

THERMAL STABILITY AND DEGRADATION OF CHITOSAN MODIFIED BY BENZALDEHYDE

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ABSTRACT

Benzylidene chitosan polymer was prepared, characterized and thermal stability was compared with chitosan. Thermal degradation products of the polymer were identified by GC-MS technique. It seems that the mechanism of degradation of benzylidene chitosan is characterized by formation of low-molecular weight radicals, followed by random scission mechanism along the backbone chain.

1. INTRODUCTION

The reaction of the amino groups of chitin and chitosan with carbonyl compounds leading to formation of Schiff bases have been reported in several literatures [**Hirano & Ohe (1975); Tirkistani (1998) and Tirkistani (1998)**]. It has been reported that chitosan is more stable than chitin to depolymerization due to stabilizing effect of free amino groups [**Bihari-Verga et al., (1975)**].

In this paper, thermal stability of benzylidene chitosan polymer is reported by thermogravimetric analysis. Thermal degradation of the modified polymer is studied using GC-MS technique.

2. EXPERIMENTAL

2.1. Materials:

Chitosan (Aldrich Chemical Co., Inc.) was used without further purification.

Benzaldehyde (BDH Chemical Ltd.) was purified by standard procedure.

All other chemicals and solvent were purified by standard procedure.

2.2. Preparation of the polymer:

An equimolar ratio of chitosan and benzaldehyde was fused for 30 min, then 50 ml of glacial acetic acid was added to the reaction mixture and refluxed for 2 h. The excess acetic acid was removed by distillation. The reaction mixture was cooled to room temperature and washed with diethyl ether and ethanol to remove the unreacted benzaldehyde. The formed solid polymer was filtered and dried in an oven at 40 °C for several days.

2.3. Analytical Techniques:

2.3.1. Infrared spectroscopy (IR):

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

2.3.2. Microanalysis:

Elemental analysis of the modified polymer was performed by Micro-analytical Unit at King Abd El Azzez University.

2.3.3. Thermal Gravimetric Analysis (TG):

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

TG was also used for the determination of rates of degradation of the polymer in the initial stages of decomposition. The activation energies were calculated by application of the arrhenius equation.

2.3.4. Thermal degradation of the Polymer:

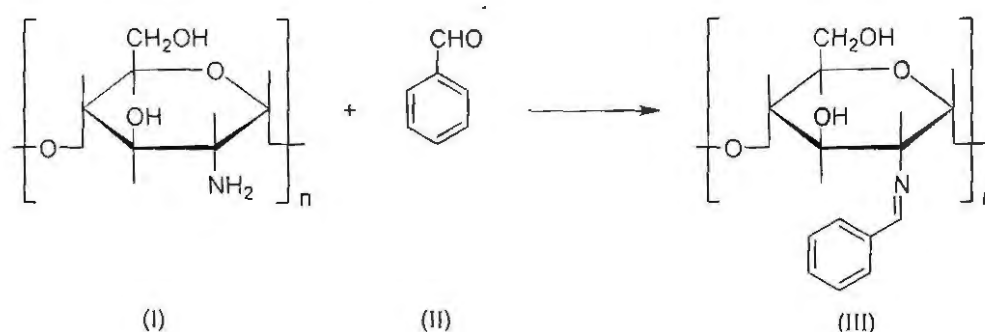
Samples of ~50 mg were heated under vacuum from ambient temperature to 500°C. The volatile degradation products were collected for qualitative analysis by GC-MS technique. A Saturn GC 3400 with a fused quartz capillary column of 30 m × 0.25 mm coated with methylsilicon, under programmed heating condition from 40 to 200°C was used for the identification of the condensable degradation products. The GC is interfaced with a Varian mass spectrometer.

3. RESULTS AND DISCUSSION

3.1. Characterization of Benzylidene Chitosan Polymer:

The IR spectrum of chitosan shows a broad band at 3423 cm^{-1} due to OH and NH_2 groups. The bands at 1655 and 1321 cm^{-1} due to the amino group. There are bands at 1458 , 1423 , 1379 and 1078 cm^{-1} due to O-C-O group. These bands are in good agreement with the IR spectrum of chitosan given [Muzzarelli et al., (1972)]. Microanalysis of $\text{C}_6\text{H}_{11}\text{O}_4\text{N}$ (calcd. C, 44.7; H, 6.8; N, 8.7 %. Found C, 44.62, H, 9.4; N, 8.67 %).

