame retardant add-on for cotton, as described in previous research [73,74], is illustrated in Figure 4-9. One publication suggests that low add-ons of flame retardant chemicals make combustible gases available at lower temperatures than untreated cotton. Therefore, the fabric can ignite and burn more readily. Similarly, another study suggests that the presence of flame

retardant chemicals at low add-ons causes a decrease in the decomposition temperature of cotton and leads to more rapid burning [74]. Still another report proposes that low add-ons of phosphorus-based flame retardant chemicals catalyzes the decomposition of cellulose at a lower temperature so that more char and less fuel are formed [71]. The authors suggest that this lower decomposition temperature combined with less available fuel causes the flame to propagate more quickly as it searches for combustible material. Therefore, the observed increases in burning rates for the treated samples in this research implies that low add-ons of the flame retardant chemicals was achieved through thermally initiated grafting.

Table 4-5. Summary of burn test results for thermally initiated treatments.

Sample	Flame Duration (s)	Burn Rate (mm/s)
Untreated cotton	11.9	16.8
Compound 1 – 10%	7.2	27.8
Compound 1 – 20%	7.8	25.6
Compound 1 – 30%	8.3	24.1
Compound 2 – 10%	8.1	24.7
Compound 2 – 20%	8.4	23.8
Compound 2 – 30%	9.1	22.0

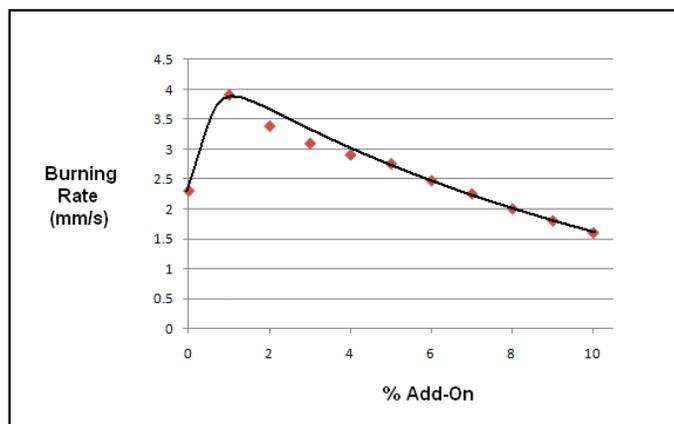


Figure 4-9. Illustration of correlation between horizontal burning rate and add-on for cotton. [71,72]

However, a 30% monomer solution (and most likely a 20% solution) should have provided a sufficient amount of the flame retardant chemicals to increase the fire resistance of the treated fabrics. To understand the reason for increased burning rates despite relatively high treatment bath concentrations, it is first necessary to consider the possible forms that the chemical may take after curing. Ideally, the flame retardant chemical would be graft polymerized to the surface of the substrate. However, it is likely that some chemical exists as a homopolymer that is not covalently attached to the substrate. Homopolymer chains may also develop to be intimately tangled within the fiber matrix of the substrate. One would also expect some of the monomer to remain unpolymerized and some of the unpolymerized molecules may become entrapped in the fiber matrix.

A phosphoramidate monomer with a very similar chemical structure to the two presented in this research had a boiling point of 135°C [61]. It is reasonable to expect Compound 1 and Compound 2 to have similar volatilities to the molecule described in that work. The heat produced by a flame is more than enough to evaporate monomers with a boiling point as low as this. Therefore, any flame retardant chemical that is present on a treated substrate that still exists in monomer form is subject to evaporation when the heat from a flame is brought near. This concept is supported by the thermogravimetric analysis of the monomers, which demonstrated that significant fractions of unreacted monomer are lost to evaporation before the temperature at which their phosphate linkage decomposes is reached. Obviously, in order to be an effective flame retardant, the chemical must remain with the substrate and release its flame suppressing functionality. With this in mind, one can see that the likely cause for the observed increase in burn rates is the low degree of conversion of the monomers into polymer as opposed to low add-on. In other words, while the add-on of the flame retardant monomers was probably sufficiently high to hinder the propagation of the flame, the low degree of conversion of these monomers into polymer meant that some of the flame retardant chemical evaporated upon heating. Once evaporated, the flame retardant chemicals were no longer present to serve their intended purpose. This evidence shows that achieving a high

degree of polymerization with these monomers is absolutely critical if they are to be used as flame retardants.

Another observation to be made from Table 4-5 is that the burn rates of the treated fabrics decreases as monomer concentration in the treatment bath increases. At this point, it is unclear if this is caused simply by higher add-ons or if higher degrees of polymerization of the flame retardant monomers is a factor. In either case, if the burn rates of these unwashed samples were plotted in a graph similar to that in Figure 4-9, they would undoubtedly fall to the right of, and decrease away from, the maximum burn rate. In contrast, the burning rates of the washed samples are very close to that of untreated cotton and increase as monomer concentration increases. Table 4-6 summarizes the burn test results of the washed samples. If these samples were plotted in a graph similar to that in Figure 4-9, they would occur to the left of, and increase towards, the maximum burn rate. The washing step would have removed any homopolymer or unreacted monomer. Even though the effect of the flame retardant chemical was barely observable after washing, the fact that it was observable at all is an indication that a very small amount of the chemical was grafted to the substrate. These results show that not only is a high degree of polymerization critical if these compounds are to perform satisfactorily as fire suppressants, but that the polymers must be covalently attached to the substrate if any semblance of durability is desired.

Table 4-6. Summary of post-wash burn test results for thermally initiated samples.

Sample	Flame Duration (s)	Burn Rate (mm/s)
Untreated cotton	11.9	16.8
Compound 1 – 10%	11.6	17.2
Compound 1 – 20%	11.1	18.0
Compound 1 – 30%	10.4	19.2
Compound 2 – 10%	11.8	17.0
Compound 2 – 20%	11.4	17.5
Compound 2 – 30%	10.7	18.7

Even though the treated samples were not capable of halting, or even slowing, the propagation of the flame, there is a very clear distinction between untreated cotton and treated samples when they are examined after burn testing. Figure 4-10 is representative of the difference observed when comparing treated samples, both unwashed and washed, with untreated cotton. The photograph on the left shows that untreated cotton is completely burned such that nothing remains. In the middle, the treated fabric shows a substantial increase in char formation. The char structure that is depicted here was seen in all treated fabrics, regardless of the monomer used or concentration in the treatment bath. Finally, the photograph on the right is representative of the char structure of a burned sample that underwent the wash procedure. While it is obvious that less char is formed when compared to the unwashed sample, the presence of char in the washed sample is further proof of a very low grafting yield. This result is encouraging, as it indicates that the monomers, once polymerized, are capable

of promoting char formation. If a high enough degree of polymerization and grafting can be accomplished, it is very likely that these monomers will be capable of producing a durable auto-extinguishing fabric through the condensed phase mechanism.

