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Synthesis, Characterization, Conductivity and Investigation of Antimicrobial and Fungus of Magnetic Polymer Including Schiff Bases

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Novel poly-Schiff base derived from the condensation reaction poly(acrylamide) and 2,2'-bipridine-4,4'-dicarboxaldehyde has been synthesized. -CH=N- and $-NH_2$ group ^{1}H NMR signals were made use of to determine the relative abundance of Schiff base and acrylamide groups in the modified polymer. Metal-aldehyde complexes ([Ni-L], [Co-L], [Mn-L], [Fe-L], [Cr-L]) were anchored poly(acrylamide). PAA_m-Schiff base and its metal complexes were characterized by magnetic susceptibility, electronic and spectral studies. The DC conductivities of the solid samples were measured using a four-probe technique. The conductivity of coordination polymers were found to be high in comparison to PAA_m including Schiff bases. *In vitro* activities against some Gram-positive (*Bacillus subtillis, Bacillus cereus, Micrococcus luteus* NRLL B4375, *Pseudomonas aeroginosa* ATCC 29212) and the fungus *Candida albicans* were determined.

Key Words: Schiff bases, Coordination polymer, Magnetic polymer, Poly(acrylamide).

INTRODUCTION

The chemistry and application of polymer including Schiff bases have received immense attention during the last few decades[1-3]. Polymers including metal ions can be showed as magnetic materials[4]. Because metal ions have unpaired electrons are paramagnetic. Polymers containing various metals show properties semi-conducting[5]. Conducting substances have attracted much attention from both fundamental and practical viewpoints. The study of aromatic substances that have a molecular structure containing π-bonds in the chains is an active research area for conducting substances[6]. Conducting substances have a number of potential technological applications as chemical transistors[7], including rechargeable batteries[8] and biochemical analyses[9]. Poly(acryl amide) (PAA_m) as a water-soluble synthetic polymer has found a significant role in many industrial applications.

Poly(acryl amide) (PAA_m) has the capability to change some of their behaviour, *i.e.*, permeability and mechanical strength, with small changes in structure[10]. Developing the properties of individual polymers can be an important approach for

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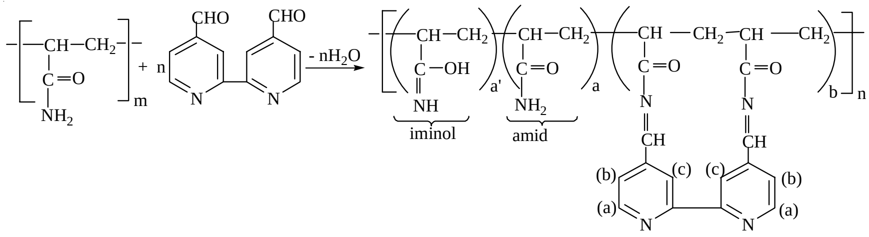
to use in new fields. In a continuation of our previous work[10,11], in this work, the synthesis and characterization of a novel polymer including Schiff bases (Fig. 1) derived from the condensation of PAA_m and 2,2'-bipridine-4,4'-dicarboxaldehyde and their metal complexes with Ni(II), Co(II), Mn(II), Fe(III) and Cr(III) are reported.



a: 8, b :1, n: 6

Fig. 1. Structure of poly(acryl amid) and aldehyde (PAA_m-SB)

EXPERIMENTAL

The solvents were used analytical grade. Poly(acrylamide), carboxaldehyde, metal salts and solvent supplied by Sigma-Aldrich Company were used. ^1H spectrum was recorded with a Bruker Avance DPX-400 using TMS as internal standard and DMSO-d_6 as solvent. IR spectra of all modified polymer were recorded on a Mattson-5000 FTIR instrument in KBr pellets. Mass spectra were recorded on a Micro Mass-UK Platfrom II mass spectrometer. Molar conductivities in DMF (10^{-3} mol/L) at 20 ºC were measured using a Siemens WPA CM 35 apparatus. Magnetic measurements were determined with a Sherwood Scientific MK1 model Evans magnetic balance. Carbon, hydrogen and nitrogen values were obtained a LECO CHNS-932 analyzer. Metal contents were determined by a Perkin-Elmer Analyst 800 model AAS. The molecular weight (M_w) overage was suggested from element analyses. The number average molecular weight (M_n) was determined with a vapour pressure osmometer using Vescor 5520X.

