Graft Copolymerization of Nitrogen- and Phosphorus-Containing Monomers onto Cellulosics for Flame-Retardant Finishing of Cotton Textiles

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ABSTRACT: Phosphoramide containing an active vinyl group (P-III) was prepared. Its structure was confirmed by elemental analysis and Fourier transform infrared, nuclear magnetic resonance, and mass spectroscopy. P-III was evaluated as a fire-retardant finishing agent for cotton fabrics. It was applied to cotton fabrics using a graft process with an Fe^{2+}/H_2O_2 redox system. The major factors affecting the reaction were studied. The finished cotton fabrics were examined for flammability, and the effect of washing on treated fabrics was also examined. The results showed that P-III can be successfully used as a flame retardant for cotton fabrics. Durably flame-retardant cotton fabrics were obtained at add-on levels higher than 38%. © 2003 Wiley Periodicals, Inc. J Appl Polym Sci 89: 2573–2578, 2003

INTRODUCTION

Protection of inflammable material against fire dates back to about 40 B.C., but the earliest attempts to fireproof textile fabrics are more recent.[1] The development of fire retardants is based on the possibility of the fire retardant reacting with the hydroxyl groups of the cellulose molecules. In this study a series of flame-retardant finishes based on phosphoramide derivatives were prepared, and their suitability as flame-retardant treatments of cotton fabrics was evaluated.[2–4] The use of phosphorus compounds as components of flame-retardant additive in polymers is well established.[5]

Many techniques for imparting durable flame resistance properties to cellulosic substrates have been described in the literature.[6] However, relatively few of them are practiced today, either because of commercial nonavailability of the chemicals, safety concerns, process control issues, or other reasons. Durable flame retardants are more complex, more expensive and more difficult to apply than the nondurable type.

To overcome such difficulties, it was thought feasible that the grafting of phosphorus- and nitrogen–containing acrylic monomers onto a cellulosic fiber might lead to durable fixation of the latter onto cellulosic fabrics.

EXPERIMENTAL

Reagents

Cotton fabric (400 g/m²; 21 picks × 61 ends/cm), from Misr Spinning and Weaving Co. (Mehalla El-Kubra, Egypt), was used after purification by scouring for 2 h at the boiling point using an aqueous solution containing 1% sodium hydroxide. It was then thoroughly washed and air-dried at room temperature.

The chemicals phosphorus oxychloride, diethylamine, hydroxyethyl methacrylate, and triethylamine used in the study were of laboratory grade. Ammonium chloride, ferrous ammonium sulfate, hydrogen peroxide, thiourea dioxide (TUDO), copper sulfate, potassium sulfate, ammonium molybdate, and ammonium nitrate were commercial-grade chemicals. Trimethylated melamine (TMM) whose commercial name was Cassurit HML, was kindly supplied by Hoechst A.G. Germany. Egyptol, a nonionic detergent, was provided by the Egyptian Company for Starch and Yeast, Egypt.

Preparation of methacryloyloxyethyl orthophosphorotetraethyl diamidate

Bis-(*N,N*-diethyl)aminochlorophosphine oxide (P-II) was prepared by the reaction of phosphorus oxychloride with diethylamine in a 1:2 ratio at −20°C in the presence of triethylamine (TEA),[7] shown in Scheme 1. It showed a molecular formula compatible with the given structure, $C_8H_{20}ClN_2OP$. The mass spectrum (*m/z,* relative intensity; Fig. 11) showed:

226 (M^+, 16%); 227 (M^+, 64%); 211 (M^+—CH_3, 100% base peak); 191 (M^+—Cl, 44%); 154 (M^+—$C_4H_{10}N$, 33%); 72(M^+—$C_4H_{10}NOPCl$, 70%). ¹H-NMR (Fig. 12) 0.8–1.1 (m, 12H, 4 CH_3 groups); 2.9–3.3 (m, 8H, 4 CH_2 groups). FTIR P=O detected at ν 1250 cm⁻1.