The reaction of chitosan (I) with benzaldehyde (II) gives the corresponding benzylidene chitosan polymer (III).



The IR spectrum of the formed polymer show bands at 3738 and 3434 cm^{-1} due to amidic group. The disappearance of the band at 1720 cm^{-1} indicates the involvement of carbonyl group of benzaldehyde in modification of chitosan. Microanalysis of $\text{C}_{13}\text{H}_{14}\text{O}_4\text{N}$ (Calcd. C, 60.6; H, 5.4; N, 5.4 %. Found C, 59.71; H, 5.93; N, 5.60 %).

3.2. Thermal methods of analysis:

3.2.1. Thermogravimetry (TG):

TG curve of chitosan is shown in Figure 1. There are two degradation stages in chitosan polymer. In the first stage, weight loss starts at $\sim 220^\circ\text{C}$ and continues to 320°C with 50% weight loss. The maximum rate of weight loss, shown by derivative equipment associated with TG apparatus, occurs at 295°C . The second stage reaches a maximum at $\sim 470^\circ\text{C}$ with a weight loss percentage of $\sim 40\%$.

There are two degradation stages in the benzylidene chitosan polymer as shown in Figure 2. The first stage starts at $\sim 170^\circ\text{C}$ with a

weight loss percentage of ~ 50 %. The maximum rate of weight loss, shown by derivative thermogravimetric occur at 235°C. The second stage starts at ~310°C with a weight loss percentage of 40 %. Comparing the TG curves of benzylidene chitosan with chitosan polymer indicate that the thermal stability of the modified polymer is less than chitosan.

The effective activation energies of the thermal degradation of the chitosan and benzylidene chitosan polymers were determined from the temperature dependence of the chain rupture rate. The rate constant of the thermal degradation plotted according to the Arrhenius relationship (Figure 3). The activation energies of chitosan and benzylidene chitosan polymers were found to be 52.2 and 23.2 kJ/mole, respectively. It is clear that the activation energies are in the same order of the stabilities.

3.2.2. Thermal degradation of benzylidene chitosan polymer:

50 mg of polymer sample was heated under vacuum from ambient temperature to 500°C. The liquid fraction from the degradation were injected into the GC – MS apparatus. Figure 4 shows the GC trace from the degradation products of benzylidene chitosan polymer. Table 1 represents the results of degradation products which were identified by mass spectroscopy. Some of the peaks could not be identified due to the lack to the reference material or due to the unclear mass spectra.

Peaks 1, 3, 4, 6 and 10 in the GC trace for the degradation products of benzylidene chitosan polymer are corresponding to 5-hydroxy-1,3-pentadiene, cyclohex-1-en-6-ol, 4,5-dihydroxypent-1-ene, 6-hydroxy-2,4-hexadienol and 3,5,6-trihydroxyhexanal, respectively similar to those suggested structures in the thermal degradation of chitosan succinimide polymer [Tirkistani (2008)]. The mechanism of formation of these compound is as follow:

