

Synthesis and characterization of the nano-structured poly (1-amino-2-hydroxy-naphthalene-4-sulfonic acid)

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Abstract

In recent years, the synthesis of polymers containing functional groups has attracted the attention of many researchers due to their interesting optical, electronic and thermal characteristics. Among them, *bi-functional* or *tri-functional polyarenes* are widely used as composite materials with high stability, photoresist or fire resistant materials. In addition, the existence of functional groups in the polymer structure allows preparing new materials. These polymers have also a potential for analytical and environmental applications. In this study, the chemical oxidative polymerization of, 1-amino-2-hydroxy- *naphthalene-4-sulfonic acid* was performed by NaOCl (oxidant) in aqueous alkaline medium. The structure of the resulting polymer was characterized by FT-IR technique. Further characterization was performed using TG-DTA analysis. The solid state degradation kinetics of the obtained polymer was analyzed by using TG-DTG and DTA data from ambient temperature to 1000 °C in nitrogen atmosphere under isothermal conditions. TGA-DTG curves showed that the thermal decomposition occurred in two stages. They are attributed to the dehydration and thermal decomposition stage of polymer. Six kinetic methods based on single heating rates were used to investigate the thermal decomposition behavior of this polymer. The values of activation energy E , frequency factor A , reaction order n , entropy change ΔH^\ddagger , enthalpy change ΔS^\ddagger and Gibbs free energy ΔG^\ddagger , related to the thermal decomposition were calculated by means of Coats-Redfern (CR), Horowitz-Metzger (HM), MacCallum-Tanner (MC), van Krevelen (vK), Madhusudanan-Krishnan-Ninan (MKN) and Wanjun-Yuwen-Hen-Cunxin (WHYC) methods. The activation energy values obtained by all the methods were in good agreement with each other.

Keywords: activation energy; 1-amino-2-hydroxy-*naphthalene-4-sulfonic acid*; thermal decomposition.

Introduction: Kinetic Theory

The kinetics of heterogeneous condensed phase reactions that occur in non-isothermal conditions is usually described by the equation,

$$\beta \frac{d\alpha}{dT} = A f(\alpha) \exp\left(\frac{-E}{RT}\right) \quad (1)$$

where α , β , A , $f(\alpha)$ are the degree of conversion, the linear heating rate, pre-exponential factor, and the differential conversion function, respectively. The kinetic parameters related to the solid state decomposition can be used by different reaction models. The degree of conversion, α and corresponding $(1-\alpha)^n$ are calculated from TG curves. Here n is the reaction order. In this study the decomposition kinetics was performed by six different methods given in the literature CR (Coats *et al.*, 1964), HM (Horowitz *et al.*, 1963), MC (MacCallum *et al.*, 1970), vK (Van Krevelen *et al.*, 1951), MKN (Madhusudanan *et al.*, 1993) and WHYC (WanJun *et al.*, 1993) can be expressed by following equations,

The Coats-Redfern method

$$\ln\left[\frac{g(\alpha)}{T^2}\right] = \ln\left[\frac{AR}{\beta E}\left(1 - \frac{2RT}{E}\right)\right] - \left(\frac{E}{RT}\right) \quad (2)$$

The van Krevelen method

$$\ln g(\alpha) = \ln \left[\frac{A(0.368/T_m)^{\frac{E_a}{RT_m}}}{\beta \left(\frac{E_a}{RT_m} + 1\right)} \right] + \left(\frac{E_a}{RT_m} + 1\right) \ln T \quad (3)$$

The MacCallum-Tanner method

$$\log g(\alpha) = \log\left(\frac{AE}{\beta R}\right) - 0.4828E^{0.4351} - \left(\frac{0.449 + 0.217E}{10^{-3}T}\right) \quad (4)$$

Madhusudanan-Krishnan-Ninan method

$$\ln\left(\frac{g(\alpha)}{T^{1.9206}}\right) = \left[\ln\frac{AR}{\beta E} + 3.7678 - 1.9206 \ln E\right] - 0.12040\left(\frac{E}{RT}\right) \quad (5)$$

