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Radical graft functional modification of cellulose with allyl monomers: Chemistry and structure characterization

Song Liu, Gang Sun *

Fiber and Polymer Science, University of California, Davis, CA 95616, United States

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Abstract

Cotton cellulose was successfully functionalized via a free radical graft polymerization process. Potassium persulfate served as an effective water soluble radical initiator to generate cellulosic radicals. The polymeric radicals could react with allyl monomers such as allyl-dimethylhydantion (ADMH) to form surface grafted cellulose. The reaction sites generated by potassium persulfate were probably at carbon 3 and 4 in glucose ring via oxidative hydrogen abstraction. The cellulosic radicals can initiate grafting polymerization of ADMH with a maximum polymerization degree of about 12 based on LC–MS results. The radical graft polymerization mechanisms were proposed based on LC–ESI/MS analysis. The ideal covalent bonding between cellulose and poly (allyl-dimethylhydantion) (PADMH) ensured permanent graft of the monomers on cotton and durability of the expected functions on the treated cotton.

Keywords: Radical graft polymerization; Solid phase reaction; Cellulose; Allyl monomer

1. Introduction

Carbohydrates such as cellulose and starch can be chemically modified to possess new functional groups. One of the chemical methods is to graft vinyl functional monomers onto glucose rings employing radical polymerization systems. Many different radical graft polymerization processes have been developed by using initiators such as peroxides and hydroperoxides (Hebeish, Abou-Zeid, Waly, & El-Alfy, 1978), diazo compounds (Hebeish, Abdel-Bary, Waly, & Bedeawy, 1980), or redox pairs (Abdel-Hafiz, 1995; El-Alfy, Waly, & Hebeish, 1985). Most of the processes were conducted in solutions containing radical initiators and functional vinyl monomers, but radical initiators can directly react with the monomers in the solution, producing a large amount of homopolymer byproducts instead of grafted products. Thus, grafting efficiencies were lower in general, which is a concern to applications in many areas. Another concern of using the radical graft polymerization is the production of long chains of the functional monomers, which may alter surface properties of the fibers and affect applications as textile materials. Due to the above reasons, commercial application of the radical graft modification was rare.

However, radical polymerization can still be employed in surface modifications of cellulose if the following conditions can be ensured during the modification processes. These conditions include rapid and preferential generation of polymeric radicals on the solid materials, solvent-free condition during graft polymerization and short chain formation of the monomers. According to the analysis, a practical surface functional modification of cellulose was designed and implemented. Several water soluble monomers were successfully grafted onto cellulose using potassium persulfate (PPS) as an initiator (Liu & Sun, 2006; Sun & Sun, 2002). In order to prove that the above conditions in modification of cellulose could lead to effective radical graft polymerization on cellulose molecules, elemental analysis, Fourier transform infrared spectroscopy (FTIR) and electron microprobe were employed in structural analysis of the grafted products. At the same time the grafted

* Corresponding author. Tel.: +1 530 752 0840; fax: +1 530 752 7584.
E-mail address: gysun@ucdavis.edu (G. Sun).

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cellulose was hydrolyzed under acidic conditions, and the hydrolyzed mixtures were analyzed by liquid chromatography–mass spectroscopy (LC–ESI/MS).

2. Experimental

2.1. Materials

Pure cotton print cloth # 400 was purchased from Test-Fabrics Inc. (West Pittston, PA). Potassium persulfate (PPS, Acros, Pittsburg, PA) was recrystallized from distilled water. 3-allyl-5,5-dimethylhydantoin (ADMH) was synthesized in this lab according to a method reported previously (Sun & Sun, 2001).

2.2. Grafting polymerization

All of the chemicals (monomers and the initiator) were mixed in distilled water at certain ratios. Cellulose fabric was dipped in the monomer/initiator solution and padded at a required expression. This "dip-pad" process was repeated twice. Padded fabric was dried at 60 °C for 10 min in an oven. The samples were then cured in an oven at 105 °C for 30 min, and then washed with large amount of hot water, dried at 60 °C. Grafting yield refers to weight percentage increase of grafted monomer on cellulose.

2.3. FTIR and elemental analysis

FTIR spectra were taken on a Nicolet 6700 spectrometer (Thermo Electron Corporation) using KBr pellets. The samples were made thin enough to ensure that the Beer–Lambert law was fulfilled. Nitrogen contents on fabric samples were examined following a total Kjeldahl nitrogen analysis method at the DANR analytical laboratory at the University of California, Davis.

2.4. LC–MS analysis

To characterize chemically modified cellulosic structures, acid hydrolysis method was used to break the carbohydrate into soluble small molecules. The modified cotton was hydrolyzed at 100 °C in 10% sulfuric acid for 6 h, and then neutralized by NaOH. LC–ESI/MS spectrum of the mixture (neutralized) was analyzed by a Finnigan LCQ Classic Ion Trap Mass Spectrometer. The analytes went through a Vydac C18 column (for positive mode) or polymer PLRP-S 100 (for negative mode) using isocratic conditions (200 μL/min) before ionization in an electrospray source and the mobile phase is a solution containing 80% MeOH, 0.1% formic acid (positive mode) or 20 mM NH_4OAc (negative mode). Ions were scanned from 50–2000 *m*/*z* with the following conditions (nebulizing gas = 50, 5 KV spray voltage) (LCQ, Thermo Finnigan, San Jose, CA). As direct injection was adopted, the spectrum was acquired by syringe infusion of the analyte at 15 μL/min into the ESI source. A good quality spectrum was obtained by averaging the acquired data over a period of 1 min.

In collision induced dissociation (CID) experiments on the LCQ instruments, nitrogen was used as the collision gas, and 35% of normalized collision energies was used to induce fragmentation.

2.5. Electron microprobe

High resolution sulfur elemental mapping and high speed back scattered electron (BSE) imaging were taken with a Cameca SX-100 electron microprobe (CAMECA Instruments Inc., USA).

2.6. Chlorination

Conversion of halamine precursor structures in the grafted samples into *N*-halamines was conducted by immersing the samples in a diluted chlorine bleach solution (300 ppm available chlorine, pH 11) at room temperature for 30 min with stirring (liquor ratio was 1:50), and the fabrics were then washed in distilled water and air dried.

2.7. Antibacterial assessment

Antibacterial properties of the grafted samples were examined according to a modified Test Method 100 of American Association of Textile Chemist and Colorists (AATCC) against a Gram-negative bacterium *Escherichia coli (E. coli*, k-12). The detail procedure can be found in the previous paper (Sun & Sun, 2001).

3. Results and discussion

To promote graft reaction and avoid homopolymerization of the monomers, radical initiators should preferably react with cellulose instead directly reacting with monomers. Radical initiators can undergo two different paths, addition to vinyl monomers or hydrogen abstraction from weak C–H sites on cellulose. Alkoxide radicals prefer to abstract hydrogen atoms from weak C–H bonds rather than addition to vinyl monomers, different from other initiator radicals (Moad & Solomon, 1995). Thus peroxide radical initiators are selected in this study. After even delivery of an aqueous solution containing both the initiator and a monomer onto the materials, water was removed before initiating the graft reactions to ensure a solvent-free graft reaction. Such conditions can minimize formation of homopolymerization of the monomers and increase graft efficiency. In addition, selection of functionalized allyl monomer can be used to reduce formation of long chains because of self-inhibition properties of allyl monomers (Schildknecht, 1972).