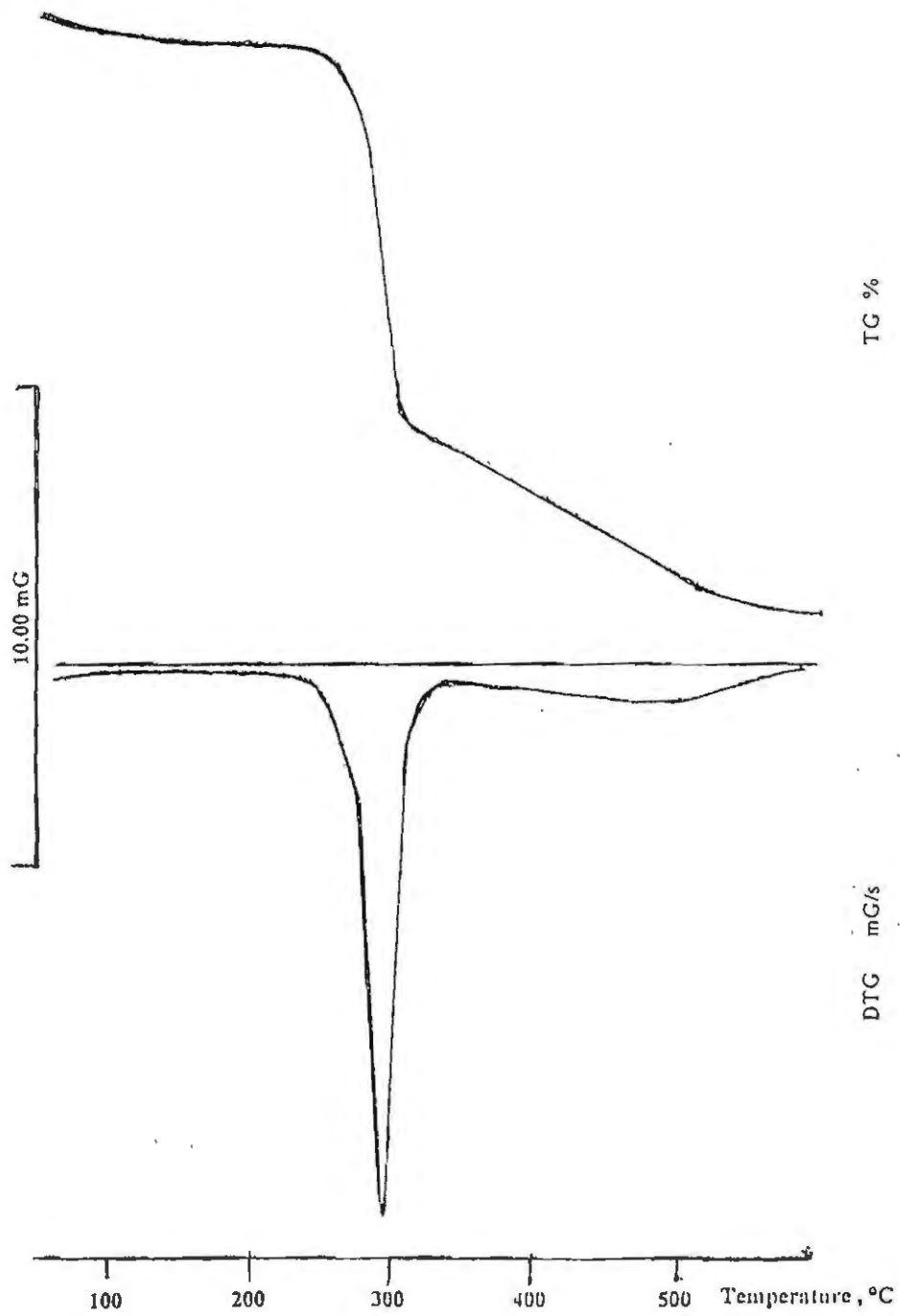


Figure 1 : TG curve of chitosan

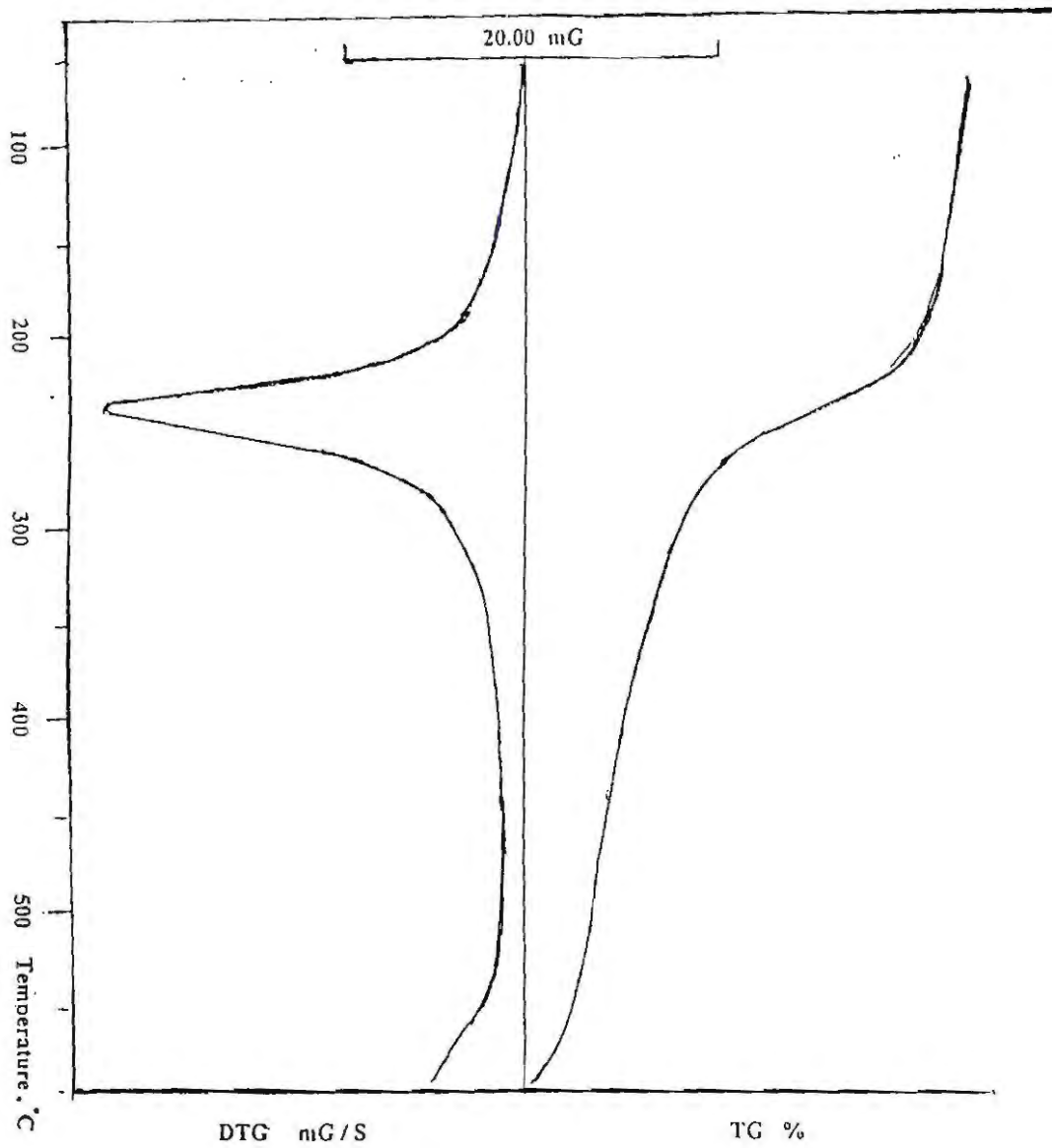


Figure 2 : TG of benzyilidene chitosan polymer

