THERMAL STABILITY AND DEGRADATION OF CHITOSAN MODIFIED BY BENZOPHENONE
التحليل والتكسير الحراري للكيتوسان المعدل باستخدام البنزوفينون

M.M. El-Halwany[1], M.A. Diab[2], A.Z. El-Sonbati[2], and D.M.D. Bader[2]
[1]Mathematical and Physical Sciencs Department, Faculty of Engineering, Mansoura University, Mansoura, Egypt.
[2]Chemistry Department, Faculty of Science, Mansoura University, Demiatta, Egypt

E.mail:- elsonbatisch@yahoo.com

يتضمن هذا البحث تحضير ن-(ثنائي فينيل ميثاليدينل) كيتوسان ومقارنه الثبات الحراري له بالكيتوسان باستخدام التحليل الوزني. وتم قياس طاقة التنشيط للتكسير الحراري للبوليمر المحضر باستخدام معادلة أرهينيوس ووجد أنها تساوي ٣٨,٧ كيلوجول/مول. كذلك تم استخدام مطياف الكتلة المتصل بالكروماتوجاف للتعرف على نواتج التكسير الحراري للبوليمر المحضر ولقد اقترحت ميكانيكية لهذا التكسير أساسها تكوين شقوق ذات وزن جزيئي صغير سرعان ما تتحد لتكوين هذه النواتج.

ABSTRACT
N-(biphenylmethylidenyl) chitosan polymer was prepared, characterized and thermal stability was compared with chitosan. Thermal degradation products of the modified polymer were identified by GC-MC technique. It seems that the mechanism of degradation of the prepared polymer is characterized by formation of low molecular weight radicals, followed by random scission mechanism along the backbone chain.
Keywords: N-(biphenylmethylidenyl) chitosan-Thermal stability and degradation-Mechanism of degradation.

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 [1-3]. It has been reported that chitosan is more stable than chitin to depolymerization due to stabilizing effect of free amino groups [4]. In spit to that, it was found that chitosan at high temperature in air undergoes degradation [5]. Thermal analysis with a derivatograph showed that this polymer can not withstand temperature higher than 200-220 °C. Tirkistani [5-7] was reported the reaction of chitosan with same cyclic oxygenated compounds with the aim of synthesis of new chitosan derivatives. Thermal stabilities of these derivatives has been studied. In this paper, thermal stability of N-(biphenylmethylidenyl) chitosan (BPMC) polymer is reported by thermogravimetric analysis. Thermal degradation of the modified polymer is studied using GC-MC technique.

2. EXPERIMENTAL
2.1. Materials
1- Chitosan (Aldrich Chemical Co., Inc.) was used without further purification
2- Benzophenone (BDH Chemical Ltd.) was purified by standard procedure.
3- All other chemicals and solvents were purified by standard procedure.

2.2. Preparation of the polymer
An equimolar ratio of chitosan and benzophenone was fused for 30 min. then 50 ml of glacial acetic acid was added to the reaction mixture and refluxed for 2h. The excess acetic acid was removed by distillation. The reaction mixture was cooled to room temperature and washed

with diethyl ether and methanol to remove the unreacted benzophenone. 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 Microanalytical Unit at Cairo 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 1oo/min in a dynamic nitrogen atmosphere (30 ml/min); the sample holder was boot-shaped, 10 mm x 5 mm x 2.5 mm deep and the temperature measuring thermocouple was placed 1 mm 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 x 0.25 mm coated with methylsilican, 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 N-(biphenylmethylidenyl) chitosan (BPMC)
The IR spectrum of chitosan (Fig.1) 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} are due to O-C-O group. These bands are in good agreement with the IR spectrum of chitosan given by Muzzarelli et al. [8]. Microanalysis of $C_6H_{11}O_4N$ (Cald. C, 44.7; H, 6.8; N, 8.7 %. Found C, 44.62; H, 6.94 and N, 8.67 %).

The reaction of chitosan with benzophenone gives N-(biphenylmethylidenyl) chitosan (BPMC) polymer.