3.1. Generating radicals on cellulose with PPS

Radical graft polymerization on cellulose depends on effective generation of polymeric radicals on cotton cellu-

lose. Potassium persulfate (PPS) was selected as a radical initiator in this approach since it is soluble in water and inexpensive though it does not produce alkoxide radicals, the best radical initiators for hydrogen abstraction. Application of PPS can be easily achieved and controlled by a dip-pad process that is widely employed in textile wet processing. The question was whether PPS is capable of producing the expected cellulosic radicals. In fact, this question can be answered by a sulfur mapping test on the PPS treated cotton cellulose since cellulose radicals could couple with persulfate radicals and produce cellulose sulfate. The cotton fabric sample was soaked in PPS solution and then dried at low temperature to avoid possible decomposition of PPS. The dried fabric sample was then heated up to 105 °C for 30 min to initiate the reaction on cellulose without existence of any monomer, and then the sample was extracted with deionized water in a Soxhlet extractor to remove any adsorbed potassium sulfate and residual potassium persulfate. The sample was evaluated by a scanning electron microprobe. The PPS treated cellulose demonstrated very strong sulfur signal along the fiber axis as shown in Fig. 1a and b, a result of successful fixation of sulfate on the cellulose substrate. The sulfur contents were further quantified based on total element analysis as listed in Table 1, which are consistent with the sulfur mapping results.

To further reveal the grafting position of sulfate on cellulose, the above PPS treated cellulose was hydrolyzed in acidic solution (1 N HCl, 60 °C for 4 h). The hydrolyzed products were subjected to liquid chromatography and mass spectroscopy. Electrospray ionization (ESI) is a technique used in mass spectrometry to produce ions and is especially useful in producing ions from macromolecules because it overcomes the propensity of these molecules to fragment when ionized. During the electrospray processes the ions observed are quasimolecular ions that are ionized by the addition of a proton (H^+) to give $[M+H]^+$ (M = analyte molecule, H = proton), or the removal of a proton $[M-H]^-$ for example. The negative mode MS spectrum of hydrolyzed PPS treated cotton is shown in the Fig. 2.

Table 1
Elemental analysis on cotton samples before and after treatment

	N (%)	S (ppm)
Untreated cotton	0.022	85
PPS treated cotton[a]	0.023	860
PADMH-g-Cotton[b]	0.146	510

[a] PPS 0.175 mM, dried at 60 °C for 10 min and cured at 105 °C for 30 min.
[b] ADMH 0.35 mM, PPS 0.175 mM, dried at 60 °C for 10 min and cured at 105 °C for 30 min.

Three major peaks of ions $[M-H]^-$ with *m/z* 215, 377 and 539 can be seen from Fig. 2a. They are spaced by 162, suggesting linkage of one or more anhydroglucose units. Collision induced dissociation (CID) is a mechanism by which fragment molecular ions could be formed in the gas phase. The CID produced fragment ions can be used to achieve partial or complete structural determination. CID spectrum of $[M-H]^-$ ion *m/z* 215 gives peaks *m/z* 197, 179 and 97. The fragment *m/z* 97 is a strong indication of the existence of sulfate ion. For diol molecules, dehydration is common in the CID process (Es-Safi, Kerhoas, Einhorn, & Ducrot, 2005; Kovacik, Bekesova, Tvaroska, &

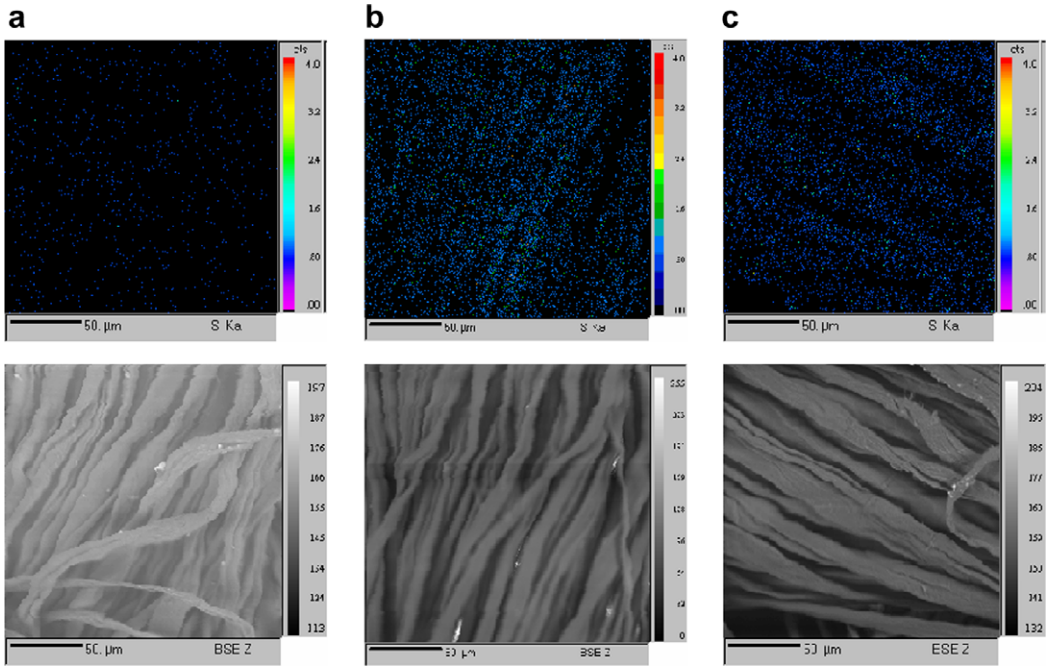


Fig. 1. Microprobe images (upper pictures: sulfur mapping; lower pictures: back scattering) of (a) untreated cotton (b) PPS treated cotton and (c) ADMH and PPS treated cotton (PADMH-g-Cotton).

