

## Thermal stability and degradation of chitosan modified with phenylacetic acid

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**Abstract**—N-(phenylacetyl) chitosan (NPAC) polymer was synthesized by the reaction of phenylacetic acid with chitosan. The chemical structure of the formed polymer was characterized by IR and microanalysis. Thermogravimetric analysis revealed that the thermal stability of the NPAC polymer was less than that of chitosan. The products of NPAC thermal degradation were identified by the GC-MS technique. The results indicate that the mechanism of degradation of NPAC polymer is characterized by the elimination of low-molecular weight radicals. A combination of these radicals and a random scission mechanism along the backbone chain are the main source of the degradation products.

Key words: N-(phenylacetyl) Chitosan, Thermal Stability, Mechanism of Degradation

### INTRODUCTION

The free amino groups of chitosan enable a variety of chemical modifications and substitution processes like carboxyalkylation, acylation, sulfation, enzymatic substitution, metal chelation, cyanoethylation, nitration and phosphorylation [1-3]. Synthesis of chitosan derivatives has recently become of great interest, with tailoring of the polymer to specific applications such as waste-water treatment [4], the food industry [5] and in medicine as wound dressing [6], gel implants [7], scaffolding materials [8] and drug delivery systems [9,10]. These modifications offer a wide spectrum of tools to enhance the sorption properties of chitosan for metals. They may increase the chemical stability of the sorbent in acid media and, especially, decrease the solubility in most mineral and organic acids. They also increase its resistance to biochemical and microbiological degradation [11,12]. It has been reported that the concentrations of acetic acid in solution and chemical modifications of chitosan affected the degradation both in the presence as well as in the absence of a degrading agent [13]. Chitosan is more stable than chitin to depolymerization due to the stabilizing effect of the free amine groups [14]. In spite of that, it was found that chitosan at high temperature in air underwent degradation [15]. Thermal analysis with a derivatograph showed that this polymer cannot withstand a temperature higher than 200-220 °C. Tirkistani [16,17] reported the reaction of chitosan with some cyclic oxygenated compounds with the aim of synthesis of new thermally stable chitosan derivatives. Sashiwa et al. described the biodegradation of chitosan and its derivatives depending on water solubility [18]. Good biodegradation was observed in modified chitosan derivatives by standard activated sludge [19]. Recently, Diab et al. [20-22] reported the thermal stability and degradation behaviors of N-(biphenylmethylidene) chitosan, N-(methylphenylidene) chitosan and N-cinnamoyl chitosan. Thermogravimetric analysis reveals that the thermal stability of chitosan is greater than that of these modified chitosan polymers. In this paper, novel N-(phenylacetyl) chitosan (NPAC) polymer was synthesized by

the reaction of chitosan with phenylacetic acid. The formed modified polymer was characterized by elemental analysis (C, H, N), IR spectroscopy and thermal gravimetric analysis. Thermal degradation of the NPAC polymer was studied and the products of the degradation were identified by GC-MS technique. A mechanism of the degradation is suggested.

### EXPERIMENTAL

#### 1. Materials

Chitosan (Aldrich Chemical Co., Inc. USA) was used without further purification. Its degree of deacetylation (DDA) was determined to be 94% by <sup>1</sup>H NMR spectroscopic method [23,24]. The molecular weight distribution and subsequent characteristics were obtained in an AVS-350 viscometer (Marimex, Germany) coupled to an automatic dilution device, Scholl Geräte Viscodoser AVS 20 (Germany). The molecular weight of the chitosan was estimated based on the parameters described by the Mark-Houwink equation:

$$[\eta] = K_m M^a$$

where  $K_m = 0.076$  and  $a = 0.76$  [25]. The average viscometric molecular weight,  $M_v = 69,000$ , was estimated from the intrinsic viscosity determined in a 0.3 mol L<sup>-1</sup> acetic acid and 0.2 mol L<sup>-1</sup> sodium acetate buffer solution at 25 ± 0.01 °C as the mean of five replicates. Phenylacetic acid (BDH Chemical Ltd., UK) was purified by degassing and being twice distilled on a vacuum line.

#### 2. Preparation of the Polymer

An equimolar ratio of chitosan repeating units and phenylacetic acid was fused for 30 min. in an oil bath at 220 °C. The reaction mixture was refluxed for 2 h. The reaction product was cooled to room temperature, washed with diethyl ether and methanol to remove the unreacted phenylacetic acid. The formed N-(phenylacetyl) chitosan (NPAC) polymer was filtered and dried in an oven at 40 °C for several days.

