Carbohydrate Polymers 92 (2013) 885–893

Contents lists available at SciVerse ScienceDirect

Carbohydrate Polymers

journal homepage: www.elsevier.com/locate/carbpol

Conferring flame retardancy on cotton using novel halogen-free flame retardant bifunctional monomers: synthesis, characterizations and applications

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ARTICLE INFO

Article history:
Received 13 June 2012
Received in revised form
25 September 2012
Accepted 27 September 2012
Available online 8 October 2012

Keywords:
Cotton
Flame retardants
Halogen-free
Phosphorus–nitrogen synergism
Monomers
Bifunctional

ABSTRACT

Two novel halogen-free phosphorous–nitrogen flame retardant bifunctional monomers were synthesized and characterized using attenuated total reflectance/Fourier transform-infrared (ATR/FT-IR) and electrospray ionization mass spectrometry ($^+$ESI-MS). The monomers were applied separately and graft polymerized on cotton in the presence of the thermal initiator $K_2S_2O_8$. The performance of each monomer was evaluated using thermal gravimetric analysis (TGA), grafting efficiency, and vertical flame test. It was shown that the performance of N,N-dimethyl di(acryloyloxyethyl)phosphoramide (DMDAEP) (monomer **2**) as flame retardant outperformed that of ethyl di(acryloyloxyethyl)phosphorodiamidate (EDAEP) (monomer **1**). The superior performance of DMDAEP was attributed to the presence of more nitrogen atoms compared to EDAEP. The increased nitrogen content in DMDAEP increased the synergistic effect of the P–N system. Cotton treated using padding methods showed more promising results than cotton treated by exhaust methods.

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1. Introduction

In United Sates only, fire has killed more people than all natural disasters combined. In the year 2009, according to National Fire Protection Association (NFPA) statistics (USFA statistics, NFPA estimates, 2009) of fires in USA, 1.35 million fires resulted in 3010 deaths, 17,050 injuries and $12.53 billion value loss of property. Astonishingly, 28% of total fires which happened in residential structures caused most of the damage as shown in Fig. 1.

It has been reported that (Hall, 2007) 70% of the home smoking material fire fatalities resulted from fires originating with upholstered furniture, mattresses or bedding. Thus in the residential structures, flame retardant treatment of the textile related articles can significantly contribute to saving lives and property. Detailed fire statistics for European countries have been reported elsewhere (Kobes, 2009; World fire statistics, October 2005).

Cotton is one of the most abundantly used fibers, but it is one of the most flammable fibers as well with low limiting oxygen index (LOI) of 18.4% and onset of pyrolysis at 350 °C. However, its thermal functionality can be modified by making them flame retardant through surface treatment either with durable (e.g. monomers containing phosphorus and nitrogen along with reactive moiety) or with non-durable (usually inorganic salts containing ammonium, urea, phosphate and poly phosphates) flame retardants. Additionally, back coating assisted by resin bonding can be done to achieve flame retardancy with antimony–bromine systems.

The most common flame retardant systems for rendering cotton fabrics flame retardant are halogen-containing compounds. However, halogen-based compounds are not environmentally friendly because they generate toxic gases, which can be endocrine disruptive (Legler & Brouwer, 2003; Rahman, Langford, Scrimshaw, & Lester, 2001). The findings of studies (Kuriyama, Talsness, Grote, & Chahoud, 2004; Prenatal exposure to flame-retardant compounds affects neurodevelopment of young children, 2010; Szabo et al., 2009) resulted in the ban of the production of two major classes including polybrominated diphenyl ethers (PBDEs) and polybrominated biphenyl (PBB) in EU and USA (DIRECTIVE, 2003/11/EC OF THE EUROPEAN PARLIAMENT, 2003; Legler & Brouwer, 2003; US EPA). All this happened because there was growing evidence that PBDEs persist in the environment and accumulate in living organisms (Legler & Brouwer, 2003; Rahman et al., 2001; US EPA). Moreover, toxicological testing indicated that these chemicals may cause liver, thyroid, and neuro developmental toxicity. It was demonstrated that PBBs cause liver cancer in laboratory rats and mice (US EPA). The Department of Health and Human Services (DHHS) and the International Agency for Research on Cancer (IARC) suggested that PBBs could be carcinogenic to human health.

P–N (phosphorous–nitrogen) containing flame retardant systems have been vastly studied over the last three decades (Cole,

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0144-8617/$ – see front matter. Published by Elsevier Ltd.
http://dx.doi.org/10.1016/j.carbpol.2012.09.081

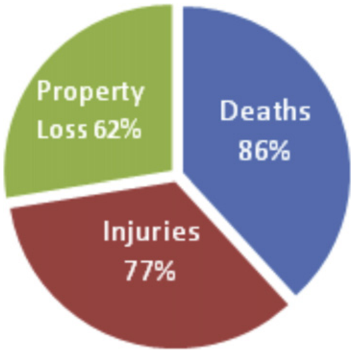
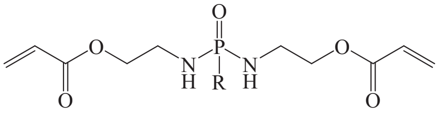


Fig. 1. Damage caused by 28% of residential fires out of total.

1979; Cole & Stephenson, 1980; Hebeish, Waly, & Abou-Okeil, 1999; Yang & Wu, 2003). Such systems attracted much attention because of their good thermal stability, low toxicity, and superior performance, owing to the synergistic effect of P–N (Hendrix, Drake, & Barker, 1972; Lewin, 1999; Pandya & Bhagwat, 1981). P–N synergism is not a general phenomenon; it depends on the nitrogen containing compound and polymer nature (Levchik, 2007; 2006). Several theories have reported the basis for P–N synergism (Cullis, Hirschler, & Tao, 1991; Gaan, Sun, Hutches, & Engelhard, 2008; Holme & Pater, 1980), and explained that P–N systems work by reducing the formation of flammable volatiles and catalyzing char formation.

