Ni(II)-MACROMOLECULAR COMPOUND DERIVED FROM POLY(4-VINYLPYRIDINE-CO-DIVINYLBENZENE) AND SCHIFF BASE NICKEL COMPLEX: THERMO-DEGRADATION AND KINETICS BEHAVIOR

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Various kinetic techniques have been developed to obtain the different kinetic parameters such as degree of conversion (α), activation energy (E), pre-exponential factor (A) and rate constant (r). Consequently, the aim of this paper is to study the decomposition kinetics of Divinylbenzene-4-vinylpyridine unmodified copolymer (**Unm-Polym**) with its modified structure with nickel Schiff base complex (**Co-Polym-Ni^{2+}-SB**) by thermal analysis. The TG/DTG analysis was conducted between 25 and 800°C using four different heating rates and four methods were chosen to calculate the previous mentioned parameters. The obtained Ea values are between 162 and 441 kJ mol^{-1} for Kissinger, Ozawa and Friedman methods. The resulting activation energies calculated by Coats-Redfern method were used to evaluate the thermodynamic parameters like ΔS, ΔH and ΔG. By using these methods, the higher obtained values of *Ea* were estimated for nickel complex that caused its lower thermostability compared to the structure of **Co-Polym-Ni^{2+}-SB**.
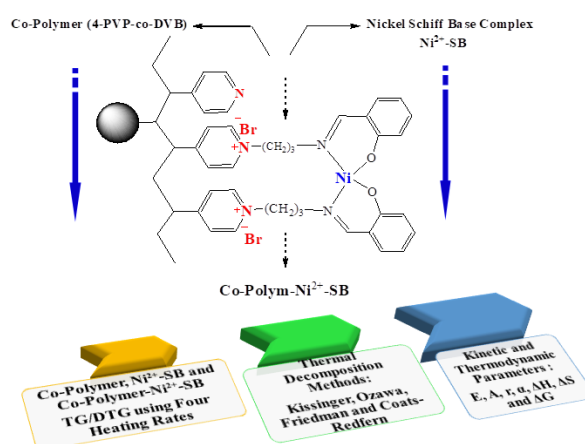
INTRODUCTION

Obtaining novel copolymers from Schiff bases complexes chemically modified with polymers is currently of interest in the development of a new class of macromolecular systems which have numerous interesting properties.[1-3] The coordination mechanism generates a strong metal-nitrogen ion interaction[4] that improves blend compatibility and can expand and diversify some properties of these materials, such as thermal stability[5-7] catalytic activity[8] and electrochromic application.[9]

Recently, and in order to develop sustainable, inexpensive, and environmentally friendly compounds, there has been a considerable effort focusing on the synthesis of new homogeneous and

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heterogeneous catalysts. As consequence, polymeric materials are frequently used because they are typically insoluble, recyclable, non-volatile and in addition to all these characteristics these materials are non-toxic. Polymers containing nitrogen atoms attracted much attention in different fields of science, technology, medicine and pharmaceutical chemistry.[10-12] Considering their interesting physicochemical properties, the polymers or copolymers based on 4-vinylpyridine (PVP) and divinylbenzene (DVB) are of great importance and it is well recognized that PVP has interesting reactivity. On the other hand, pyridine is known as a good electron donor and as a ligand capable of forming coordination bonds with the complex form of poly(4-vinylpyridine) which can be applied as conductive polymers.[13]

Therefore, it is commonly practical to combine this polymer with other compounds to obtain interesting structural characteristics.[14] So, modifying the structures of these compounds with transition metal complexes, are intriguing materials with many important applications, especially in catalysis.[15,16] These materials are becoming increasingly important in other technological fields such as the properties of fluorescence, biological activities as well as their applications in photoluminescence.[17-20] Added to this, other applications are also marked for these copolymers such as polyelectrolyte,[21] and gas separation membranes.[22]

In addition to the spectral approaches, significant attention has been paid to the employment of the thermal analysis as a complementary technique to provide more information of the thermal behavior needed for several applications.[23] Determining of thermal degradation mechanism of synthetic materials remains problematic for researchers. However, defining through diverse thermal analysis methods the different kinetic parameters play a significant role in the evaluation of combustion characteristics of these materials. Recently, many non-isothermal kinetic methods have been technologically advanced to obtain the different kinetic parameters. These methods were based essentially on relationships between heating rates and applicable different temperatures. The most well-known approaches are Kissinger, Ozawa, Friedman and Coats-Redfern methods.[24]

Even though the 4-PVP-co-DVB crosslinked copolymer was extensively studied but only a few have been published on the thermal stability and degradation kinetics of this material.[25,26] Specifically, there are few studies on thermal degradation of PVP crosslinked with divinylbenzene that contain coordination complexes.[27] The evaluation and the determination of the thermal stability and the different kinetic parameters of these kinds of materials deliver significant further information for its use and applications as novel and innovative functional and reactive materials.