N-(biphenylmethylidenyl) chitosan (BPMC)
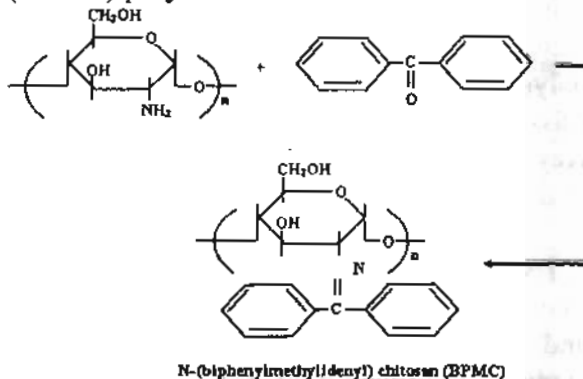
The IR spectrum of BPMC polymer (Fig. 2) shows bands at 3444 and 3423 cm^{-1} are due to the imidic group in the modified prepared polymer. Microanalysis of $C_{19}H_{19}O_4N$ (Calcd. C, 70.2; H, 5.8; N, 4.3 %- Found C, 69.81; H, 5.98; N, 4.51 %).

3.2. Thermal methods of analysis
3.2.1. Thermogravimetry (TG)
TG curve of chitosan is shown in Fig. 3. There are two degradation stages in chitosan polymer. The first stage, weight loss starts at ~ 220 °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 ~ 470 °C with a
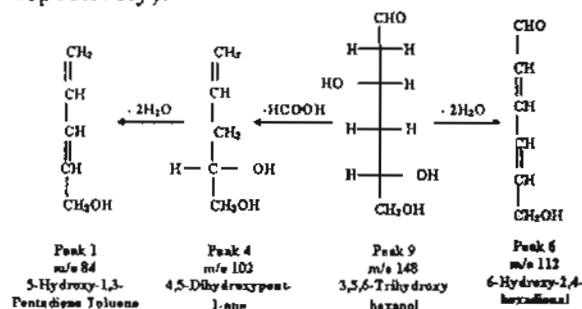
weight loss percentage of ~ 40 %. These are two degradation stages in BPMC polymer as shown in Fig. 4. The first stage starts at ~ 151 °C with a weight loss percentage of 40 %. The maximum rate of weight loss at ~ 299 °C. The second stage starts at ~ 345 °C with a weight loss percentage of ~ 50 %. TG curves reveal that the thermal stability of chitosan polymer is greater than BPMC polymer. The effective activation energies of the thermal degradation of chitosan and BPMC 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 (Fig. 5). The activation energies of degradation of chitosan and BPMC polymers were found to be 52.2 and 38.7 KJ/mol, respectively. It is clear that the activation energies are in the same order of the stabilities.

3.2.2. Thermal degradation of BPMC polymer

50 mg of the modified polymer was heated under vacuum from ambient temperature to 500 °C. The degradation products were injected into the GC-MS apparatus. Fig. 6 (a & b) show the GC trace of the thermal degradation products of polymer sample. Table 1 represents the degradation products which were identified by mass spectropic apparatus. Some of the peaks could not be identified because of their small size or due to the unclear mass spectra. From the degradation products it seems that the mechanism of degradation products is characterized by the elimination of low molecular weight radicals, followed by random scission mechanism along the backbone chain:


Peak 9
m/e 148
3,5,6-Trihydroxyhexanol
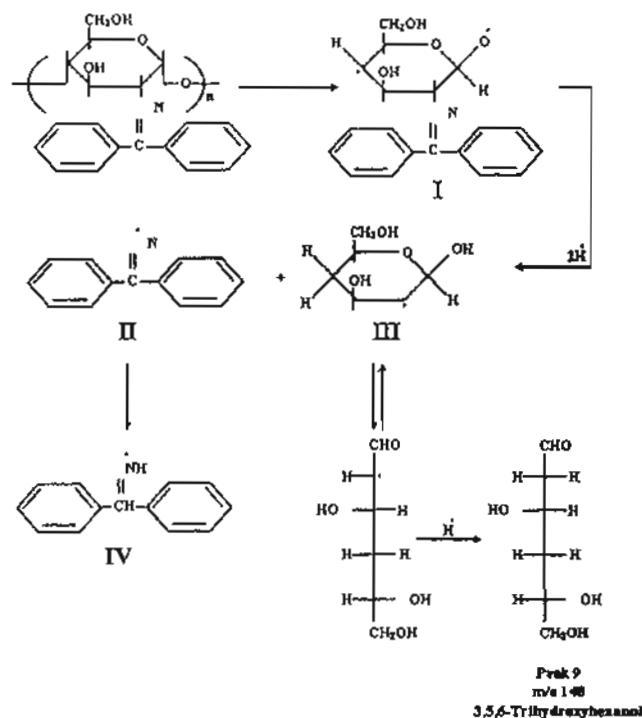
The aldehydic compound, namely,3,5,6-trihydroxyhexanal represented in peak 9 in Table 1 was confirmed by mass spectroscopy. 3,5,6-Trihydroxyhexanal may lose two molecules of water or formic acid forming 6-hydroxy-2,4-hexadienal and 4,5-dihydroxypent-1-ene (Peaks 6 and 4, respectively).