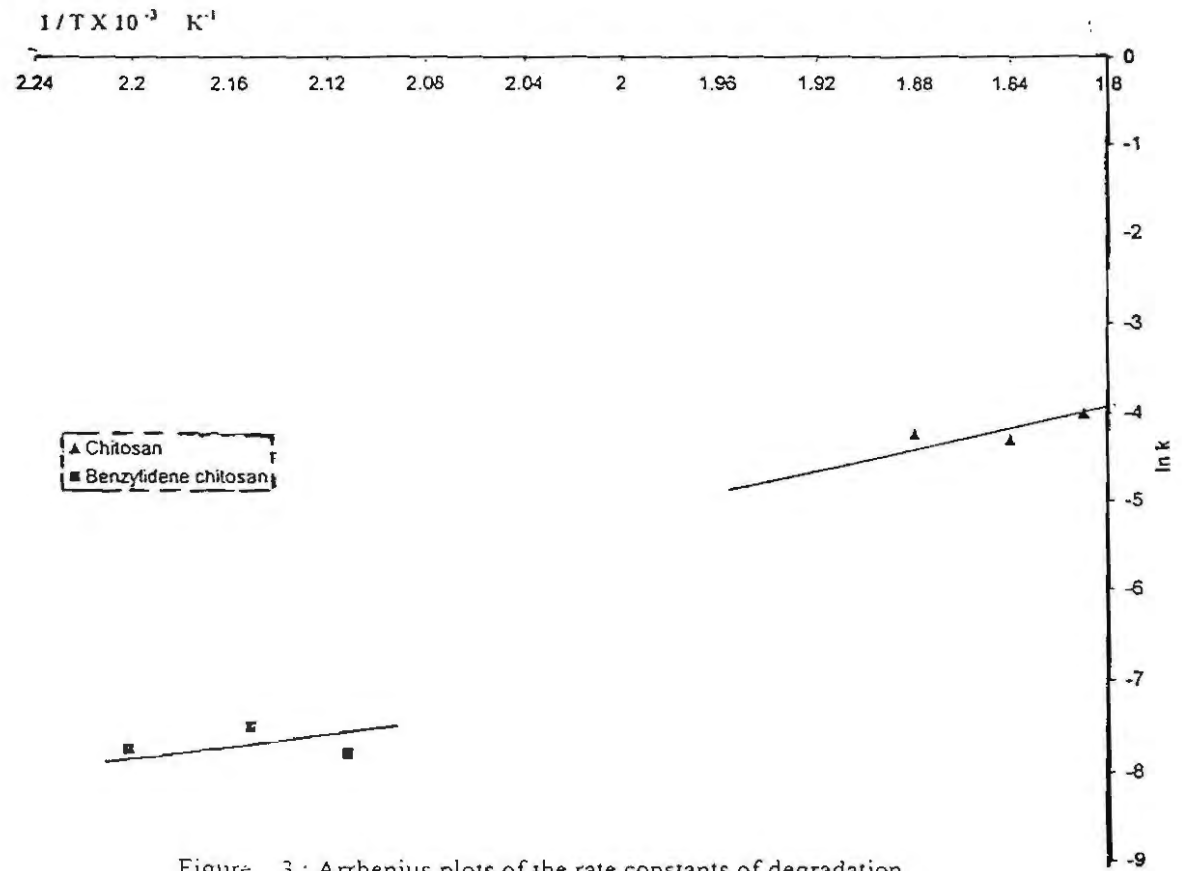


Figure 3 : Arrhenius plots of the rate constants of degradation of chitosan and benzyldene chitosan polymers