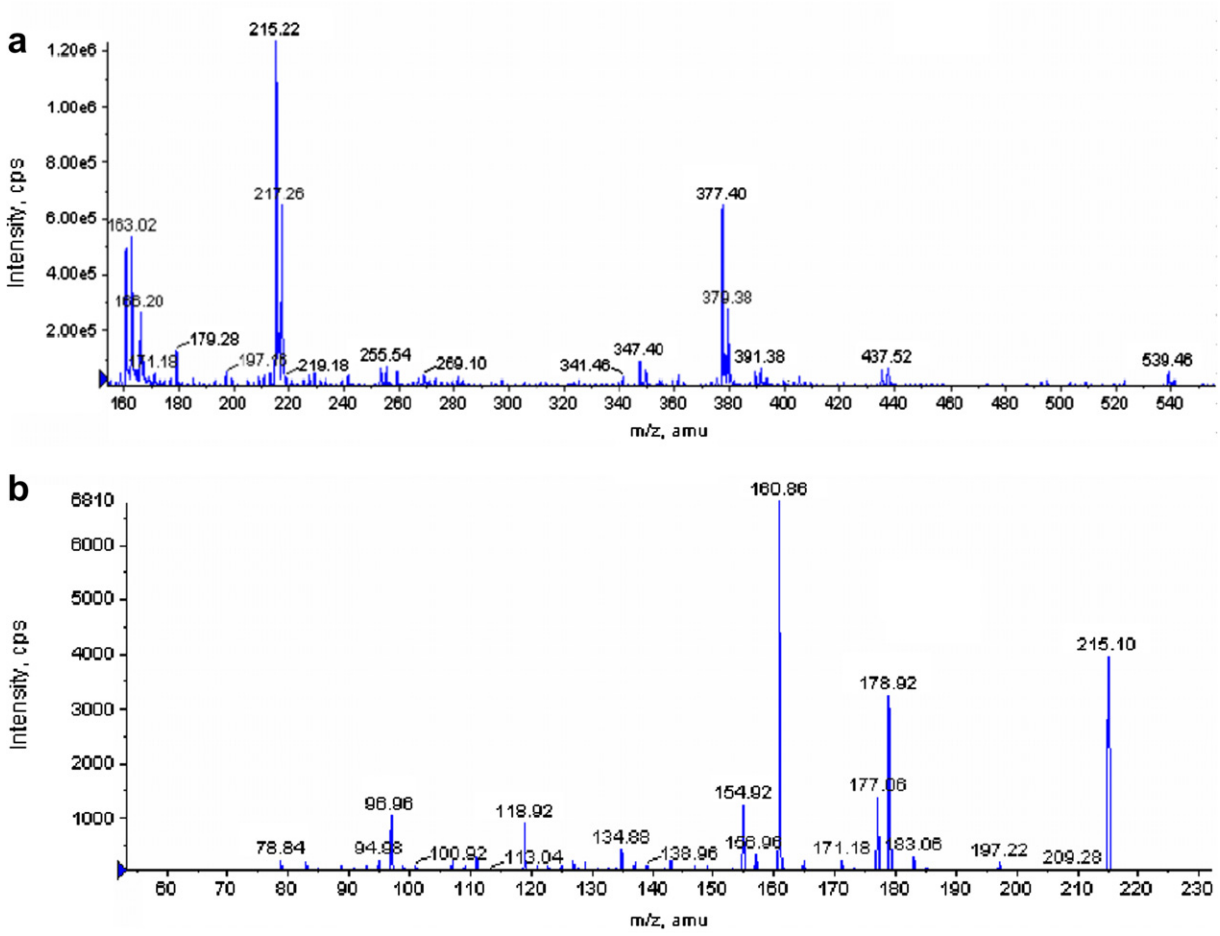


Fig. 2. Mass spectra of the hydrolytic mixture of PPS treated cotton cellulose (a) total ion chromatography and (b) collision induced dissociation (CID) of ion *m/z* 215.

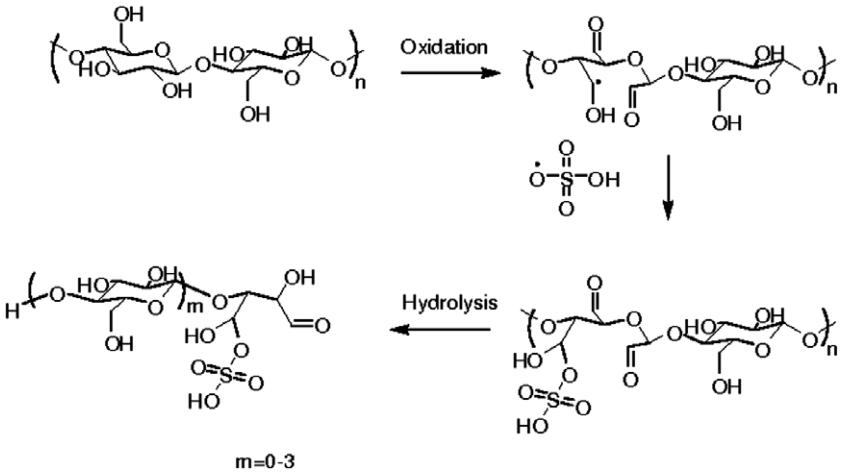
Kovac, 2006). The $[M-H-18]^-$ and $[M-H-36]^-$ ions in the product-ion spectra (Fig. 2b) obviously resulted from loss of one and two H_2O molecules from the $[M-H]^-$ ion. Those isotopic $[M+H+2]^+$ peaks for *m/z* 215, 377 and 539 (*m/z* 217, 379 and 541) also proved the existence of sulfur in those ions. These results confirmed formation of sulfate grafted cellulose on the PPS treated cotton, which also further proved that cellulosic radicals were effectively generated by PPS.

Common oxidative pathways for polysaccharides include oxidization of C6 alcohol to aldehyde or even to carboxylic acid, oxidation of C2, C3 alcohol to ketone, breakage of the C2–C3 bond (Nevell, 1985). The smallest polysaccharide fragment linking with sulfate has a molecular weight of 120 Da. The molecular weight difference between glucose (MW = 180) and the fragment is 180 − 120 = 60, indicating ring structure rupture. Combined with all those possible oxidative pathways, a mechanism is proposed in Scheme 1. The radical arising from oxidative breaking of C2–C3 bond can combine with sulfate radical to result in a molecule with MW of 218. The actual MW of 216 suggests the oxidation of C6 alcohol to aldehyde. So the radical could be generated at C3 on the glucopyranoid ring, and *m/z* 216 could be sulfate attached 2,3,4-trihydroxy butanal. The glucose negative ion can be seen as *m/z* 179. Another peak *m/z* 163 may come from fragmented glucose (Fig. 2b).

3.2. Mechanism of graft reaction

Addition of an allyl monomer such as 3-allyl-5,5-dimethylhydantoin (ADMH) in the graft system significantly reduced the sulfur signal in microscope mapping (sulfur content decreases from 860 to 510 ppm), indicating that some generated cellulosic radicals reacted with monomer molecules instead of persulfate radicals (Fig. 1c and Table 1). Since only the monomer ADMH contains nitrogen, nitrogen analysis of the samples was employed to reflect the grafting yield. Kjeldahl nitrogen analyses revealed that the nitrogen contents on the PPS treated and ADMH grafted cotton samples were 0.023% and 0.146%, respectively, which further confirmed the cellulosic radicals could react with allyl monomers rapidly. The calculated grafting yield was 0.738%.

After confirming the formation and reactions of cellulosic radicals, location of the real grafting reaction on cellulose and grafted chain length were also explored by using the same mass chromatographic approach. The modified



Scheme 1. Proposed mechanism for interaction between PPS and cotton cellulose.

and untreated cotton samples were hydrolyzed under the acidic condition (10% H_2SO_4, 100 °C for 6 h) and neutralized with NaOH; the solutions were then employed in liquid chromatography and mass spectroscopy study. Direct hydrolysis of ADMH under the same acidic condition resulted in 2-dimethyl-2-amino-*N*-2-propenyl acetamide (DAPA) with MW of 142 Da. The cellulosic radical generated by PPS, as shown in Scheme 1, was expected to add to ADMH so to give negative ion peaks as *m/z* $120 + 142 - 1 = 261$, $261 + 142 = 403$, etc. and positive ion peaks as *m/z* $120 + 142 + 1 = 263$, $263 + 142 = 405$, etc., from the hydrolyzed samples. As expected, the negative mode mass spectrum (Fig. 3a) of the hydrolysates shows the ion series of *m/z* 261 ($120 + 142 - 1$), 403, 545, 687, 829 and 971, which should be 2,3,4-trihydroxy butanal attached oligomer series. Due to the increased acidity of the hydroxyl group to carbonyl, the 2,3,4-trihydroxyl butanyl attached oligomer series show good signal intensity in negative mode (Ding et al., 2006). This consistent finding shows that the cellulosic radical generated at C-3 can initiate grafting polymerization under the described solvent-free condition. Besides the *m/z* 261 ions series, there is another ion series of *m/z* 239 ($98 + 142 - 1$), 381, 523, 665, 807 and 949, which are homopolymer of DAPA end attached with sulfate. There is still the residue unattached homopolymer in the cotton substrate even after extensive water extraction. The positive mode mass spectrum is more complicated (Fig. 3b).