As a continuation of our recent works related to the synthesis of bidentate Schiff base compounds,[28] as well as the synthesis of a modified copolymer with nickel complex.[29] Herein, we report the use of the unmodified divinylbenzene-4-vinylpyridine copolymer with its modified structure by a coordination nickel complex (See below Scheme 1) to shed some light on its thermal stability. However, the different kinetic and thermodynamic parameters corresponding to thermal decomposition of these materials have also been calculated using different methods such as Kissinger, Ozawa, Friedman and Coats-Redfern.
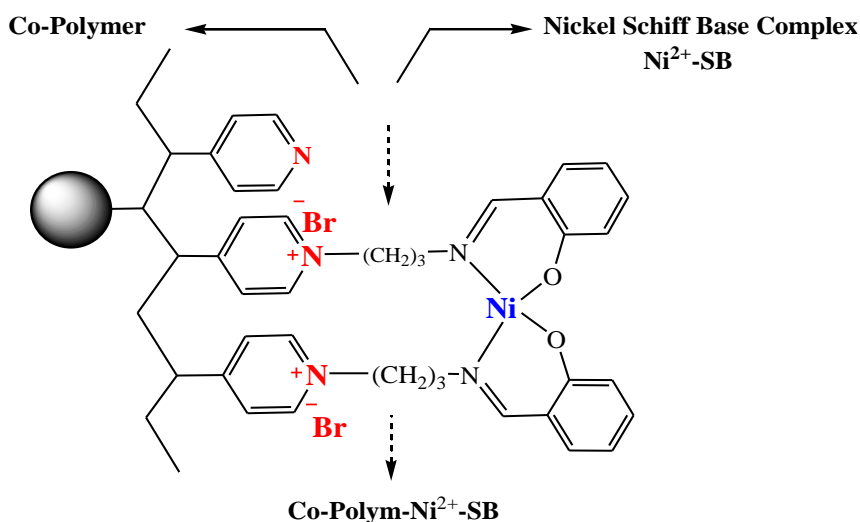
Scheme 1 – Schematic representation of **Co-Polym-Ni²⁺-SB** macromolecular complex.

EXPERIMENTAL

1. Thermogravimetric analysis

Thermogravimetric analysis of the three compounds was performed using a thermogravimetric analyzer TGA Q500 TA Instruments in dynamic mode under nitrogen atmosphere (Flow rate 60 mL min^{-1}). About 6 mg of each sample was placed in a small Alumina crucible for each run and heated from 25 to 800°C at different heating rates of 5, 10, 15 and 20°C min^{-1}.

During the heating, variation of the weight loss and its derivative with respect to time and temperature were collected automatically by the thermal analyzer software. Each run of the selected conditions was repeated to check the reproducibility of the results.

2. Kinetic and thermodynamic analysis theory

In the thermal analysis process, the rate of reaction may be expressed by:

$$r = \frac{d\alpha}{dt} = k(T)f(\alpha) \tag{1}$$

where **T:** The absolute temperature (K);
α : The degree of conversion;
r: The rate of change of conversion or composition per time unit (t).
The temperature-dependent term **k(T)** in Eq. (1) is:

$$k(T) = A exp\left(-E/RT\right) \tag{2}$$

where **E:** The activation energy (kJ mol^{-1});
A: The pre-exponential factor (s^{-1});
R: The universal constant of the perfect gases (kJ mol^{-1} K^{-1}).
The conversion function **f(α)** in Eq. (1) is:

$$f(\alpha) = (1-\alpha)^n \tag{3}$$

Combining Eqs. (1)-(3), the overall rate of weight loss of active material is given by:

$$\frac{d\alpha}{dt} = A(1-\alpha)^n exp\left(-E/RT\right) \tag{4}$$

For non-isothermal TGA measurements, the heating rate is constant Eq. (4) will be written as:

$$\beta \frac{d\alpha}{dT} = A(1-\alpha)^n exp\left(-E/RT\right) \tag{5}$$

Published methods of deriving kinetic and thermodynamic parameters from TGA data, involve either a single thermogram or multiple thermograms obtained at different heating rates. They may be either differential (Involving the derivative term, -), or integral based upon integration of Eq. (5) after rearrangement and variables separation.[30]

In the present work, four methods were used: Kissinger,[31] Ozawa,[32] Friedman[33] and Coats-Redfern.[34]

2.1. Kissinger method

The Kissinger method calculates the activation energy using the maximum decomposition temperature (T_p) at which the rate of the weight loss is the highest.[31] The differentiation of Eq. (4) gives:

$$\frac{E\beta}{RT_p^2} = A_n(1-\alpha)_p^{n-1} exp\left(-E/RT\right) \tag{6}$$

This method assumes that the decomposition product is independent of and nearly equal to unity for a first order reaction deducing the following expression:

$$ln\left(\frac{\beta}{T^2_p}\right) = \left\{-ln\left(\frac{E}{RT_p}\right) + ln[n(1-\alpha_p)^{n-1}]\right\} - \frac{E}{RT_p} \tag{7}$$

where**:** The heating rate (°C min^{-1}),
E: The apparent activation energy (kJ mol^{-1}),
T$_p$: The peak temperature (°C) of the maximum rate (% s^{-1}),
A: The pre-exponential factor (s^{-1}).