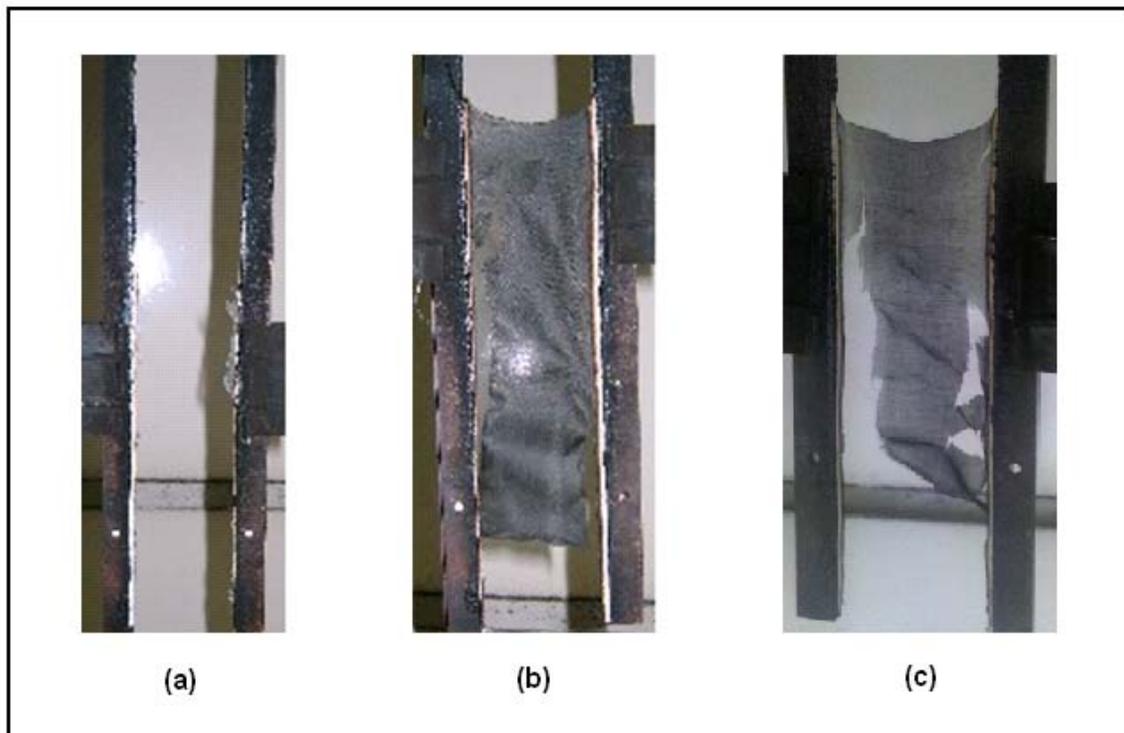


Figure 4-10. Char formation in (a) untreated cotton, (b) treated sample, and (c) treated and washed sample.

The burn rates expressed in Table 4-5 and Table 4-6 show that the fabrics treated with Compound 2 burned slightly slower than those treated with Compound 1. However, the burn rates and char structures are similar enough that it is difficult to conclude that one monomer is superior to the other. If one monomer is a more effective fire suppressant, it should become more apparent in

future work as higher degrees of conversion and grafting are reached and flame propagation is significantly slowed or halted.

4.3.1.2 Plasma-Induced Samples

Table 4-7 summarizes the results from the burn testing of the plasma treated samples. As with the samples that were applied in conjunction with a thermal initiator, the plasma treated samples demonstrated accelerated burn rates when compared to untreated cotton. Once again, this is most likely because of a low degree of conversion of the monomer into polymer. Some of the unreacted monomer evaporates, leaving only a fraction of the flame retardant chemical behind as grafted polymer, homopolymer, or entrapped monomer. When this remaining chemical degrades and releases phosphoric acid, there is acid-catalyzed decomposition of the cellulose which causes the fabric to degrade at a lower temperature and burn more readily.

Table 4-7. Summary of burn testing for unwashed fabrics treated with 20% monomer solutions containing 10% EGDMA.

Monomer	Plasma Exposure – Pretreatment (seconds per side)	Plasma Exposure – Post Treatment (seconds per side)	Flame Duration (s)	Burn Rate (mm/s)
Untreated	0	0	11.9	16.8
Compound 1	0	0	6.7	29.9
	15	15	7.3	27.4
	30	30	9.2	21.7
Compound 2	0	0	7.0	28.6
	15	15	7.5	26.7
	30	30	9.6	20.8

It is encouraging that a correlation can be observed that relates plasma exposure time to burn rate. As the dwell time of the treated fabric within the discharge increased, the burning rate of the fabric decreased. If plotted in a chart similar to Figure 4-9, the burn rates of these unwashed samples would fall to the right of, and decrease away from, the maximum burn rate. However, unlike the thermally initiated samples, the monomer concentration in the treatment baths was the same for all plasma treated fabrics. The only variable in this set of samples was plasma exposure time, meaning that plasma polymerization must be the sole contributor to this perceived effect. Therefore, it can be said that the decrease in burn rates with increasing dwell time is due to higher degrees of plasma polymerization of the flame retardant monomers.

Since more of the chemical exists in polymer form, less evaporates upon heating and more is available to release its flame retardant fraction. This is evidence that the flame retardant molecules presented in this work can be polymerized under atmospheric plasma conditions. Moreover, if plasma exposure times are increased beyond the range that was examined in this work, it is likely that high enough degrees of polymerization can be attained to produce effective flame retardant fabrics.

As with the thermally initiated samples, the plasma treated samples were subjected to the wash procedure described in Section 3.2.5 to remove any ungrafted homopolymer or unreacted monomer. The results of the burn tests on these washed samples are presented in Table 4-8. As plasma exposure time increases, so do the burn rates. Should the burn rates of these samples be plotted in a graph such as the one in Figure 4-9, they would be on the left of, and increase towards, the maximum burn rate. Consequently, the fact that the post-wash burn rates increase with plasma exposure time is actually an indication that grafting yields are increasing. Since only the effect of fixed flame retardant polymer is observed after washing, it is apparent that, like the thermally initiated samples, an extremely low degree of grafting was achieved. Nevertheless, the presence of a correlation between the burn rate of the washed samples and plasma exposure time is a hint that longer dwell times within the discharge do increase grafting yields.

Table 4-8. Summary of post-wash burn test results of plasma treated samples.

Monomer	Plasma Exposure – Pretreatment (seconds per side)	Plasma Exposure – Post Treatment (seconds per side)	Flame Duration (s)	Burn Rate (mm/s)
Untreated	0	0	11.9	16.8
Compound 1	15	15	11.3	17.7
	30	30	10.1	19.8
Compound 2	15	15	11.4	17.5
	30	30	10.0	20.0

In regards to char structure, there are very obvious differences between the treated samples, both unwashed and washed, and untreated cotton. The photographs in Figure 4-11 illustrate the dissimilarities that were seen. On the left, it is obvious that untreated cotton burns completely, leaving no charred material. In the middle photograph, one can see that the char structure of an unwashed sample after burning is very well defined. This was seen in all unwashed plasma treated samples, regardless of the monomer used or the plasma exposure time. Finally, the image on the right is representative of a washed sample. The char structure of this specimen is less distinct, but the fact that this amount of char was present indicates that some of the flame retardant chemical remained with the substrate after the washing procedure. These are very good signs that speak to the ability of the compounds presented in this work to promote char formation.