Besides the expected ion series of *m/z* 263, $263 + 142 = 405$, $263 + 2 * 142 = 547$, $263 + 3 * 142 = 689$, $263 + 4 * 142 = 831$, etc., there are homopolymer ion series of *m/z* 383($98 + 2 * 142 + 1$), 525, 667, 809 and 951, etc. and *m/z* 307, 449, 591, etc. A gradient in eluent composition (methanol concentration changes from 5% to 90% in 40 min.) was adopted to aid the separation of those compounds. The results are shown in Fig. 4. The ion series (*m/z* 307, 449,

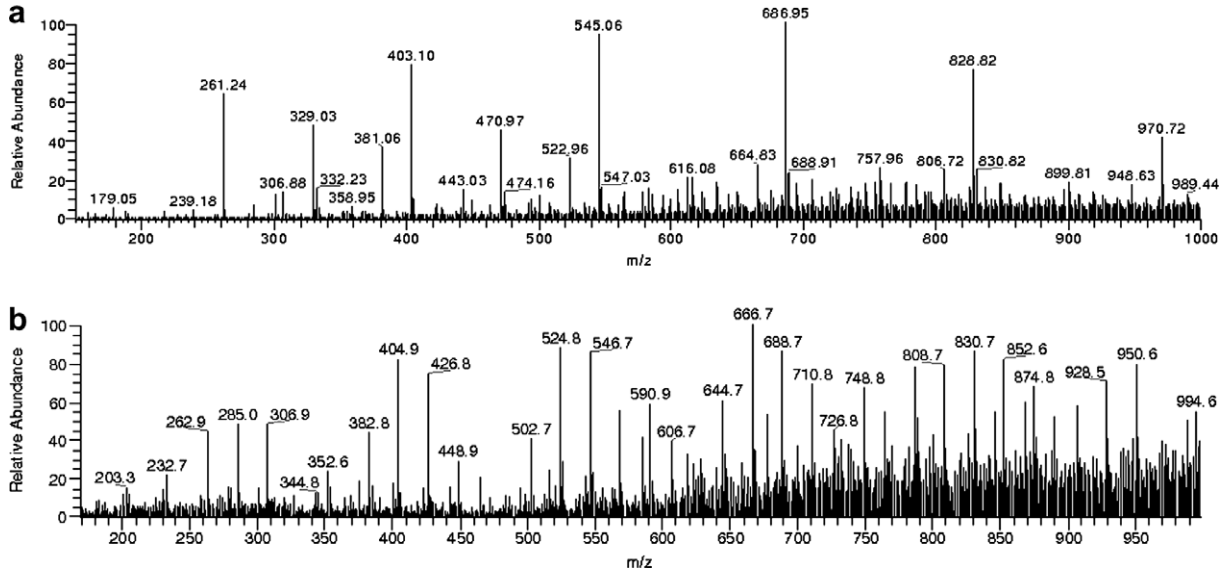


Fig. 3. ESI/MS of the hydrolytic mixture of ADMH grafted cotton (a) negative mode and (b) positive mode.

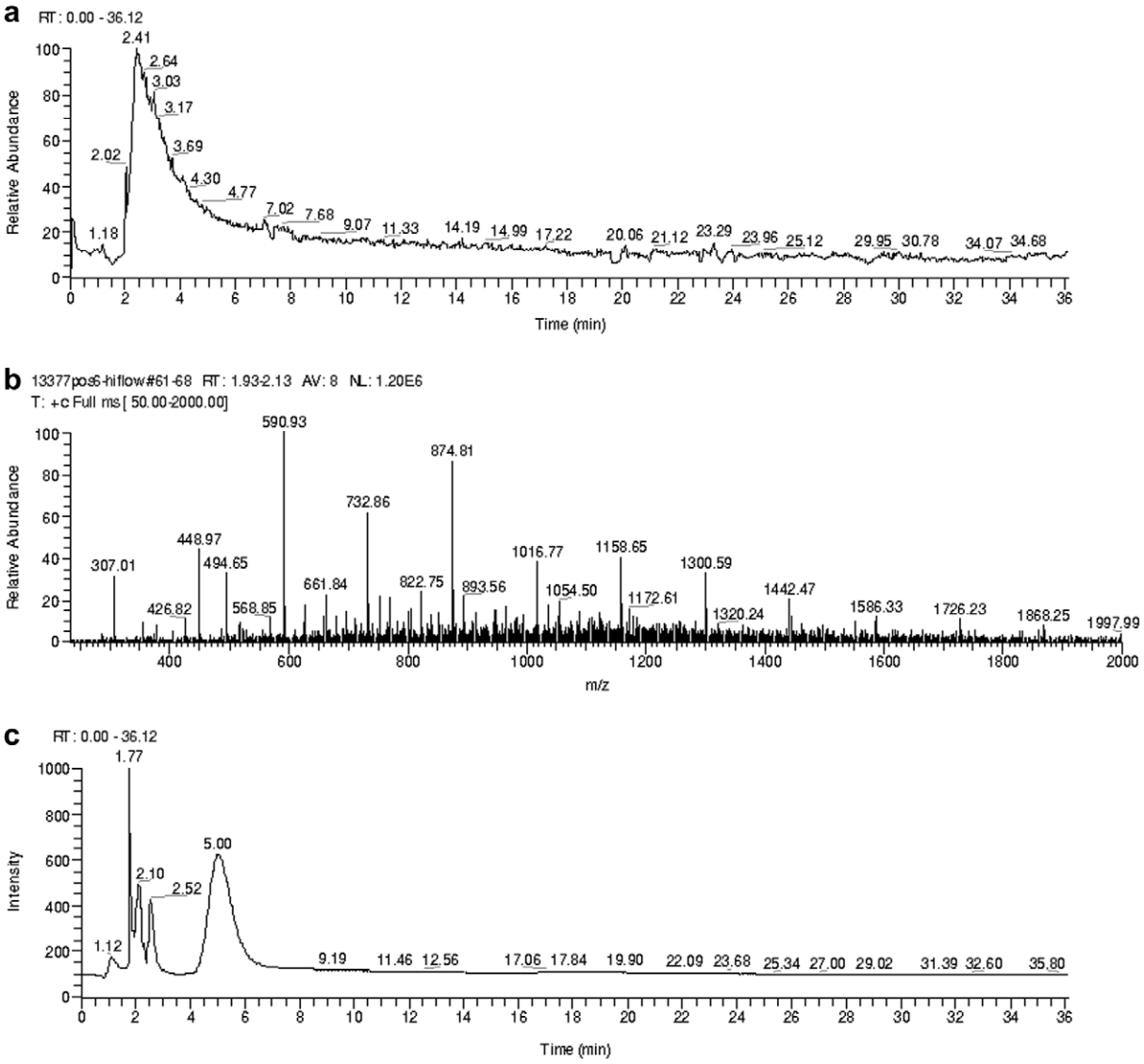


Fig. 4. HPLC–MS chromatograph (a), spectrum (b) and HPLC–UV chromatograph (c) of PADMH-g-Cotton hydrolysates.