Peak 1	Peak 4	Peak 9	Peak 6
m/e 84	m/e 102	m/e 148	m/e 112
5-Hydroxy-1,3-Pentadiene Toluene	4,5-Dihydroxypent-1-ene	3,5,6-Trihydroxy hexanol	6-Hydroxy-2,4-hexadienal

4,5-Dihydroxypent-1-ene may lose water molecule to form 5-hydroxy-1,3-pentadiene (peak 1).

The enolic form of 3,5,6-trihydroxyhexanol may cyclized to form cyclohex-1-en-6-ol as shown in Peak 3.

Peak 3
m/e 95
Cyclohex-en-6-ol
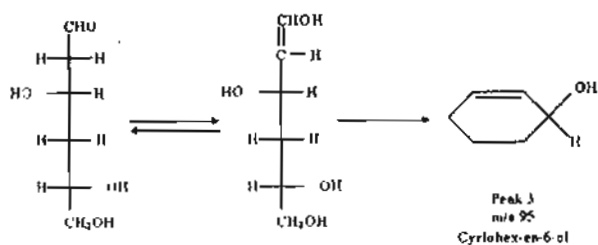
The radical IV may abstract H˙ or OH˙ to produce diphenylmethaneamine and N-hydroxydiphenylmethaneamine,respectively (Peak 11 and 13).
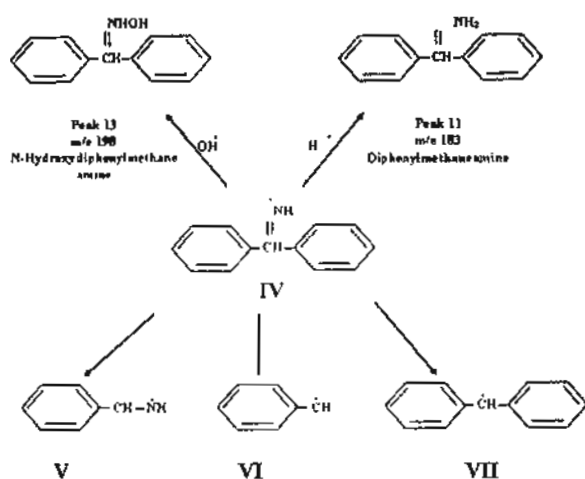
The radical V may abstract H˙ or OH˙ to produce phenylmethaneamine and benzyl hydroxylamine, which represented in Peaks 5 and 8, respectively.
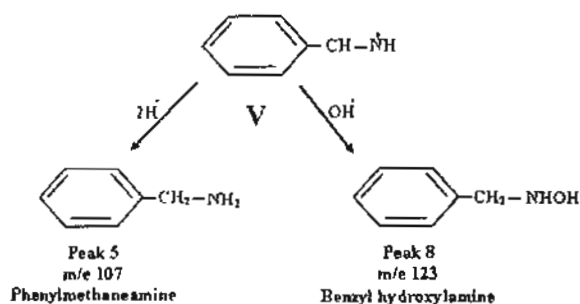
The radical VI may abstract H˙ to produce toluene (Peak 2) and could be oxidized to produce benzoic acid as represented in Peak 7.