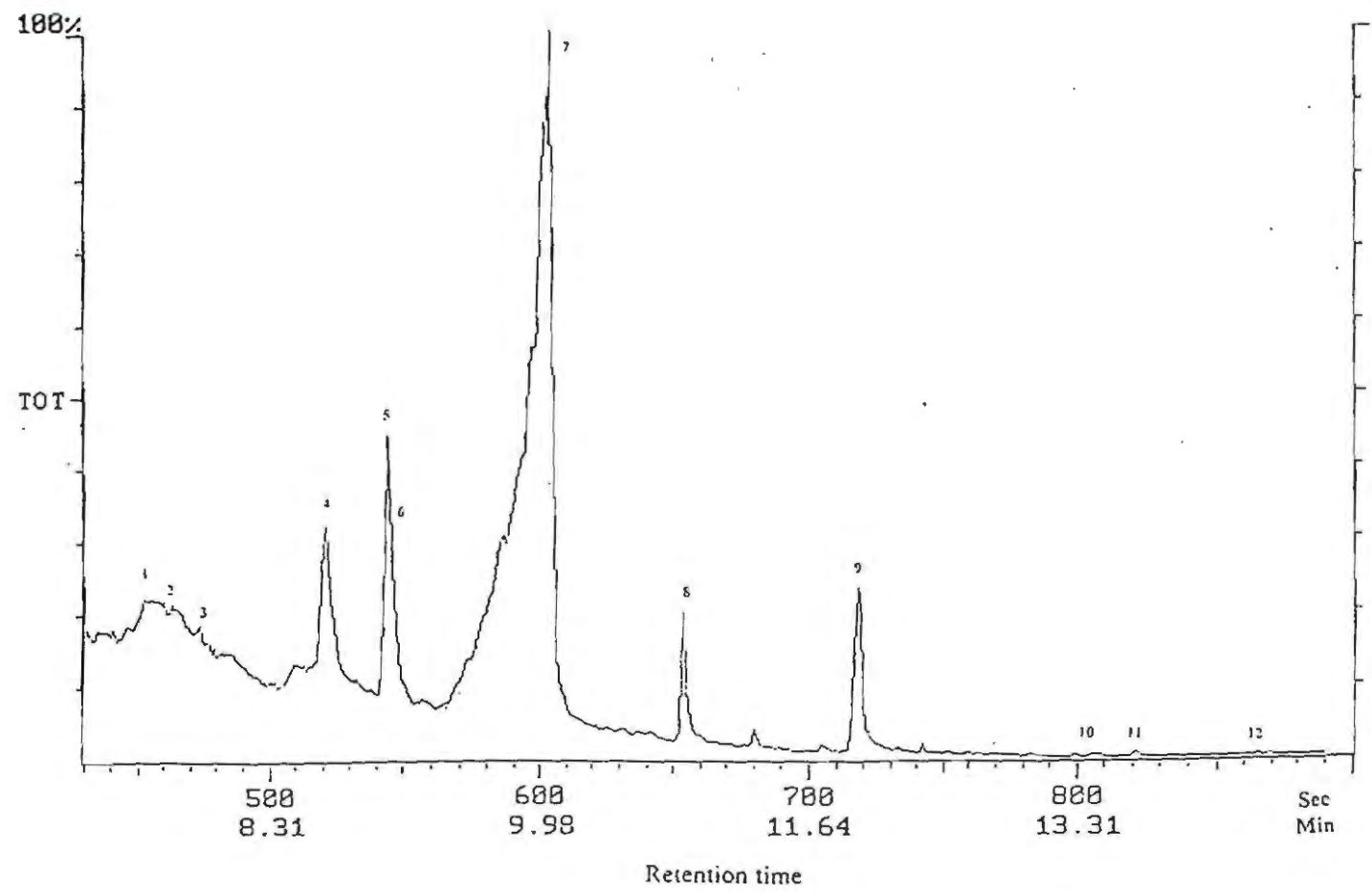
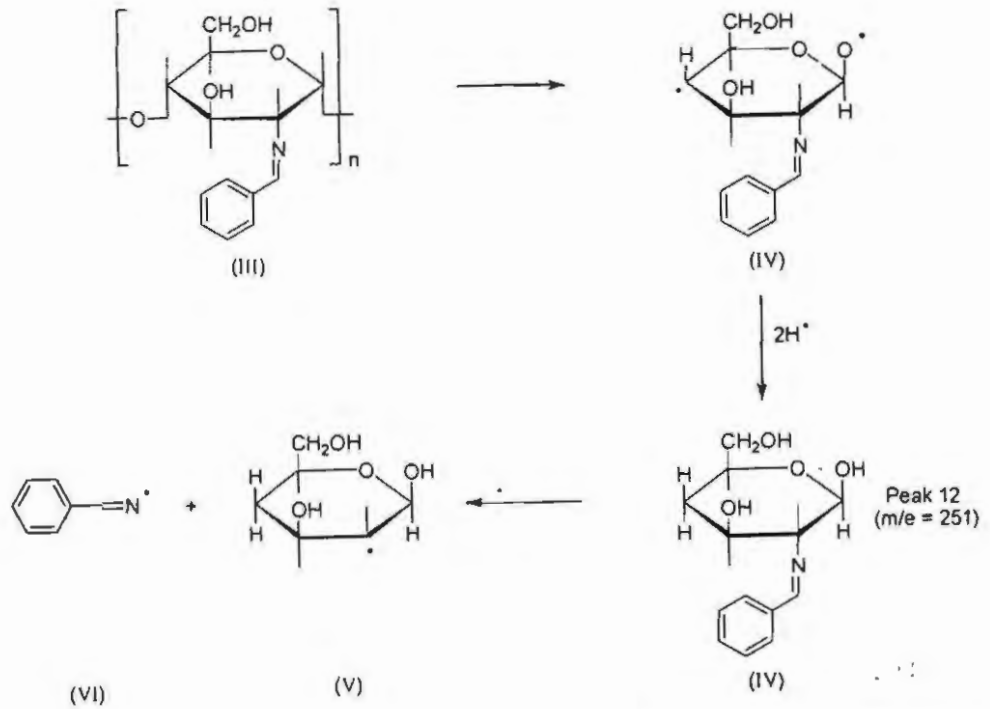