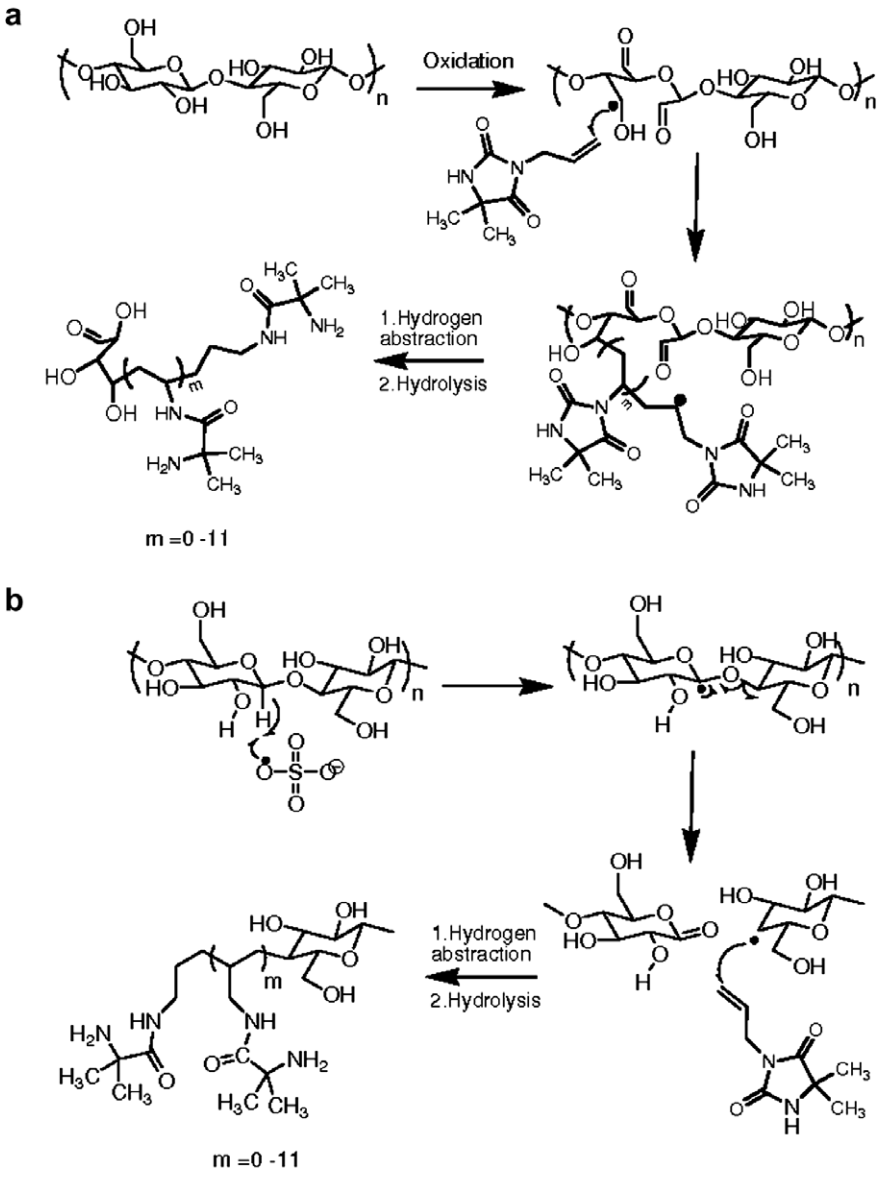
591, 733, 875, 1017) with *m*/*z* difference of 142 Da ($z = 1$, $m = m/z$) can be seen clearly in the Fig. 4(b) spectrum (retention time 1.93–2.13). Again the 142 Da spacing is a clear indication of DAPA oligomer series (Table 2).

In a simple system comprised of only ADMH, potassium persulfate, substrate cotton cellulose and sulfuric acid, the deduced fragment attached to ADMH monomer, dimer, trimer and so on with the MW of 164 should be 4-deoxy-β-D-xylo-hexopyranose. This also explains the *m*/*z* 163 peak in negative mode MS spectrum (Fig. 2a) of the hydrolyzed PPS treated cotton cellulose. Here, the loaded PPS molecules are much less than the substrate glucopyranoid rings in quantity, and the distribution of PPS is uniform in the fiber level (20 μm) but not in the molecular level. Thus, the PPS generated primary radicals escaping from the initiator cage reaction can oxidize cotton to create cellulosic radicals at C3, and the C3 radical can combine with another sulfate radical (Scheme 1). Another possibility is H abstraction at C1, and the formed C1 radical will transfer to C4 in the adjacent glucopyranose ring where no sulfate radical exists in the nearest proximity. So, sulfate radical combination with radical of *m*/*z* 164 was seldom observed. Such a pathway of radical reactions was proposed and shown in Scheme 2b.

Free radicals could be generated by breakage of either C–H or O–H bonds. However, abstraction from the former seemed to be more likely due to the lower bond dissociation energy (typically 410 kJ/mol for C–H compared with 460 kJ/mol for O–H). It is known that in secondary alcohols the hydroxyl group has a moderately activating effect on the geminal C–H bond (Hon, 1976). This effect is the strongest on C–H at C1 in the glucopyranoid ring due to the anomeric effect (lone electron pairs of two neighboring oxygen atoms interact with antibonding orbit of C–H so to weaken the bond). Consequently, sulfate primary radicals formed *in situ* could abstract the hydrogen atoms on C1 positions preferentially (Hon, 1979). Driving force for the fragmentation according to the second step of the proposed

Table 2
Summary of ion series

	Mass *m/z*	Assignment
Hydrolysate from PPS treated cotton		
Positive $[M+H]^+$	N/A	N/A
Negative mode $[M-H]^-$	163	4-deoxy-β-D-xylo-hexopyranose
	215, 377, 539	Sulfate attached 2,3,4-trihydroxy butanal
Hydrolysate from ADMH grafted cotton		
Positive $[M+H]^+$	307,449,591,733, 875, 1017	DAPA oligomers attached 4-deoxy-β-D-xylo-hexopyranose
Negative mode $[M-H]^-$	261, 403, 545, 687, 829, 971	DAPA oligomers attached 2,3,4-trihydroxy butanal
	239, 381, 523, 665, 807, 949	DAPA oligomers attached sulfate



Scheme 2. Proposed mechanisms for PPS initiated grafting polymerization on cellulose.

mechanism is provided by formation of a strong carbonyl double bond. Enthalpy (ΔH) calculated for this step was −5.44 kJ/mol (AM1 semi-empirical method, geometry optimization was employed for all of the species). Obviously it is also entropy favored reaction since two pieces products were formed.