In accordance, P-II reacted with hydroxyethyl methacrylate in the presence of TEA at 0°C–5°C to produce methacryloyloxyethyl orthophosphorotetra-
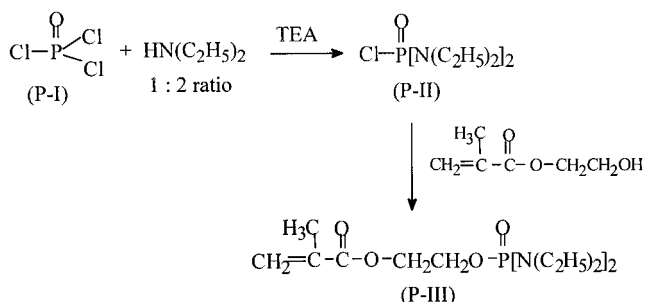
Scheme 1

ethyl diamidate (P-III). The P-III structure was given to the obtained product based on its spectral data. The product had olefinic protons that appeared as singlets at δ 6.2 ppm along with three sets of multiplets at δ 3.6, δ 4.0, and δ 4.3 ppm assignable to N—CH$_2$, O—CH$_2$, and CH$_2$—OP=O, respectively (Fig. 13), whereas its Fourier transform infrared (FTIR) spectra showed absorption at ν 3400, 2970, 1720, and 1240 cm^{-1} attributed to the OH, alphatic protons, CO, and PO, respectively (Fig. 14. In addition, its mass spectrum revealed fragments at 58 (100%), 72 (40%), 86 (62%) and 191 (10%) assigned to the glycoxal, 2-methyl propanaldehyde, α-methyacrylate, and orthophosphoro tetraethyl diamidate, respectively (Fig. 15).

Fabric treatment

The cotton fabric was first thiocarbonated using a solution of 1% NaOH (w/v), 1% CS$_2$ (v/v), and a suitable wetting agent to increase the efficiency of the thiocarbonation reaction.

Unless otherwise indicated, the thiocarbonated cotton fabric samples were grafted with methacryloyloxyethyl orthophosphorotetraethyl diamidate (P-III) using a Fe^{2+}–H$_2$O$_2$–TUDO redox system.[8]

Fe^{2+}–H$_2$O$_2$–TUDO has been reported to form an effective redox system capable of initiating grafting of different vinyl monomers onto cotton cellulose.[9] The initiation mechanism involves the following reactions:

$$H_2O_2 + Fe^{2+} \rightarrow HO^- + HO^\bullet + Fe^{3+}$$

$$H\dot{O} + Cell\text{-}OH \rightarrow Cell\text{-}\dot{O} + H_2O$$
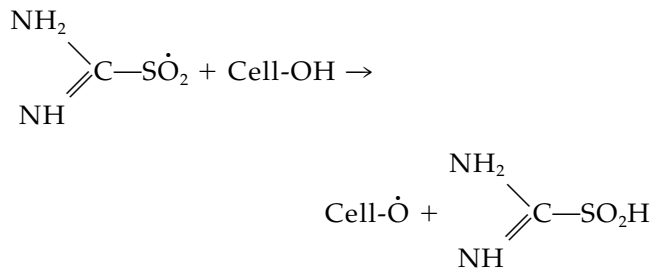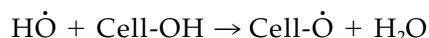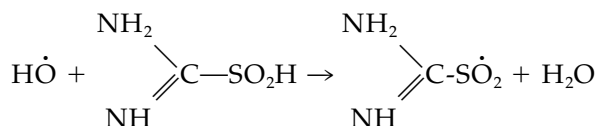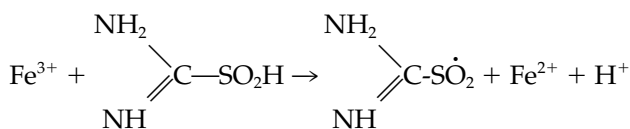
In the presence of vinyl monomer grafting occurs via addition of the cellulose macroradical (Cell-O$^\bullet$) to the double bond of the monomer followed by the subsequent addition of the monomer molecule:

$$Cell\text{-}O^\bullet + M \rightarrow Cell\text{-}OM$$

The graft polymerization was carried out at 40°C–8°C, for 0.5–4 h in an H$_2$O$_2$ concentration of 0.05%–0.3% using a P-III monomer concentration of 50%–300% based on the weight of cotton fabric sample (ows).

The cotton fabric samples were treated on pilot scale in a "jigger" under the same experimental conditions and with the same polymerization solution as explained above. The samples were under continuous movement during the reactions to avoid heterogeneous deposition on the sample surface.[10]

The graft yield (GY %) was determined from the gain in the weight of the cotton sample because of the graft polymerization after removing ungrafted polymer with a proper solvent.