#### 3. Analytical Techniques

##### 3-1. Infrared Spectroscopy (IR)

Spectra of the polymer samples in the form of KBr discs were recorded on a Pye Unicam SP 2000 (UK) spectrometer.

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### 3-2. Microanalysis

Elemental analysis of the modified polymer was performed by the Microanalytical Unit at Cairo University.

### 3-3. Thermogravimetric Analysis (TG)

TG measurements were made with a Mettler TG 3000 (USA) apparatus. Finely powdered (~10 mg) samples were heated at 10°/min in a dynamic nitrogen atmosphere (30 ml/min); the sample holder was boot-shaped, 10 mm×5 mm×2.5 mm deep and the temperature measuring thermocouple was placed 1 mm from the sample holder.

### 3-4. Thermal Degradation of the Polymer

Samples of ~50 mg were heated under vacuum from ambient temperature to 500 °C. The volatile degradation products were collected for qualitative analysis by GC-MS technique. A Saturn GC 3400 (USA) with a fused quartz capillary column of 30 m×0.25 m coated with methylsilicon and a flame ionization analyser was used for identification of the condensable degradation products. The carrier gas was nitrogen at a flow rate 20 ml/min, and the programmed heating rate was 10°/min from 40 to 200 °C. The GC was interfaced with a Varian mass spectrometer (USA) equipped with the standard electron impact or chemical ionization (CI) sources and a DS 55 data system scans from *m/e* 200 to 20 at a scan rate of 10 s/decade. Perfluorokerosene (PFK) was used for computer calibration, and the ion source was maintained at 200 °C. Accurate mass measurements of the CI mass spectra were performed at 10000 resolving power using PFK as internal reference and by a computer interpolation data system.

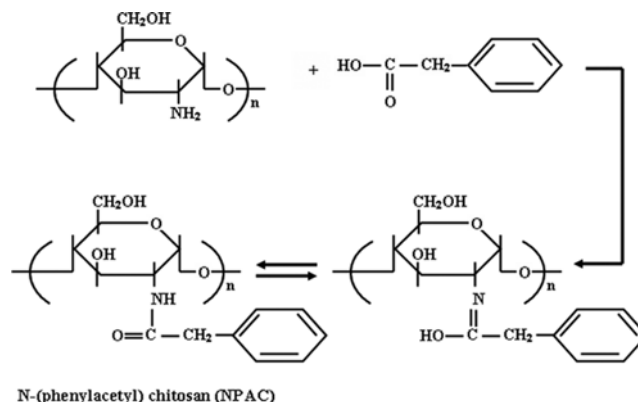
## RESULTS AND DISCUSSION

### 1. Characterization of N-(phenyl acetyl) Chitosan (NPAC) Polymer

The IR spectrum of chitosan (Fig. 1) shows a broad band at 3,423  $\text{cm}^{-1}$  due to OH and  $\text{NH}_2$  groups. The bands at 1,655 and 1,321  $\text{cm}^{-1}$

are due to the amino groups. There are bands at 1,458, 1,423, 1,379 and 1,078  $\text{cm}^{-1}$  due to the O-C-O groups. The spectrum is in good agreement with the IR spectrum of chitosan reported by Muzzorella et al. [26]. Microanalysis results for of chitosan  $\text{C}_6\text{H}_{11}\text{O}_4\text{N}$  were as follows: (Calcd. C, 44.7; H, 6.8; N, 8.7%. Found C, 44.62; H, 6.94; N, 8.67%).