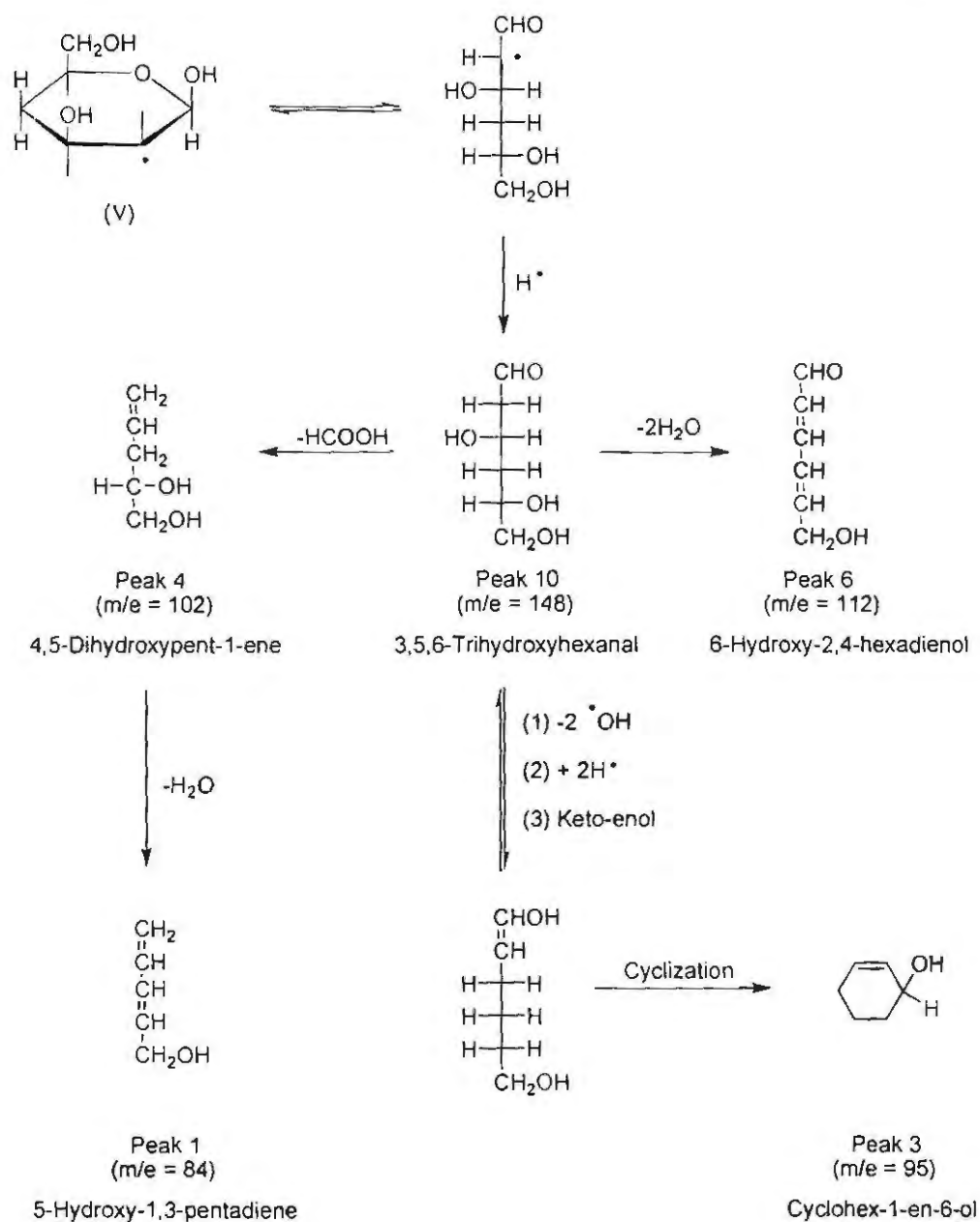


