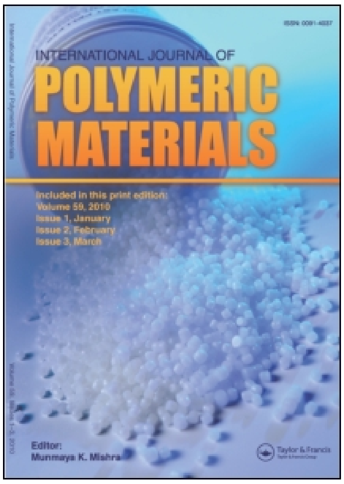

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Thermogravimetric Studies of Chitin Derivatives I

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Thermogravimetric Studies of Chitin Derivatives I.

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The thermal stabilities of chitin derivatives (chitin; chitin iodine, acetate, phenylthiourea, tosylate, butyl xantate, benzyl xantate, isocyanate hexane, benzoate and benzoylate) have been studied by thermogravimetry (TG) between 278 K and 823 K under nitrogen flow. The kinetic data thus obtained indicate that the thermostabilities decrease in the order: chitin-acetate > chitin-phenylthiourea > chitin-isocyanate hexane > chitin-butylxantate > chitin-benzoate > chitin-benzylxanthate > chitin-iodine > chitin benzoylate.

The thermal stability seems to depend on the kind of bond established between the chitin and the reactant. Tosylate exhibits the lowest Ea, probably due to its property as a good leaving group. Furthermore, chitin-acetate has the highest Ea due to its similarity with the pendant group which enables the macromolecule to achieve better electric resonance stabilization.

The reaction order for the thermal decomposition of these chitin polymers is zero. This means that we are concerned with a single step decomposition mechanism. The pre-exponential factor, the reaction order, the decomposition temperature and the activation energy of the decomposition for chitin derivatives have been determined.

KEY WORDS Chitin, natural polymers, crab shells, reaction order, decomposition temperature, activation energy

INTRODUCTION

Chitin is a natural polymer available in the exoskeletons of crabs and lobsters with around 25% of chitin in dry weight.[1]

The hydrolysis of chitin yields 2-deoxy-2-amino glucose and acetic acid in an equimolar ratio. This is an indication that this homopolymer is acetylated glucosamine. The crystal structure of chitin has been studied by x-ray diffraction and polarized infrared spectroscopy.[2,3] The unit cell contains two chains having extensive intra- and inter-molecular hydrogen bonding with a bent conformation similar to cellulose. The two chains must be arranged in opposite directions in order to avoid steric hinderance.

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The second most common portion of biomass comes from a polysaccharide, chitin, which is produced by a variety of marine animals, insects and fungi.

It is estimated that more than a million tons of this material is produced annually, mainly by sea animals.[4] Since these invertebrates have a short life, they have enormous regeneration capacity. However, the natural production of chitin is primarily located in places near the sea.

Chitinase is an enzyme hydrolyzing the β-(1,4)-glycosidic linkage in chitin.[5] Some fungi produce a variety of chitinases with different properties. In common with all polysaccharases, chitinases under certain conditions can act as transglycolyases,[6] and may be responsible for some of the covalent crosslinking of chitin to other wall components. For some nematodes, chitinases are involved in the hatching of the eggs.[7]

The existence and high specificity of these natural products, polyoxine, nikkomycine and allosamidins, gives hope for future developments of compounds of use in medicine and agriculture.

EXPERIMENTAL

Synthesis of Chitin and its Derivatives

The synthesis of chitin and its derivatives has been reported elsewhere.[8] Chitin was obtained from crabs from the Concepción coast by standard methods.[1] Chitin solutions in *N,N*-dimethylacetamide and LiCl (5%) were prepared, and then reacted with the substrates to obtain derivatives.

Elemental Analysis

The samples for microanalysis were dried under vacuum (10^{-3} Torr) for 24 hrs.

Solubility

The solubility of the chitin derivatives was tested using the following solvents: acetonitrile, dimethylformamide, dimethylsulfoxide, acetone, 2-butanone, dichloromethane, chloroform, acetic acid, toluene and benzene.