Durability to washing of efficient flame retardant systems is a long standing problem. Covalent bonding is the best way to achieve durability on textile substrate by surface treatment. Previously (Hochart, De Jaeger, & Levalois-Grützmacher, 2003; Tsafack & Levalois-Grützmacher, 2006) subsequent grafting and polymerization were reported to achieve durable flame retardancy. Our research group extended this work by introducing bifunctionality into monomers containing P–N as shown in Fig. 2. Monomer **2** has $-N(CH_3)_2$ directly attached to central phosphorous atom as compared to $-O(C_2H_5)$ in monomer **1**, which will allow us to systematically study the influence of increasing the number of nitrogen atoms on the flame retardancy performance of these monomers. Bifunctionality was introduced with the goal of increasing the number of reactive cites on the monomer to furnish better durability coupled with good flame retardancy due to P–N synergism.

Here we reported the synthesis and evaluation of two potential flame retardant monomers as depicted in Fig. 2. The monomers were characterized by ATR–FTIR and ESI-MS in the positive mode. Grafting was evaluated by calculating % dry-add-on (%DAO) and SEM analysis on the treated samples. The thermal stability and fire retardancy were studied by TGA and vertical flame test, respectively.



	R
Monomer **1**	OC_2H_5
Monomer **2**	$N(CH_3)_2$

Fig. 2. Phosphorodiamidate and phosphoramide monomers **1** and **2** synthesized in the study.

2. Experimental

2.1. Materials and reagents

Cotton fabric used for this research was Test Fabric # 400, with gsm of 102 g/m^2. The construction was 78 × 76 plain weave and come in bleached desized form. Ethyl dichlorophosphate, N,N-dimethylphosphoramic dichloride, triethylamine, ethanolamine, acryloyl chloride, dichloro methane, potassium persulphate, and Mohr's salt were purchased from Sigma Aldrich, USA and used as received. The other reagents were of laboratory grade and used as received.

2.2. Synthesis of monomers

The synthesis of each monomer was completed in two similar steps. In the first step, the intermediates were synthesized as shown in Schemes 2.1 and 2.3 (Supplemental information). In the second step, acryloyl chloride was reacted with the intermediate to form the final products, ethyl di(acryloyloxyethyl)phosphorodiamidate (EDAEP) named monomer **1**, and N,N-dimethyl di(acryloyloxyethyl)phosphoramide (DMDAEP) named monomer **2**, as shown in Schemes 2.2 and 2.4 (Supplemental information).

2.3. Characterization

Monomers **1** and **2** and their intermediates were characterized using attenuated total reflectance/Fourier transform-infrared (ATR/FT-IR) and electrospray ionization mass spectrometry ($^+$ESI-MS). ATR/FT-IR spectrum was recorded on a Nicolet Nexus 470 spectrophotometer. For each sample, a drop of the monomer under investigation was placed directly onto the germanium crystal of the Avatar OMNI-Sampler, and a background spectrum was collected prior to each sample. The instrument was set to collect the spectra at a resolution of 4 cm^{-1} and a total of 32 scans.

Mass spectrua were collected at the North Carolina State University, Department of Chemistry Mass Spectrometry Facility. High resolution exact mass measurements were collected for the sodiated or protonated molecular ions of the samples. The spectra were recorded on an Agilent Technologies 6210 LC-TOF mass spectrometer. Samples were diluted with methanol and analyzed using 1 μL flow injection at 300 μL/min using a mixture of water: methanol (25:75, v/v) containing 0.1% formic acid as an eluent. The instrument was operated in the positive-ion mode with a capillary voltage of 4 kV, nebulizer pressure of 30 psig, and a drying gas flow rate of 10 L/min at 350 °C. The fragmenter voltage was set at 110 V, and the skimmer voltage was 60 V. Reference ions of purine at m/z 121.0509 and HP-0921 at m/z 922.0098 were used as internal standards, and were simultaneously introduced through the use of a second orthogonal sprayer.

2.4. Application of monomers

The thermal initiator used for this study was potassium persulphate (KPS) ($K_2S_2O_8$) 5% along with Mohr's salt 1% for preventing homopolymerization and promoting free radical graft polymerization of the monomer on the substrate.

For each monomer, the application recipe includes monomer, thermal initiator (KPS) and Mohr's salt. Each monomer was evaluated at concentration of 300 g/L prepared by dissolving the monomer in CH_3OH. However, thermal initiator (5%) and Mohr's salt (1%) were dissolved in distilled water separately. Then these two solutions were pad applied separately on the cotton sample. A 140 mm × 220 mm swatch of cotton fabric was first padded with solution containing initiator and Mohr's salt at pick up of 85–90%. Then the sample was dried and padded with a monomer solution.

The cotton sample was allowed to dry. At the end, treated samples were cured at 120 °C for 3.5 min.

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

A 140 mm × 220 mm swatch of cotton fabric was immersed in a monomer solution and agitated for 3 min. Subsequently, the cotton sample was taken out of the monomer solution and allowed to dry and then cured at 120 °C for 3.5 min.

Washing durability up to 25 accelerated washes was evaluated by slightly modifying McSherry, Drake, Cooper, and Markezich (1974) method. The only modification was that the samples were washed for 2 h, which is supposedly equal to 25 accelerated washes instead of 4 h washing equivalent to 50 accelerated washes, according to McSherry et al. method.

2.5. Evaluation of fabrics

To determine the effectiveness of the monomers as a potential flame retardant, the finished fabrics were analyzed using scanning electron microscopy (SEM), thermal gravimetric analysis (TGA), burning test, and grafting efficiency.