VI

Peak 2
m/e 92
Toluene

Peak 7
m/e 122
Benzoic acid
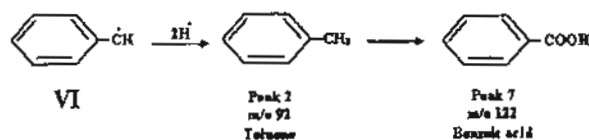
The radical VII may abstract H˙ or OH˙ to produce diphenylmethane and diphenylmethanol (Peak 10 and 12, respectively).
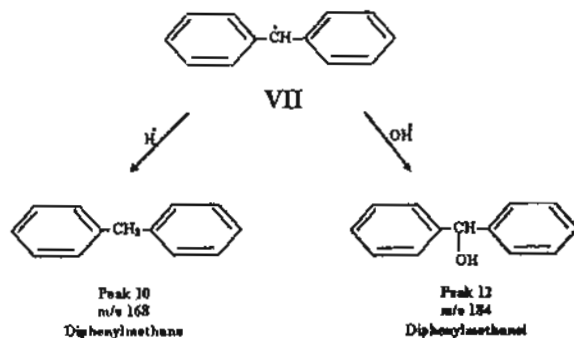
Table 1. GC-MS of the degradation products of BPMC polymer

| Peak No.	Rotation (Time, min.)	Major MS Fragment	Suggested Structures (Most Probable)