Analysis

FTIR spectra were recorded on a Jasco FT/IR-300 E Fourier transform infrared spectrophotometer. The ^{1}H-NMR were obtained on a Jeol nuclear magnetic resonance (NMR) EX-270 spectrometer. Also, molecular formula determination was obtained by mass spectrometry with a Finnigan mat SSQ 700 (England). FTIR, NMR, and mass spectrometry of the National Research Centre.

Evaluations of fabric properties

The extent of reaction of the prepared phosphorus compounds with cotton fabric was expressed as the contents of nitrogen and phosphorus. The nitrogen content was determined according to the Kjeldahl method.[11] The phosphorus content was determined according to a method described elsewhere.[12] The property of flame retardance was monitored according to the vertical test method.[13]
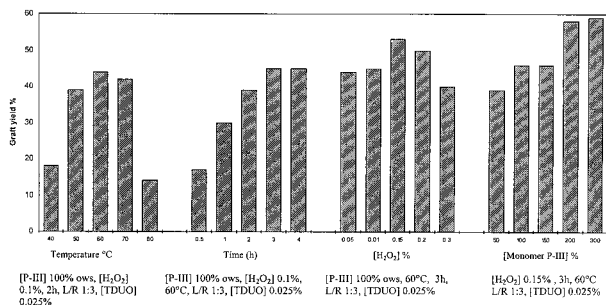
Figure 1 Effect of reaction conditions on graft yield percent method of preparation: Fe^{2+}–H_2O_2–TUDO redox system.

RESULTS AND DISCUSSION

Graft polymerizations

Figure 1 shows that graft percentage increased by increasing the temperature from 40°C to 60°C and then decreased with a further increase in temperature. This trend could be associated with the effect of temperature on: (1) stability of the emulsion of monomer and diffusion of the latter from the aqueous phase to the fiber phase, (2) adsorption of monomer on the substrate, (3) swellability of the substrate, (4) rate of initiation of polymerization, (5) rate of propagation of the growing polymer add-on, (6) rate of termination of the growing polymer add-on, and (7) rate of homopolymer formation. Although the first five items would positively affect the graft percent percentage, the last two would have the opposite effect. The obtained data reveal that above 60°C, the adverse effects of rate of termination the polymer add-on and rate of
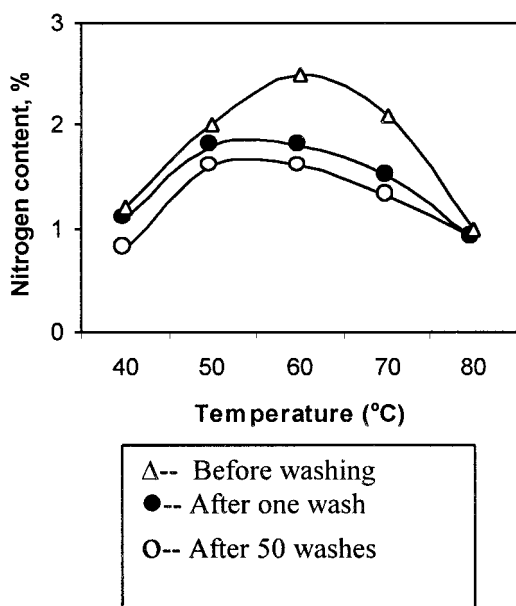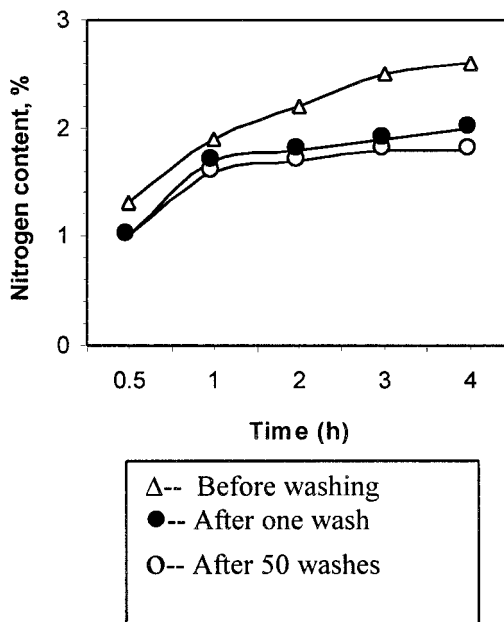