The surface morphology of the treated and untreated samples was studied by SEM. The images were recorded on PHENOM FEI model number 800-03103-02 under vacuum. The fabric samples were first sputter coated with sputter coater EMITECH SC7620. The sputtering was done to make the samples conductive. Char from treated samples was also scanned to see the difference in surface morphology of char that resulted from burning of samples treated with different monomers.

Grafting efficiency was calculated using the following formula.

$$\text{Grafting efficiency} = \frac{W_g - W_o}{W_o} \times 100$$

where W_g is the weight of sample after grafting and W_o is the weight of sample before grafting.

The thermal decomposition profile of treated and untreated samples was assessed by TGA. Perkin Elmer Pyris 1 TGA (serial number 537N9071908) was used for this analysis. Nitrogen gas was used to purge the balance head and furnace at a flow rate of 20 mL/min. The furnace was programmed to heat from 25 °C to 800 °C at a rate of 20 °C/min.

The burning test according to ASTM D 6413-08 was used to compare the flammability of treated and untreated samples. A fabric sample of size 63 × 204 mm was mounted in a sample holder. The flame from a Terrill burner was placed at a distance of 0.75 in. from the bottom of sample. The flame was introduced to the sample for 3 s. After the flame was removed, the sample was observed for burning time, after glow and char length for both treated and untreated cotton.

3. Results and discussion

The monomers synthesized in the present work were bifunctional because they posses two vinyl groups per molecule, to enhance the % degree of grafting and hence the washing durability. The synthesis of these monomers was achieved in two steps as given in supplemental information.

3.1. Synthesis of monomers **1** and **2**

In step 1, the reaction was performed in the presence of triethylamine (Et_3N) as an acid scavenger and dichloromethane (CH_2Cl_2) as a solvent. This is an S_N2 type reaction. Triethylamine was used in excess in order to speed up the reaction by readily scavenging the acid formed during the reaction. The phosphorous containing compound was first dissolved in excess of CH_2Cl_2 and then added dropwise to the reaction mixture. In step 1, the nucleophilic attack took place via the nitrogen not the oxygen due to the strong nucleophilic nature of NH_2 group compared to the OH group in ethanolamine. The addition of phosphorous containing compound was done in slow dropwise manner to hinder the oxidation of phosphate (Zhao, 2010). At the completion of the first step, the precipitates were separated by vacuum filtration, and the filtrate was used in second step.

In the second step, acryloyl chloride pre-dissolved in excess of CH_2Cl_2 was added to a mixture of the filtrate (from the first step) and triethylamine. This reaction proceeds via the nucleophilic attack of the OH on the electrophilic carbonyl carbon of acryloyl chloride, to replace the chloride in the acid chloride. It was noticed that the addition of acryloyl chloride was the most important factor for optimizing reaction conditions. Dissolving acryloyl chloride in excess of CH_2Cl_2 and then adding this mixture to the reaction vessel (three-neck round bottom flask containing intermediate and triethylamine) dropwise controlled the rate of the reaction. Before calculating the molar ratio's of the reactants for step 2, it is important to calculate the yield of step 1. It was shown that excess of acryloyl chloride hinders the synthesis of the final product. The esterification reaction (step 2) was optimized in terms of reaction time. Excessively longer reaction time for step 2 can lead to unwanted products and shorter reaction time can result in insufficient reaction yield. Step 2 for bifunctional monomers took less time (3 h at 0 °C) than monofunctional monomers step-2 time with overnight stirring at room temperature (Tsafack & Levalois-Grützmacher, 2006).

3.2. Characterization of monomers

3.2.1. Characterization of monomer **1**

For monomer **1**, the FT-IR spectrum (cm^{-1}) (Fig. 3a) showed peaks at 3393.8 cm^{-1} (N—H Stretch), 1720.0 cm^{-1} (C═O), 1664.3 cm^{-1} (C═C), 1199.7 cm^{-1} (P═O), 1035.8 cm^{-1} and 988.8 cm^{-1} (P—O—C). The peak at 3393.3 cm^{-1} corresponds to the secondary amine (NH). According to Thomas and Chittenden (1964), the presence of organophosphorus compounds can be confirmed by the presence of P═O in the range of 1156–1287 cm^{-1}. The peak at 1199.7 cm^{-1} corresponds to the P═O, which confirms the molecular structure of monomer **1**.

The theoretical mass for the compound was 320.1029. The mass for the sodiated ion appeared at 343.1029, measured using electrospray ionization mass spectrometry (ESI-MS), which confirmed the molecular structure of monomer **1**.

3.2.2. Characterization of monomer **2**

Monomer **2** has different structure because it has —$N(CH_3)_2$ attached to phosphorus rather than —$O(C_2H_5)$ as in monomer **1**, shown in Schemes 2.2 and 2.3. Because of difference in the molecular structure of monomer **2**, it reacted differently in step-2, Scheme 2.3, and resulted in a different product with different FT-IR signatures. The FT-IR peaks (cm^{-1}) for monomer **2** appeared at 3469.5 cm^{-1} (N—H), 1721.1 cm^{-1} (C═O), 1674.9 cm^{-1} (C═O in secondary or tertiary amides), 1621.2 cm^{-1} (C═C), 1240.1 cm^{-1} (P═O), 1322.6 cm^{-1}, 1004.6 cm^{-1}, and 742.1 cm^{-1} (P—N ($CH_3)_2$).