Preparation of the polymer including Schiff bases: The polymeric-Schiff bases were prepared by adding drop-wise with stirring the PAA_m (1 mmol) in hot water (25 mL) with the appropriate 2,2'-bipridine-4,4'-dicarboxaldehyde (6 mmol) in hot CH_3OH solution (10 mL). The stirring was continued until the solution was dense *ca.* 4 d. The mixture was evaporated until about the ratio 1:3 of its original volume, cooled and collapsed with acetone. A crystalline yellow precipitate was obtained. The crystalline solids were filtered, washed with a mixture of water-methanol (1:1 v/v) and dried in desiccators over anhydrous $CaCl_2$.

Synthesis and isolation of complexes

First step: Preparation of metal-aldehyde complexes: 2,2'-Bipridine-4,4'-dicarboxaldehyde (L) complexes of Ni(II), Co(II), Mn(II), Fe(III) and Cr(III) were prepared by mixing aqueous solutions of metal chloride with ethanol solutions of the aldehydes in 1:1 mole ratio[10]. The resulting solutions was stirred for *ca.* 1 h, filtered and allowed to stand. On standing for 8 h, solid complexes formed which were collected by filtration, washed with a small volume of diethyl ether and dried in a desiccators over $CaCl_2$ (Fig. 2). The results indicate the ML nature of Ni(II), Co(II), Mn(II), Fe(III) and Cr(III) complexes according to the LC-Mass spectroscopy $[M+H]^+$ 339.8 (m/z: 27.2 %), $[M+H]^+$ 335.7 (m/z : 31.8 %), $[M-2H]^+$ 336.7 (m/z: 18.2 %), $[M]^+$ 374.7 (m/z: 32.1 %), $[M+H]^+$ 370.7 (m/z: 27.8 %); for [Ni-L], [Co-L], [Mn-L], [Fe-L] and [Cr-L], respectively. The decomposition temperature for all of the metal-aldehyde complexes was >200 ºC. Yields: 80-84 %.

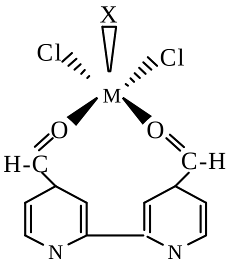


Fig. 2. Structure of metal-aldehyde complexes [X: Cl for M: Fe(III) and Cr(III)]

Second step: Preperation of coordination polymers: A solution of poly(acrylamide) (1 mmol, 4 mL) in water (15 mL) was added to a solution of the metal-aldehyde complexes (4 mmol) in methanol (10 mL). The solution was mixed until the viscosity increased and the colour of the solution changed (*ca.* 4 d). After cooling, the complexes were washed repeatedly with methanol and then dried. The coordination polymers are coloured, crystalline solids, which are soluble in water, DMSO and DMF. Yields: 63-77 %.

Solid state conductivity measurements: Solid state electrical conductivities (σ) were measured with a Nippon NP-900 multimeter using a four-probe technique[12,13]. The pellets of the Schiff bases were prepared at loading of *ca.* 8 tons and thickness of *ca.* 0.05 cm.

Bactericidal and fungicidal testing screening: *In vitro* antibacterial activities of the Schiff bases and the complexes were studied using the well-diffusion method in the bactericidal and fungicidal testing screening. The strains chosen were *Bacillus subtillis, Bacillus cereus, Micrococcus luteus* NRLL B4375, *Pseudomonas aeroginosa* ATCC 29212 and the yeast (*Candida albicans* ATCC 10239). The bacterial and yeast cultures were incubated at 37 ºC for 18 h. The ligands and the complexes were stored dry at room temperature and dissolved 250 µg/mL in DMSO. Molten nutrient agar (15 mL) kept at *ca.* 45 ºC was then poured in the Petri-dishes and allowed to solidify. Then holes of 6 mm diameter were punched carefully using a sterile cork borer and these were completely filled with the test solutions. The plates were incubated for 24 h at 37 ºC. The mean value obtained for the two holes was used to calculate the zone of growth inhibition of each sample.