Horowitz-Metzger method

By using $\Theta = T - T_m$

$$\ln(g(\alpha)) = \ln\frac{ART_m^2}{\beta E} - \frac{E}{RT_m} + \frac{E\Theta}{RT_m^2} \quad (6)$$

WanJun-Yuwen-Hen-Cunxin method

$$\ln\left(\frac{g(\alpha)}{T^{1.8946}}\right) = \left[\ln \frac{AR}{\beta E} + 3.6350 - 1.8946 \ln E \right] - 1.0014 \left(\frac{E}{RT} \right) \quad (7)$$

In the equations above, $g(a)$, T_m , E , R , are the integral function of conversion, DTG peak temperature, activation energy and gas constant, respectively. The kinetic parameters were calculated from the linear plots of the left-hand side of kinetic equations against $1/T$. For vK equation the left-hand side is plotted against $\ln T$. The values E and A were calculated from the slope and intercept of the straight lines, respectively.

Material and Methods

1-amino-2-hydroxy-*naphthalene*-4-sulfonic acid, hydrochloric acid (HCl, 37%) and other all chemical compounds were supplied from Merck Chem. Co. (Germany) and they were used as received. Sodium hypochlorite (NaOCl), (30% aqueous solution) was supplied from Paksoy Chem. Co. (Turkey).

Synthesis of poly(1-amino-2-hydroxy-*naphthalene*-4-sulfonic acid)

P[1A2HN4S] was synthesized from the oxidative polymerization reaction of 1A2HN4S in aqueous solution of NaOCl (30%). The 1A2HN4S (0.242 g, 0.001 mol) was dissolved in an aqueous solution of KOH (10%, 0.056 g, 0.001mol) and placed into a 50 ml three-necked round-bottom flask. It was fitted with a condenser, thermometer, and stirrer. After heating to 30 °C, NaOCl was added drop wise to this solution for about 20 min. Then, the mixture was cooled to room temperature and 0.001 mol HCl (37%) was added. Unreacted monomer was separated from the reaction product by washing CHCl_3 . The mixture was filtered and washed with hot water (3×25 ml) for separating from mineral salts and then dried in the oven at 110 °C. Synthetic procedure and the proposed structure for P[1A2HN4S] is outlined in Figure 1. Also, the FT-IR results of P[1A2HN4S] are illustrated in Figure 2. IR (KBr) (λ_{max} : cm^{-1}): 3074 (–OH), 1674 (–C=N), 1479(–C=C-aromatic), 1454 (–C=C- aromatic), 1280, 1230, 1152, 1114, 1085, 752.

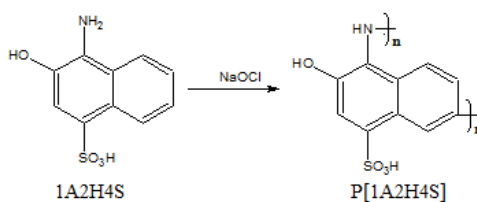


Figure 1. The synthetic procedure for P[1A2HN4S]

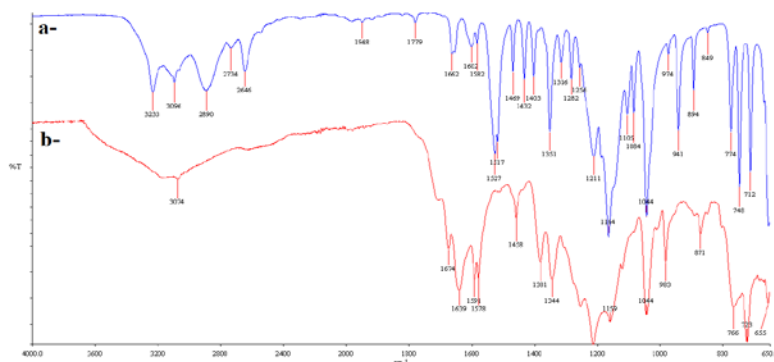


Figure 2. FT-IR spectra of monomer (a) and resulting polymer (b)

Instrumental techniques

Thermogravimetric analysis was performed with TGA-DTA Perkin-Elmer Diamond system apparatus. The thermal measurements were carried out from the ambient temperature up to 1000 °C at heating rate of 10°C /min. TGA-DTG and DTA curves were recorded in dynamic nitrogen atmosphere at a flow rate of 60 ml/min. For thermogravimetric analysis, the polymer sample was evaluated in the form of 4 mg weight. A platinum crucible was used as a sample container. Al₂O₃ was used as a reference material

Results and Discussion

The kinetic analysis of resulting polymer was studied by thermogravimetric analysis from ambient temperature to 1000 °C in nitrogen atmosphere. Typical TG, DTG and DTA curves for resulting polymer are shown in Figure 3.