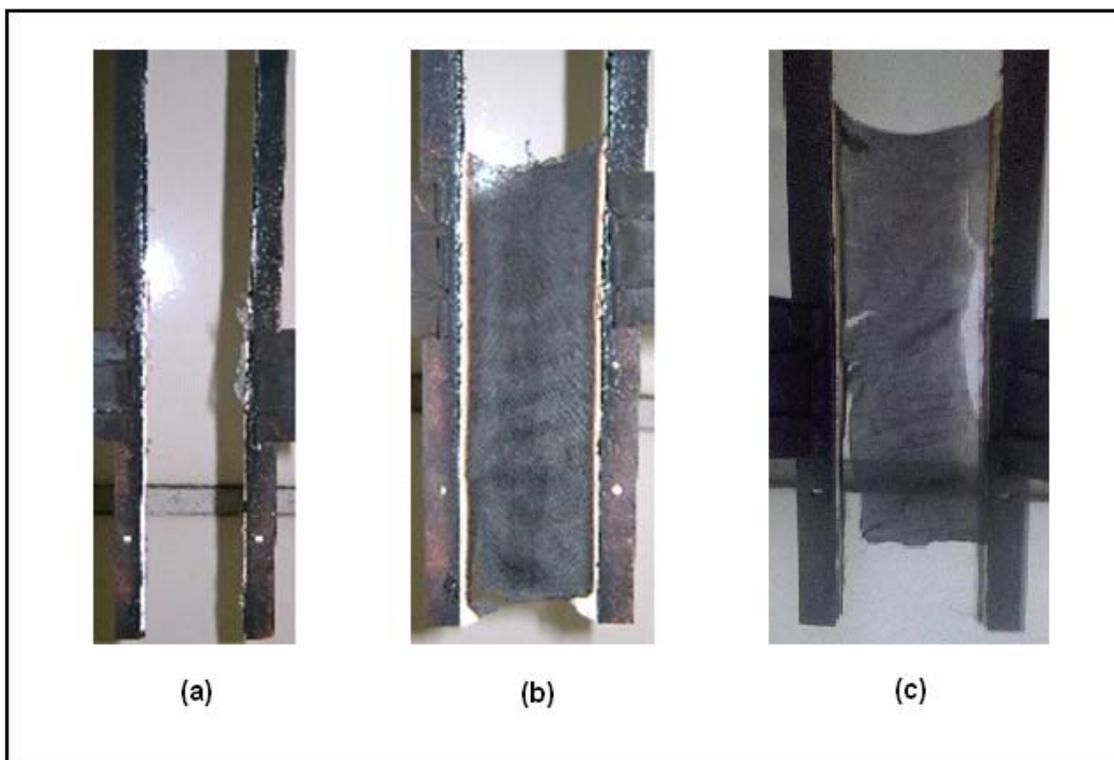


Figure 4-11. Char formation in (a) untreated cotton, (b) treated sample, and (c) treated and washed sample.

Once again, it is difficult to conclude that one monomer offers superior flame protection over the other. In most cases, fabrics treated with Compound 2 seemed to burn a little more slowly than fabrics treated with Compound 1. However, the burn rates were too similar to state that one monomer was more effective. If one monomer is better than the other, it will become more evident as future work attains higher degrees of polymerization and grafting.

4.3.2 Thermogravimetric Analysis Results

The thermograms from the unwashed treated samples are provided in Appendices G – M. The results from these thermograms are summarized in Table 4-9. Based on the data gathered from the burn testing, one would predict a decrease in degradation temperatures of the treated samples accompanied by an increase in char formation. In fact, this is exactly what was observed. Untreated cotton degraded over a range of 361.38 – 400.84°C, reaching a maximum at 385.46°C. In contrast, the thermally initiated samples that were treated with a 30% monomer solution began to degrade at 274.31°C (Compound 1) and 288.66°C (Compound 2). The plasma treated samples all began to degrade at around 300°C. The decreases in degradation temperature are surely evidence of phosphoric acid catalyzed decomposition of cellulose and prove the presence of the flame retardant chemical on all substrates.

Table 4-9. Summary of thermograms from unwashed treated fabrics.

Sample	Onset of Degradation		Maximum Degradation		End of Degradation		Char Residue Remaining at 950°C
	Temp. (°C)	Weight (%)	Temp. (°C)	Weight (%)	Temp. (°C)	Weight (%)	Weight (%)
Untreated	361.38	94.630	385.46	46.454	400.84	7.123	5.008
Compound 1 (30%) – Thermal Initiator	274.31	93.007	307.52	61.662	332.48	39.639	28.332
Compound 2 (30%) – Thermal Initiator	288.66	93.987	315.80	61.760	337.33	38.263	27.689
Compound 1 – Plasma 15s	302.34	95.243	324.73	58.475	343.87	29.592	24.384
Compound 1 – Plasma 30s	298.30	94.572	323.72	57.932	341.88	29.956	25.645
Compound 2 – Plasma 15s	301.13	94.173	322.09	59.027	335.85	33.883	26.443
Compound 2 – Plasma 30s	301.12	94.748	319.93	63.655	339.67	31.617	26.470

The second important observation to be taken from this data is the significant increase in char formation that was found for all treated samples. At 950°C, only around 5% of the untreated cotton remained as char residue. On the

other hand, the amount of char residue that remained at 950°C for the treated samples varied between 24.384% and 28.332%. When combined with the increase in char formation that was observed for treated samples during burn testing, this result is further proof of the value of the flame retardant chemicals presented in this work as char promoters.

If the thermally initiated samples are compared to the plasma treated samples, it is apparent that the thermally initiated samples degrade at lower temperatures and generate more char. In order to lower the degradation temperature, more acid-catalyzed decomposition must occur. For this to happen, more phosphoric acid, and thus more of the flame retardant chemical, must be present. Furthermore, if more phosphoric acid is present, then it follows that more cross-linking and char formation will occur. For this reason, the somewhat lower degradation temperature and the slightly higher char formation in the thermally initiated samples is attributed to the presence of more of the flame retardant chemical. This observation is consistent with the fact that the thermally initiated samples were immersed in 30% monomer solutions and the plasma treated samples were immersed in 20% monomer solutions.

When the monomers are evaluated against one another, it is unclear if one offers greater flame protection than the other. With the thermally initiated samples, the fabric treated with Compound 1 degraded at a lower temperature and produced more char than the equivalent fabric that was treated with

Compound 2. The temperatures at the onset of degradation for the plasma treated samples were all very similar. However, the fabrics treated with Compound 2 had a slightly higher char yield. As mentioned previously, further testing is needed to determine if one of the monomers is a more successful flame retardant.

5 CONCLUSIONS

The intention of this research was to develop novel phosphorus-based flame retardant monomers that could be graft polymerized to a substrate using atmospheric pressure plasma. It was shown that a two-step synthetic route could be utilized to generate such monomers from a chlorophosphate, ethanolamine, and acryloyl chloride. Both reactions in this process follow an S_N2 mechanism. The reactions are simple to perform and yield an acceptable quantity of the target monomer.

Preliminary attempts at applying these monomers by thermal initiation and plasma-induced graft polymerization failed to produce an auto-extinguishing fabric. In fact, the burn rates of all treated samples exceeded that of untreated cotton. This phenomenon is observed in other works at low add-ons of phosphorus-based flame retardant chemicals to cotton. This increase in burn rate is attributed to the phosphoric acid catalyzed decomposition of cellulose, which generates combustible material at lower temperatures and allows the fabric to burn more readily. However, flame retardant chemical bath concentrations in this work should have been sufficiently high to impart flame retardancy to the fabrics. Instead, it is likely that any monomer that was left unreacted after the curing or plasma post-treatment step would simply evaporate when the heat of the flame was applied. Once the flame retardant chemicals had evaporated from the substrate, they were incapable of providing any flame

protection to the fabric. The reduction in the degradation temperature of the treated samples was confirmed by thermogravimetric analysis. Treated samples showed degradation temperatures around 60°C to 85°C below that of untreated cotton. These observations show that the monomers are ineffective if they are not polymerized and that achieving high degrees of polymerization and grafting is essential if they are to be used satisfactorily.