RESULTS AND DISCUSSION

Analytical data and some of the physical properties of the magnetic polymer including Schiff bases are summarized in Table-1. All the complexes are soluble in water and common organic solvents such as ethanol, methanol, DMF and DMSO. Elemental analyses are consistent with a polymer including Schiff base to metal ratio of 1:1 where a = 8 and b = 1. However, deviations from these values should be noted and may be attributed to the polymeric nature of coordination polymers[11]. The assigned absorption bands are consistent with suggested structure polymer including Schiff base and their complexes. Table-2 summarizes the main IR and UV-visible bands of the compounds. IR bands in the 1748-1742, 3100-2937, 3230-3200, 3418-3386 and 3450-3442 cm^{-1} regions are characteristic of ν(C=O), ν(NH), $\nu(NH_2)_{asym}$, $\nu(NH_2)_{sym}$ and ν(OH), respectively. The IR spectra of the polymeric-Schiff bases and their complexes have ν(NH) and ν(OH) stretching vibrations, which indicates that both classes of compounds have enol and keto forms[14].

TABLE-1
ANALYTICAL DATA AND PHYSICAL PROPERTIES OF MAGNETIC POLYMER INCLUDING SCHIFF BASES

Abbreviation M_v / M_w M_w (a:8, b:1, n:*6/4)	Main Unit [Empiric formula] M_w	Colour, Yield (%) μ_{eff} (BM)	Elemental analysis %: Found (Calcd.)			
			C	H	N	M
*(PAA$_m$-SB)	$*[(C_3H_5ON)_a(C_{18}H_{14}O_2N_4)_b]_n$	Yellow,	57.46	6.55	19.51	-
10900 / 5316	$[886]_n$	35, -	(56.88)	(6.09)	(18.96)	-
Co(PAA$_m$-SB)	$[(C_3H_5ON)_a(C_{18}H_{14}O_2N_4Co)_b]_n$ 2nCl	Dark blue, 81, 4.33	44.10	5.63	12.40	5.07
12200 / 4348	$[1087]_n$		(46.37)	(4.97)	(15.46)	(5.43)
Ni(PAA$_m$-SB)	$[(C_3H_5ON)_a(C_{18}H_{14}O_2N_4Ni)_b]_n$ 2nCl	Green, 87	44.15	5.70	12.89	4.78
12250 / 4344	$[1086]_n$	Diamagnetic	(46.41)	(4.97)	(15.47)	(5.34)
Mn(PAA$_m$-SB)	$[(C_3H_5ON)_a(C_{18}H_{14}O_2N_4Mn)_b]_n$2nCl	Yellow, 61	47.12	5.79	13.22	5.99
12240 / 4332	$81083]_n$	Diamagnetic	(46.54)	(4.99)	(15.51)	(5.08)
Fe(PAA$_m$-SB)	$[(C_3H_5ON)_a(C_{18}H_{14}O_2N_4Fe)_b]_n$ 3nCl	Viyolet,	42.80	5.73	2.16	5.79
12260 / 4620	$[1155]_n$	72, 2.68	(43.64)	(4.68)	(14.55)	(4.85)
Cr(PAA$_m$-SB)	$[(C_3H_5ON)_a(C_{18}H_{14}O_2N_4Cr)_b]_n$ 3nCl	Claret red, 78, 4.72	44.37	4.44	12.86	4.91
12250 / 4604	$[1151]_n$		(43.79)	(4.69)	(14.60)	(4.52)

The azomethine (-CH=N-) stretching mode at 1650 cm^{-1} for the polymeric-Schiff bases is not observed due to overlap with $\nu(NH_2)$.

Bands appearing at 1515, 1255 and 485 cm^{-1} are assigned to ν(CN) + δ(NH), δ(NH) and ν(C=O) vibrations, respectively, for the polymeric-Schiff bases[10]. These observations indicate that the aldehyde reacts with the polymer.

On compelling, the ν(CN) + δ(NH), δ(NH) and ν(C=O) frequencies generally increase. Such frequency shifts, when compared to those of the polymeric-Schiff bases, may be attributed to coordination of the metal ion with the azomethine nitrogen and the imine oxygen of the carboxylate group (Fig. 3). Furthermore, the appearance of new bands in the 420-410 and 520-495 cm^{-1} can be assigned to ν(M-O) and ν(M-N), respectively[15].