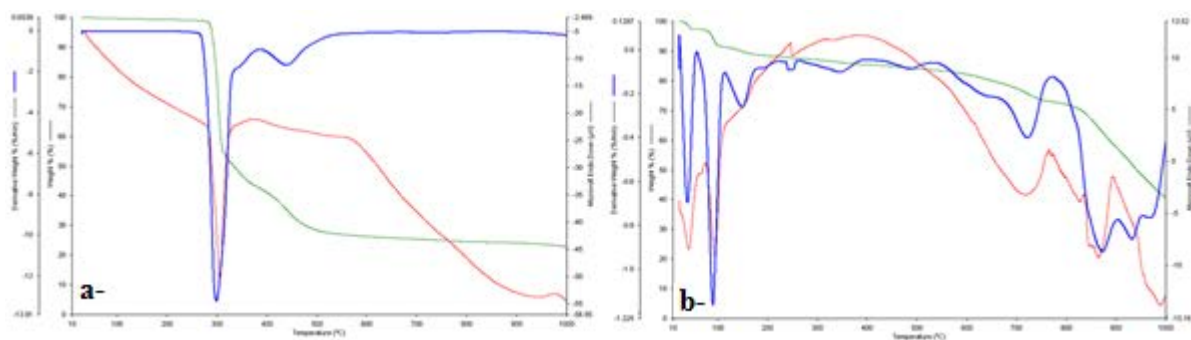


Figure 3. Typical TG, DTG and DTA curves for monomer (a) and resulting polymer (b)

From the TG curve for compound a (monomer), it appeared that the sample decomposed in one stage over the temperature range 278-309 °C with a mass loss 22.2 % in weight. From the corresponding DTA profiles, only one endothermic peak for monomer was noted. The maxima of these peaks attributed to the thermal decomposition of monomer. The decomposition process of resulting polymer was very different to monomer. The stability of resulting polymer was less than that of monomer as it decomposed at 88 °C. First stage (thermal dehydration) occurred at the temperature range of 88-122 °C and second stage occurred at the temperature range of 443-516 °C. From the corresponding DTA profile, two exothermic peaks for resulting polymer were noted. The maxima of these peaks attributed to thermal dehydration (97.8 °C) and decomposition steps of resulting polymer (832.7 °C), respectively. Thermal data obtained at a single heating rate (10 °C min⁻¹), were evaluated by the methods based on the single heating rates for kinetic analysis. The reaction order, n , activation energy, E , pre-exponential factor, A , and the linearization curves of the thermal dehydration and decomposition of the resulting polymer were determined. According to the CR method, the plot of $\ln [g(a)/T^n]$ versus $1/T$ gave straight lines with slopes equal to $-E/R$ for all the decomposition steps of the resulting polymer (Figure 4). The activation energies of the dehydration and decomposition obtained by this approach at $0.05 < \alpha < 0.95$ are 103.11 and 114.70 kJ/mol for resulting polymer, respectively.

