Gamma-Induced Polymerization and Grafting of a Novel Phosphorous-, Nitrogen-, and Sulfur-Containing Monomer on Cotton Fabric to Impart Flame Retardancy

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ABSTRACT: Diethyl (acryloyloxy) ethylthiophosphoramidate (DEAETPN), a novel phosphorus-, nitrogen-, and sulfur-containing monomer, was synthesized in a two-step reaction. The monomer was polymerized and grafted onto cotton fabric by gamma radiation method. Effect of methyl methacrylate (MMA) on percentage grafting (Pg) of DEAETPN on cotton fabric was studied, and it was found that small amount of MMA increases Pg on cotton fabric. The monomer, polymer, and the grafted cotton fabric were characterized by spectroscopic and thermogravimetric techniques. Flame retardant property of the modified cotton fabric was studied by the Shirley Manual Flammability Tester. The flame retardancy of cotton-*g*-DEAETPN by gamma radiation method and living radical polymerization method was compared. J Appl Polym Sci 125: 1506–1512, 2012

Key words: gamma polymerization; flame retardant; modified monomers; cotton fabric

INTRODUCTION

The persistent fire resistance of textiles is an unsolved problem, and it even became more problematic when textiles such as cotton fabric (LOI = 18.4%) are concerned. Halogen-free phosphorus-based compounds are the flame retardants most frequently used on cotton textiles. Numerous studies[1–3] have shown that they reduce the formation of flammable volatiles and catalyze char formation. The most common method of incorporation of this desired functionality (e.g., phosphorous and nitrogen) in polymer involves the postpolymerization or the postgrafting reactions.[4–8] These methods have lot of advantages but suffer from the inherent property of low reactivity of the polymers that lowers the amount of phosphorus and nitrogen introduced on the polymer backbone. According to the literature,[9] the amount of char residue and flame retardancy increases with the phosphorus content added to the polymer. Furthermore, the postgrafting reaction damages the original structure of the polymer. To overcome these limitations, synthesis of new monomers with desired functionality and their polymerization and grafting is of great importance to propose original materials of target applications.[10–14]

Various phosphorous- and nitrogen-containing monomers were synthesized and grafted on cotton fabric and studied for their flame retardant property.[15–17] It was observed that phosphorous and nitrogen together show synergic effect to achieve flame retardancy. It will be a win–win situation if the addition of a new element to these basic elements increases flame retardancy. Recently, we have synthesized and grafted a novel phosphorus-, nitrogen-, and sulfur-containing monomer diethyl (acryloyloxy) ethylthiophosphoramidate (DEAETPN) on cotton fabric by living radical polymerization method using benzyl *N*,*N*-diethyl thiocarbamate as suriniferter and studied its flame retardant property.[18] It was observed that all these elements increase the flame retardancy of cotton fabric. In the present work, grafting of DEAETPN has been carried out by use of gamma radiations.

The use of high-energy radiations, for example, gamma radiations for creating active sites has revolutionized the field of polymerization and graft copolymerization.[19,20] This method has advantages over the method of initiation, which involves a tedious task of purification of the graft from the catalyst while the former method is cleaner in this respect. In this method, the backbone (specially polymers containing labile hydrogen atoms) or monomer or the mixture irradiated with high energy radiation leads to the formation of peroxides and hydroperoxides, which can be used in subsequent reactions for initiating the polymerization of a monomer thus leading to the formation of graft copolymers.

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Despite of a lot of advantages associated with functionalized monomer synthesis and the gamma-radiation-induced polymerization/grafting method, no attempt was found in literature where phosphorus-containing monomers were polymerized or grafted by the gamma-induced polymerization method. Further, despite of a number of phosphorus- and nitrogen-containing monomers (amides as well as esters), no monomer other than DEAPTN having phosphorus, nitrogen, and sulfur was found in the literature.

In this work, therefore, a novel phosphorus-, nitrogen-, and sulfur-containing monomer DEAETPN was synthesized, polymerized, and grafted onto cotton fabric by the gamma radiation polymerization method.

EXPERIMENTAL

Materials

Commercial grade reagents and solvents were used. All reagents and solvents were purified before use. Ethanol amine, benzoyl chloride, methyl methacrylate (MMA), thionyl chloride, and benzyl chloride were distilled before use. Diethyl thiochlorophosphate and acylic acid were used as received.