2.2. Ozawa method

Ozawa method is based on the following expression:[32]

$$log(g(\alpha)) = log\left(AE/R\right) - log\beta + log\, p\left(E/RT\right) \tag{8}$$

Using Doyle's approximation:[30]

$$log[p(E/RT)] \cong -2.315 - 0.4567\left(\frac{E}{RT}\right) \tag{9}$$

Substitution of (9) into (8) gives the final expression of the previously mentioned method:

$$log\beta = log\left(\frac{AE}{RT}\right) - 2.315 - 0.4567\left(\frac{E}{RT}\right) \tag{10}$$

2.3. Friedman method

In Friedman method,[33] the following expression is obtained:

$$ln\left(\frac{d\alpha}{dT}\right) = ln\left\{\beta\left(\frac{d\alpha}{dt}\right)\right\} = lnA + nln(1-\alpha) - \frac{E}{RT} \tag{11}$$

2.4. Coats-Redfern's method

For Coats-Redfern's method,[34] the following expressions were given:

$$log\left[\frac{-log\,(1-\alpha)}{T^2}\right] = log\left[\frac{AR}{\beta E}\right] - \frac{E}{2.303RT}$$

$$for\ n = 1 \tag{12}$$

$$log\left[-log\left\{\frac{1-(1-\alpha)^{1-n}}{(1-n)T^2}\right\}\right] = log\left[\frac{AR}{\beta E}\right] - \frac{E}{2.303RT} \quad for \ n \neq 1 \tag{13}$$

The thermodynamic parameters as: change in enthalpy (ΔH), entropy (ΔS), free energy (ΔG) and frequency factor (A) are calculated using equations (14-16).

$$\Delta S = 2.303 \, R \, log\left(\frac{Ah}{kT}\right) \tag{14}$$

where **h** and **k** are Plancks' and Boltzmanns' constants, respectively.

$$\Delta H = E - RT \tag{15}$$

$$\Delta G = \Delta H - T\Delta S \tag{16}$$

RESULTS AND DISCUSSION

The synthesis of these compounds and their full structural characterization have been reported previously.[28,29] The nickel Schiff base complex used in this study is presented in Scheme 1. It was synthesized in situ, by the reaction of the appropriate carbonyl (salicylaldehyde) and aminopropylbromide. The formed Schiff base was used to prepare the corresponding nickel complex.[28] The quaternization reaction of this nickel Schiff base complex was obtained using poly(4-vinylpyridine-*co*-divinylbenzene) copolymer that contain 2% amount of divinylbenzene crosslinker.

1. Thermal decomposition studies

The TG/DTG curves of **Co-Polymer**, **Ni^{2+}-SB** complex and **Co-Polym-Ni^{2+}-SB** complex selected for the heating rate of 10°C min^{-1} appear on the respective thermograms as a single step for the copolymer, four steps for **Ni^{2+}-SB** Schiff base complex and three steps for **Co-Polym-Ni^{2+}-SB** complex (Fig. 1). During the degradation of these samples, the temperature range of distinct stages was associated with the decomposition of the components, and this range was determined using the limit temperatures corresponding to the two neighbor minimums on the DTG curve.[35]

Within temperatures of 120–450°C, the DTG profile of **Co-Polymer** exhibited only one peak temperature at **Tp1** = 419.0°C, while the DTG profile of **Ni^{2+}-SB** Schiff base complex exhibited three peak temperatures at about **Tp1** = 129°C, **Tp2** = 303°C, and **Tp3** = 389°C. Within the same

temperature range, the third sample (**Co-Polym-Ni^{2+}-SB** complex) exhibited two peak temperatures (**Tp1** = 282°C and **Tp2** = 362°C).

These decomposition steps could be assigned to the degradation of the organic part in the structures of the components. At temperatures over 450°C, the mass losses were only observed with the nickel complex and the copolymer nickel complex mainly caused by the decomposition of remaining organic part. The maximum peak of degradation at the final stage is observed at **Tp3** = 518°C and **Tp3** = 633°C for the nickel complex and the copolymer nickel complex, respectively, leading finally to the nickel oxide as a residue. Based on the combined analysis of the TG and DTG curves, the onset decomposition temperature (**T$_{onset}$**) and the end temperature (**T$_{end}$**) were found respectively: 371.0°C and 439.0°C for **Co-Polymer**, 289°C and 797°C for **Ni^{2+}-SB** and 289.0°C and 799.0°C for **Co-Polym-Ni^{2+}-SB**.