Figure 4: GC curve of the degradation products of benzylidene chitosan polymer

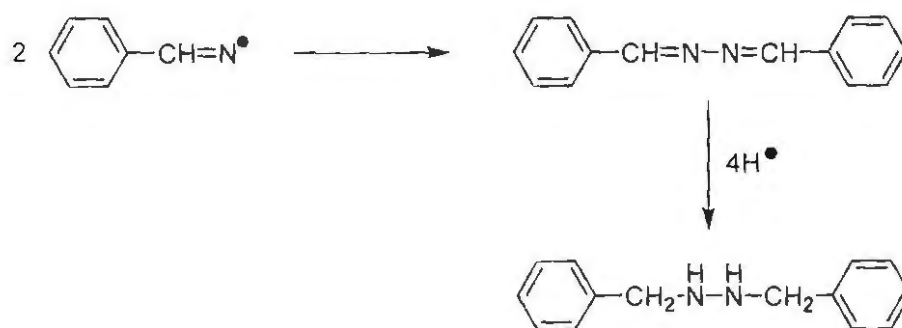


2,4-Dihydroxy-3-benzylideneamino-6-hydroxymethyl-tetrahydropyran



The radical V may abstract two H^\bullet and produces 2,4-dihydroxy-3-benzylideneamino-6-hydroxymethyltetrahydropyran (peak 12).

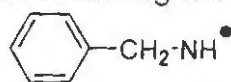
Two moles of VI abstract four hydrogen radicals forming N,N-dibenzylhydrazine (peak 11).