Cotton fabric with the following specifications 124 g/m^2, peaks, and end 55/in and 35/in were used. The fabric was washed thoroughly with a soap solution followed by extensive washing with water. The washed fabric was further extracted with Na_2CO_3, water, and hexane in a Soxhlet apparatus to remove any remaining waxy material and other impurities. The samples were removed from the Soxhlet and dried. Samples (3 cm $\times$ 4 cm) were prepared by sewing from all the ends with the thread from the same fabric to avoid any loss of weight during the reaction. The cotton samples were then dried under vacuum for constant weight.

Techniques

Gamma chamber-900, supplied by BARC, Trombay, Mumbai, containing Co^{60}, 2000 ci at a constant dose of 2.052 kGy/h, was used as a source of gamma radiations. ^{1}H-NMR, ^{13}C–NMR, and ^{31}P spectra were recorded on a Bruker AV-400 FT-NMR spectrometer in $CDCl_3$ at 25°C. FTIR was obtained by using the Perkin–Elmer spectrometer using KBr pressed pellets. Thermogravimetric analysis (TGA) was carried out in a nitrogen atmosphere on Rheometric scientific Thermogravimetric Analyzer at a heating rate of 20°C/min under a nitrogen atmosphere. Qualitative determination of the flammability behavior of the fabric was carried out by burning the samples, placed vertically over the candle flame, whereas quantitative determination of flammability of all the samples was carried out on the Shirley Manual Flammability Tester, which follows the relevant BS 5438: 1989 standard tests.

Synthesis and characterization of monomer

The monomer was synthesized in three steps with ethanol amine as the starting material. The detailed procedure and characterization of the monomer synthesized have been reported in our earlier work.[18]

Polymerization of DEAETPN

A known amount of monomer DEAETPN (1.87 $\times$ 10^{-3} to 11.22 $\times$ 10^{-3} moles) was dissolved in known quantity of toluene (5–15 mL) in a flask and placed in the gamma chamber for irradiation for desired dose (4.104–69.768 kGy) at constant dose rate of 2.052 kGy/h. After the stipulated time period, the solvent was removed from the reaction mixture, and polymer was dissolved in minimum quantity of dichloromethane and precipitated out by slow addition of petroleum ether. The percentage conversion of polymerization, Pc, was calculated from the weight of monomer taken and weight of polymer formed.

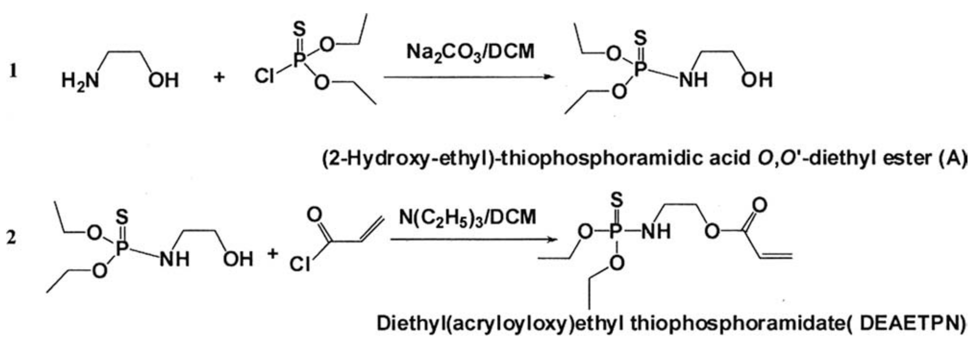
$$\text{Percent Conversion (Pc)} = \frac{\text{Weight of polymer formed}}{\text{Weight of monomer used}} \times 100$$