2. Effect of heating rate

Thermal decomposition studies (TG and DTG) with different heating rates of the **Co-Polymer**, **Co-Ni^{2+}-SB** complex and **Co-Polym-Ni^{2+}-SB** complex were carried out in the temperature range 25-800°C at different heating rates of 5, 10, 15 and 20°C min^{-1}. The results obtained from these reveal that the thermal decomposition curves of the studied samples are quite similar. The selected steps of the thermal pattern of decomposition of these samples are used to calculate both kinetic and thermodynamic parameters. Thus, as it can be seen in Fig. 2, the TG and DTG thermograms of the studied samples shifted to higher temperatures region. So, as the heating rates are increased, a neat increase is immediately observed of all decomposition characteristics as summarized in Table 1. This fact is mainly ascribing to the influence of the heat transfer efficiency at the higher heating rates. On the other hand, the heating of the particles occurred more gradually leading to an improved and more effective heat transfer to the inner portions when testing them at lower heating rate.[36]
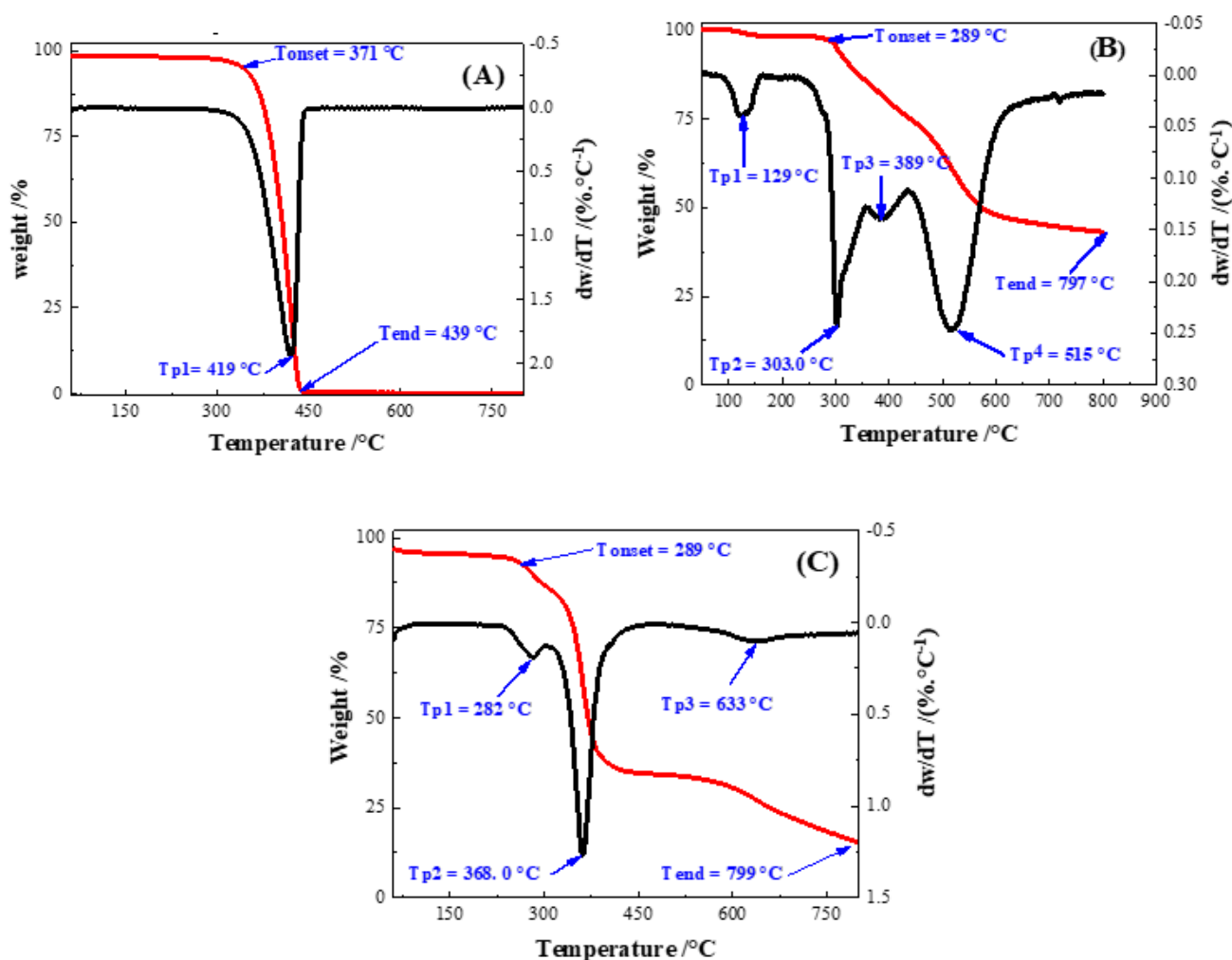
Fig. 1 – TG and DTG thermograms of (**A**)- **Co-Polymer**, (**B**)- **Ni²⁺-SB** complex and (**C**)- **Co-Polym-Ni²⁺-SB** complex performed at 10 °C min⁻¹ in nitrogen atmosphere.

Table 1

Thermogravimetric decomposition parameters of **Co-Polymer**, **Ni²⁺-SB** complex and **Co-Polym-Ni²⁺-SB** complex determined from TG/DTG experiment at different heating rates in N_2 atmosphere