Thermogravimetry

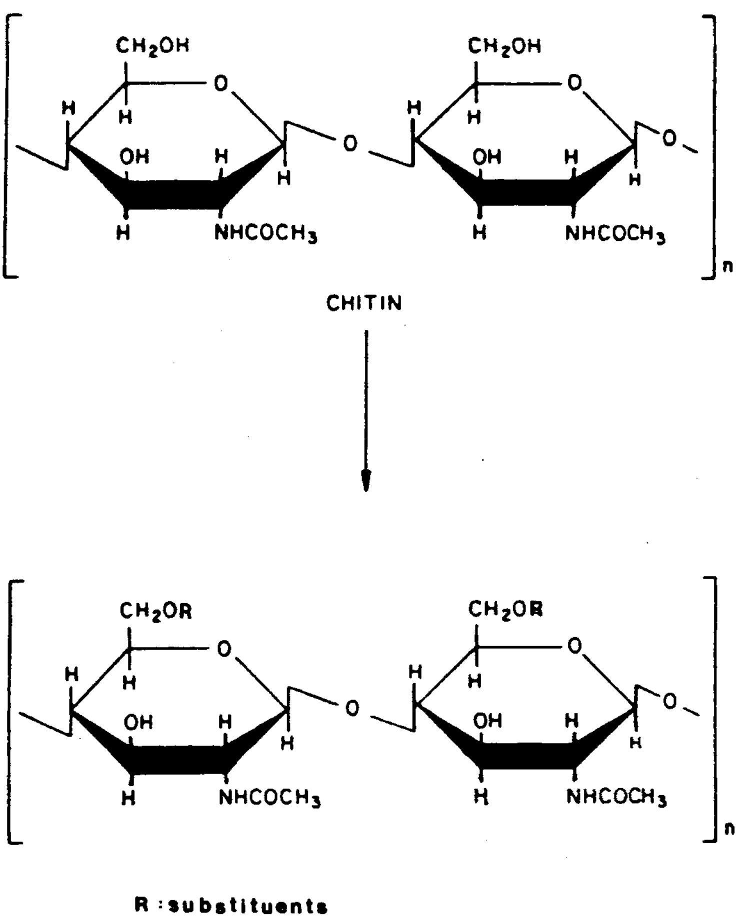
A Perkin-Elmer Model TGS-2 Thermogravimetric System, with a microprocessor-driven temperature control unit and a TA data station, was used. The mass of these samples was generally in the range of 4–10 mg.

The sample pan was placed in the balance system equipment and the temperature was raised from 25 to 550°C at a heating rate of 10°C/min. The mass of the sample pan was continuously recorded as a function of the temperature.

Data generally showed different and consistent nonreversible loss in mass, attributed to the pyrolysis of chitin in the temperature interval of 573–673 K.

RESULTS AND DISCUSSION

The synthesis of chitin derivatives has been recently reported.[8] We prepared chitin using as starting materials crab shells from Tomé, Chile. These modified polymers were prepared by using the following scheme:



The percentage mass loss as a function of time and temperature when the nine compounds are heated from 298 K to 823 K is displayed in Table I. Table II shows the thermal decomposition temperature (T_D) for each macromolecule. These values were taken from the first large change in the slope of the TG curve. This value was corroborated with the first derivative of the curve.

The macromolecules degrade mainly in one stage and exhibit a T_D around 600 K, with chitin-benzoate having the lowest and chitin tosylate the highest. The data suggest that the thermal stability of the macromolecules is related to the nature of the atom and group directly bonded to the chitin. It is difficult to establish a relationship between the thermal stability and activation energy of the decomposition reaction.