Collision induced dissociation spectrum of *m/z* 307 (in Fig. 3a) is shown in Fig. 5. Losing one H_2O molecule

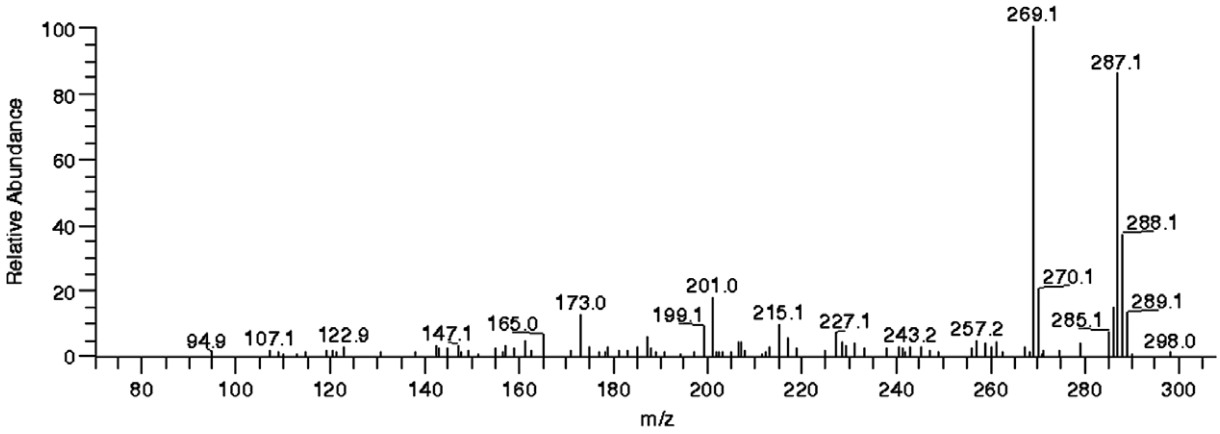


Fig. 5. Collision induced dissociation (CID) of the ion *m/z* 307.

from the protonated molecule ion 307 will produce fragment ion *m/z* 289. The multiple loss of H$^{\cdot}$ could generate *m/z* 287, which is another proof of alcohol molecule (Crews, Rodriguez, & Jaspars, 1998). Loss of another H_2O molecule from the *m/z* 287 ion will result in the ion of *m/z* 269, which was abundant in the product-ion spectra of the $[M+H]^+$ ion. Such a loss of multiple water molecules also is very common for a polyol compound (Es-Safi et al., 2005; Kovacik et al., 2006). So far, the chemical attachment of allyl monomer in the solvent-free heterogeneous reaction condition is confirmed from the LC–MS analysis, and the grafting polymerization may happen according to two mechanisms (Scheme 1a and b). The detectable longest grafting chain size was 12 (nominal *m/z* 1869 in Fig. 4b).

The grafted ADMH on cellulose were also confirmed from FTIR spectra, shown in Fig. 6. After subtracting pure cotton spectrum from that of PADMH-g-Cotton, two strong peaks 1758 and 1704 cm^{-1} can be seen clearly, which fit well with the ADMH spectrum and are due to two carbonyl groups in ADMH.

3.3. Unattached byproducts

Although the grafting reaction was quite efficient, a few side reactions are likely to take place simultaneously, par-

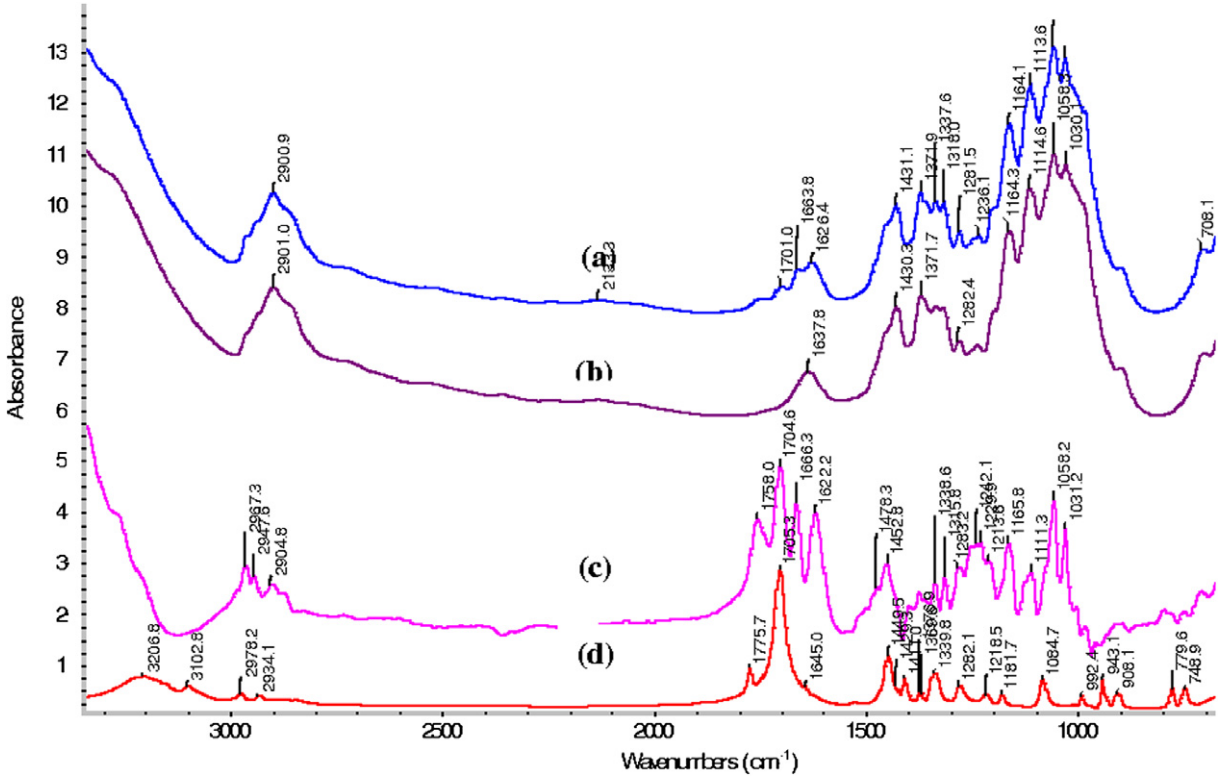


Fig. 6. IR spectra of (a) PADMH-g-Cotton; (b) untreated cotton; (c) difference spectrum between PADMH-g-Cotton and cotton; (d) standard spectrum of ADMH.