The reaction of chitosan with phenylacetic acid gives the corresponding N-(phenylacetyl) chitosan (NPAC) polymer



The IR spectrum of the NPAC polymer (Fig. 2) showed a broad band at ~1,731  $\text{cm}^{-1}$  indicating the involvement of phenyl acetic acid in the modification of chitosan. The band at 1,639  $\text{cm}^{-1}$  is attributed to the amide group [27]. IR spectroscopy also confirms the imine formation represented by the absorption at 1,563  $\text{cm}^{-1}$ , which is not present in the original chitosan sample. The absorption at 711  $\text{cm}^{-1}$  is due to the C=C stretching in the aromatic ring. Microanalysis of NPAC  $\text{C}_{14}\text{H}_{17}\text{ON}$  gave: Calcd. C, 63.8; H, 6.4; N, 5.3%. Found C, 63.71; H, 6.51; N, 5.31%. The elemental analysis results of chitosan and NPAC were quite different from those expected for a 100% degree of substitution (~90%), suggesting that the substitution was

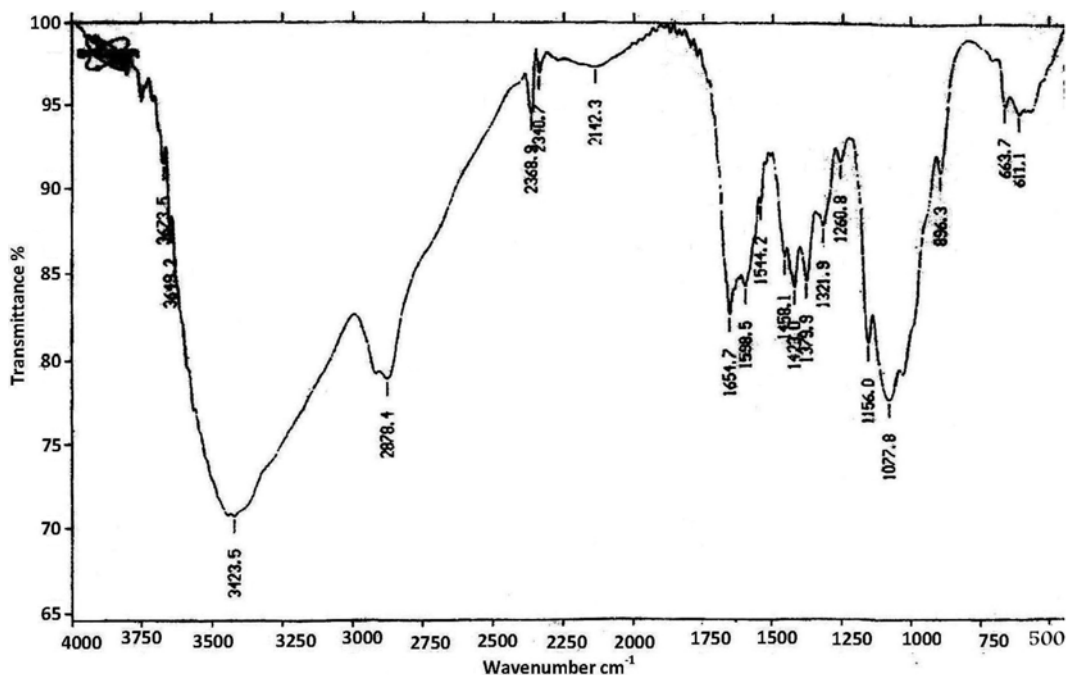


Fig. 1. IR spectrum of chitosan.