1	7.49	84, 61, 47	5-Hydroxy-1,3-Pentadiene Toluene
2	7.52	92, 75, 61, 48	Toluene
3	7.69	95, 70, 47	Cyclohex-en-6-ol
4	8.70	102, 83, 61, 47	4,5-Dihydroxypent-1-ene
5	9.05	107, 91, 75, 61, 48	Phenylmethaneamine
6	9.44	112, 83, 56, 42	6-Hydroxy-2,4-hexadienal
7	10.32	122, 105, 47	Benzoic acid
8	10.92	123, 105, 47	Benzyl hydroxylamine
9	13.38	148, 132, 114, 61, 47	3,5,6-Trihydroxyhexanol
10	15.02	168, 137, 107, 61, 47	Diphenylmethane
11	15.75	183, 123, 105, 61	Diphenylmethaneamine
12	16.00	184, 122, 105, 47	Diphenylmethanol
13	16.58	198, 177, 149, 61, 48	N-Hydroxydiphenylmethaneamine
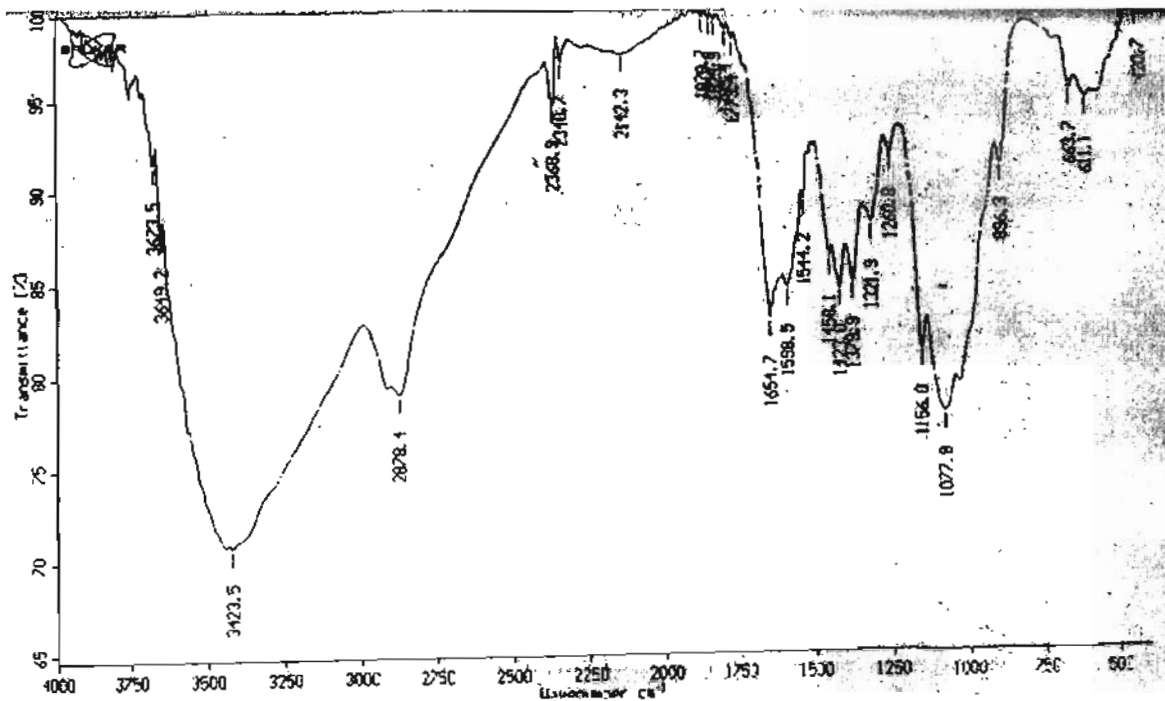
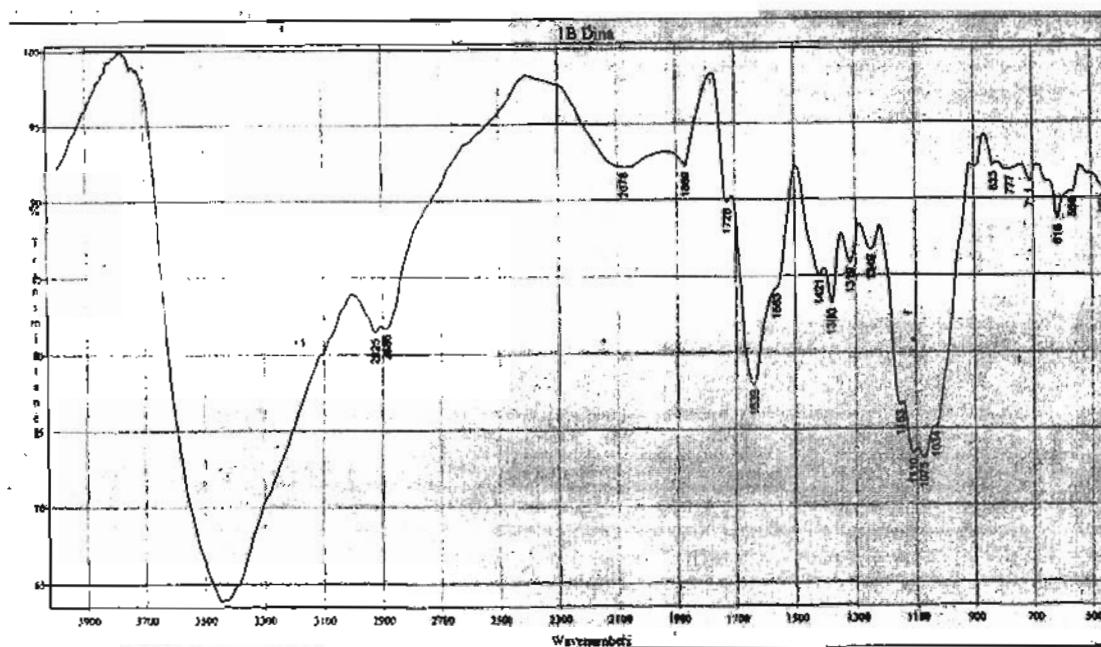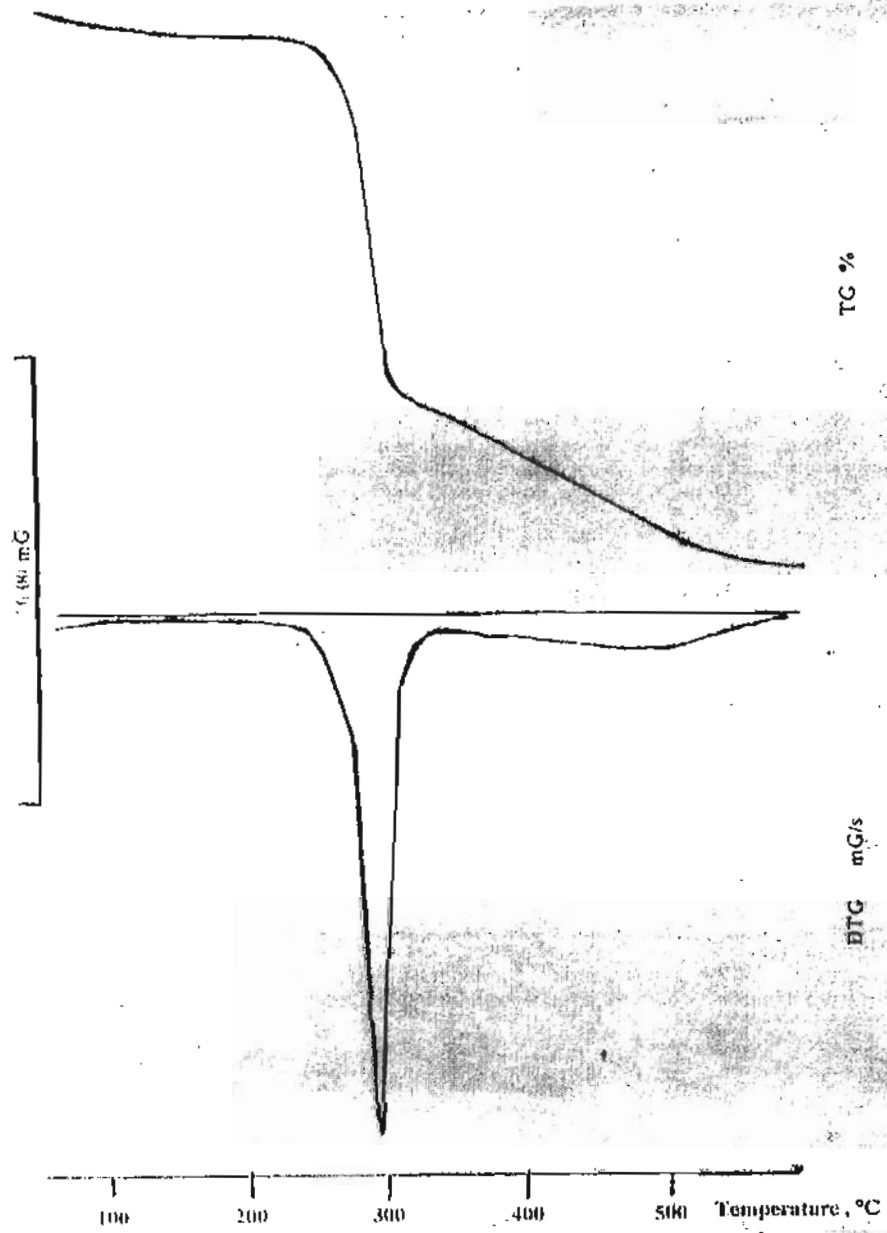Fig. 1: IR Spectrum of Chitosan