FT-IR shows a weak peak at 1721.1 cm^{-1}, which corresponds to the carbonyl of the ester group as in monomer **1**. It showed

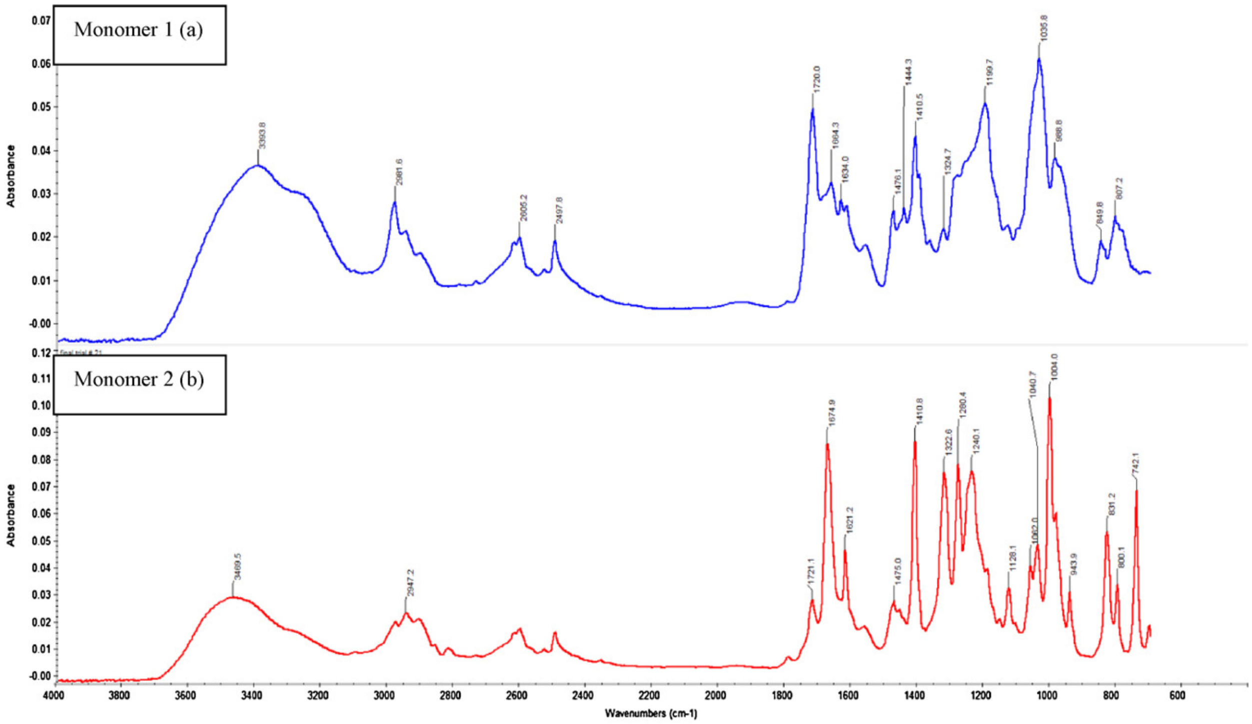


Fig. 3. FT-IR spectra of monomers **1** and **2**.

all the required peaks confirming the presence of P—N $(CH_3)_2$ vibration at 1322.6 cm^{-1}, 1004.6 cm^{-1}, and 742.1 cm^{-1} (Chittenden & Thomas, 1966). However, the FT-IR spectrum showed a strong peak at 1674.9 cm^{-1}, which indicated that the acylation step did not exclusively took place on the OH to form the corresponding ester and most of the acylation took place at the NH as shown in Scheme 2.3, which explains why the C═O peak of the ester group was weak in the case of monomer **2**.

The FT-IR spectra for monomers **1** and **2** are compared in Fig. 3. In contrast to the molecular structures of monomer **1**, the attachment of —$N(CH_3)_2$ to the phosphorous atom in monomer **2** increases the nucleophilic character of the —NH group and makes it a stronger nucleophile than that of the OH, which explains the reason for the presence of the two carbonyls of both ester and amide. However, monomer **2** can still act as a potential flame retardant.

3.3. *P═O absorption frequency and flame retardancy*

According to Kandola, Horrocks, Price, and Coleman (1996) cotton treated with phosphorus-based flame retardants catalyzes the dehydration of cellulose at temperature lower than the decomposition temperature of cellulose by the formation of phosphoric acid. This dehydration results furnished thermally stable double bonds in the cellulose chains, which produces significant char yield. Further investigations into the chemical structure dependence of phosphorus compound on conjugated double bond formation were carried by Katsuura and Inagaki (Inagaki, Tomiha, & Katsuura, 1974), which demonstrated that the formation of conjugated double bonds in cellulose chains depends on the electron density of phosphoryl group. This was further supported by FT-IR analysis of the vibrational frequency of P═O, which was consistent with the experimental results. Hence, it could be concluded that there is a strong relationship between the flame retardancy and the presence of P═O stretching frequency in the treated fabric. The stronger the P═O vibrational frequency, the better the flame retardancy.

Similar results were observed in the present study as well. The P═O vibrational frequencies for monomers **1** and **2** were 1199.7 cm^{-1} and 1240.1 cm^{-1}, respectively. In the case of monomer **2**, phosphoryl group has higher electron density due to the electron donating nature of nitrogen compared to oxygen in monomers **1**. Hence, it could be expected that monomer **2** would show better flame retardancy than monomers **1**. Moreover, it was reported that the presence of electron withdrawing groups such as cyano and carboxyl has an adverse effect on the flame retardancy function of phosphoryl group (Inagaki, Nakamura, Asai, & Katsuura, 1976).

3.4. *Evaluation of fabrics*

The treated fabrics were evaluated by SEM, grafting efficiency, TGA, and vertical burning test.

3.4.1. *Scanning electron spectroscopy (SEM)*

Surface morphology can provide useful information about the surface morphology for the substrates following any chemical changes on the surface. To address any surface changes following the monomer applications, SEM analysis was performed on both treated and untreated cotton samples. Moreover, SEM images of the charred samples were also analyzed to determine the efficiency of each monomer as a flame retardant. The SEM images showed remarkable difference in the treated and un-treated cotton samples as shown in Fig. 4. These SEM images showed clearly the presence of a coating on treated samples, which confirmed the polymerization of the monomers.

3.4.2. *Grafting efficiency*

Table 1 shows the grafting efficiency obtained for each monomer. The grafting efficiency obtained by the exhaust method was much lesser than that of the padding method.