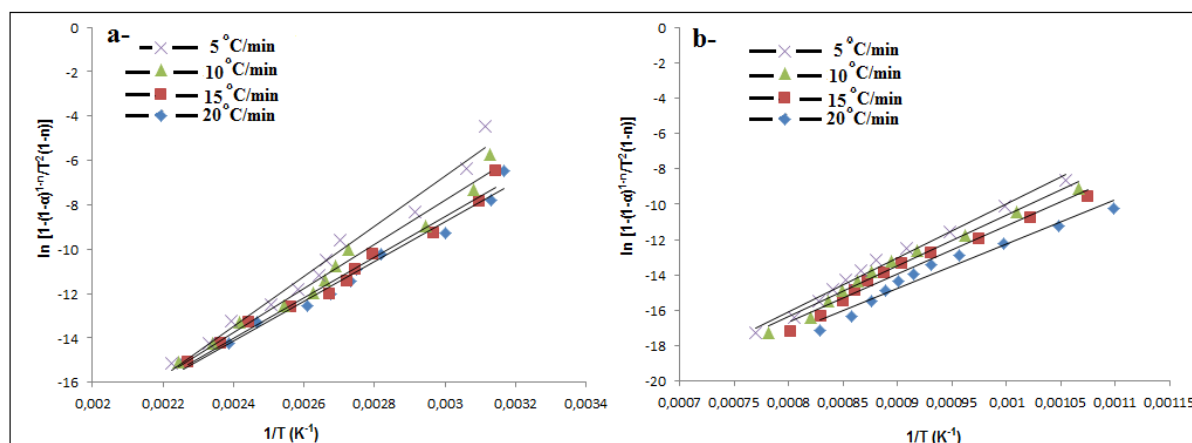


Figure 4. Coats-Redfern plots of the dehydration (a) and decomposition step (b)

Moreover, for all of the methods, it is possible to determination of the pre-exponential factor and reaction order is possible from the expression of $g(a)$ in eqns where $n \neq 1$:

$$g(\alpha) = \frac{1 - (1 - \alpha)^{1-n}}{1-n}$$

n , A , and E can be calculated from the linearization curves of the dehydration and decomposition steps obtained using the methods mentioned above. n , A , r and E obtained by all the methods using in this study was presented in Tables 2 and 3. The results are in good agreement with the values obtained from all of them. As can be seen in Tables 2 and 3, the value of correlation coefficients of linearization curves for both the dehydration and decomposition steps are approximately 1.00. The kinetic data obtained by different methods agree with each other. In order to calculate the $\Delta H^\#$, $\Delta S^\#$, and $\Delta G^\#$, of both the dehydration and decomposition steps following relations were used [11]:

$$\Delta S^\# = 2.303 \log \left(\frac{Ah}{kT} \right)_R ; \Delta H = E - RT; \Delta G^\# = \Delta H - T \Delta S^\#$$

Where h , T and A are the Planck constant, temperature at the maximum rate of weight loss, pre-exponential factor. The thermodynamic parameters calculated were reported in Tables 2 and 3.

Table 2. The Kinetic data on the dehydration step of resulting polymer

Heating rate	methods	n	E/kJ mol^{-1}	$\ln A/s^{-1}$	$\Delta S^\#$ $mol^{-1}K^{-1}$	$\Delta H^\#/kJ$ mol^{-1}	$\Delta G^\#/kJ$ mol^{-1}	Correlation, r
5	CR	1,4	103,1	-32,8	-519,8	-522,8	-238,5	0,98791
	WHYC	1,4	107,3	-34,2	-531,0	-534,7	-244,3	0,98769
	MKN	1,4	109,6	-32,4	-536,1	-520,2	-226,9	0,98760
	MC	1,4	107,2	-27,9	-478,3	-482,5	-220,8	0,98719
	HM	1,2	109,4	14,4	-125,7	-129,4	-60,6	0,96397
	vK	1,3	104,9	452,5	3516,5	3513,5	1589,9	0,96076
10	CR	1,6	107,3	-32,6	-518,2	-521,5	-238,0	0,98783
	WHYC	1,6	113,8	-36,9	-534,6	-557,0	-264,6	0,98757
	MKN	1,5	111,4	-34,3	-528,5	-536,0	-246,9	0,98765
	MC	1,5	111,2	-27,5	-475,7	-479,0	-218,8	0,98719