Figure 3 Effect of time on nitrogen content. Fe^{2+}–H_2O_2–TUDO redox system (P-III): 100% ows; H_2O_2: 0.1%; 60°C; L/R 1:30.

homopolymer formation on the graft percentage prevail over the favorable effects resulting from the first five characteristics.[9]

As to time characteristics, Figure 1 shows that in the beginning the graft polymerization was characterized by an initially fast rate, then the rate slowed down. The slowing down of the rate of polymerization could be ascribed to depletion in both monomer and initiator concentration, as well as a shortage in accessible cel-
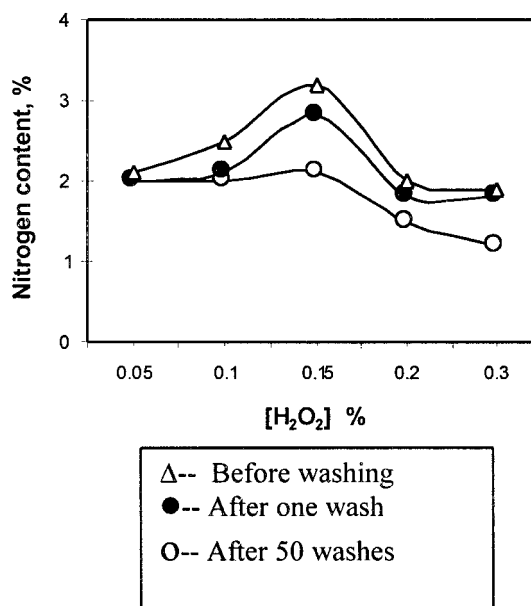

Figure 2 Effect of temperature on nitrogen content. Fe^{2+}–H_2O_2–TUDO redox system (P-III): 100% ows; H_2O_2: 0.1%; 3 h; L/R 1:30.

Figure 4 Effect of H_2O_2 concentration on nitrogen content. Fe^{2+}–H_2O_2–TUDO redox system (P-III): 100% ows; TUDO: 0.025%; 60°C; 3 h; L/R 1:30.
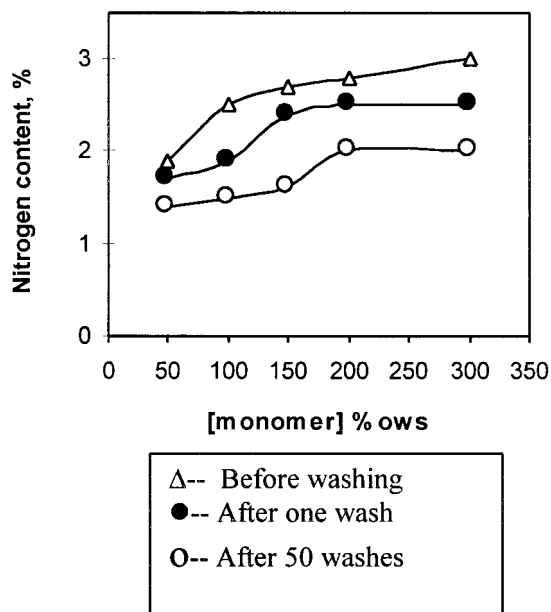
Figure 5 Effect of monomer content on nitrogen content. Fe^{2+}–H_2O_2–TUDO redox system (P-III): 100% ows; TUDO: 0.025%; 60°C; 3 h; L/R 1:30.