A promising conclusion that can be made from the burn testing is that both monomers that are presented in this thesis are capable of producing significant amounts of char. While untreated cotton burned completely, there was a distinct char structure that remained after treated samples were burned. Thermogravimetric analysis was used in an endeavor to quantify this observation. Untreated cotton exhibited about 5% char residue after being heated to 950°C. On the other hand, all treated fabrics showed char residues in the vicinity of 25 – 28%. This is both significant and encouraging because it demonstrates the condensed phase mode of action of these monomers.

While an auto-extinguishing fabric was not produced, much was learned about the use of these monomers. The data shows that the degrees of polymerization and grafting that are achievable using the parameters set forth in this study are too low to produce an effective flame retardant fabric. Still, the data also seems to suggest that these monomers would be capable of

generating durable flame retardant cotton fabrics if high enough degrees of polymerization and grafting are accomplished.

6 RECOMMENDATIONS FOR FUTURE WORK

The opportunities for future research into the plasma-induced graft polymerization of these flame retardant monomers are many. The first thing that needs to be examined is the kinetics of homopolymerization of these monomers by plasma. As it stands, we know that the polymerization and grafting of these monomers is perhaps the most critical factor in their use. However, we know very little about the parameters that are needed to achieve these high degrees of conversion. The monomers should be spread uniformly and thinly onto a glass microscope slide and passed through the plasma discharge. By varying plasma device parameters such as power, exposure time, and inter-electrode gap distance, one could determine the ideal processing conditions for conversion of the monomers into polymer. Degrees of conversion can be monitored through FTIR by following the disappearance of the vinyl absorption and through ^1H NMR by measuring the intensity of the vinyl protons. If high enough degrees of conversion are not attained through the use of the monomer and plasma alone, a cross-linking agent can be added and the effect of its concentration could be examined. Finally, a photoinitiator may be needed to further enhance the degree of conversion. The effects of varying photoinitiator concentration could be investigated. Once high degrees of polymerization are achieved, the polymer films should be analyzed by TGA to determine the temperature at which the phosphate linkage decompose.

Once suitable processing conditions are established, attempts at applying the monomers to substrates can be made. The effects of monomer concentration, crosslinking agent concentration, and photoinitiator concentration on grafting yield should be thoroughly investigated. Other analytical methods can be used to supplement burn testing for this evaluation. SEM photomicrographs of untreated cotton fibers should be relatively rough. On the other hand, SEM photomicrographs of treated fibers with high grafting yields should be more smooth and uniform as the flame retardant polymer coats their surface. It may also be beneficial to examine treated fabrics with SEM to ensure that the polymer has not clogged their pores and compromised their breathability. Thermogravimetric analysis should also be performed on treated samples. It is expected that the pyrolysis of the treated samples would occur at lower temperatures than untreated cotton and that the weight loss of the treated samples would be reduced. Char yields could be calculated for each monomer based on the weight of the remaining residue at extremely elevated temperatures (around 1000°C). The treated samples could be digested in the MARS 5 microwave digester and submitted for ICP analysis to determine the percentage of phosphorus add-on. Since we know the ratios of phosphorus to nitrogen in the monomers, the percentage of phosphorus add-on could be used to calculate the percentage of nitrogen add-on. Finally, these tests could be repeated following an accelerated wash cycle to explore the durability of the treatments.

A different method for evaluating the flame retardancy of the treated fabrics should be considered. The current burn testing procedure requires large strips of treated fabric, preferably 250-300 mm long and 75 mm wide. In order to obtain sufficient polymerization and grafting yields, the concentration of monomer in the treatment baths is very high. Because it is necessary to treat such sizeable areas of fabric, a large quantity of each monomer is needed to test each set of variables. For example, a minimum of 10 mL of a 20% monomer solution are needed to treat each 250 mm by 75 mm fabric swatch. That equals 2 grams of monomer that are required to test just one set of variables. This does not even take into consideration that an additional identically treated fabric swatch will be needed for durability testing and that another, smaller, treated sample will be needed for other destructive analytical tests such as TGA and ICP. Therefore, in order to thoroughly investigate just one set of processing conditions, more than 4 grams of monomer are needed. For this reason, it is advisable to seek an alternative burn testing procedure, such as LOI testing, which uses smaller fabric samples.

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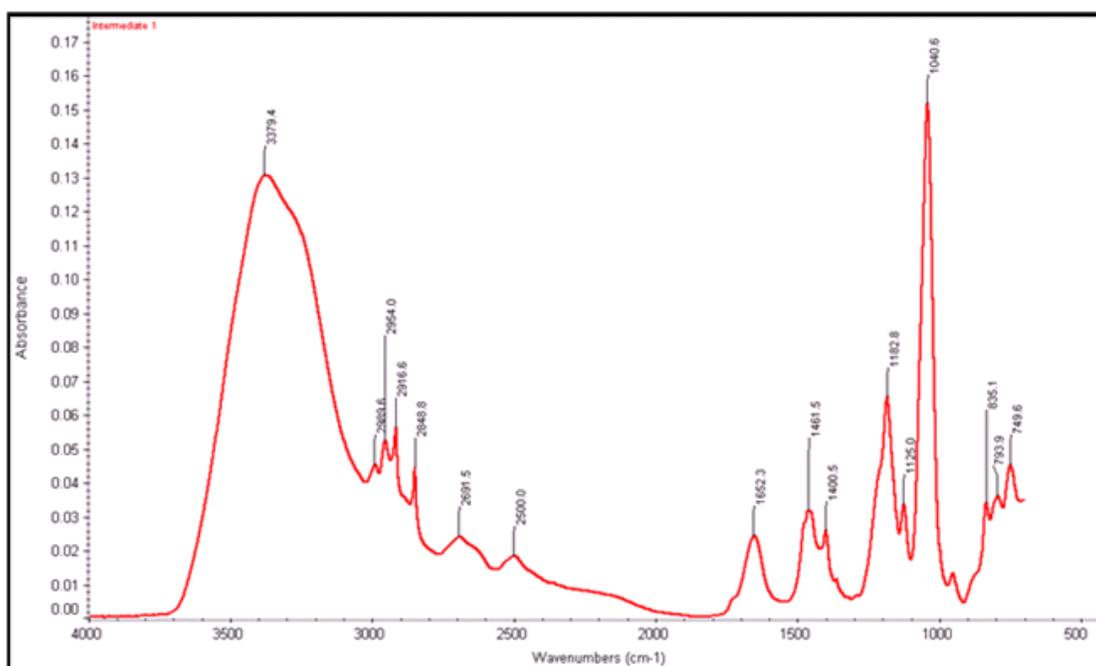
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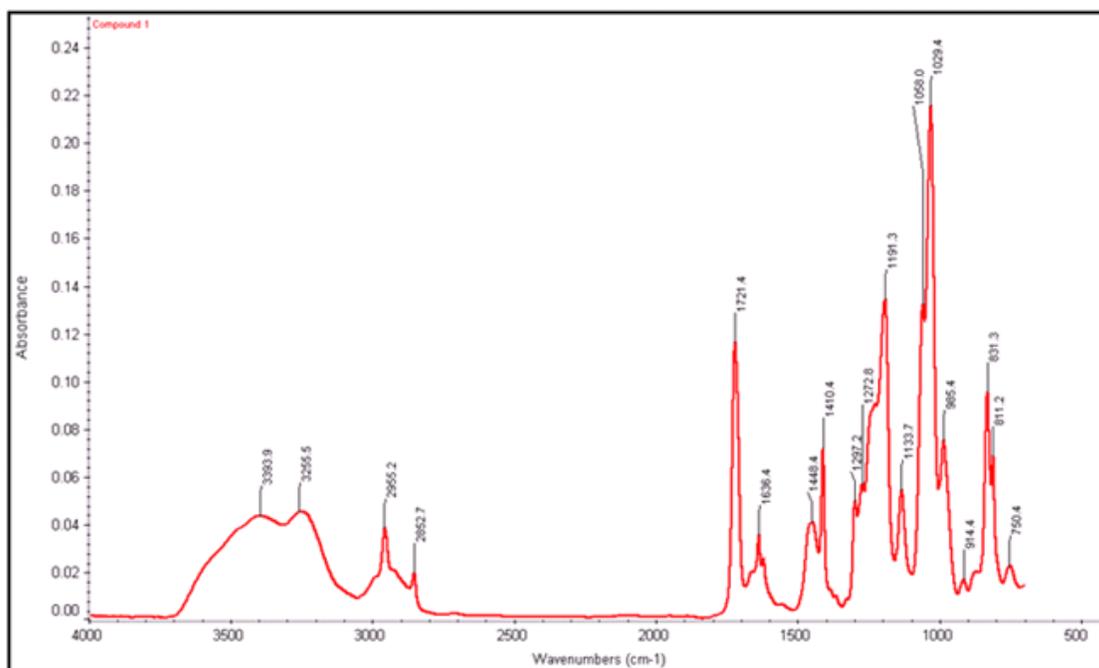
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8 APPENDICES