	HM	1,3	115,1	14,0	-130,3	-133,5	-62,2	0,94555
	vK	1,4	106,1	436,6	3383,5	3380,9	1530,1	0,94644
15	CR	1,7	114,5	-33,8	-525,7	-531,2	-243,6	0,98083
	WHYC	1,8	116,3	-34,4	-531,2	-536,7	-246,1	0,98011
	MKN	1,6	113,9	-33,6	-525,1	-530,1	-242,9	0,98697
	MC	1,5	113,7	-27,3	-472,1	-477,6	-219,3	0,97706
	HM	1,4	118,1	13,8	-133,3	-135,0	-62,1	0,96785
	VK	1,4	107,2	395,2	3123,5	3036,3	1327,7	0,97896
20	CR	1,7	117,2	-33,9	-529,5	-532,6	-242,9	0,98368
	WHYC	1,7	119,1	-34,6	-535,0	-538,0	-245,4	0,98307
	MKN	1,6	116,0	-34,9	-534,4	-540,7	-248,3	0,98306
	MC	1,6	110,6	-27,5	-472,1	-478,8	-220,6	0,97706
	HM	1,5	122,3	13,7	-136,4	-135,2	-60,6	0,97896
	VK	1,5	109,5	376,4	3019,5	2880,4	1228,7	0,97897

Table 3. The Kinetic data on the decomposition step of resulting polymer

Heating rate	methods	<i>n</i>	E/kJ mol ⁻¹	lnA/s ⁻¹	$\Delta S^\#$ /J mol ⁻¹ K ⁻¹	$\Delta H^\#$ /kJ mol ⁻¹	$\Delta G^\#$ /kJ mol ⁻¹	Correlation co, <i>r</i>
5	CR	2,1	214,7	-25,4	-467,6	-461,3	-205,5	0.98890
	WHYC	2,1	213,4	-25,3	-467,2	-461,0	-205,4	0.98778
	MKN	2,2	213,8	-25,3	-466,8	-461,0	-205,7	0.98681
	MC	2,3	220,9	-17,5	-402,0	-395,8	-175,9	0.98673
	HM	2,1	221,3	10,0	-172,5	-166,2	-71,9	0.98650
	vK	2,2	223,3	339,5	2567,0	2573,8	1169,6	0.98490
10	CR	2,2	218,9	-24,5	-460,1	-453,9	-202,2	0.98423
	WHYC	2,2	217,7	-24,4	-459,7	-453,5	-202,0	0.98412
	MKN	2,3	218,0	-24,4	-459,3	-453,0	-201,8	0.98415
	MC	2,3	224,7	-16,4	-393,4	-387,1	-171,9	0.98264
	HM	2,2	225,4	11,3	-162,2	-155,8	-67,1	0.98096
	vK	2,3	231,3	350,6	2658,6	2665,4	1211,1	0.97823
15	CR	2,3	223,7	-24,2	-458,1	-451,7	-201,1	0.98769
	WHYC	2,3	222,5	-24,2	-457,7	-451,3	-200,9	0.98761
	MKN	2,3	222,8	-24,1	-457,3	-451,1	-201,0	0.98760

	MC	2,5	229,1	-16,1	-390,7	-384,3	-170,5	0.98056
	HM	2,3	231,1	11,7	-158,8	-152,3	-65,4	0.97290
	VK	2,4	236,7	354,1	2687,9	2694,9	1224,6	0.96145
	CR	2,4	231,6	-24,4	-459,6	-453,3	-201,9	0.99899
	WHYC	2,4	230,3	-24,3	-459,2	-452,8	-201,6	0.99899
	MKN	2,4	230,1	-24,3	-458,6	-452,1	-201,2	0.99899
20	MC	2,6	237,1	-16,2	-391,7	-385,3	-171,0	0.98925
	HM	2,5	237,5	12,1	-155,1	-148,6	-63,76	0.98900
	VK	2,6	244,1	363,1	2762,4	2769,4	1258,4	0.97936

Conclusions

A study on the thermal dehydration and decomposition steps of polymer, P[1A2HN4S] was carried out by using the methods based on a single heating rate. E , A , n , ΔH^\ddagger , ΔS^\ddagger and ΔG^\ddagger related to the dehydration and decomposition kinetics was obtained by the dynamic thermogravimetric data. It was found that the mean activation energies of polymer were 103.11 kJ/mol for the dehydration step, and 114.70 kJ/mol for decomposition step

Acknowledgments

This work was financially supported by the TUBITAK Grants Commission (Project No: KBAG- 113Z587).