Grafting of DEAETPN on cotton fabric

Dried and weighed cotton fabric sample (3 cm $\times$ 4 cm) was suspended in toluene (3–12 mL) in a flask. A definite amount of the monomer DEAETPN (1.87 $\times$ 10^{-3} to 11.22 $\times$ 10^{-3}) was added to the flask and placed in the gamma chamber for irradiation at a constant dose of 2.052 kGy/h for total dose of (10.26–73.87 kGy). After the stipulated time of reaction, the fabric was removed from the reaction mixture and washed thoroughly with acetone to remove any homopolymer formed during the reaction. Monomer and homopolymer are soluble in acetone, so chances of physical adsorption on cotton fabric could be eliminated. The grafted fabric free from homopolymer was dried and weighed to a constant weight. The percentage of grafting (Pg) was calculated from the increase in the initial weight of the cotton fabric.

$$\text{Percent Grating} = \frac{W_1 - W_0}{W_0} \times 100,$$

where W_0 and W_1 are the initial weight of the original cotton fabric and weight of the grafted cotton



Scheme 1 Synthesis of monomer.

fabric after complete removal of the homopolymer, respectively.

Flammability test

Quantitative determination of flammability of all the samples was carried out on the Shirley Manual Flammability Tester, which follow the relevant BS 5438: 1989 standard tests. A sample size of 80 mm × 200 mm was prepared, and the test specimen was placed on the pins of the appropriate specimen holder, making sure that the pins pass through the points marked off from the template and the material is resting on blunt pins. The distance between the tip of the burner and bottom of specimen was kept at 20 mm. The burner after lighting was preheated for 10 min and a flame height of 40 ± 2 mm was adjusted using the gas flow fine control valve. The flame was applied to the bottom edge of the test specimen for the minimum time at which the specimen catches the fire. The time is noted and the application flame is continued till 12 s.

RESULTS AND DISCUSSION

Synthesis of DEAETPN

The synthesis of DEAETPN was developed in our laboratory and was carried out in two steps (Scheme 1).

Effect of various reaction parameters on percentage conversion and percentage grafting

The effect of various parameters such as monomer concentration, amount of solvent and total dose on percentage conversion, (Pc) and percentage grafting (Pg), has been studied, and the results are presented in Tables I and II, respectively. It is observed from the Table that the maximum Pc (46%) was obtained using 5.61×10^{-3} moles of DEAETPN, 10 mL of toluene at 69.768 kGy of total dose, whereas maximum Pg (32%) was obtained using same amount of the monomer and toluene but at higher total dose (73.87 kGy).

TABLE 1
Effect of Various Reaction Parameters on Percentage Conversion (Pc) of DEAETPN

S.No	[DEAETPN] $\times 10^3$ Mole	Solvent (mL)	Total dose (kGy/h)	Pc (%)
1	1.87	10	10.26	4.0
2	3.47	10	10.26	15.0
3	5.61	10	10.26	24.0
4	9.35	10	10.26	19.0
5	11.22	10	10.26	12.0
6	5.61	5	10.26	16.5
7	5.61	8	10.26	20.0
8	5.61	12	10.26	21.3
9	5.61	15	10.26	16.5
10	5.61	10	4.10	0
11	5.61	10	20.52	38.0
12	5.61	10	30.78	44.0
13	5.61	10	41.04	44.0
14	**5.61**	**10**	**69.77**	**46.0**

TABLE II
Effect of Various Reaction Parameters on Percentage Grafting (Pg) of DEAETPN on Cotton Fabric

S.No	[DEAETPN] $\times 10^3$ Mole	Solvent (mL)	Total dose (kGy/h)	Pg (%)
1	1.87	10	20.52	4.0
2	3.47	10	20.52	30.8
3	5.61	10	20.52	9.5
4	9.35	10	20.52	18.33
5	11.22	10	20.52	16.7
6	5.61	5	20.52	5.3
7	5.61	8	20.52	17.1
8	5.61	12	20.52	17.7
9	5.61	15	20.52	16.0
10	5.61	10	10.26	0
11	5.61	10	17.04	12.0
12	5.61	10	30.78	22.0
13	5.61	10	49.25	27.0
14	**5.61**	**10**	**73.87**	**32.0**
15	5.61	10	92.5	32.0