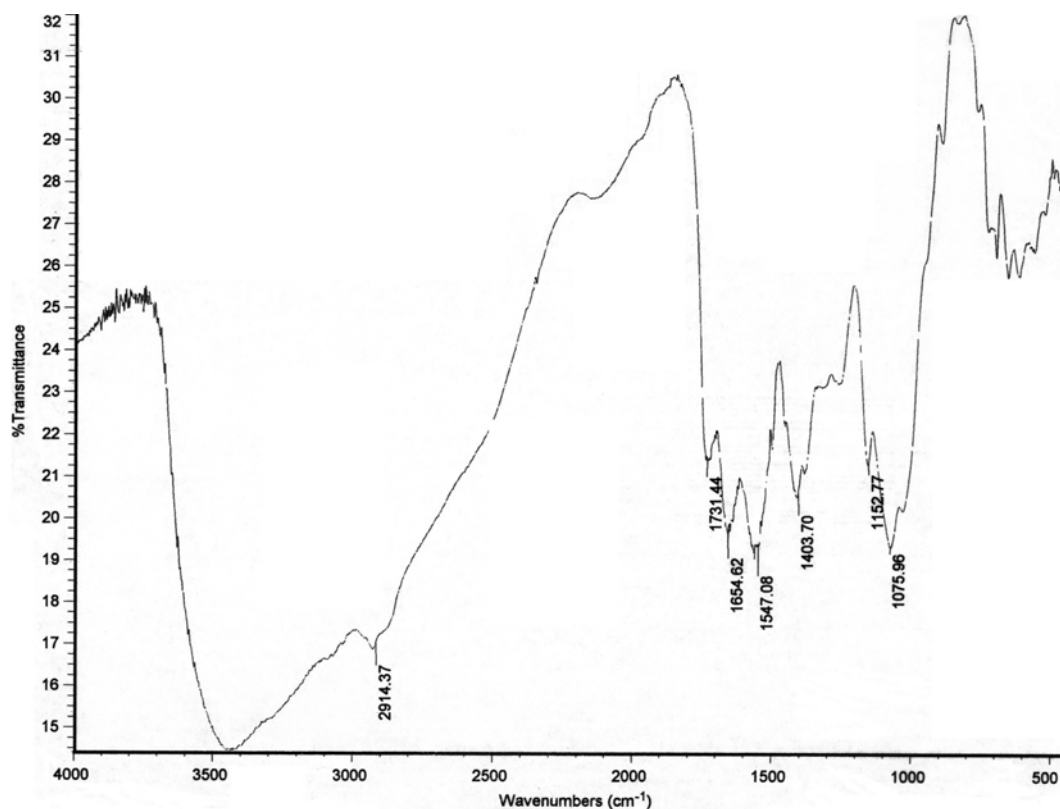


Fig. 2. IR spectrum of NPAC polymer.

not complete. However, the presence of phenylacetic acid in the chitosan modification caused an increase in the carbon and hydrogen content in the resulting material compared with the starting chitosan. A decrease in the nitrogen/carbon ratio suggests that the substitution occurred.

## 2. Thermal Analysis Methods

### 2-1. Thermogravimetry (TG)

The TG and DTG curves of chitosan are shown in Fig. 3. There are two degradation stages in chitosan polymer. In the first stage, weight loss starts at  $\sim 220^\circ\text{C}$  and continues to  $\sim 320^\circ\text{C}$  with  $\sim 50\%$  weight loss. The maximum rate of weight loss, shown by the derivative of the curve occurs at  $\sim 295^\circ\text{C}$ . The second stage reaches a maximum at  $\sim 470^\circ\text{C}$  with a weight loss percentage of  $\sim 25\%$ .

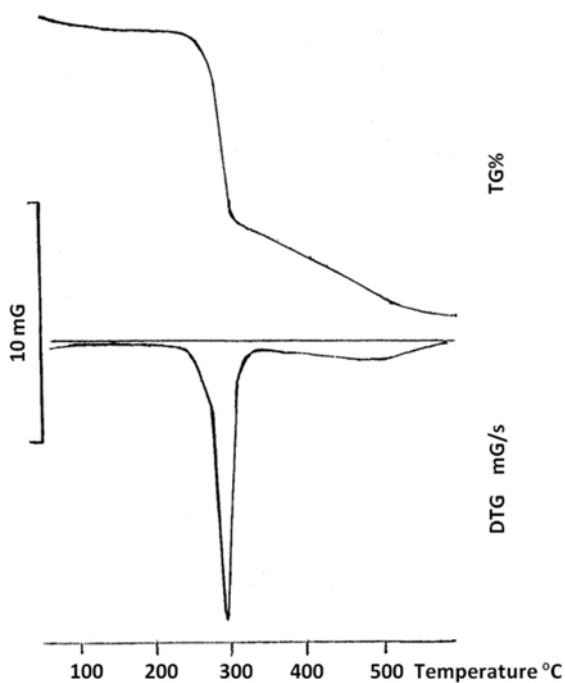


Fig. 3. TG and DTG curves of chitosan.

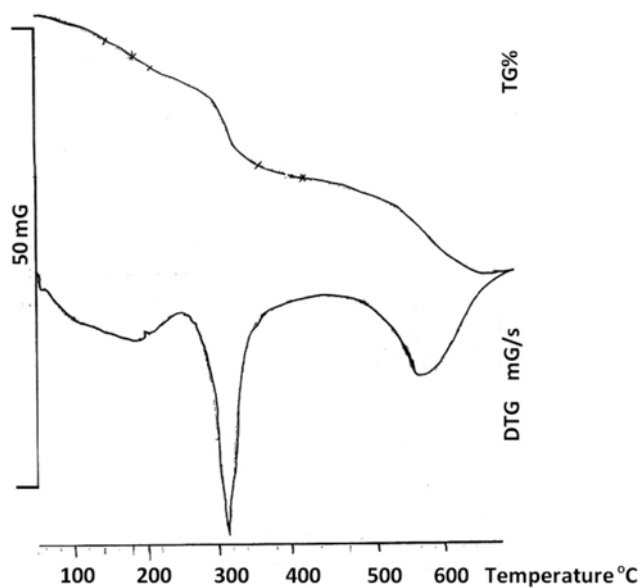


Fig. 4. TG and DTG curves of NPAC polymer.