Samples	Heating rates /°C min⁻¹	Temperature /°C					
		Tp1	**Tp2**	**Tp3**	**Tp4**	**T onset**	**T end**
Co-Polymer	**5**	405	-	-	-	368	433
	10	419	-	-	-	369	439
	15	431	-	-	-	404	456
	20	432	-	-	-	398	461
Ni²⁺-SB	**5**	132	293	382	515	263	625
	10	129	303	389	518	270	616
	15	131	308	396	527	268	656
	20	129	312	399	536	277	697
Co-Polym-Ni²⁺-SB	**5**	275	352	554	-	-	-
	10	282	362	633	-	-	-
	15	283	368	655	-	-	-
	20	286	373	629	-	-	-
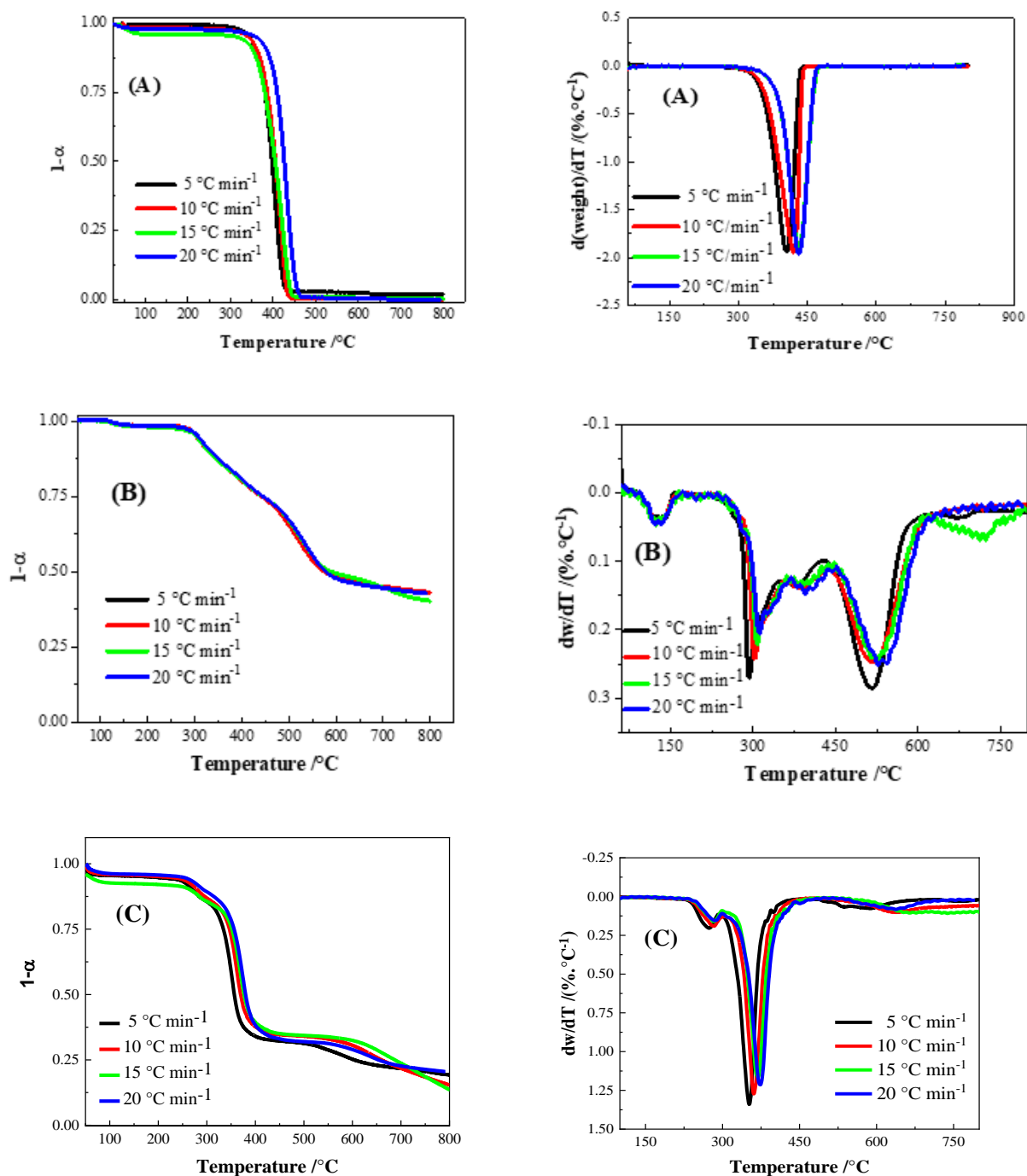
Fig. 2 – TG and DTG thermograms of **(A)- Co-Polymer**, **(B)- Ni^{2+}-SB** complex and **(C)- Co-Polym-Ni^{2+}-SB** complex performed at different heating rates 5, 10, 15 and 20 °C min^{-1} in nitrogen atmosphere.

3. Determination of Kinetic parameters of thermal decomposition processes of studied samples

3.1. *Kissinger and Ozawa methods*

Kissinger and Ozawa methods are used to fit the curve. The fitting curves of the prepared samples are showed in Figs. 3 and 4. The obtained