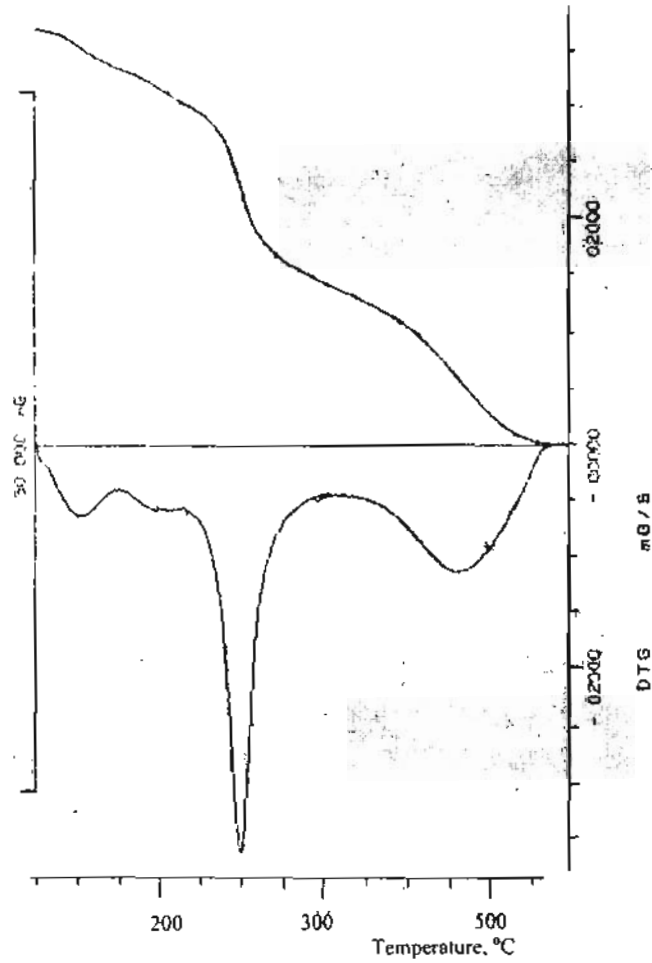Fig. 2: IR Spectrum of BMBA Polymer

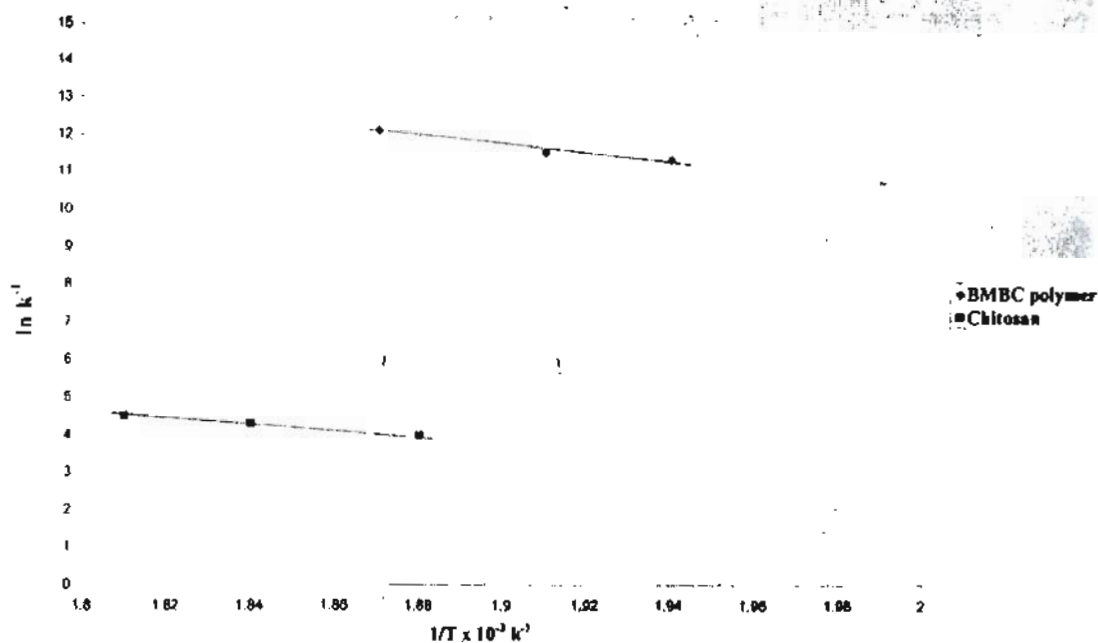Fig. 3: TG Curve of Chitosan

Fig. 4: TG curve of PBMC polymer

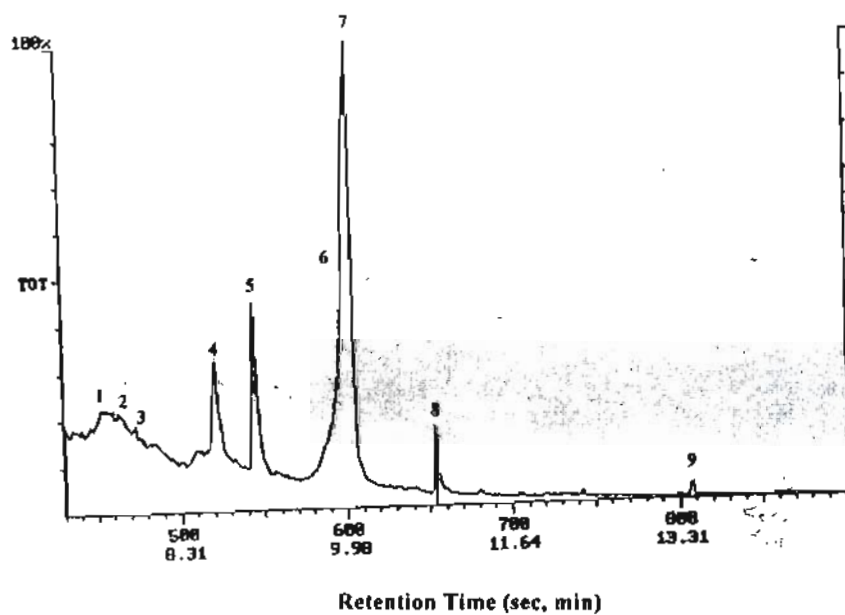Fig.5: Arrhinus plots of the rate constants of degradation of chitosan and PBMC polymers.