3.4.3. *Thermogravimetric analysis*

TGA results for treated and untreated cotton are shown in Fig. 5. It was shown before (Kandola et al., 1996; Tsafack &

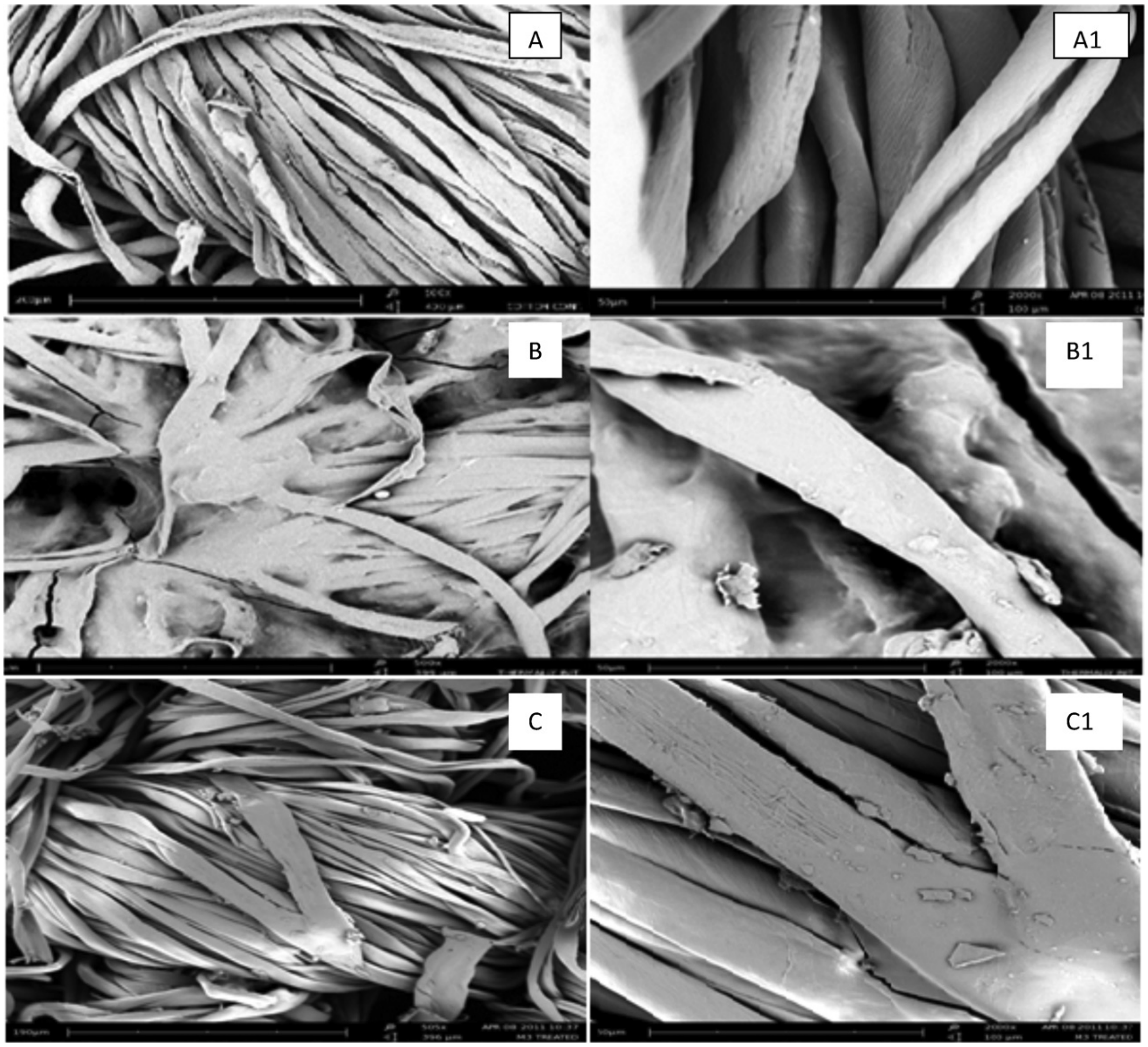


Fig. 4. SEM monographs (A and A1) un-treated cotton, and (B and B1), (C and C1) cotton treated with monomers **1** and **2** (unwashed and exhaust method) at 500× and 2000× magnification, respectively.

Levalois-Grützmacher, 2006) that cotton treated with phosphorus-based flame retardants starts decomposing at lower temperature than control cotton, due to phosphoric acid catalyzed hydrolysis, which eventually produces more char.

In the present work, the control sample degraded over the range 298–399 °C with 80% weight loss with the maximum rate of decomposition begininning at 378 °C. The % weight left beyond 399 °C was less than 20%, and the % weight left at 800 °C was less than 9%. On the other hand, the cotton treated with monomer **1** and monomer **2** degraded in the range 230–320 °C with only 40% weight loss with the maximum rate of decomposition at 278 °C. Also, the weight left at 800 °C was more than 25% for monomer **1** and 18% for monomer **2** treated samples, compared to less than 9% for cotton control.

Table 1
Grafting efficiency for monomers **1** and **2**.

Monomer	Grafting efficiency Exhaust method (50% o.w.f.) (without washing)	Grafting efficiency Padding method (300 g/L) (without washing)	Grafting efficiency Padding method (300 g/L) (after 25 accelerated washes)
1	25%	46%	12%
2	17%	43%	23%

Previous research (Tsafack & Levalois-Grützmacher, 2006) showed that for a polymer to be effective as a flame retardant it should have a decomposition temperature close or lower than that of the substrate, in order to interfere with the burning process, which is consistent with the thermal behavior of monomers **1** and **2**, as they both exhibited decomposition temperature lower than that of the untreated cotton. Furthermore, the weight loss for the untreated cotton in the decomposition range was due to the formation of flammable volatiles. However, in the case of cotton treated with monomers **1** and **2**, the weight loss decreased by 40%, potentially due to the formation of less volatiles and more char. The char residues left at 800 °C for cotton treated with monomers **1** and **2** were 20% and 10% more than the untreated cotton, respectively. Hence, it can be stated that the treatment with monomers **1** and **2** rendered cotton remarkably thermally stable. TGA thermograms were similar for cotton treated by the exhaust and padding methods. Except for monomer **2**, char residue at 800 °C was higher for the padding method compared to the exhaust method.