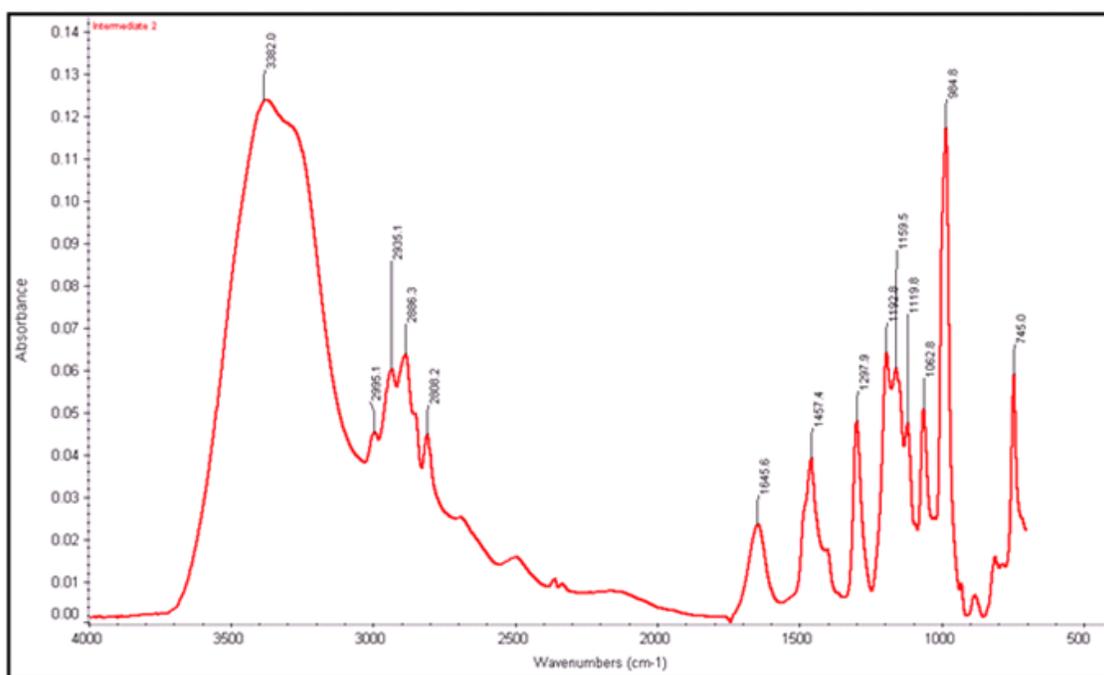
Appendix A



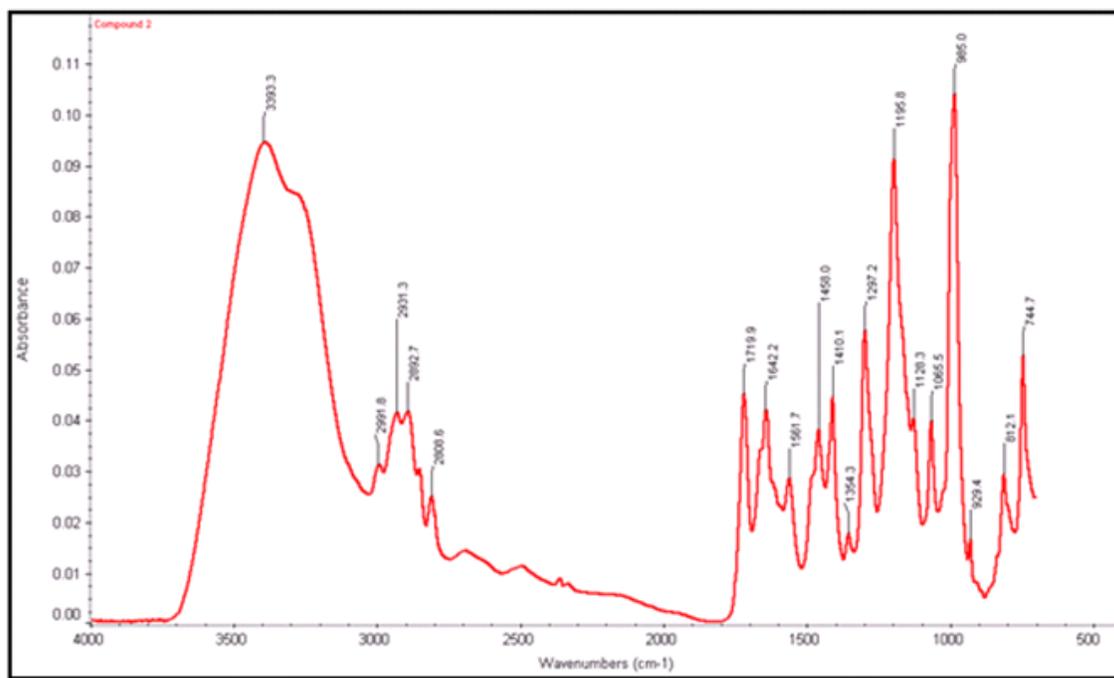
Appendix B



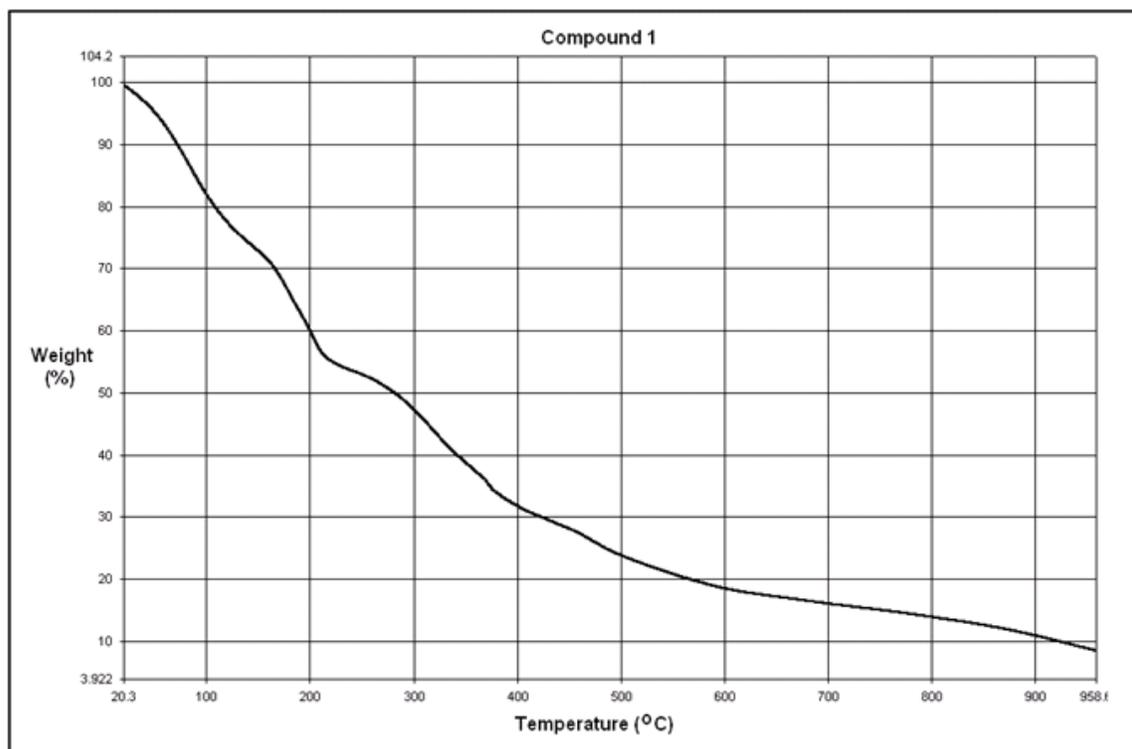