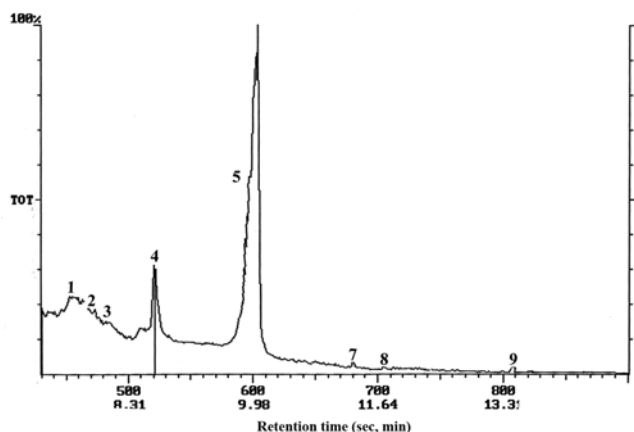


Fig. 5. GC curve of the degradation products of NPAC polymer.

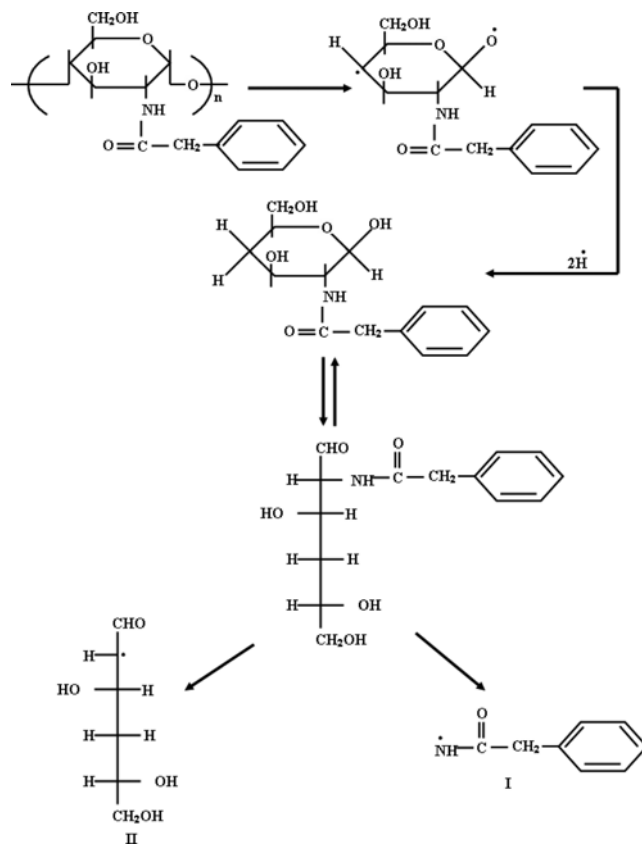
The TG and DTG curves of the NPAC polymer are shown in Fig. 4. There are three degradation stages in the NPAC polymer. The first stage starts at  $\sim 110^\circ\text{C}$  with a weight loss percentage of  $\sim 30\%$ . The maximum rate of weight loss is at  $\sim 190^\circ\text{C}$ . The second stage starts at  $\sim 270^\circ\text{C}$  with a weight loss percentage of  $\sim 25\%$  and maximum rates of weight loss at  $315^\circ\text{C}$ . The third peak shows a weight loss percentage of  $\sim 30\%$ . TG curves reveal that the thermal stability of the chitosan polymer was greater than that of the NPAC polymer.