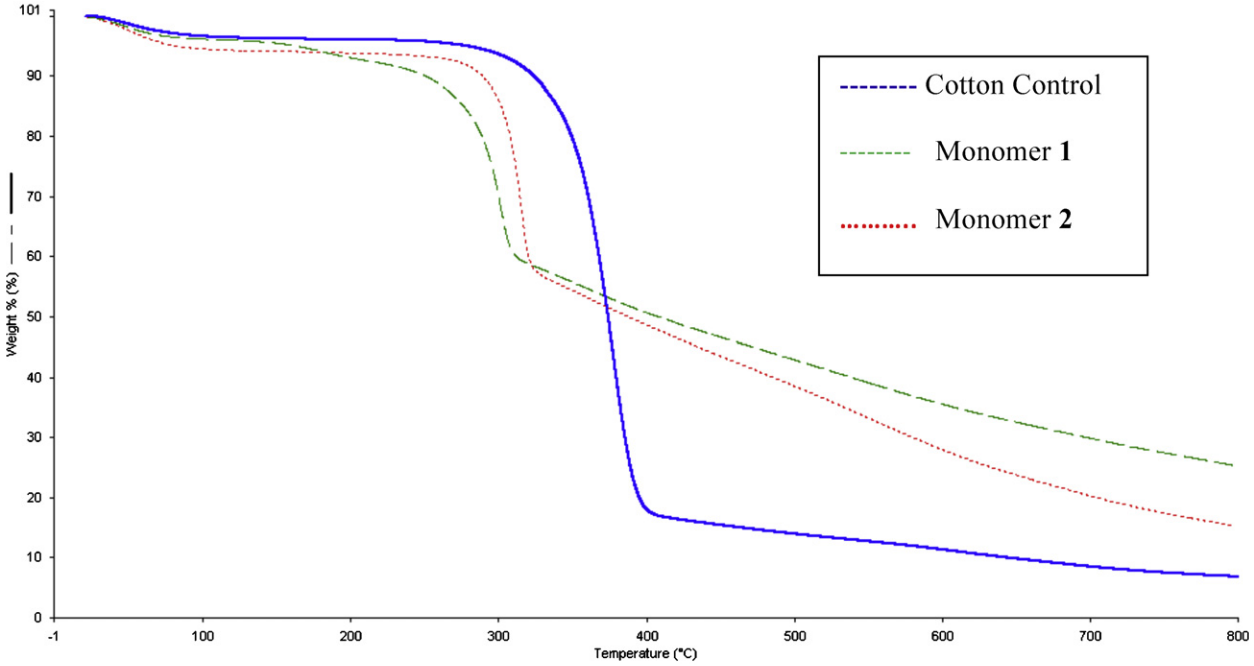


Fig. 5. TGA graphs thermally grafted cotton monomers **1** and **2** (padding method).

3.4.4. Burning test

Vertical flame test was performed to compare and evaluate the flammability of the treated and untreated cotton samples. A 63 mm × 204 mm sample of cotton treated with monomer **1**, monomer **2** and untreated cotton was used for this test. Table 2 shows the results of the burning time for each of the treated samples and the control.

It can be seen from Table 2 that the burning time decreases remarkably for the treated samples both by the exhaust and padding methods. Burning time can be attributed to the performance of each monomer such that the shorter the burning time the more efficient the monomer as a flame retardant and in char formation, which is consistent with previous studies (Alongi, Ciobanu, & Malucelli, 2011; Hobart & Rowland, 1978). The padding method gave better results than the exhaust method. Thus burning test results were consistent with the grafting efficiency obtained as shown in Table 1.

The underlying reason for such burning behavior was linked to the lower decomposition temperature for the treated sample. According to Hobart and Rowland (1978), lower decomposition temperature for the treated cotton combined with less available fuel due to the presence of flame retardant causes the flame to propagate quickly in search of combustible fuel, which was observed during the burning test for monomers **1** and **2**. For the treated cotton, the flame runs through the whole sample very quickly. However, the main difference among the treated and untreated cotton was the after glow. There was absolutly no after glow for the treated samples, where the untreated cotton fabric burns vigrously, with much stronger flame and flame higher from the surface of the sample with high heat of combustion and no char at all. However, for the treated samples, the flame was weak, with very little heat of combustion and significant charring. The increase in the char for the treated cotton was very high so that the burnt samples kept their structual integrity. The results of the burning tests are summarized in Figs. 6 and 7 for visual assessment of the char left both for exhaust and padding methods respectively. Monomer **2** (C) produced greater char compared to monomer **1**, applied by the exhaust method. For monomers applied by the padding method, unwashed samples for monomers **1** (E) and **2** (G) furnished self extinguishing cotton, showing better performance compared to the exhaust method results, which is consistent with the results obtained from grafting efficiency and burning time. After washing, the flame retardancy was reduced significantly as shown by samples (F) and (H) due to decrease in grafting efficiency, and increase in burning time (close to untreated cotton). Hence, more work needs to be done to enhance the durability of the flame retardant finish on cotton. However, these results were promising and can be improved potentially by incorporating a cross linking agent.

Table 2
Burning time for treated and untreated cotton based on the vertical flame test.