lulose hydroxyls as the polymerization reaction proceeded. In addition, attachment and/or intimate association of the vinyl polymer with the cellulose molecules during the initial stages of polymerization would render them less amenable to polymerization during the later stages of reaction.
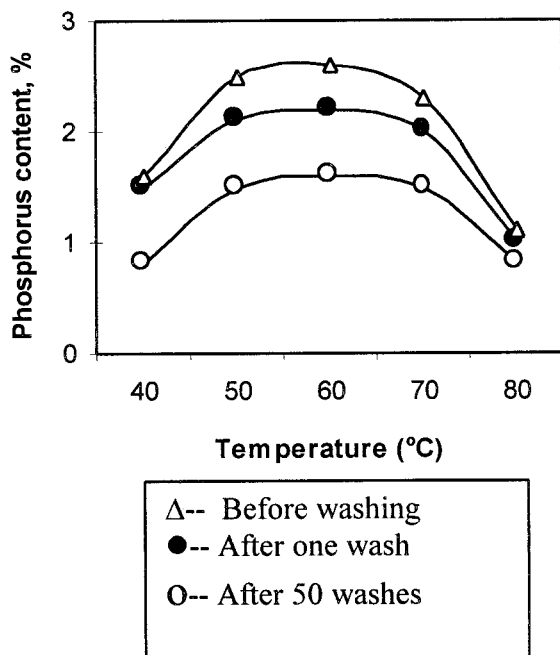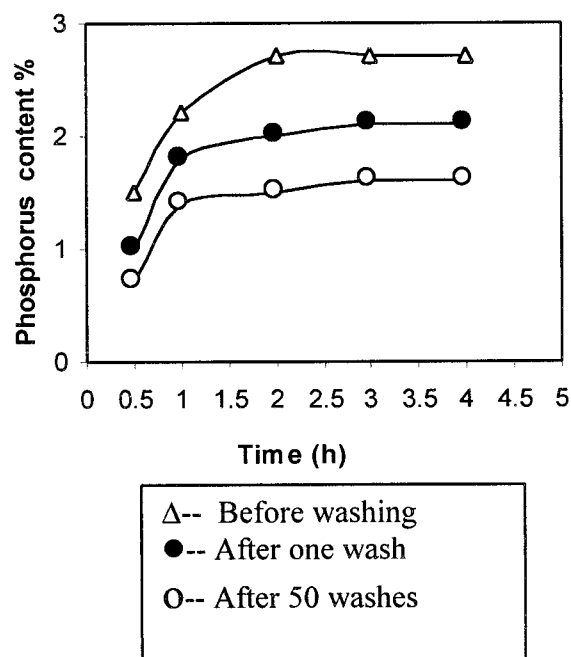

Figure 7 Effect of time on phosphorus content. Fe^{2+}–H_2O_2–TUDO redox system (P-III): 100% ows; H_2O_2: 0.1%; 60°C; L/R 1:30.

Figure 1 also shows that the increase of H_2O_2 concentration up to 0.15% was accompanied by an increment in the graft yield percent. Increasing the H_2O_2 concentration above 0.15% caused a decrement in the graft yield. Enhancement in percentage of add-on by increasing H_2O_2 concentration up to 0.15% could be
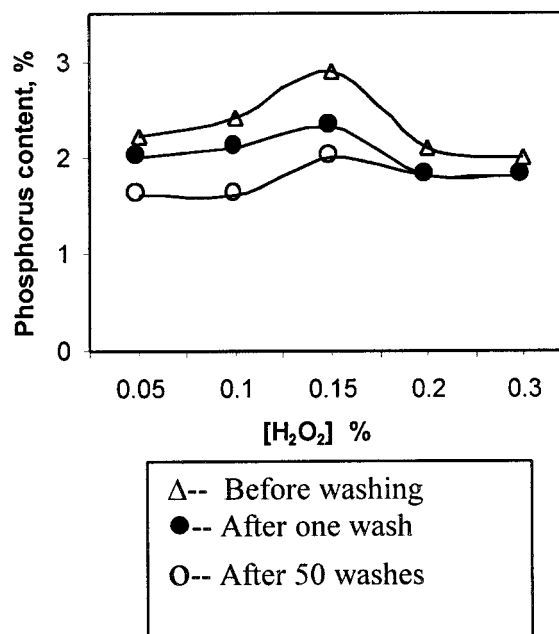

Figure 6 Effect of temperature on phosphorus content. Fe^{2+}–H_2O_2–TUDO redox system (P-III): 100% ows; H_2O_2: 0.1%; 3 h; L/R 1:30.