TABLE-2
KEY IR BANDS (cm^{-1}) AND ELECTRONIC SPECTRAL DATA (nm) (ε_{max} M^{-1} cm^{-1}) OF THE PAA$_m$ INCLUDING SCHIFF BASE AND IT'S METAL COMPLEXES

Compound	ν(CH=N) ν(CN)+δ(NH)	ν(NH) δ(NH)	ν(NH$_2$) asym sym	ν(C=O) ν(M-O)/ ν(M-N)	λ_{max} ($\varepsilon \times 10^5$)
(PAA$_m$-SB)	Overlap 1518	2935 1256	3202 3420	483 -	236 (26), 285 (2.9)
Co(PAA$_m$-SB)	Overlap 1521	3022 1257	3211 3435	484 492/518	236 (320), 286 (31) 603 (1.3)
Ni(PAA$_m$-SB)	Overlap 1524	3088 1258	3220 3447	485 495/520	235 (280), 287 (36) 490 (1.3)
Mn(PAA$_m$-SB)	Overlap 1522	3042 1260	3215 3433	484 490/516	236 (16), 285 (2.3) -
Fe(PAA$_m$-SB)	Overlap 1526	3075 1259	3217 3448	487 492/519	235 (29), 286 (2.6) 543 (0.6)
Cr(PAA$_m$-SB)	Overlap 1523	3063 1258	3219 3437	486 490/518	237 (26), 285 (3.1) 345 (0.42), 380 (0.19), 604 (0.68)

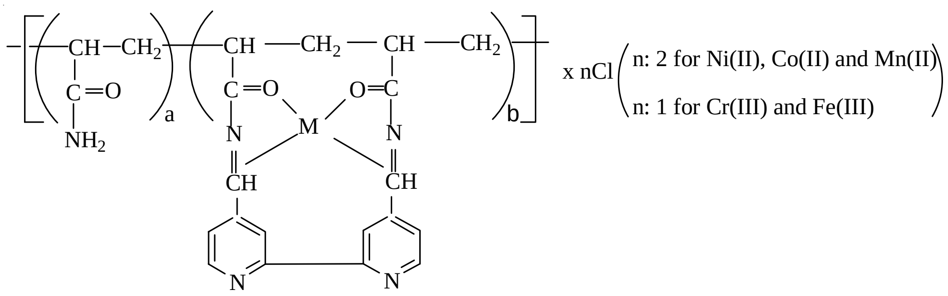
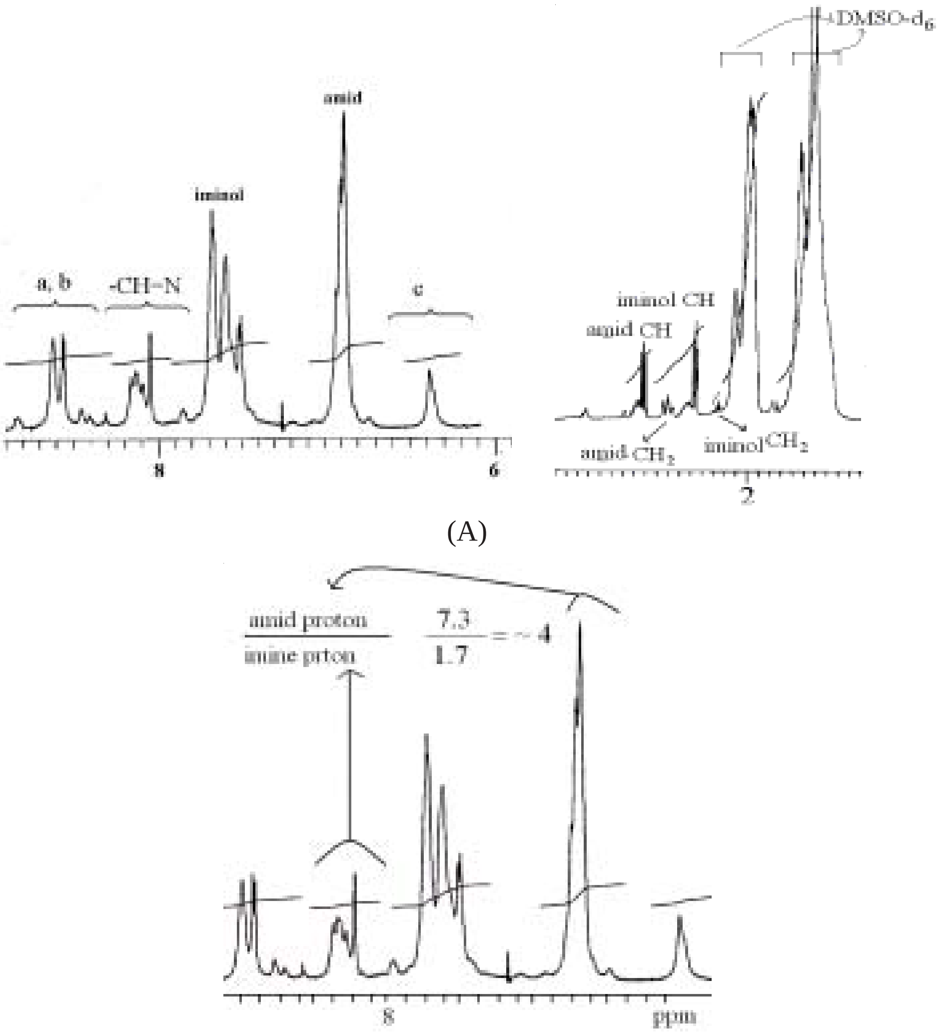