Monomer	Burning time (s) Exhaust method	Burning time (s) Padding method (without washing)	Burning time (s) Padding method (after washing)
Untreated cotton	23.9	23.9	N/A
Monomer **1**	13.4	3[a]	21
Monomer **2**	8.5	4[a]	15

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

[a] Self extinguishing.

The increase in char formation for the cotton samples treated with phosphorus-based flame retardant is consistent with the proposed condensed phase mechanism. The presence of phosphorus-based flame retardant alters the pyrolysis path of the substrate by lowering the decomposition temperature, eventually reducing the formation of gaseous combustibles and favors the formation of char, which was confirmed using the TGA results shown in Fig. 3, and the flame test (Figs. 6 and 7) results. Franklin and Rowland (1979) in a study for cotton treated with seven different commercially available flame retardants concluded similar results. According to Franklin and Rowland, chemical processes occurring during the pyrolysis of untreated and treated cotton are similar. For flame retardant treated cotton, pyrolysis products were formed at lower temperatures. These observations were interpreted as an indicator that the presence of a flame retardant finish enhances all the pyrolysis processes, dehydration, and char formation at the expense of processes leading to the formation of combustible

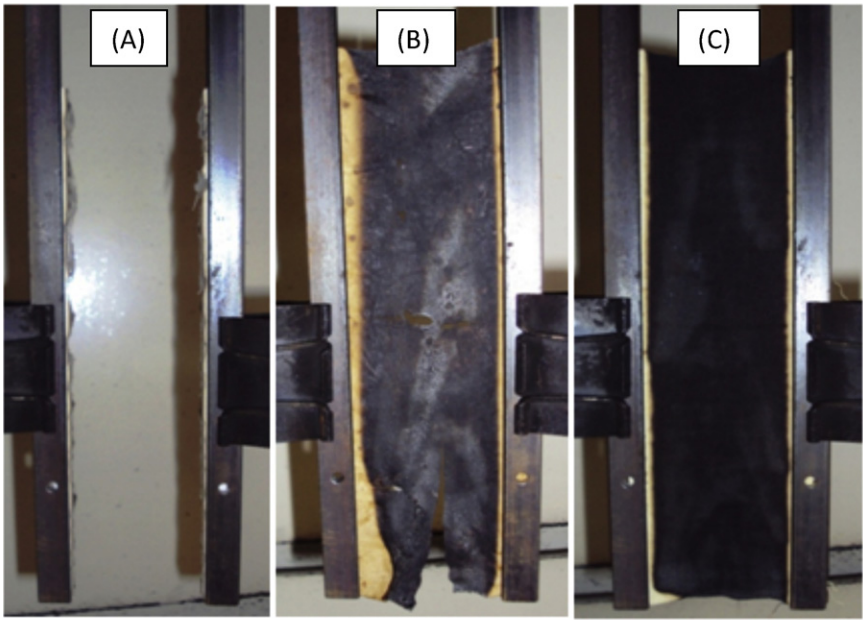


Fig. 6. Char residue for (A) untreated, (B) monomer **1** and (C) monomer **2** (exhasut method) treated cotton.

volatiles that lead to flamed combustion. This could be the underlying reason for shorter burning time and higher amount of char except Fig. 7(E) and (G) where the presence of monomers had made the cotton self extinguishing.

3.4.5. *Surface morphology of char*

After the burning test, it was observed that all the treated samples formed chars as compared to no char left at all for untreated cotton. Char from samples treated with different monomers were different in appearance. The surface morphology of char is related to the performance of the relevant flame retardant. It was shown previously (Hendrix et al., 1972) that more effective flame retardants left a noticeable coating on the surface of char which not only serves as a barrier to heat but also keep the char firm and intact. The surface scans of the char left from samples treated with monomer **1** and monomer **2** are shown in Fig. 8 at 500× and 2000× magnification.

In Fig. 8, char formed from cotton samples treated with monomer **1** (A, A1) and monomer **2** (B, B1) show a coating which is continuous and all over the surface of fibers. Char from monomer **2** (B, B1) treated samples was more firm and intact as compared to char from monomer **1** (A, A1) treated sample, which can be seen from Fig. 8. Due to extra nitrogen attached to phosphorus in monomer **2** as compared to oxygen in monomer **1**, electron density on phosphorus of monomer **2** is much higher. Hence, it can be concluded that higher the electron density on phosphorylating group in flame retardant monomer higher