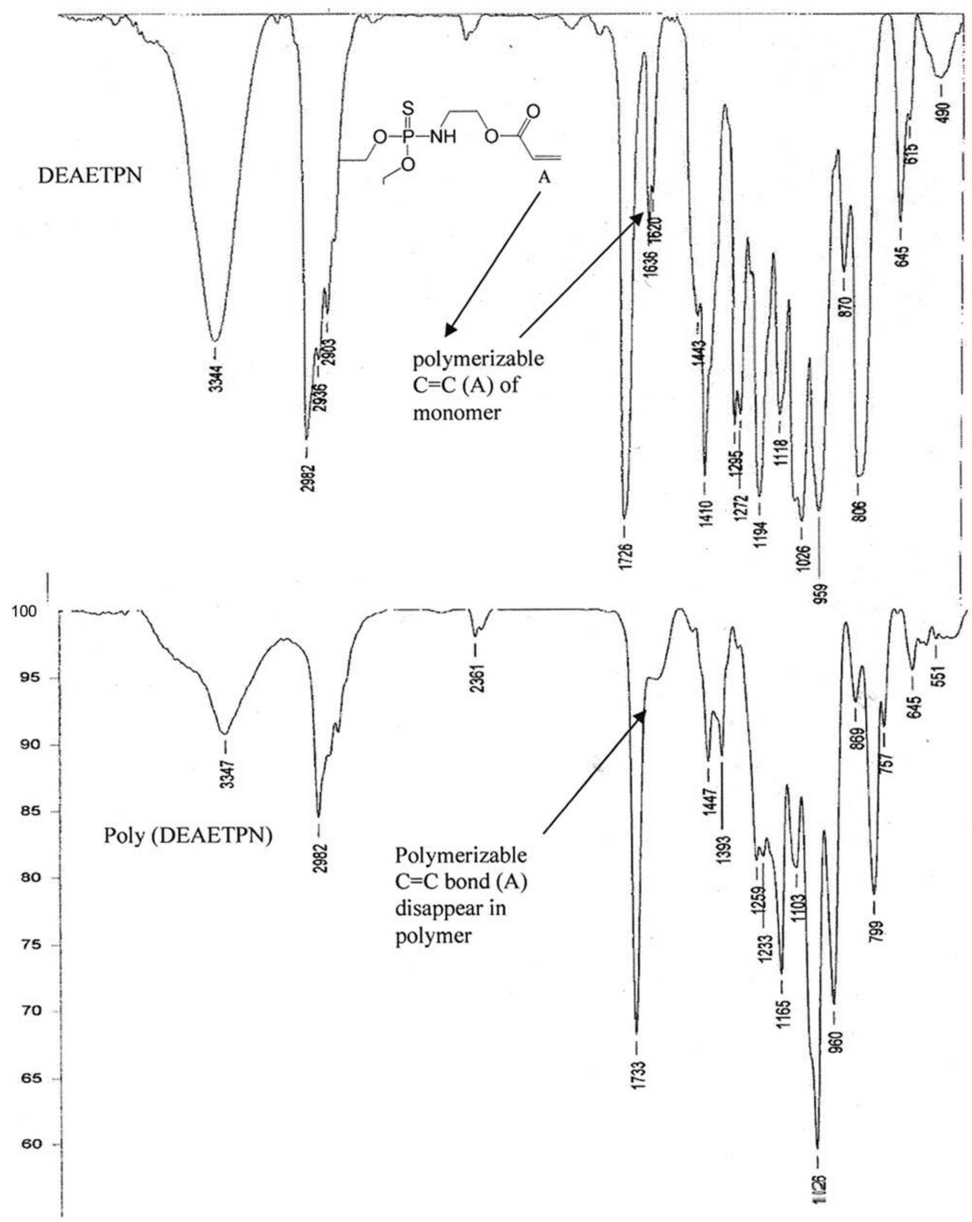


Figure 1 Comparison of the FTIR between monomer and polymer.

Beyond the total dose, Pc remains almost constant but Pg starts decreasing.

Effect of [MMA]

Grafting of DEAETPN on cotton fabric has been studied in the presence of MMA in the reaction mixture. It was found that the percentage of grafting of DEAETPN increases by addition of a small amount of MMA in the reaction mixture. The percentage of grafting of DEAETPN in the presence of 1×10^{-4} mol of MMA increases to 41% under optimum conditions. The increase in the percentage of grafting in the presence of MMA may be due to the reason that MMA being sterically less crowded reacts with DEAETPN to give growing co polymeric chain that reacts with the active site on the cotton fabric to give higher percent grafting.