Kinetic parameters calculated by these two models are the activation energy, correlation coefficient (R^2) and the pre-exponential factor A (Conversion rate α is 0.25-0.85, 0.55-0.95 and 0.50-0.85 for **Co-Polymer**, **Ni^{2+}-SB** Schiff base complex and **Co-Polym-Ni^{2+}-SB** complex respectively). These results are summarized in Table 2.
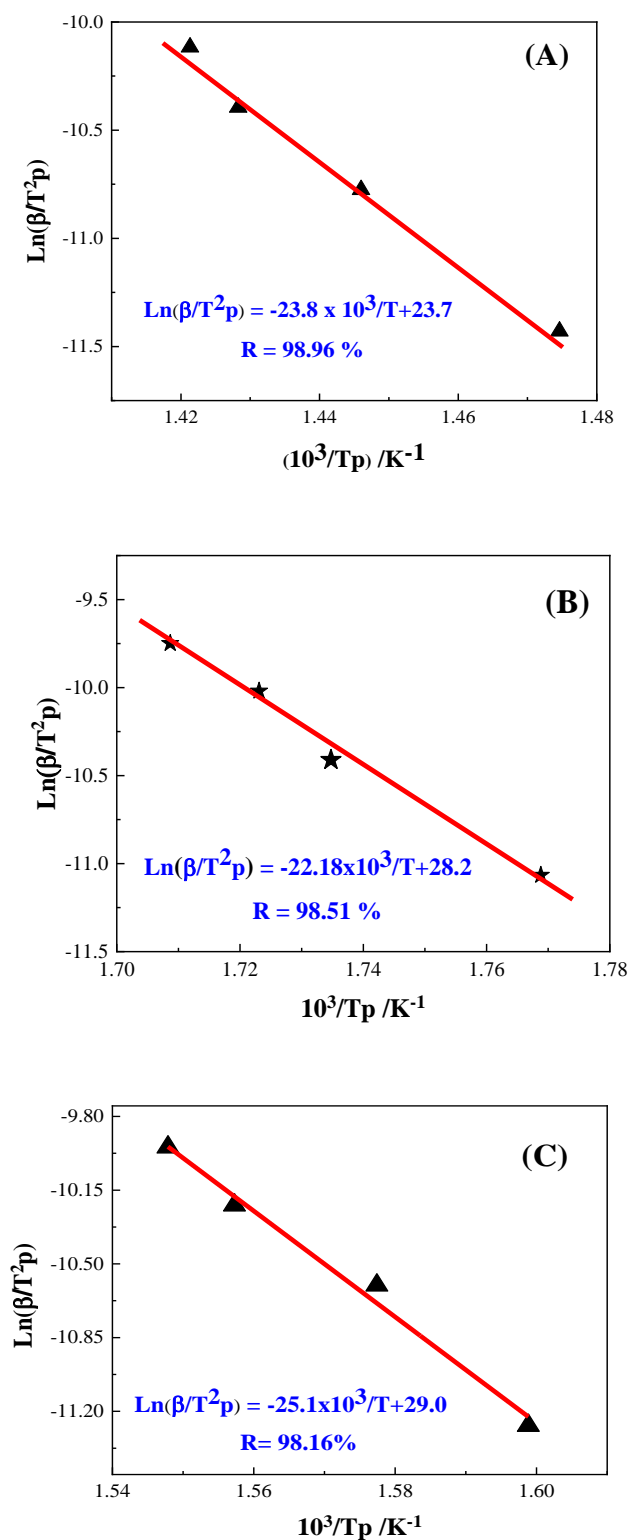
Fig. 3 – Kissinger's plots for **(A)- Co-Polymer**, **(B)- Ni^{2+}-SB** complex and **(C)- Co-Polym-Ni^{2+}-SB** complex.
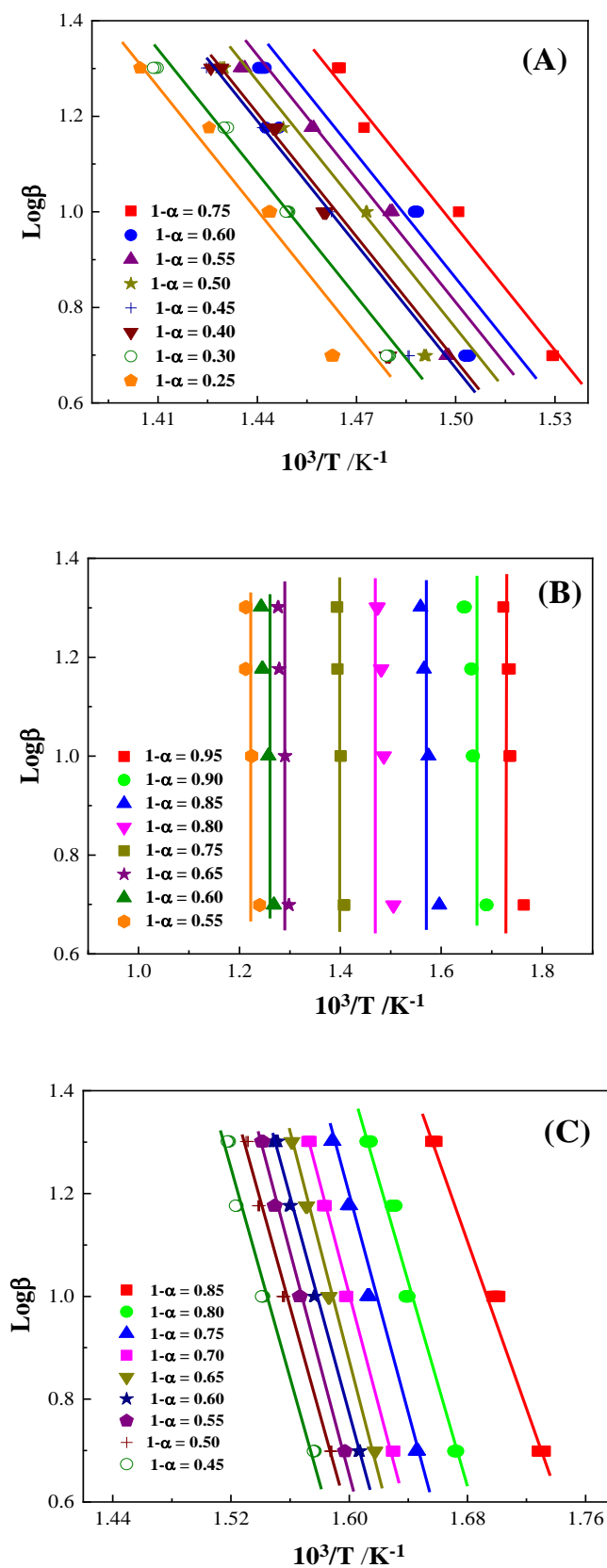
Fig. 4 – The fitting plots illustrated with Ozawa method for **(A)- Co-Polymer**, **(B)- Ni²⁺-SB** complex and **(C)- Co-Polym-Ni²⁺-SB** complex.