TABLE I

Percentage mass loss at several temperatures for chitin and derivatives[a]

Temp. (K)	Chitin[b] (%)	Chitin-1 (%)	Chitin-2 (%)	Chitin-3 (%)	Chitin-4 (%)
298	100	100	100	100	100
373	99.8	98.5	98.9	98.6	93.5
423	99.8	95.4	96.9	95.9	89.5
483	99.4	90.2	93.0	92.4	84.4
503	98.9	88.1	92.0	91.5	80.1
523	98.6	86.7	90.0	90.7	74.6
533	97.4	85.4	88.7	90.1	72.2
553	95.8	82.3	85.0	88.8	68.2
563	44.6	80.0	82.2	87.9	66.7
573	93.5	77.3	78.3	86.7	65.6
583	91.6	73.6	73.3	85.1	64.2
603	87.2	63.5	59.0	80.3	63.3
623	80.8	50.7	35.5	61.4	61.4
643	71.6	41.1	35.5	61.4	61.7
653	65.0	38.6	34.4	54.5	61.4
663	56.6	37.5	33.7	47.9	61.0
673	48.1	36.7	33.2	40.7	60.8
683	39.7	36.1	32.7	34.2	60.6
693	33.4	35.5	32.2	30.4	60.0
703	30.4	34.9	31.8	29.2	59.9
723	29.1	33.7	31.2	28.4	59.5
743	28.5	32.5	30.7	27.6	58.2
763	27.9	31.4	30.2	26.9	55.3
783	27.4	30.8	29.8	26.4	53.5
823	26.6	28.0	28.8	25.4	52.2

Temp (K)	Chitin-5 (%)	Chitin-6 (%)	Chitin-7 (%)	Chitin-8 (%)	Chitin-9 (%)
298	100	100	100	100	100
373	99.4	95.7	99.1	99.8	98.2
423	98.0	93.0	97.3	97.4	95.6
483	94.9	90.5	95.4	90.9	90.1
503	93.3	88.9	93.9	87.6	88.0
523	90.3	87.8	92.0	83.1	83.6
533	88.1	86.1	90.9	80.1	82.0
563	80.4	77.0	86.7	65.3	73.3
573	76.3	72.8	84.6	59.5	69.6
583	71.6	68.3	81.7	51.1	
603	61.8	60.1	73.9	41.1	51.3
613	56.9	58.2	67.3	37.7	43.9
623	52.2	53.1	58.6	35.7	38.9
633	49.1	50.1	49.6	34.2	32.6
643	47.2	48.1	43.4	33.6	29.2
653	46.0	46.1	39.3	33.0	27.3
663	44.8	46.0	36.6	32.5	26.5
673	44.4	45.8	34.7	31.9	26.0
683	43.8	44.9	33.5	31.5	25.6
693	43.2	44.3	32.5	32.1	25.2
703	42.7	43.8	31.6	30.6	24.9
723	41.7	42.7	29.1	29.8	24.2
743	40.8	41.9	26.2	29.1	23.7
763	40.4	41.1	23.8	28.6	23.2
783	40.4	40.4	22.3	28.0	22.7
813	40.4	39.4	21.3	27.4	22.1
823	40.3	39.1	21.1	27.1	21.8

[a]Heating rate of 10°C min^{-1} under nitrogen atmosphere.

[b]Chitin; chitin-1 (chitin iodine); chitin-2 (chitin-o acetate); chitin-3 (chitin phenylthiourea); chitin-4 (chitin tosylate); chitin-5 (chitin butylxantate); chitin-6 (chitin benzylxantate); chitin-7 (chitin isocyanate hexane); chitin-8 (chitin benzoate); chitin-9 (chitin benzoylate).

TABLE II

Decomposition temperatures of chitin derivatives

Polymer[a]	T_D(K)
Chitin	670
Chitin-1	617
Chitin-2	609
Chitin-3	671
Chitin-4	758
Chitin-5	607
Chitin-6	612
Chitin-7	623
Chitin-8	573
Chitin-9	615

[a]Chitin; chitin-1 (chitin-iodine); chitin-2 (chitin-acetate); chitin-3 (chitin-phenylthiourea); chitin-4 (chitin-tosylate); chitin-5 (chitin-butylxantate); chitin-6 (chitin-benzylxantate); chitin-7 (chitin-isocyanate hexane); chitin-8 (chitin-benzoate); chitin-9 (chitin-benzoylate).

Since the decomposition reaction is irreversible, the rate dependent parameters such as activation energy and order of reaction may be calculated from a single experimental curve.[9] The specific rate constant (k) can be expressed in the Arrhenius form

$$k = Z \exp(-E/RT) \tag{1}$$

where Z is the frequency factor, E the activation energy, R the gas constant and T the absolute temperature.