#### 2-2. Thermal Degradation of NPAC Polymer

50 mg of NPAC polymer sample was heated to  $500^\circ\text{C}$  under vacuum and the degradation products were injected into the GC-MS apparatus. Fig. 5 shows the GC curve of the thermal degradation products of NPAC polymer sample. Table 1 represents the degradation products which were identified by the mass spectroscopic apparatus. Some of the peaks could not be identified because of their small size or due to unclear mass spectra. According to the degradation products of the NPAC polymer, it seems that the degradation occurred mainly by forming low-molecular weight radicals I and II (Scheme 1), followed by random scission mechanism along the backbone chain. These radicals may stabilize themselves by abstraction of  $\text{H}^\bullet$  or  $\text{OH}^\bullet$  radicals.

The radicals I may abstract  $\text{H}^\bullet$  to produce 2-phenylacetamide (Scheme 2) as shown in peak 8 in Fig. 5.

The radical III may abstract  $\text{H}^\bullet$  to produce toluene which is oxidized to benzoic acid as represented in peaks 2 and 6, respectively, and shown in Scheme 3.



Scheme 1.

The radical IV produces 2-phenylacetic acid (peak 7) after abstraction of  $\text{H}^\bullet$  as shown in Scheme 4.

3,5,6-Trihydroxyhexanol (peak 9) was formed among the degradation products of NPAC polymer by abstraction of  $\text{H}^\bullet$  of the aldehydic radical II (Scheme 5).

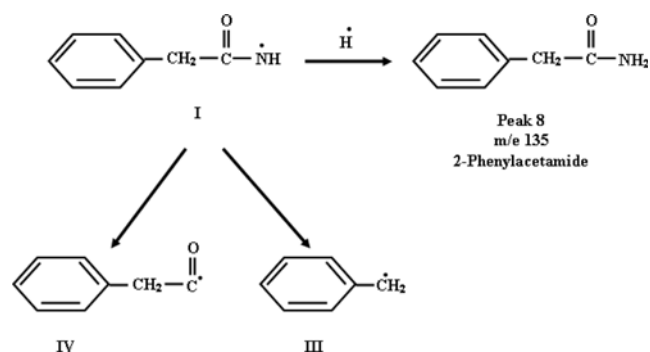
5-Hydroxy-1,3-pentadiene, cyclohex-1-en-6-ol, 3,5-dihydroxypent-1-ene and 6-hydroxy-2,4-hexadienal were formed among the degradation polymer of NPAC polymer as represented in peaks 1,3,4 and 5, respectively. The mechanism of formation of these compounds (Scheme 6) is as follows:

#### 3. Conclusions

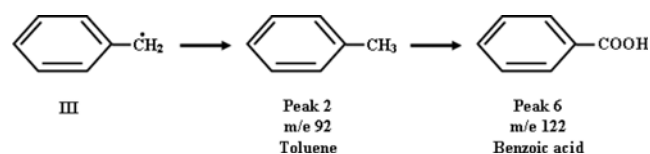
Novel N-(phenylacetyl)chitosan (NPAC) polymer was synthesized by the reaction of chitosan with phenylacetic acid. The formed modified polymer was characterized by elemental analysis (C, H,

Table 1. GC-MS of the degradation products of NPAC polymer

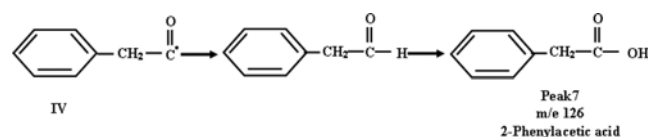
Peak no.	Retention time, min	Major MS fragments	Suggested structures (most probable)
1	7.49	84, 61, 47	5-Hydroxy-1,3-pentadiene
2	7.52	92, 75, 61, 48	Toluene
3	7.69	95, 70, 47	Cyclohex-1-en-6-ol
4	8.70	102, 83, 61, 47	4,5-Dihydroxypent-1-ene
5	9.44	112, 83, 56, 42	6-Hydroxy-2,4-hexadienal
6	10.32	122, 105, 47	Benzoic acid
7	11.34	126, 111, 83, 47	2-Phenylacetic acid
8	11.73	135, 115, 75, 61, 47	2-Phenylacetamide
9	13.38	148, 132, 114, 61, 47	3,5,6-Trihydroxyhexanol



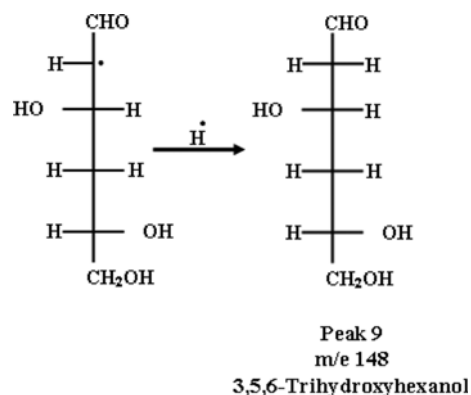
Scheme 2.