Fig. 3. Suggestion structures for M(PAA$_m$-SB) complexes

The ^{1}H NMR spectra of the polymeric-Schiff bases exhibits a signals at 8.10 ppm due to imine protons (-N=CH-). The ring proton signals appear at 8.42-8.61 and 6.41 ppm in the (PAA-SB). Most polydispersed polymers exhibit broad and multiple peaks in the NMR spectra[16]. Multiple peaks are shown in (PAA-SB). Therefore, the d values were reported in terms of data in the midpoint of multiple peaks.

For (PAA-SB), signals at 3.40/3.20, 2.11/2.10 and 2.78, 2.61 ppm are assigned to the -CH/-CH$_2$ of imine group and -CH/-CH$_2$ of keto and -CH/-CH$_2$ of enol group, respectively. These data strongly support the presence of keto and enol forms in polymeric-Schiff bases (Figs. 1 and 4, Table-3). Peak high (one unit) of imine proton (-CH=N) and total peak high (six unit) -CH of keto-enol group was compared in the polymeric-Schiff base. From the ^{1}H NMR spectrum it can be concluded that imine (-CH=N-)/acryl amide (keto group + enol group) can be 1/8 in the unit structure (Fig. 4B).



(A)

(B)

Fig. 4. ^{1}H NMR spectrum (A) and evaluation of -NH_2 and -CH=N peaks in main brim (B) for (PAA-SB)

The electronic spectra of the (PAA-SB) in water were recorded in the range of 200-800 nm. The strong absorption bands which appeared in the range of 221, 264 and 230 nm are due to intra-ligand electronic transition. The magnetic moment 4.34 BM is commensurate with tetrahedral geometry about Co(II) in the complexes[17]. Electronic spectra of Co(II) complexes shows a medium intense assigned to $^4A_2 \rightarrow$ $^4T_1(P)$ (448 nm) transition for tetrahedral coordination about Cobalt(II). The magnetic moment 3.18 BM is commensurate with octahedral geometry around Ni(II) ion[17]. Ni(II) complexes show two *d-d* bands between 693 and 397 nm, indicating an octahedral structure. The spectra of the Fe(PAA_m-SB) complexes shows band in the range of 542 nm. Hence, tetrahedral geometry may be assigned to this complex[18]. The magnetic moments for the Cr(III) complexes is 4.7 BM indicating the presence of three unpaired electrons. The electronic spectrum of the Cr(III) complex exhibits band at 604, 380 and 345 nm which may be assigned to $^4B_{1g} \rightarrow {}^4E_g$, $^4B_{1g} \rightarrow {}^4E_g$ and $^4B_{1g} \rightarrow {}^4A_{2g}$ transitions, respectively. The position of these bands is consistent with a distorted octahedral geometry with D_{4h} symmetry[18].

Solid state conductivity measurements: The conductivity range for semi-conductive materials is known to be 10^{-7}–10^{2} S cm^{-1}. Complexes are found to be semi-conductive, although including polymer Schiff bases do not conduct. The conjugation length in complexes may be attributed to high conductivity[19]. Moreover, these metals improve inter chain charge transfer, *e.g.*, high molecular weight complexes show high conductivities due to intermolecular charge transfer[20].