The thermal decomposition kinetics of the thermogravimetric mass loss can be described in terms of the kinetic equation

$$-d\alpha/dt = k(1 - \alpha)^n \tag{2}$$

where α is the fraction of the sample mass reacted at time t, n is the reaction order and k is the specific rate constant. The reaction rate ($d\alpha/dt$) was calculated using a differential technique with a heating rate v.

We can establish that

$$\frac{d\alpha}{dt} = v\,\frac{d\alpha}{dT} \tag{3}$$

After combining Equations (1) to (3) we obtain the logarithmic form

$$\beta = \ln\left[-\frac{(d\alpha/dT)}{(1 - \alpha)^n}\right] = \ln A - \frac{E}{RT} \tag{4}$$

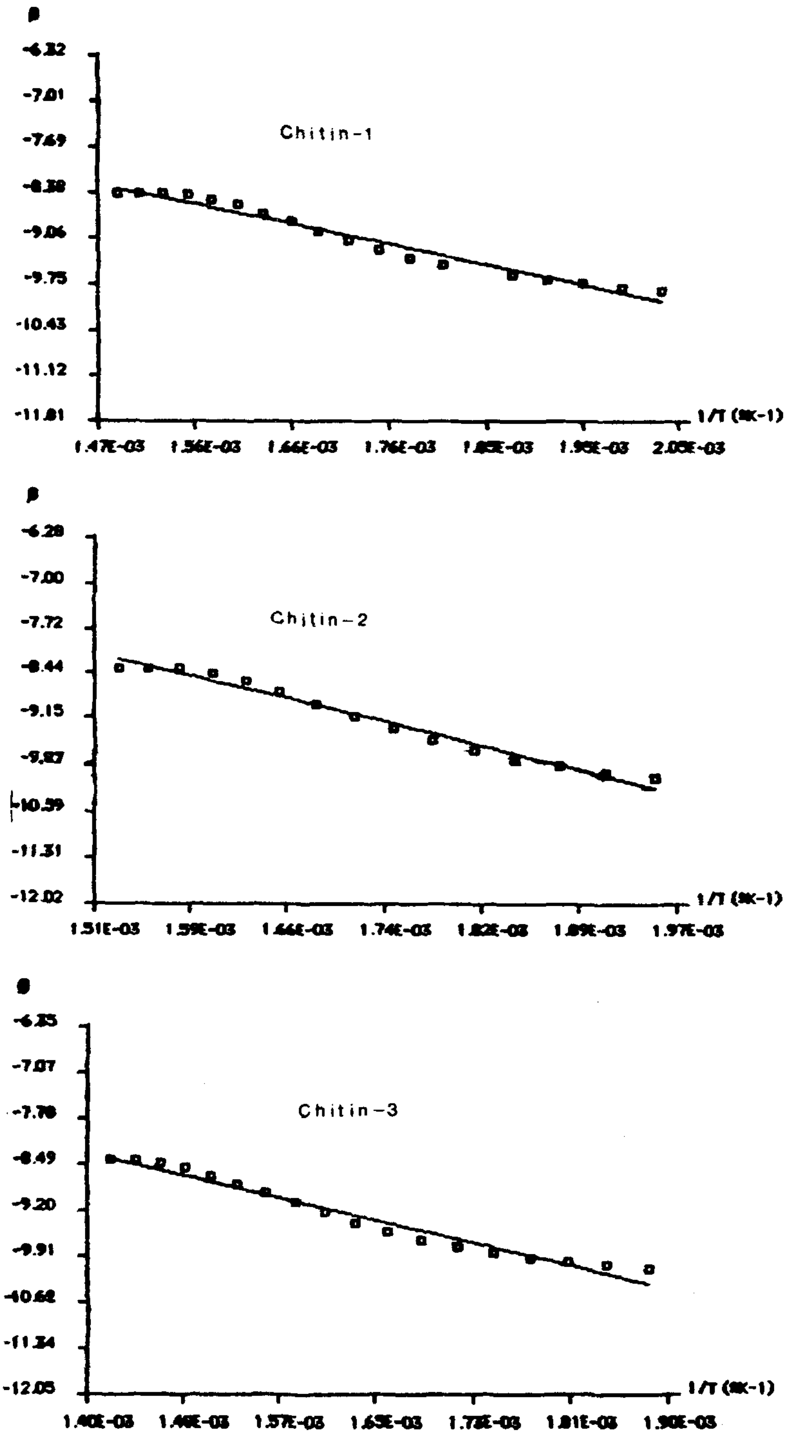

Chitin-1
-7.01
-7.69
-9.75
-10.43
-11.12
1/T (ºK-1)
Chitin-2
-7.00
-7.72
-8.44
-9.15
-12.02
1/T (ºK-1)
Chitin-3
-7.07
-8.49
-9.20
-9.91
-12.05
1/T (ºK-1)

FIGURE 1

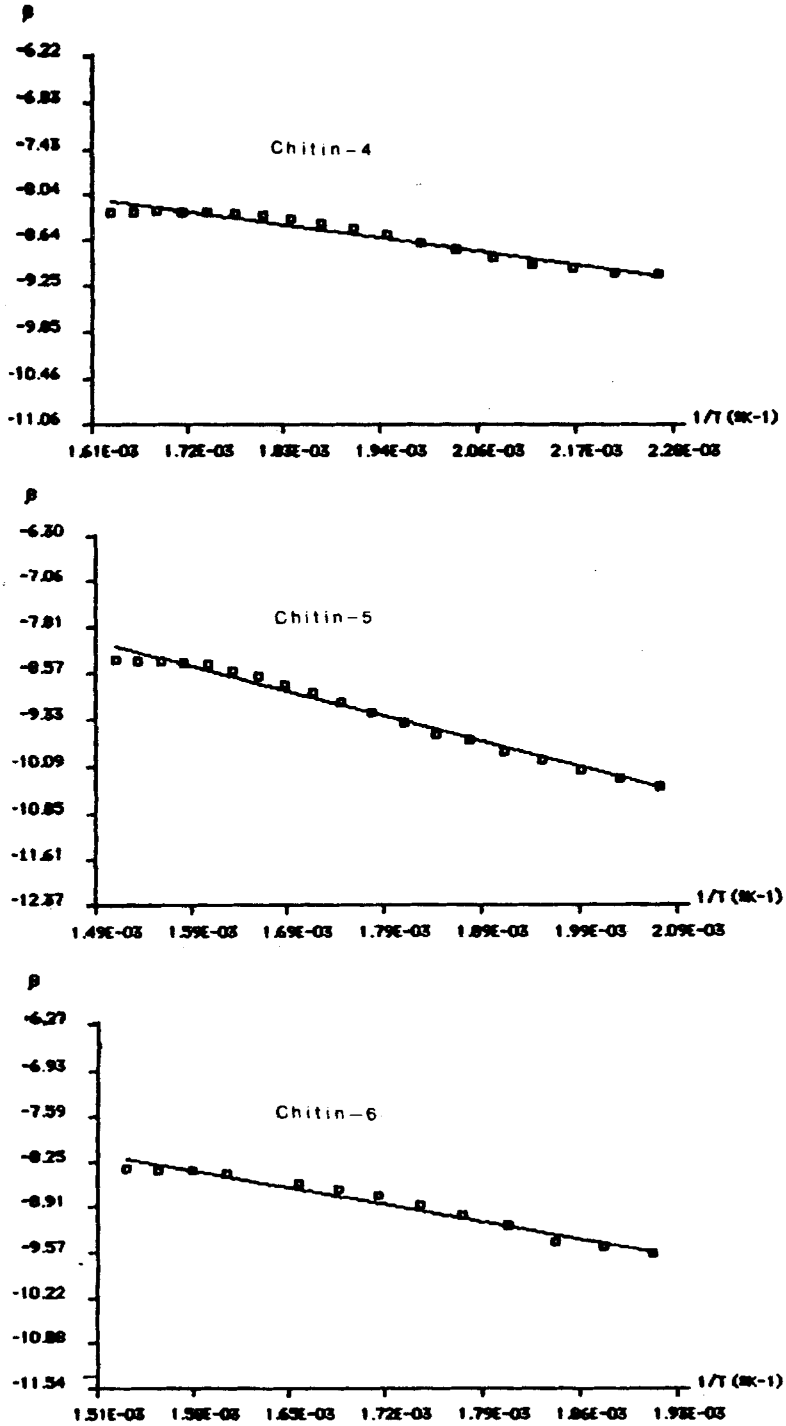


FIGURE 1 (*Continued*)