Table 2

Kinetic parameters derived from Kissinger and Ozawa methods

Compounds	α	T_p/ °C				Kissinger			Ozawa		
		5	10	15	20	E/kJ mol^{-1}	A/ s^{-1}	R^2 /%	E/kJ mol^{-1}	A /s^{-1}	R^2/ %
(A)-Co-Polymer	0.25-0.85	405	418	430	430	198±12	4.7 · 10^{14}	98.96	179±12	5.6 · 10^{16}	95.87
(B)- Ni^{2+}-SB	0.55-0.95	132	129	123	122	-	-	-	315±17	3.0 · 10^{27}	96.6
		292	302	307	311	183±9	3.7 · 10^{13}	98.51			
		379	388	387	398	265±14	5.4 · 10^{17}	99.15			
		509	520	527	536	261±20	7.2 · 10^{13}	98.25			
(C)- Co-Polym-Ni^{2+}-SB	0.50-0.85	-	-	-	-	-	-	-	161.7±4.1	1.3 · 10^{17}	99.10
		273	280	284	285	288±26	4.0 · 10^{19}	97.54			
		352	361	369	373	209±16	2.1 · 10^{15}	98.36			

Table 3

Kinetic parameters derived from Friedman method

Compounds		Friedman		
		E/ kJ mol^{-1}	A/ s^{-1}	R^2/ %
(A)- Co-Polymer	0.30-0.85	188±10	3.9 · 10^{13}	96.96
(B)- Ni^{2+}-SB	0.55-0.95	441±19	2.8 · 10^{27}	96.95
(C)- Co-Polym-Ni^{2+}-SB	0.40-0.90	190±9	2.3 · 10^{17}	97.78

3.2. Friedman method

Friedman method show relatively similar range of activation energy compared to Kissinger and Ozawa methods. These values are 187.7 kJ mol^{-1}, 440.7 kJ mol^{-1} and 190.6 kJ mol^{-1} for non-modified copolymer, nickel complex and modified copolymer, respectively. The above-mentioned samples exhibit high correlation factor (average R^2 > 96.9%).

3.3. Coats-Redfern method

For kinetic analysis of these samples, the Coats-Redfern method was used to determine the activation energy, regression coefficient and pre-exponential factor. The kinetic parameters were calculated at four heating rates of 5, 10, 15 and 20°C/min. We can observe from Table 4, regression coefficient (R²) varies from 97.60 to 99.0%. Thermodynamic parameters (ΔH, ΔG, ΔS) were also calculated at the selected peaks temperature as shown in Table 4.

Using Friedman method, the average value of A varied in a wide range of α from 10^{17} to 10^{32}, implying that the composition of these samples was complex and induce competitive reactions

may be occurred during the thermal decomposition process.[37,38] The activation energy can inform us on the reliability of the rate at which a chemical reaction proceeds and less significant activation energy means reaction occurs more easily.

From Tables 2, 3 and 4 we can observe that the average values of the activation energy for non-modified polymer **Co-Polymer** are 160.4 kJ mol^{-1}, 178.6 kJ mol^{-1}, 187.7 kJ mol^{-1} and 198.1 kJ mol^{-1} through Coats-Redfern, Ozawa, Friedman and Kissinger methods, respectively. Higher values of the activation energy with Kissinger method demonstrate that the thermal stability of this polymer is due to the covalent character of their bonds.[39] However, comparing the activation energy values of **Co-Polymer** with the **Ni^{2+}-SB**, we can observe that this complex has more thermal stability for all used methods except for Coats-Redfern one (99 kJ mol^{-1}). For the modified polymer with the corresponding nickel complex (**Co-Polym-Ni^{2+}-SB**) through these methods, the average values calculated are 183.0 kJ mol^{-1} and 269.0 kJ mol^{-1} for Kissinger method, 315.0 kJ mol^{-1}, 441.0 kJ mol^{-1}, and 97.0 kJ mol^{-1} for Ozawa, Friedman and Coats-Redfern Methods.