Figure 8 Effect of H_2O_2 concentration on phosphorus content. Fe^{2+}–H_2O_2–TUDO redox system (P-III): 100% ows; TUDO: 0.025%; 60°C; 3 h; L/R 1:30.
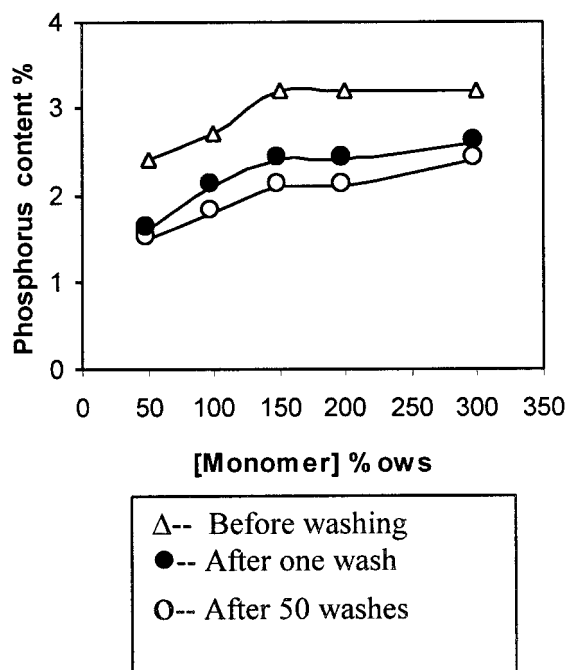
Figure 9 Effect of monomer content on phosphorus content. Fe^{2+}–H_2O_2–TUDO redox system (P-III): 100% ows; TUDO: 0.025%; 60°C; 3 h; L/R 1:30.

interpreted as the creation of more active species (free radicals) that contribute largely in the initiation of polymerization on the substrate. A higher H_2O_2 concentration seems to result in an abundance of free radicals, which participate in termination of cellulose macroradicals as well as in termination of growing polymer chains, leading to add-on of low-molecular-weight polymer. An abundance of free-radical species favors termination among themselves through combination. Hence, the ultimate effect of free-radical abundance is a faster rate of termination, giving rise to a lower percentage of polymer add-on observed when H_2O_2 concentration is higher than the 0.15% that was used.

Figure 11 ^{1}H-NMR spectra of P-II compound (in $CDCl_3$, Sppm).

Figure 1 shows that increasing monomer concentration, from 50% to 300% (based on weight of the substrate), is accompanied by progressive increase in graft percent, which is a direct consequence of the greater availability of monomer molecules in the vicinity of the cellulose at higher monomer concentrations. It is understandable that cellulose macroradicals are immobile and that their reaction with the monomer molecules would essentially rely on the availability of the latter in the proximity of the cellulose. Nevertheless, the contribution of the gel effect,[14] in which a polymer is soluble in its own monomer, cannot be ruled out.

Nitrogen and phosphorus contents

Figures 2–9 show that the nitrogen and phosphorus contents were affected according to the factors under consideration, those that affect the graft yield—that is, nitrogen and phosphorus contents increase as graft yield increases.

It can be seen that the nitrogen and phosphorus content was decreased by washing. This can be attrib-
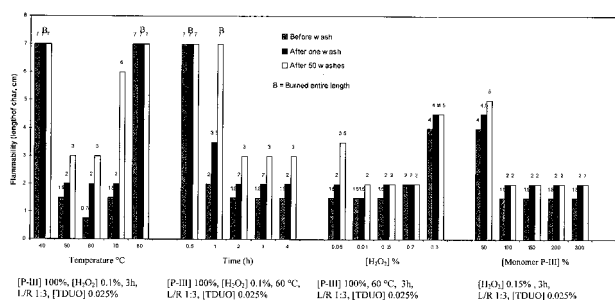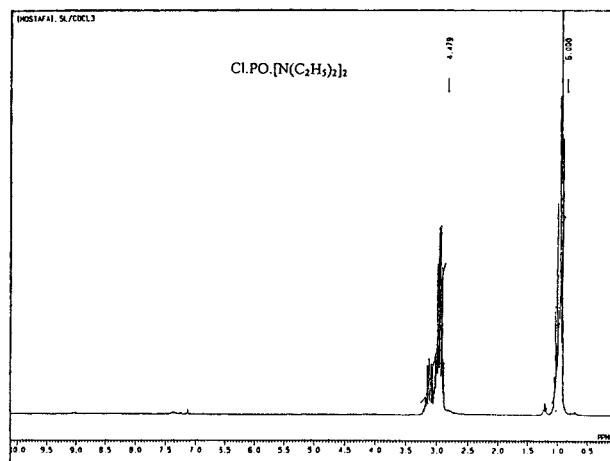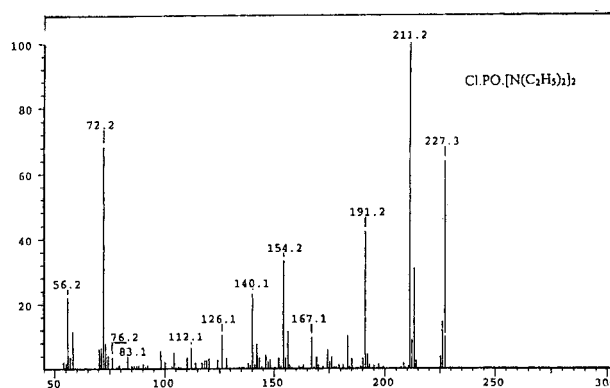