Characterization of the poly (DEAETPN) and cotton-*g*-DEAETPN

The polymers formed have been characterized by spectroscopic methods including FTIR, ^{1}H-NMR, and TGA.

Spectroscopy

FTIR, ^{1}H-NMR, and ^{31}P spectra of poly (DEAETPN) were compared with monomer DEAETPN. In the FTIR spectrum of poly (DEAETPN), the disappearance of band at 1636 cm^{-1} (Fig. 1) corresponds to νC=C (A) of polymerizable acrylic unit, and in the

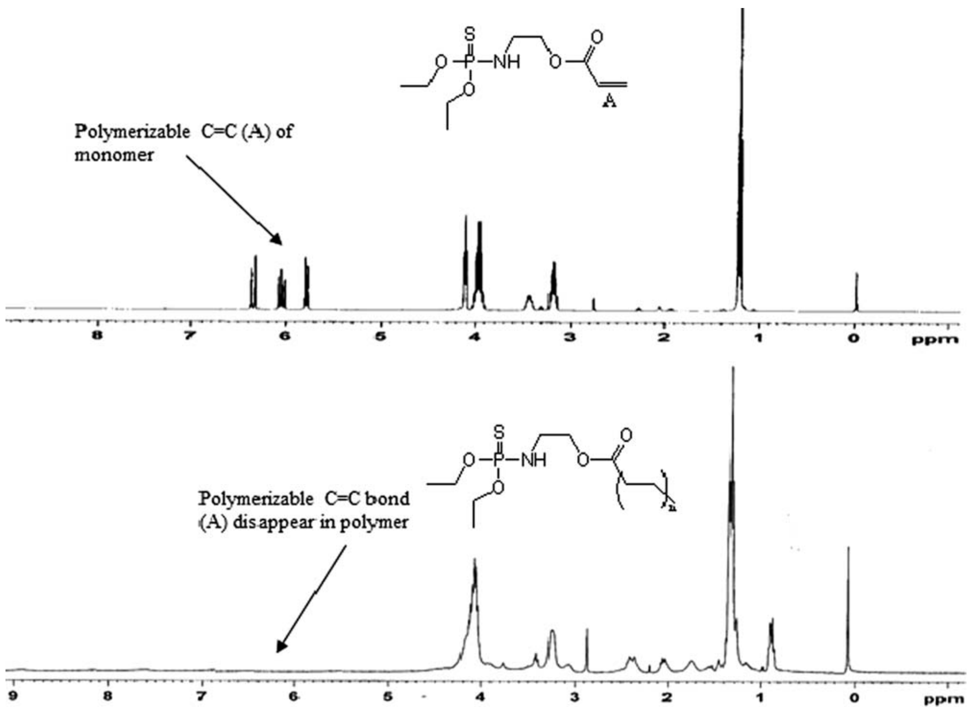


Figure 2 Comparison of the ^{1}H-NMR between monomer and polymer.

^{1}H-NMR spectra, disappearance of peaks between δ 6.37 and 5.78 (Fig. 2), which corresponds to C=C was observed. Small shift in the values of other peaks in the FTIR and ^{1}H-NMR was also observed. The ^{31}P-NMR spectra also show a small shift in peak from δ 71.66 in the monomer to 71.75 in poly (DEAETPN).

The FTIR spectra of cotton-*g*-DEAETPN show prominent peaks due to hydroxyl groups of cotton cellulose at 3445 cm^{-1} (intermolecular H-bonding), 2819 cm^{-1} (νC—H str.), 1417 cm^{-1} (νC—H def.), 1152 cm^{-1} (anti sym bridge νC—O—C), and additional band at 1727 cm^{-1} corresponding to carbonyl stretching vibration of DEAETPN grafted onto cotton. The presence of additional bands confirms the graft copolymer of cotton fabric with DEAETPN through covalent bonding.