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Synthesis and characterization of the nano-structured poly(1-amino-2-hydroxy-naphthalene-4-sulfonic acid)

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Introduction

The kinetics of heterogeneous condensed phase reactions that occur in non-isothermal conditions is usually described by the equation, $\frac{\beta \frac{d\alpha}{dt}}{1-\alpha} = A f(\alpha) \exp\left(\frac{-E}{RT}\right)$ where α , β , A , $f(\alpha)$ are the degree of conversion, the linear heating rate, pre-exponential factor, and the differential conversion function, respectively. The kinetic parameters related to the solid state decomposition can be used by different reaction models. The degree of conversion, α and corresponding $(1-\alpha)^n$ are calculated from TG curves. Here n is the reaction order. In this study the decomposition kinetics was performed by six different methods given in the literature: Coats-Redfern [1] (CR), Horowitz-Metzger (HM) [2], MacCallum-Tanner (MC) [3], van Krevelen (vK) [4], Madhusudan-Krishnan-Ninan (MKN) [5] and Waniun-Yuven-Hen-Cunxin (WHYC) [6] can be expressed by following equations,

$$\frac{\beta \frac{d\alpha}{dt}}{1-\alpha} = A f(\alpha) \exp\left(\frac{-E}{RT}\right) \quad (1)$$

$$\ln\left(\frac{g(\alpha)}{1-\alpha}\right) = \ln\left(\frac{AR}{E}\right) - \left(\frac{E}{RT}\right) \quad (2)$$

$$\ln g(\alpha) = \ln\left[\frac{A(0.568T_m)^n}{E(RT_m - 1)}\right] - \left(\frac{E}{RT_m} - 1\right) \quad (3)$$

$$\log g(\alpha) = \log\left[\frac{AE}{RT_m^2} - 0.482E\right] + 0.449 + \frac{0.217E}{10^3 T_m} \quad (4)$$

$$\ln\left(\frac{g(\alpha)}{1-\alpha}\right) = \ln\left(\frac{AR}{E}\right) + 3.7678 - 1.9206 \ln E - 1.1204 \left(\frac{E}{RT}\right) \quad (5)$$

$$\ln\left(\frac{g(\alpha)}{1-\alpha}\right) = \ln\left(\frac{AR}{E}\right) + 3.6350 - 1.8946 \ln E - 1.001 \left(\frac{E}{RT}\right) \quad (7)$$

In the equations above, $g(\alpha)$, T_m , E , R , are the integral function of conversion, DTG peak temperature, activation energy and gas constant, respectively. The kinetic parameters were calculated from the linear plots of the left-hand side of the kinetic equations (Eqns 2, 4, 5, 6 and 7) against $1/T$. For van Krevelen equation (Eqn. 3) the left-hand side is plotted against $\ln T$. The values E and A were calculated from the slope and intercept of the straight lines, respectively.

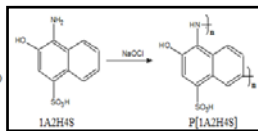


Figure 1. The synthetic procedure for P[1A2HN4S]

Method

1-amino-2-hydroxy-naphthalene-4-sulfonic acid, hydrochloric acid (HCl, 37%) and other all chemical compounds were supplied from Merck Chem. Co. (Germany) and they were used as received. Sodium hypochlorite (NaOCl), (30% aqueous solution) was supplied from Paksoy Chem. Co. (Turkey).

Synthesis of poly(1-amino-2-hydroxy-naphthalene-4-sulfonic acid)

P[1A2HN4S] was synthesized from the oxidative polymerization reaction of 1A2HN4S in aqueous solution of NaOCl (30%). The 1A2HN4S (0.242 g, 0.001 mol) was dissolved in an aqueous solution of KOH (10%, 0.056 g, 0.001mol) and placed into a 50 ml three-necked round-bottom flask. It was fitted with a condenser, thermometer, stirrer. After heating to 30 °C, NaOCl was added dropwise to this solution for about 20 min. Then, the mixture was cooled to room temperature and 0.001 mol HCl (37%) was added. Unreacted monomer was separated from the reaction product by washing CHCl_3 . The mixture was filtered and washed with hot water (3x 25 ml) for separating from mineral salts and then dried in the oven at 110 °C [7-9]. Synthetic procedure and the proposed structure for P[1A2HN4S] is outlined in Figure 1.