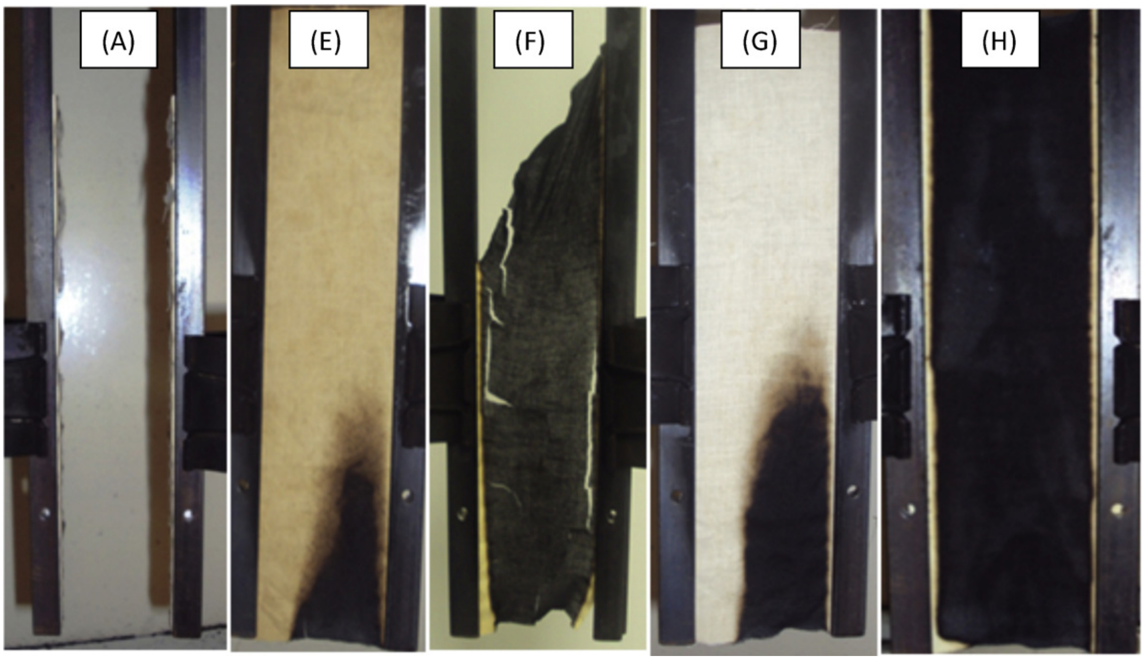


Fig. 7. Char residue for (A) untreated, (E and F) monomer **1** (G and H) monomer **2** (padding method) treated unwashed and washed samples, respectively.

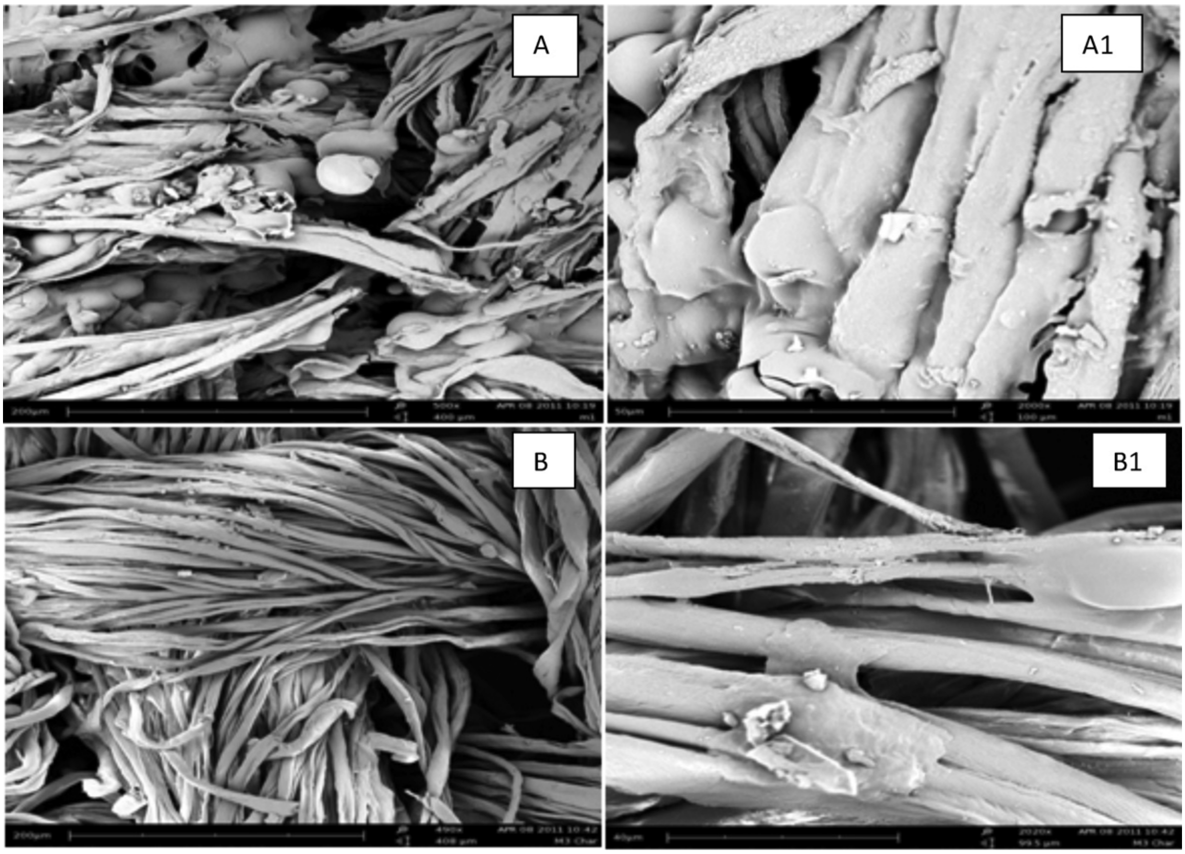


Fig. 8. SEM images of char (A and A1), and (B and B1) cotton treated with monomer **1**, and monomer **2** (exhaust method), at 500× and 2000× magnification respectively.

will be its ability to form coating and better will be its flame retardancy.

This might be the underlying reason for better synergistic effect of P–N in monomer **2** as compared to monomer **1**.

4. Conclusion

The performance of monomers **1** and **2** was evaluated as a flame retardant using TGA, grafting efficiency and vertical flame test. The TGA results collected for monomer **1** and monomer **2** were very similar for the exhaust and padding methods. The burning test results for monomer **1** showed less char length than monomer **2** in the case of padding method. However, the char formation after washing, firmness of char and presence of even coating in SEM images for monomer **2** makes it superior than monomer **1** in performance. Monomer **2** demonstrated the shortest burning time and more char formation even at low grafting efficiency compared to monomer **1** for the exhaust method. The superior performance of monomer **2** can be attributed to the presence of one more nitrogen atom, which increases the P–N synergistic effect, producing more thermally stable and highly cross linked matrix residue, which holds the cellulose fragments in the condensed phase for longer time, thus furnishing more and integrated charring. Further research is underway to design and synthesize more efficient halogen-free flame retardant systems for cotton and more effective grafting methods.

Acknowledgements

The authors are grateful to the Fulbright Program and the Textile Engineering, Chemistry, and Science Department at NC State for financially supporting this project.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.carbpol.2012.09.081.

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