Themogravimetric analysis and the flame retardant property

Primary thermograms of poly (DEAETPN), gray cotton, cotton-*g*-poly (DEAETPN), and cotton-*g*-poly (DEAETPN-*co*-MMA) are presented in Fig. 3, respectively, and the thermal data are presented in Table III. It is observed from the thermogram of gray cotton that decomposition takes place in single stage, while poly (DEAETPN), cotton-*g*-poly (DEAETPN), and cotton-*g*-poly (DEAETPN-*co*-MMA) undergo double stage decomposition. The initial decomposition temperature (IDT) values of poly (DEAETPN), cotton-*g*-poly (DEAETPN), and cotton-*g*-poly (DEAETPN-*co*-MMA) (259.0, 305.0, and 291.7°C, respectively) and the respective final decomposition temperature (FDT; 264.0, 353.7, and 313.9°C) are lower than that of the gray cotton fabric (342.8 and 387.9°C, respectively). The first stage of decomposition of poly (DEAETPN) begins at 257.3°C and continues up to 263.6°C with only 30% of the weight loss within a temperature range of 6.3°C. It remains constant up to 267.9°C from where the second stage of decomposition begins. It is further observed that the rate of decomposition is very slow. The residue left is 30%. Thus, it becomes evident that phosphorus, nitrogen, and sulfur as elements in the polymer

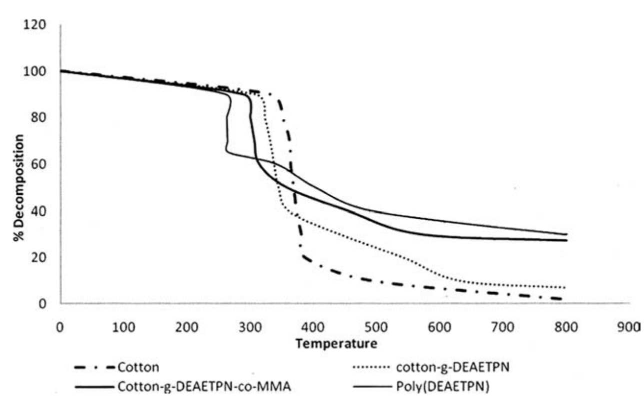


Figure 3 Primary thermogram of poly(DEAETPN), cotton, cotton-*g*-poly (DEAETPN), Cotton-*g*-poly (DEAETPN and MMA).

TABLE III
Primary Thermographs of Poly(DEAETPN), Cotton-*g*-poly(DEAETPN), and Cotton-*g*-poly (DEATPN-*co*-MMA)

S. No.	Sample	IDT (%)	FDT (%)	DT (°C) at every 10% weight loss									Residue left (%)
				10%	20%	30%	40%	50%	60%	70%	80%	90%	
1	Poly (DEAETPN)	259.0	264.0	260.1	262.5	263.6	340.9	402.8	492.3	790.0			30.8
2	Gray cotton	333.3 (10.65%)	387.9 (82.84%)	331.0	351.0	362.1	363.6	368.6	373.0	380.6	387.2	494.2	1.9
3	Cotton-*g*-MMA	374.4	430.0	342.9	377.8	390.1	397.7	404.0	409.7	415.5	422.4	446.6	4.1
4	Cotton-*g*-DEATPN	308.2	354.4	308.4	322.7	331.1	337.4	344.5	361.0	443.2	544.2	637.5	7.1
5	Cotton-*g*-DEATPN and MMA	293.7	324.3	289.1	299.6	306.0	313.7	357.8	445.5	571.5			27.8

provide high stability toward high temperature variation.

The first stage of decomposition of cotton-*g*-poly (DEAETPN) lies between 312.9 and 353.7°C during which 60% of weight is lost. The decomposition is fast up to 50% weight loss from where the loss in weight occurs with increasing temperature difference and continues to increase during second stage of decomposition (353.7–637.0°C). The fabric is stable up to 637.5°C where 10% of residue is left. It is observed from the figure that the decomposition of cotton-*g*-poly (DEAETPN-*co*-MMA) during the first stage of decomposition (291.7–313.9°C) is fast up to 40% weight loss with a small temperature difference between each 10% weight loss. Beyond 313.85°C from where begins the second stage, the rate of decomposition becomes slow with increasing temperature difference between each 10% weight loss. The second stage continues up to 571.5°C and the percent residue left (30%) is much higher. In comparison to the grafted fabric, the percent residue left in the case of gray cotton fabric is only 1.9%.