Figure 10 The effects of variable polymerization parameters and washing process on the flammability of cotton fabrics treated with methacryloyloxyethyl orthophosphorotetraethyl diamidate (P-III) method of preparation: Fe^{2+}–H_2O_2–TUDO redox system

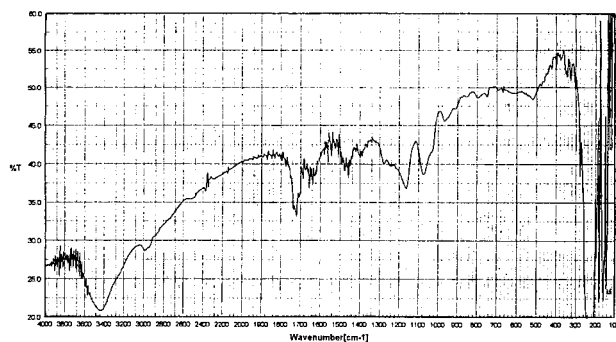**Figure 12** Mass spectra (% rel. int.) for P-II compound.

Figure 13 FTIR spectra (in K Br) cm^{-1} for P-II compound.

uted to the removal of ungrafted monomer (P-III) from the fabric during washing and also to the hydrolysis of the amide, also through washing.

Flammability

Figure 10 shows that using P-III in finishing cotton fabrics makes the fabric exhibit flame-retardant properties before and after washing when the graft yield is more than 40%. Needless to say, there is better flame retardance at higher graft yields, that is, at higher phosphorus and nitrogen contents.

It can be seen that washing reduces flame retardance to some extent. This can be attributed to the lowering of the phosphorus and nitrogen contents by washing from hydrolysis of the methyl ester groups on fire-retardant molecules.

CONCLUSIONS

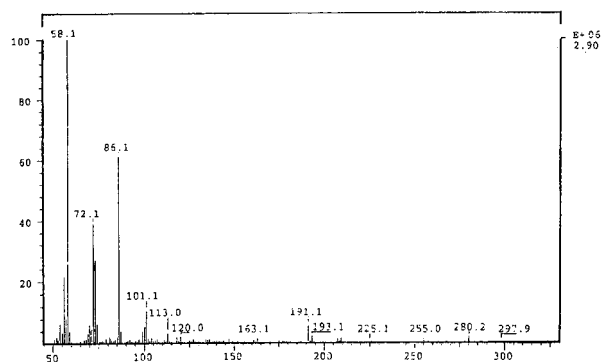Application of acrylic monomers as a reactive binder have proven feasible in the fixation of organophos-

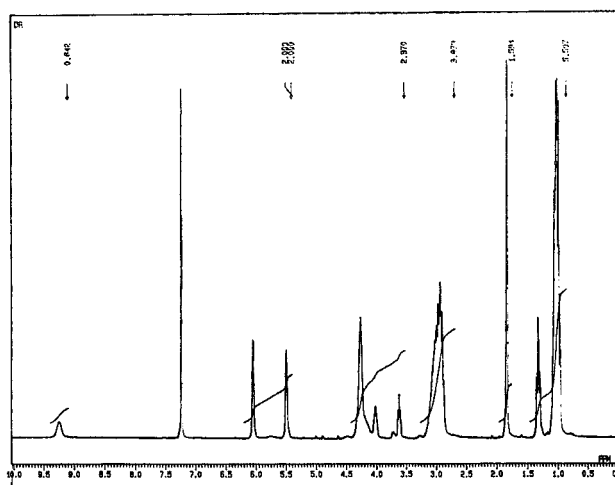**Figure 14** Mass spectra (% rel. int.) for P-III compound.

Figure 15 ^{1}H-NMR spectra of P-III compound (in CDCl$_3$, Sppm).

phorus compounds into cotton cellulose through grafting processes using the Fe^{2+}/H$_2$O$_2$ redox system. The results have shown that the functional finish on a cotton fabric is durable, surviving 50 washes without compromising its flame retardance.

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