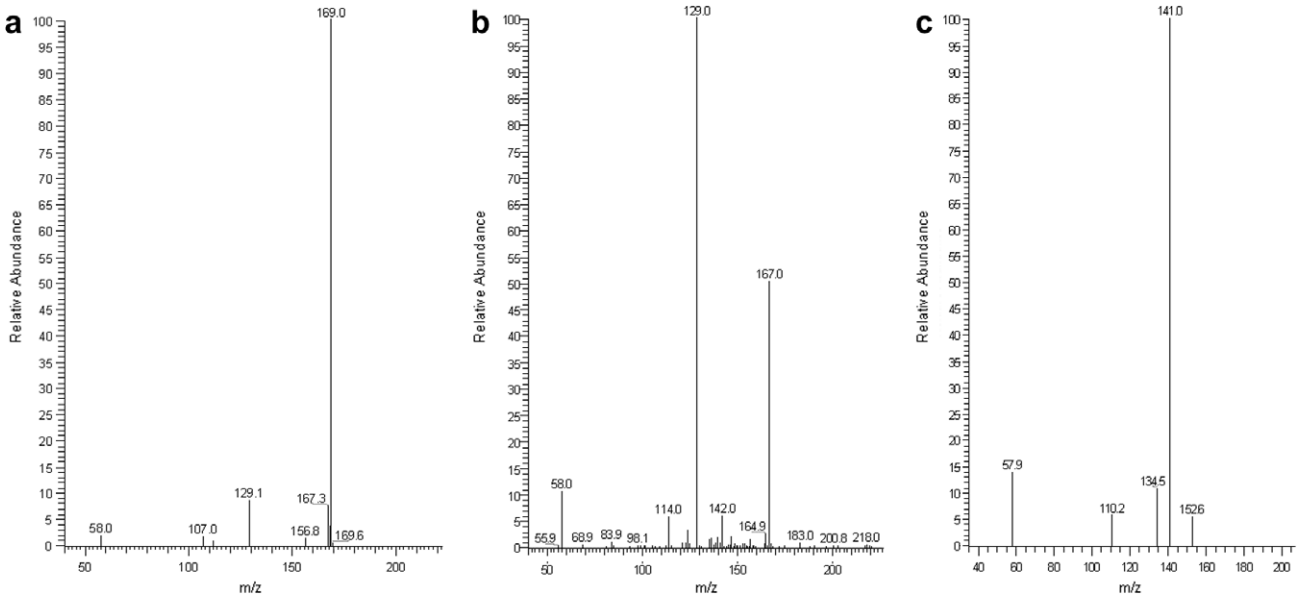
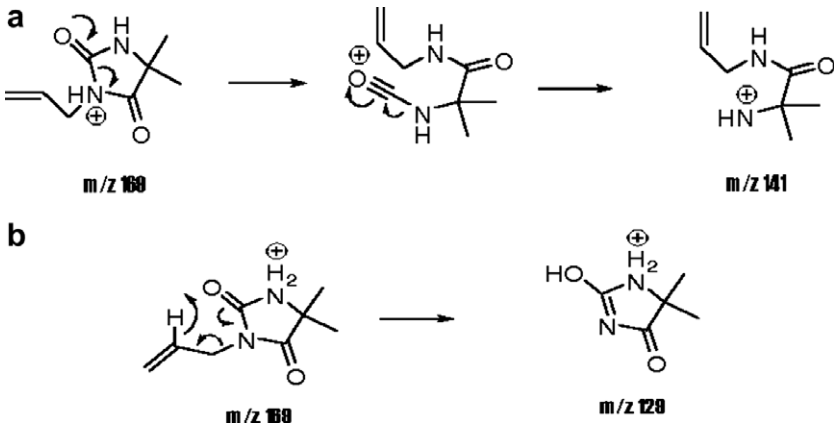


Fig. 7. Product-ion spectra of three ions m/z = (a) 169, (b) 185 and (c) 187 acquired on ion trap instrument.



Scheme 3. Proposed collision induced dissociation (CID) pathway of ion 169.

ticularly when the allyl monomer ADMH was employed as the functional monomer in the modification of cellulose. More specifically, initiator radicals still can react with monomers directly even it is not a preferred reaction. To characterize any ungrafted products formed during the chemical modification process, the processed cotton fabrics were thoroughly extracted with water to remove any unattached monomer and formed water soluble oligomers. The extracted solution was analyzed using LC–ESI/MS. In positive mode LC–ESI/MS spectrum of the extraction, strong ion peaks with m/z of 185 and 187 were found besides m/z 169 which is in accordance with the molecular weight of protonated ADMH. CID spectrum of ions with m/z = 169, 185 and 187 are shown in Fig. 7.

The CID spectrum of ion m/z 169 fits well with the standard $[ADMH+H]^+$ ion. In gas phase, a loss of 28 (m/z 169 → m/z 141) often suggests elimination of carbon monoxide. The pathway is shown in Scheme 3a. Ions with m/z 185, 187 suggest the existence of compounds A and B, shown in Fig. 8. 3-(1-Hydroxyl propyl)-5,5-dimethyl hydantoin (B) comes from hydroxyl radical addition to monomer ADMH since persulfate radicals can react with water to generate hydroxyl radical. Because allyl hydrogen can be abstracted by primary radical like persulfate or hydroxy radical, the combination of hydroxyl radical and ADMH allyl carbon radical gives 3-(1-propen-3-ol)-5,5-dimethyl hydantoin (A). The CID spectra in Fig. 7 confirm

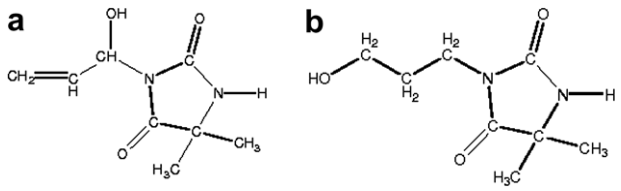


Fig. 8. Unattached compounds in grafting ADMH onto cotton.