From the thermal data, it is thus observed that IDT of both cotton-*g*-poly (DEAETPN) and cotton-*g*-poly (DEAETPN-*co*-MMA) is lower, and the grafted polymeric chains start decomposing before the raw material and form a protective layer on cotton fabric, which will inhibit the spreading of the flame. This is further substantiated by the increased amount of the residue left in the case of the grafted fabric in comparison with the gray fabric. Thus, it is evident that grafting improves on the thermal behavior of cotton fabric.

Flammability test

Qualitative determination

When the fabric samples were burnt with the direct flame, it was observed that untreated cotton fabric burnt immediately with negligible ash content, whereas the cotton-*g*-poly (DEAETPN0, and cotton-*g*-poly (DEAETPN)-*co*-MMA burnt much slower than gray cotton.

Quantitative determination

The flammability behavior of gray cotton fabric, cotton-*g*-poly (DEAETPN), and cotton-*g*-poly (DEAETPN-*co*-MMA) was tested on the Shirley Manual Flammability Tester using the standard BS 5438: 1989 standard test. The results are presented in Table IV and were compared with grafted cotton by living radical polymerization method.[18] The after glow favors the improvement in the inhibition posed to the flame to spread. It is observed from the table that after the flame was applied to the sample for 12 s, all the samples burnt completely; however, the time taken for complete burning and after glow temperature was increased when compared with gray cotton. The maximum ash content was also observed to increase from grey cotton fabric (0.02 g). It was further observed that the cotton fabric grafted with phosphorus-, nitrogen-, and sulfur-containing monomers maintained the weaved structure of the fabric after burning indicating that fabric attains stability and strength when grating toward burning phenomena. The time taken for complete burning after glow

TABLE IV
Results of Vertical Flammability Tests for Gray, Cotton-*g*-poly(DEAETPN), Cotton-*g*-poly (DEATPN-*co*-MMA)

S. No.	Type of sample	Time of flame (s)	% Grafting A(B)	Time to complete burn (s) A(B)	After glow (s) A(B)	Ash content (g) A(B)
1	Untreated cotton	12	0(0)	19(19)	10(10)	0.02(0.02)
2	Cotton-*g*-poly (DEAETPN)	12	32(21)	46(41)	86(78.24)	0.140(0.119)
3	Cotton-*g*-poly (DEAETPN-*co*-MMA)	12	41(30)	54(48)	94(85)	0.234(0.197)

[a]Polymerization by gamma radiation method.
[b]Polymerization by living radical method.

time and ash content of gamma grafted cotton fabric was observed to be better than living radical polymerization method as indicated by Table IV. The improvement might be due to higher degree of grafting when compared with living radical polymerization method. Thus, grafting by gamma radiation method and living radical polymerization method in general improves the flammability behavior of cotton, especially in the case when the monomer contains phosphorus and sulfur element along with nitrogen rending synergistic effect toward imposing inhibition to the propagation of the flame.

Comparison between living radical grafting and gamma-induced grafting of DEAETPN on cotton fabric

Gamma-induced grafting method was compared with living radical grafting method. In living radical grafting method, surface iniferter moiety (benzyl *N*,*N*-diethyl thiocarbamate) capable of initiation, chain transfer, and termination (ini + transfer + termination) was introduced on cotton fabric.[18] The monomer was grafted onto cotton fabric by the living radical polymerization method using benzyl *N*,*N*-diethyl thiocarbamate as sur iniferter. Both the methods of grafting have their own advantages. Living radical polymerization gave homogeneous grafting on the whole cotton surface with no change in the color of cotton fabric, whereas during gamma radiation method, the color of the fabric becomes slightly yellowish. This may be due to the higher Pg obtained in gamma radiation method.

The improvement in flame retardant property was also observed with gamma-induced polymerization and living radical polymerization method. The improvement also attributed to higher Pg in case of gamma radiation method.

CONCLUSIONS

A novel phosphorus-, nitrogen-, and sulfur-containing monomer, DEAETPN, was synthesized, polymerized, and grafted on cotton fabric by gamma radiation method. The qualitative and quantitative estimation indicates that flame retardant property of the polymer has been increased with grafting.

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