Thermogravimetric (TGA) analysis: Thermal data of the polymer-metal complexes are given in Table-3. As seen from Table-3, decomposition temperatures (T_i, T_m, T_f) of the polymer-metal complexes are same. The PAA-metal complexes decompose with three steps. I-VI complexes are thermally stable up to 60, 50, 45, 62, 67 and 64 ºC, respectively. In the decomposition process of the I-VI complexes, the mass losses corresponded to absorption H_2O or CH_3OH leaving in the first stages of the decomposition. The second and third steps occur within the temperature range 185-330 ºC. The second step corresponds to polymer-metal decomposition and third step leads to the decomposition of polymer-metal to metal salts.

TABLE-3

^{1}H-NMR CHEMICAL SHIFT (ppm) OF THE PAA_m INCLUDING SCHIFF BASE

Functional groups	(PAA_m-SB)
$\text{-C-N}\underline{\text{H}}_{2\text{ (keto form)}}$	6.92, 2H
$\text{-C}\underline{\text{H}}_{\text{(keto form) /}}\text{–C}\underline{\text{H}}_{2\text{ (keto form)}}$	2.11, 1H / 2.10, 2H
$\text{-C-}\underline{\text{OH}}_{\text{ (enol form)}}$ / $\text{–C=}\underline{\text{NH}}_{\text{ (enol form)}}$	7.50, 1H / 7.70, 1H
$\text{-C-}\underline{\text{CH}}_{\text{ (enol form) /}}\text{–CH-}\underline{\text{CH}}_{2\text{ (enol form)}}$	2.78, 1H / 2.61, 2H
$\text{-N=}\underline{\text{CH}}$	8.1, 1H
$\text{(CH)}_{\text{aromatic-a,b; c}}$	8.6, 4H; 6.4, 2H
$\text{-C}\underline{\text{H}}_{2\text{ (imine group) /}}\text{-CH}_{\text{ (imine group)}}$	3.2, 2H / 3.4, 1H

Bactericidal and fungicidal screening: The results of the antibacterial and antifungal screening of the magnetic polymers including Schiff with three bacteria and a yeast, namely *Bacillus subtillis, Bacillus cereus, Micrococcus luteus, Pseudomonas aeroginosa* and *Candida albicans,* are given in Table-4.

A significant activity was observed by compounds polymer including metal against *Candida albicans* (Table-4). Increased activity of the metal chalets can be explained on the basis of chelation theory[21]. Orbital of the metal ion is made up overlap with the ligand orbital. Increase enhances the lipophilicity of complexes due to delocalization of π-electrons in chelate ring. In cases, increased lipophilicity leads to breakdown of the permeability barrier of the cell[16]. Magnetic polymers including Schiff were found to be inactive against *Bacillus subtillis, Bacillus cereus, Micrococcus luteus* and *Pseudomonas aeroginosa*.

TABLE-4
BIOLOGICAL ACTIVITY STUDIED POLYMER-METAL COMPLEXES (ZONE OF INHIBITION, mm) AND THERMOGRAVIMETRIC ANALYSIS

Compd.	BS	BC	PA	ML	CA	Thermally decomposed			Conductivity × 10^{-6} (σ, Scm^{-1})
						T_i	T_{max}	T_f	
(PAA$_m$-SB)	–	–	–	–	8	60	87	210	6.01
						210	269	291	
						374	380	489	
Co(PAA$_m$-SB)	–	–	–	–	21	50	87	113	8.22
						185	214	252	
						360	440	625	
Ni(PAA$_m$-SB)	–	–	–	–	22	45	89	110	9.98
						231	265	299	
						374	380	620	
Mn(PAAm-SB)	–	–	–	–	25	62	96	109	7.43
						147	216	260	
						379	382	630	
Fe(PAAm-SB)	–	–	–	–	13	67	96	109	7.98
						237	241	320	
						330	385	630	
Cr(PAAm-SB)	–	–	–	–	11	64	96	109	6.57
						240	256	324	
						351	372	637	

BS = *B. subtillis*, BC = *B. cereus*, PA = *P. aeroginosa*, ML = *M. luteus*, CA = *C. albicans*;
T_i = Inital degradation temperature; T_{max} = Maximum degradation temperature;
T_f = Finally degradation temperature

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