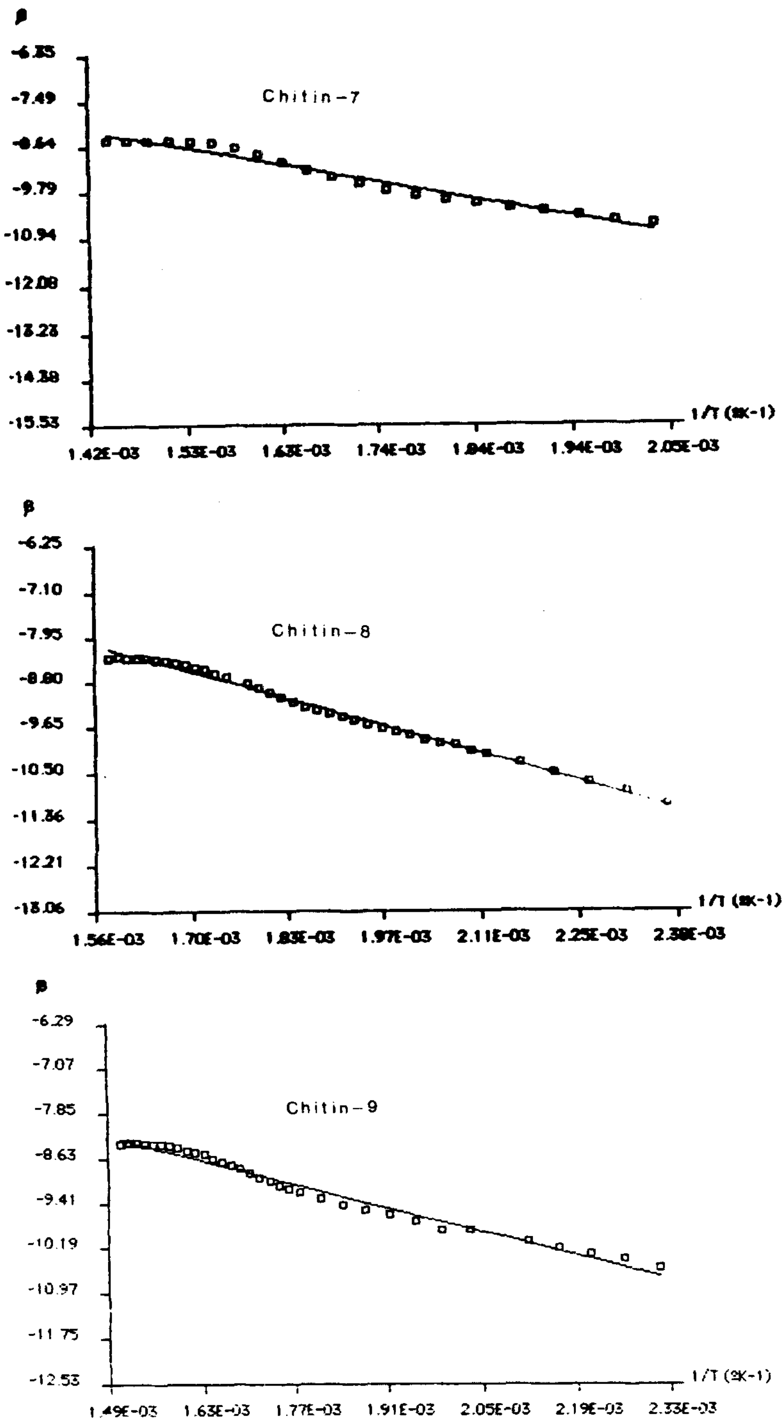


FIGURE 1 (*Continued*)