Scheme 3.

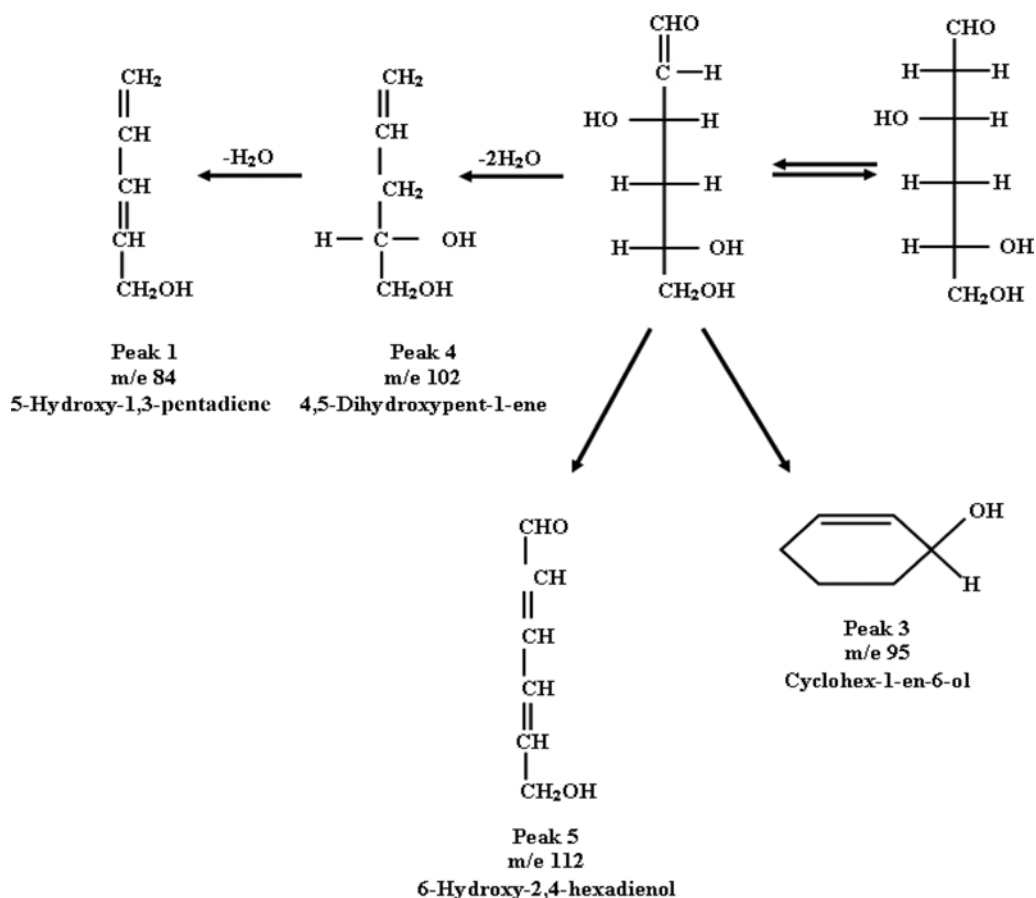


Scheme 4.



Scheme 5.

N), IR spectroscopy, and the thermal stability was compared with chitosan. Thermal degradation of NPAC polymer was studied and the products of degradation were identified by the GC-MS technique. 5-Hydroxy-1,3-pentadiene, toluene, cyclohex-1-en-6-ol, 4,5-dihydroxy-2,4-hexadienal, benzoic acid, 2-phenylacetic acid, 2-phenylacetamide and 3,5,6-trihydroxyhexanol were the main degradation products. Accordingly, it seems that the mechanism of degradation of NPAC polymer is characterized by elimination of low-molecular weight radicals. The combination of those radicals and a random scission mechanism along the backbone chain are the main source of the degradation products.



Scheme 6.

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