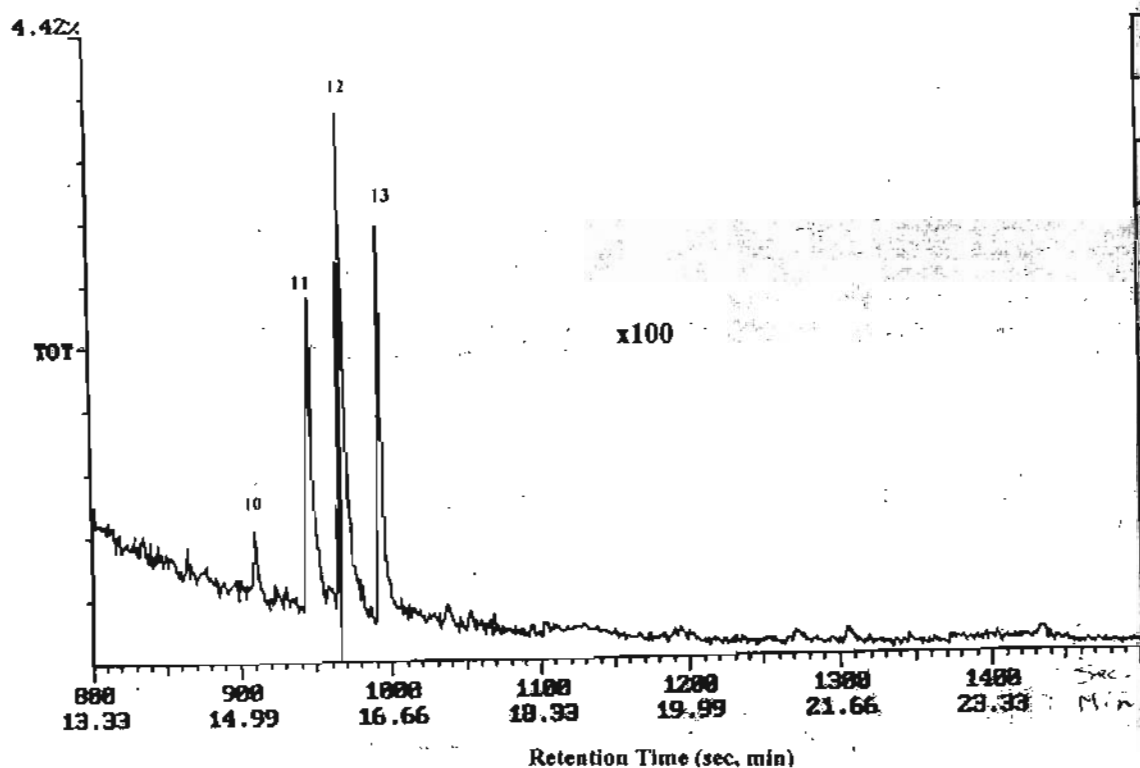Fig. 6-a: GC curve of the degradation products of PBMC polymer.

Fig. 6-b: GC curve of the degradation products of PBMC polymer.

5. REFERENCES

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CAPTION FOR FIGURES

Figure 1: IR spectrum of chitosan.
Figure 2: IR spectrum of PBMC polymer
Figure 3: TG curve of chitosan.
Figure 4: TG curve of PBMC polymer
Figure5: Arrhinus plots of the rate constants of degradation of chitosan and PBMC polymers.
Figure 6: GC curve of the degradation products of PBMC polymer.