Appendix C



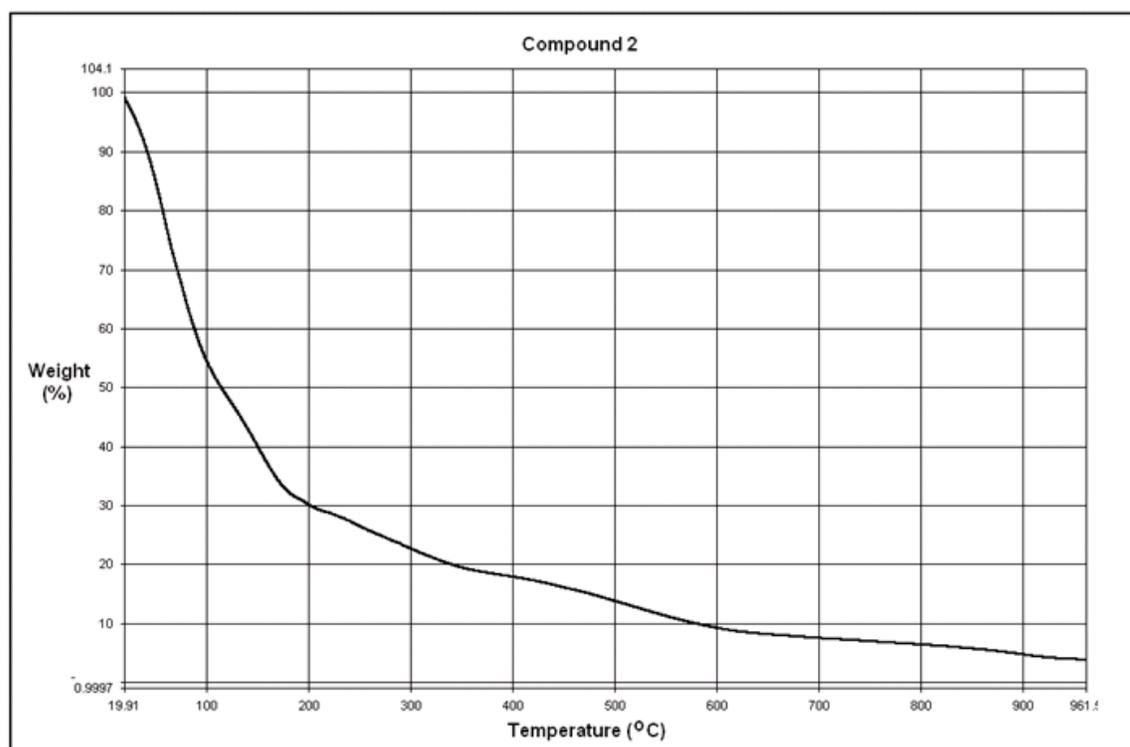
Appendix D



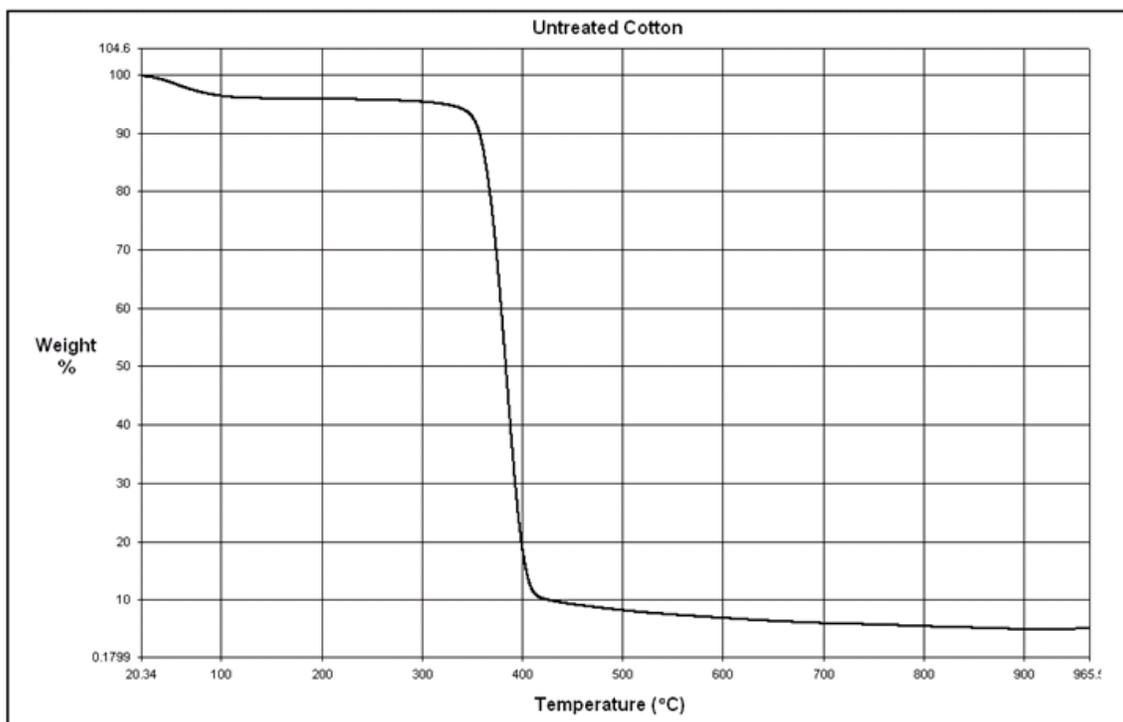
Appendix E