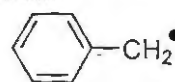
Peak 11
(m/e = 212)

N,N'-Dibenzylhydrazine

Thermal breakdown in N,N'-dibenzylhydrazine occurs in the N-N or C-N bonds forming low molecular radicals such as:



(VII)

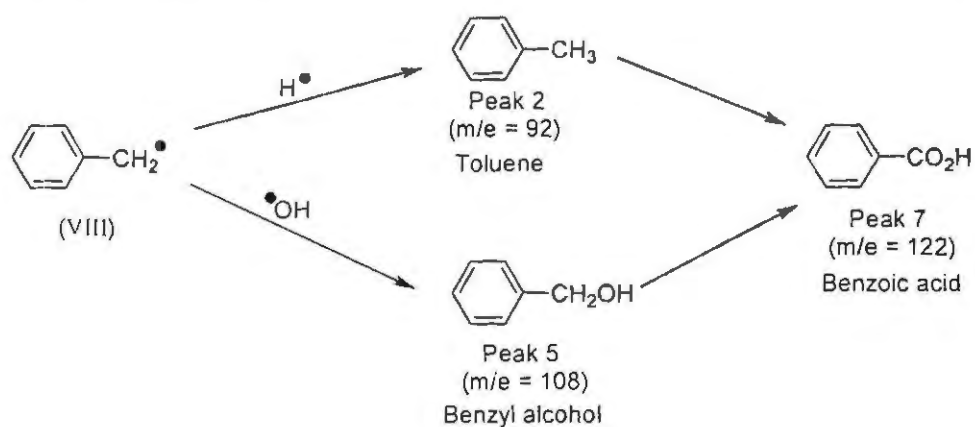


(VIII)

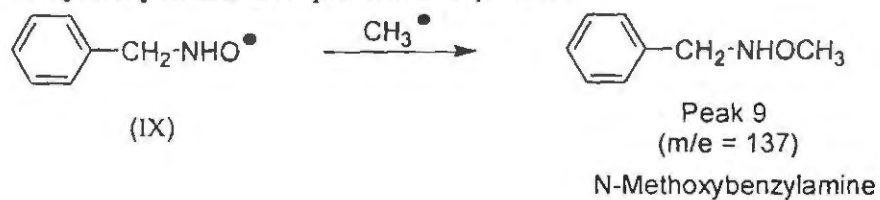
The radical VII abstract $\bullet\text{OH}$ to form benzyhydroxylamine (peak 8), followed by breakdown to form the radical IX.



The radical VIII abstract H^\bullet or $\bullet\text{OH}$ forming toluene (peak 2) or benzyl alcohol (peak 5), respectively. Oxidation of these two compounds gives benzoic acid (peak 7).



The radical IX abstract methyl radical to produce N-methoxybenzylamine as represented in peak 9.



According to these degradation products, it seems that the mechanism of degradation of benzylidene chitosan is characterized by formation of low-molecular weight radicals, followed by random scission mechanism along the backbone chain.

Table (1): GC-MS of the degradation products of benzylidene chitosan 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, 82, 61, 47	4, 5 -Dihydroxypent-1-ene
5	9.02	108, 83, 71, 61, 48	Benzyl alcohol
6	9.44	112, 63, 56	6-Hydroxy- 2 , 4-hexadienol
7	10.32	122, 105, 47	Benzoic acid
8	10.93	123, 105, 47	Benzyl hydroxylamine
9	11.94	137, 107, 61	N-Methoxybenzylamine
10	13.38	148, 132, 114, 61, 47	3 , 5 , 6-Trihydroxyhexanal
11	13.71	212, 194, 123, 105, 61	N , N'-Dibenzylhydrazine
12	14.41	251, 219, 97, 74, 55	2,4-Dihydroxy-3-benzyl-deneamino-6-hydroxymethyl-tetrahydropyran

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الملخص العربي

يتضمن هذا البحث تحضير بولي بنزالدين كيتوسان ومقارنة الثبات الحراري له بالكيتوسان باستخدام التحليل الوزني. وتم قياس طاقة التنشيط للتكسير الحراري للبوليمر المحضر باستخدام معادلة أرهينيوس ووجد أنها تساوي 23,2 كيلو جول /مول. استخدم مطياف الكتلة المتصل بالكروماتوجراف للتعرف على نواتج التكسير الحراري للبوليمر المحضر ولقد اقترحت ميكانيكية لهذا التكسير اساسها تكوين شقوق ذات وزن جزيئي صغير سرعان ما تتحد لتكوين هذه النواتج.