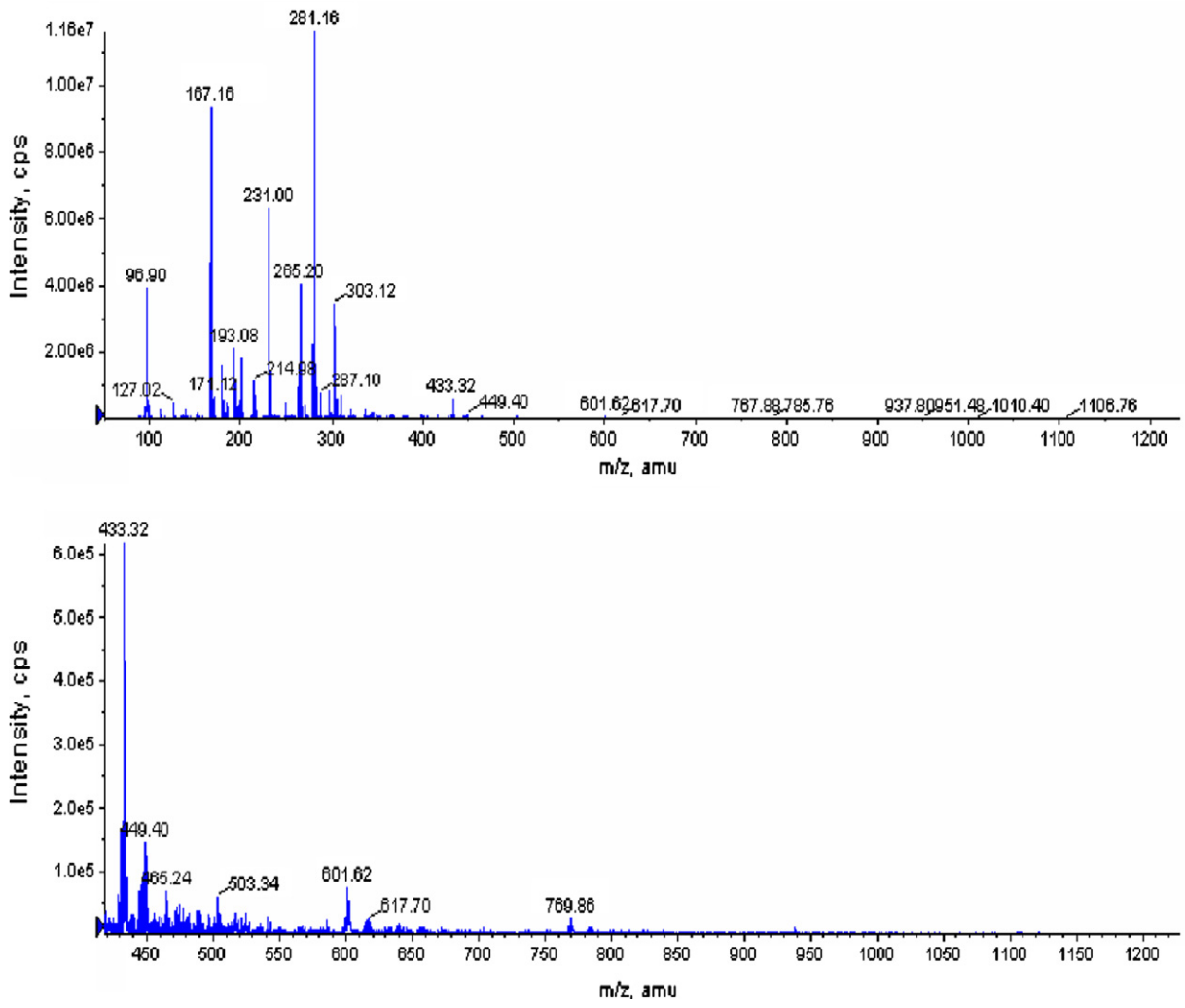


Fig. 9. Negative ESI/MS of unattached compound extracted from PADMH-g-Cotton.

that reaction path. In both CID spectra of ions *m/z* 185, 187, $[M+H-H_2O]^+$ were noticed, indicating that these ions are alcohol. Allyl linkage can be broken to give daughter ion *m/z* 129 as shown in Scheme 1b. Liquid chromatography of the aqueous extraction showed that the molar percentage of unreacted ADMH based on peak area was 82.9% in all three detected unattached byproducts. Even though the grafting yield of allyl monomer was low, the unreacted monomer can be easily removed from the grafted substrate and recycled. It was also found the grafting yield can be improved by adding crosslinker such as poly (ethylene glycol) diacrylate (Sun & Sun, 2002).

The expected homopolymer byproduct did not show up with significant signal intensity in positive mode ESI/MS. Due to the acid nature of sulfate at the end of homopolymer if it exists, the negative mode MS spectrum was acquired with the spectra are shown in Fig. 9. The first ion that can be assigned without doubt is *m/z* 96.9: HSO_4^-. The fact that the proton at N1 in the hydantoin ring is acidic justifies the $[M-H]^-$ ion *m/z* 167. Besides that, the homopolymer ion series *m/z* 265 (=97 + 168), 433, 601, 769 and 937 shows up in the spectrum, which suggests again that ADMH can be polymerized under the solvent-free condition adopted in this study.

3.4. Durable grafted structure and regenerable antibacterial function

Hydantoin can be converted to effective *N*-Chloramine biocide after chlorine treatment (Worley & Williams, 1988). ADMH was previously synthesized and chemically grafted onto many textile substrates such as polyester, nylon and cotton to produce durable and renewable antimicrobial materials (Sun & Sun, 2002). However, whether the ADMH was chemically grafted onto or its homopolymer was entrapped in the substrates was not completely distinguished in the previous modifications of the materials due to the use of a crosslinker, triallyl-1,3,5-triazine-2,4,6(1H,3H,5H)-trione (Sun & Sun, 2002). Now, the current work using LC–MS and modern instrumentations has revealed the true chemical grafting reaction of ADMH onto cotton cellulose using potassium persulfate as the radical initiator. Thus, the chlorinated PADMH-g-Cotton was tested against *E. coli* following a modified AATCC test

Table 3
Antibacterial performance of chlorinated PADMH-g-Cotton

	Grafting yield (%)	Chlorine (ppm)	Percentage reduction of *E.coli* at different contact time (%)	
			30 min	60 min
PADMH-g-Cotton	0.74	216 ± 10	99.999	99.999

ADMH 0.35 mM, PPS 0.175 mM, dried at 60 °C for 10 min and cured at 105 °C for 30 min.

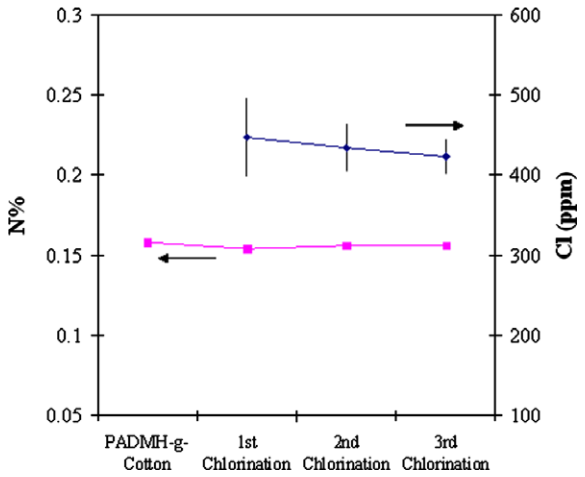


Fig. 10. Durability of the grafted structure and regenerability of N–Cl on PADMH-g-Cotton (grafting: ADMH 0.35 M, PPS 0.0875 M, dried at 60 °C for 10 min. and cured at 105 °C for 30 min; chlorination: 300 ppm available chlorine, pH 11, 30 min shaking; excess amount of Na_2SO_3 was used to quench active chlorine on the samples between 1st, 2nd and 3rd chlorinations).

method 100 to prove its biocidal efficacy. Table 3 shows the antibacterial results of the cotton product with a 5-logarithmic reduction of *E. coli* in a contact time of 30–60 min, equal to or consistent with the previous results. Moreover, the durability and regenerability of halogenated PADMH-g-Cotton were tested. Fig. 10 represents the nitrogen and chlorine contents in grafted and chlorinated PADMH-g-Cotton (chlorinated under basic condition, pH 11). The nitrogen contents are essentially constant upon repeated chlorination, which indicates stable grafted structure and supports the true chemical grafting claim. However, as suggested by the proposed mechanisms (Scheme 1), the grafted structure was vulnerable to acidic hydrolysis. Interestingly, this was evidenced by 12.7% loss of nitrogen on the same PADMH-g-Cotton sample after chlorination under acidic condition (pH 4). There was also no significant loss of chlorine on those repeatedly chlorinated samples (Fig. 10). Since chlorine content is proportionally associated with biocidal efficacy of *N*-chloramine material, the regenerable chlorine loading on PADMH-g-Cotton elucidates that the biocidal function is rechargeable without concerns of cleaving off grafted structures.

4. Conclusion

Cellulose macroradicals were generated effectively by potassium persulfate on cotton cellulose fibers under solvent-free condition, and coupling reactions occurred between sulfate and cellulose radicals. In the presence of allyl monomer the cellulosic macroradicals initiated a graft polymerization and the grafted cotton cellulose structures were confirmed. The grafting sites generated by potassium persulfate are probably at C3 and C4 on glucose ring via oxidative hydrogen abstraction without existence of any monomers. Two grafting mechanisms are proposed in Scheme 2. The polymerization degree of the longest grafted chain was 12. The chemically grafted cotton can be converted to biocide after chlorine treatment and the grafting PADMH is durable during the chlorination.

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