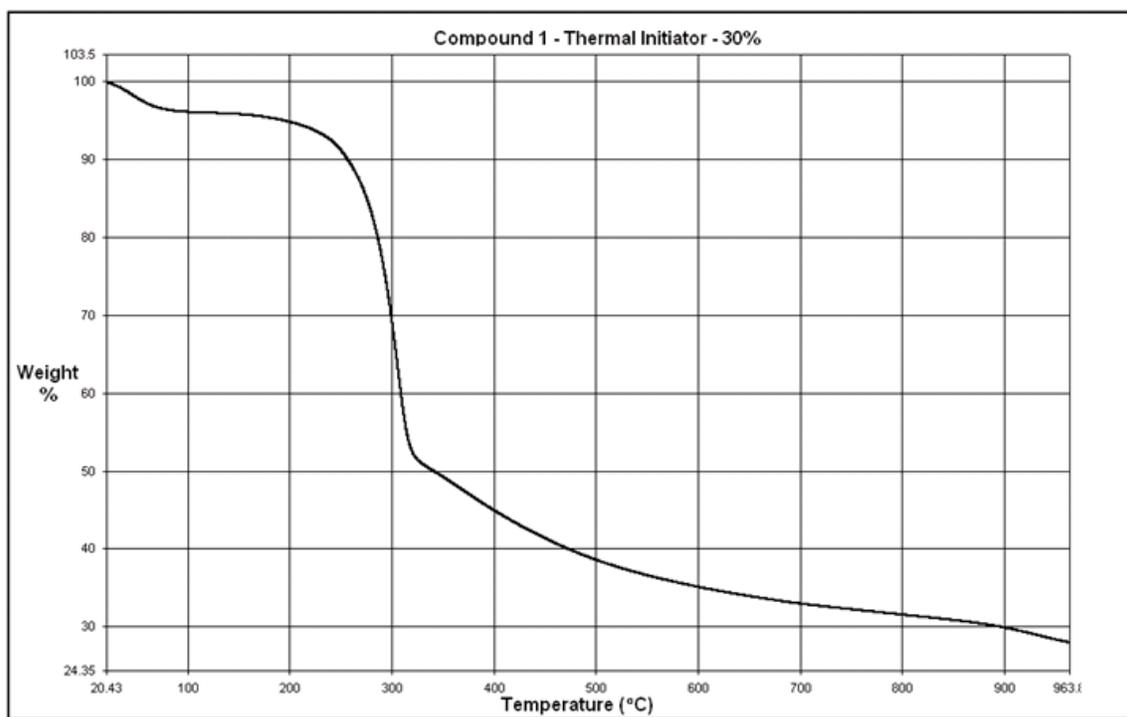
Appendix F



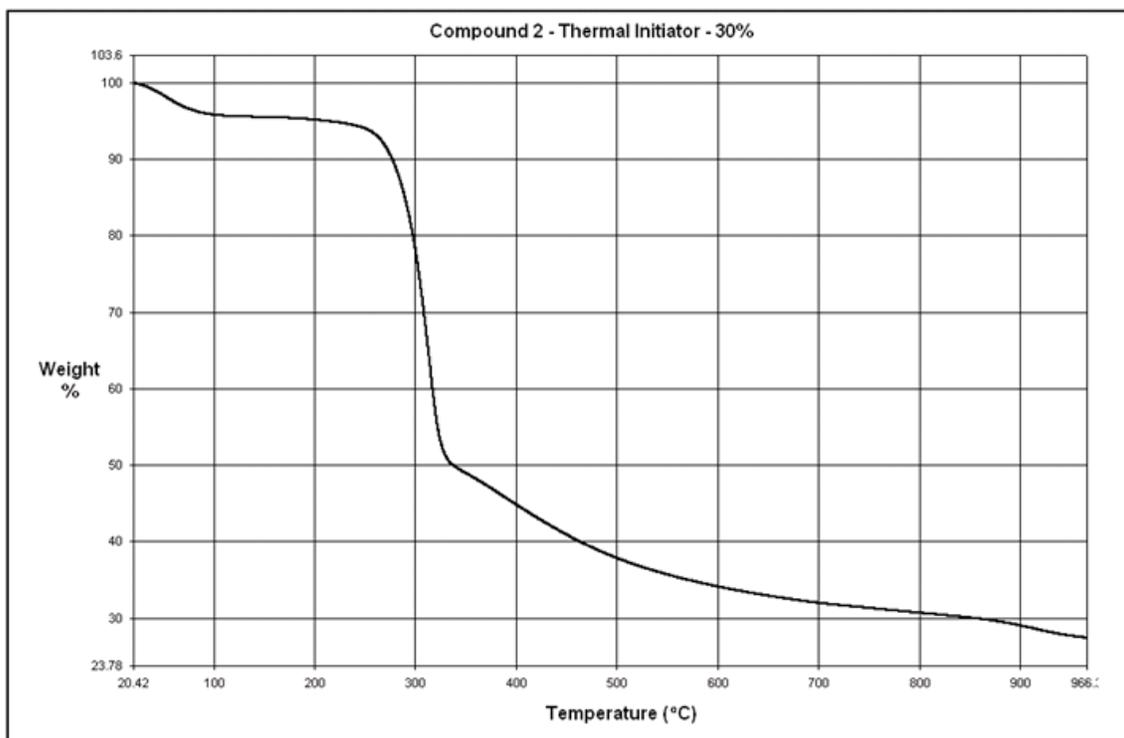
Appendix G



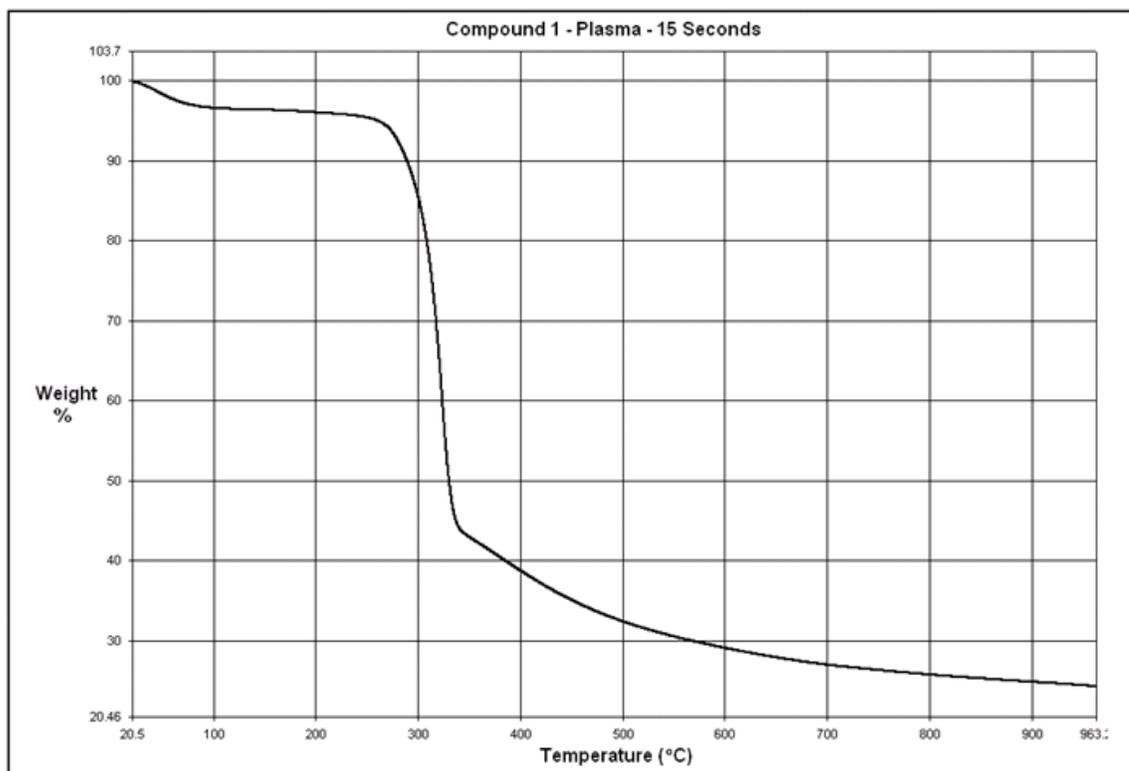
Appendix H