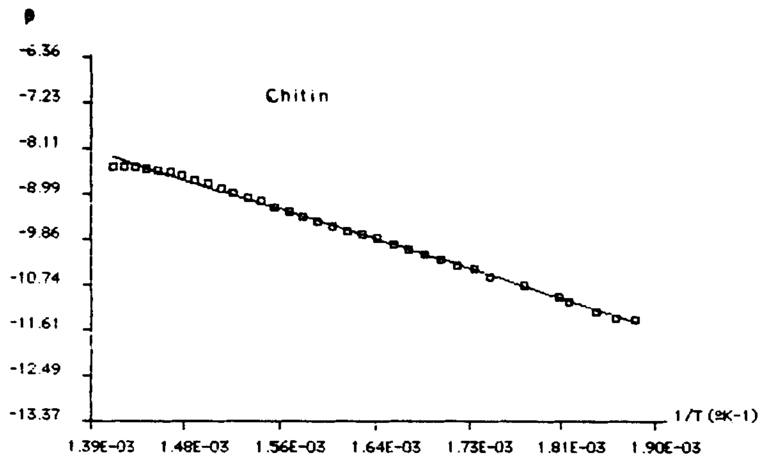


FIGURE 1 (*Continued*)

Finally, by incorporating v (10°C/min), in K/sec we obtain

$$\beta = \ln\left[-\frac{(d\alpha/dT)}{6(1-\alpha)^n}\right] = \ln A - E/RT \qquad (5)$$

Assuming a first-order reaction model, a multiple regression program was used to plot β against $1/T$ (see Figure 1). A straight line should be obtained, and E and A can be calculated from the slope and intercept, respectively. This program is very similar to that reported by Ma.[10]

The coefficients of linear correlation vary from 0.974 to 0.996. There are several values very similar to the activation energy: this is mainly due to the steric difficulties of the substrate to accommodate the polymeric backbone of the chitin helix.

Table III summarizes the kinetic parameters of chitin and its derivatives. Chitin-1 and chitin-9 have similar and the lowest Ea (13.4 and 13.0 kJ/mol^{-1}, respectively). Conversely, chitin-2 exhibits the highest Ea of 20.3 kJ mol^{-1}, probably due to the presence of the acetate group which is of similar nature to the acetamido characteristic of the chitin macromolecule.

The low T_D values could possibly be explained because the acetyl group is stable and volatilizes easily from the polymeric chain. The lowest T_D value belongs to the chitin-benzoate with 573 K, but its Ea is not the lowest.

Another similar pair is chitin-3 and 5 with Ea of 18.0 kJ·mol^{-1}: the presence of sulfur in the adduct probably increases the stability of their macromolecules. (T_D of 671 K and 623 K, respectively). In general, most of the chitin derivatives exhibit an Ea value lower than chitosan,[11] mostly due to the different kind of substrates incorporated into the backbone of the macromolecule. These values are in the range of metal poly(methylmethacrylates), which have been reported previously.[12]

TABLE III

Kinetic parameters for chitin derivatives

Polymer[a]	*Z* (s^{-1})	*Ea* ($kJmol^{-1}$)	*n*	Temp. range (K)
Chitin	5.31	29	0	533-708
Chitin-1	3.1×10^{-2}	13	0	493-673
Chitin-2	4.9×10^{-1}	20	0	513-653
Chitin-3	1.2×10^{-1}	18	0	533-703
Chitin-4	4.2×10^{-3}	7	0	443-613
Chitin-5	1.6×10^{-1}	17	0	483-663
Chitin-6	7.1×10^{-1}	15	0	523-653
Chitin-7	1.5×10^{-1}	18	0	493-693
Chitin-8	1.3×10^{-1}	16	0	423-633
Chitin-9	2.6×10^{-2}	13	0	433-663

[a]Chitin; chitin-1 (chitin-iodine); chitin-2 (chitin-acetate); chitin-3 (chitin-phenylthiourea); chitin-4 (chitin-tosylate); chitin-5 (chitin-butylxantate); chitin-6 (chitin-benzylxantate); chitin-7 (chitin-isocyanate hexane); chitin-8 (chitin-benzoate); chitin-9 (chitin-benzoylate).

This is an introduction report concerning the activation energies and decomposition order reaction for chitin and its derivatives.

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