Table 4

Kinetic and thermodynamic parameters derived from Coats-Redfern Method

(A)- Co-Polymer

β (°C/min)	T_p/°C	ΔT/°C	$10^3/T_{i0}$ /K⁻¹	Slope	Intercept	E_a/kJ mol⁻¹	A/s⁻¹	ΔS/J K⁻¹ mol⁻¹	ΔH/kJ mol⁻¹	ΔG/kJ mol⁻¹	R^2/%
5	405	107	0.737	-8.28±0.045	6.10±0.07	159±1	$2.0 \cdot 10^9$	-74	153	103	98.03
10	419	107	0.747	-8.24±0.07	6.235±0.05	160±9	$5.5 \cdot 10^9$	-66	155	200	98.15
15	426	118	0.722	-8.74±0.32	6.31±0.46	167±6	$1.0 \cdot 10^{10}$	-76	162	215	98.55
20	430	94	0.761	-9.24±0.06	7.04±0.85	177±1	$7.7 \cdot 10^{10}$	-44	171	202	98.89

(B)- Ni²⁺-SB

β (°C/min)	T_p/°C	ΔT/°C	$10^3/T_{i0}$ /K⁻¹	Slope	Intercept	E_a/kJ mol⁻¹	A/s⁻¹	ΔS/J K⁻¹ mol⁻¹	ΔH/kJ mol⁻¹	ΔG/kJ mol⁻¹	R^2/%
5	132	72	1.289	-6.95±0.80	8.96±0.49	134±4	$1.3 \cdot 10^{12}$	-16	130	137	94.66
	293	70	0.692	-6.71±0.06	4.637±0.11	128±1	$5.7 \cdot 10^7$	-118	124	190	98.72
10	129	55	0.363	-5.171±0.034	1.879±0.05	99±1	$1.5 \cdot 10^5$	-168	94	204	98.75
15	123	24	1.429	-7.04±0.13	10.07±0.32	135±2	$4.7 \cdot 10^{13}$	15	132	126	96.97
20	122	22	1.526	-7.86±0.13	12.00±0.34	151±3	$6.0 \cdot 10^{15}$	55	147	126	97.62

(C)- Co-Polym-Ni²⁺-SB

β (°C/min)	T_p/°C	ΔT/°C	$10^3/T_{i0}$ /K⁻¹	Slope	Intercept	E_a/kJ mol⁻¹	A/s⁻¹	ΔS/J K⁻¹ mol⁻¹	ΔH/kJ mol⁻¹	ΔG/kJ mol⁻¹	R^2/%
5	352	63	0.309	4.82±0.03	1.49±0.05	92±1	$2.8 \cdot 10^4$	-166	87	191	98.43
10	361	58	0.333	5.04±0.03	1.68±0.05	96±1	$1.0 \cdot 10^5$	-156	91	190	98.58
15	369	-	0.241	4.76±0.04	1.15±0.06	91±1	$3.8 \cdot 10^4$	-130	86	169	98.50
20	373	75	0.155	4.50±0.05	0.70±0.07	86±1	$1.7 \cdot 10^4$	-170	81	191	97.92

3.4. Thermodynamic analysis

The average values of Eα derived from Coats-Redfern's methods were used to calculate the average values of A, ΔH, ΔG and ΔS at different heating rates from 5 to 20°C min⁻¹. The corresponding activation energy E, the pre-exponential factor A, enthalpy of activation (ΔH), entropy of activation (ΔS), and the Gibbs free energy change (ΔG) were listed in Table 5. As expected ΔG values are positive, indicating non-spontaneous chemical processes of the thermal decomposition of **Co-Polymer**, **Ni²⁺-SB** Schiff base complex and **Co-Polym-Ni²⁺-SB** complex

samples. On the other hand, the negative values of ΔS of thermal decomposition demonstrate that these compounds are more ordered.[40] Furthermore, the corresponding values of the enthalpy of activation (ΔH) are also positive and are in the range between 80.0 and 87.0 kJ mol^{-1}. These positive values mean endothermic process of thermal degradation under the inert nitrogen atmosphere.[41]

CONCLUSION

After using non modified copolymer **Co-Polymer**, a Schiff base nickel complex **Ni^{2+}-SB** and the modified copolymer with this complex, **Co-Polym-Ni^{2+}-SB** by quaternization reaction, this study provided information on their combustion characteristics and decomposition kinetic parameters that could be summarized as follows:

The kinetic parameters of the prepared samples were determined and compared through four different methods.

The entire mentioned samples exhibit high correlation factor (average $94 < R^2 < 99$ %).

The activation energy determined by Kissinger method is 289 Kj mol^{-1}, whereas the values derived from Ozawa, Coats-Redfern and Friedman methods are 162, 97 and 191 kJ mol^{-1}, respectively.

These higher values with all the used methods reproduce a reasonable high thermal stability. So, the obtained higher values of *Ea* were estimated for nickel complex that caused its lower thermostability compared to the structures of unmodified and modified co-polymer.

These differences could be explained by diverse experimental conditions such as the sample masses, the particle size or heat transport, which can have an important influence on the nature of the decomposition reactions.

Finally, thermodynamic parameters calculated using Coats-Redfern's method furnish negative values of entropy of activation. These negative values express a change in the order due to the complexity of the non-modified copolymer and the modified copolymer thermal decomposition process compared to the free nickel complex.

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