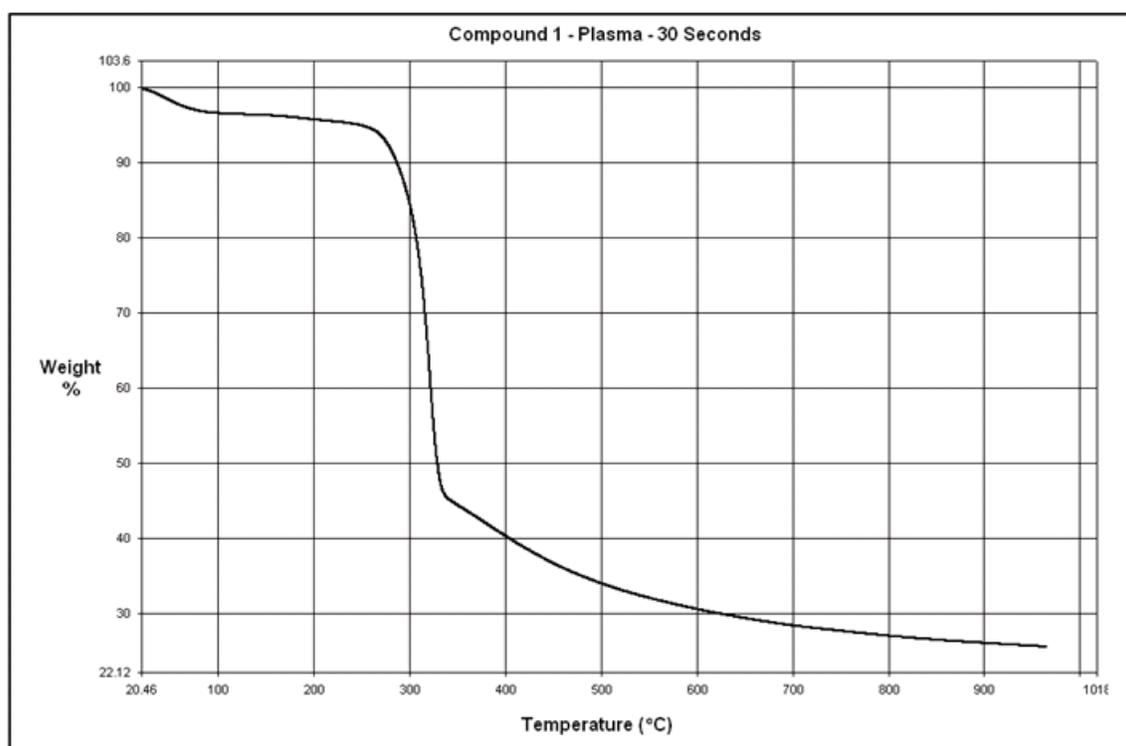
Appendix I



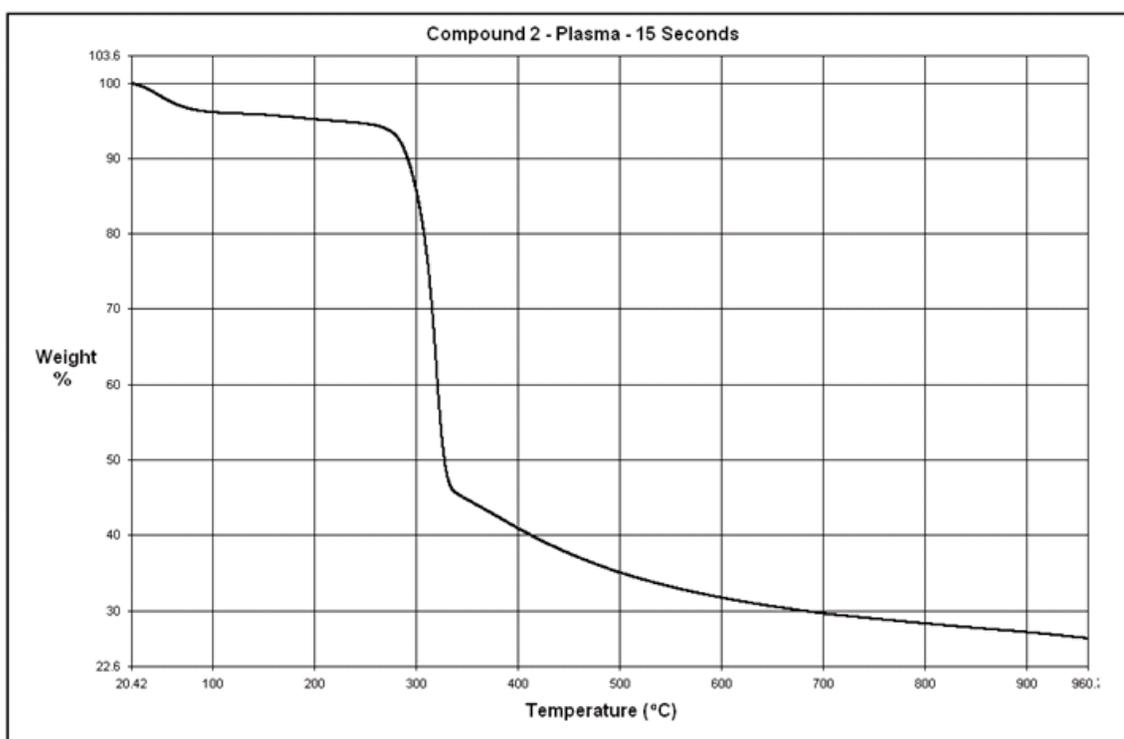
Appendix J



Appendix K



Appendix L



Appendix M