Instrumental techniques

Thermogravimetric analysis was performed with TGA-DTA Perkin-Elmer Diamond system apparatus. The thermal measurements were carried out from the ambient temperature up to 1000 °C at heating rate of 10 °C/min. TGA-DTG and DTA curves were recorded in dynamic nitrogen atmosphere at a flow rate of 60 ml/min. For thermogravimetric analysis, the polymer sample was evaluated in the form of 4 mg weight. A platinum crucible was used as a sample container. All the experiments were performed twice for repeatability and the results show good reproducibility with the smaller variations in the kinetic parameters. Al_2O_3 was used as a reference material.

Discussion

The kinetic analysis of resulting polymer was studied by thermogravimetric analysis from ambient temperature to 1000 °C in nitrogen atmosphere. Typical TG, DTG and DTA curves for resulting polymer are shown in Figure 3.

From the TG curve for compound a (monomer), it appeared that the sample decomposed in one stage over the temperature range 278-309 °C with a mass loss 22.2 % in weight. From the corresponding DTA profiles, only one endothermic peak for monomer was noted. The maxima of these peaks which were attributed to the thermal decomposition of monomer (95.6 °C). The decomposition process of resulting polymer was very different to monomer.

The stability of resulting polymer was less than that of monomer as it decomposed at 88 °C. First stage (thermal dehydration) occurred at the temperature range of 88-122 °C and second stage occurred at the temperature range of 443-516 °C. From the corresponding DTA profile, two exothermic peaks for resulting polymer were noted. The maxima of these peaks which were attributed to thermal dehydration (97.8 °C) and decomposition steps of resulting polymer (832.7 °C), respectively. Thermal data obtained at a single heating rate (10 °C min⁻¹), were evaluated by the methods based on the single heating rates for kinetic analysis [10].

According to the Coats and Redfern method, the plot of $\ln(g(\alpha)/T^2)$ versus $1/T$ gave straight lines with slopes equal to $-E/R$ for all the decomposition steps of the resulting polymer (Figure 4). The activation energies of the dehydration and decomposition obtained by this approach at 0.05 < α < 0.95 are 103, 11 and 114,70 kJmol⁻¹ for resulting polymer, respectively.

Moreover, for all of the methods, it is possible to determination of the pre-exponential factor and reaction order is possible from the expression of $g(\alpha)$ in eqns (3, 4, 5, 6 and 7) where $n \neq 1$:

$$g(\alpha) = \frac{1-(1-\alpha)^{1-n}}{1-n}$$

As can be seen in Tables 2 and 3, the value of correlation coefficients of linearization curves for both the dehydration and decomposition steps are approximately 1.00. The kinetic data obtained by different methods agree with each other. In order to calculate the enthalpy ΔH^\ddagger , activation entropy ΔS^\ddagger , and the free energy of activation ΔG^\ddagger , of both the dehydration and decomposition steps following relations were used [11]:

$$\Delta S^\ddagger = 2.303 \log \left(\frac{Ah}{kT} \right) R; \Delta H = E - RT; \Delta G^\ddagger = \Delta H - T \Delta S^\ddagger$$

Results

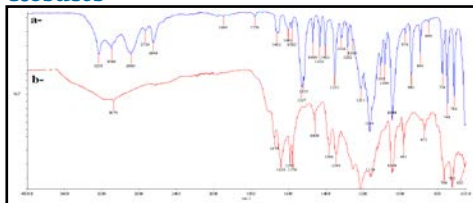


Figure 2. FT-IR spectra of monomer (a) and resulting polymer (b)

FT-IR results of P[1A2HN4S] are illustrated in Figure 2. IR (KBr) (λ_{max} : cm⁻¹): 3074 (-OH), 1674 (-C=N), 1479(-C-C-aromatic), 1454 (-C-C- aromatic), 1280, 1230, 1152, 1114, 1085, 752.

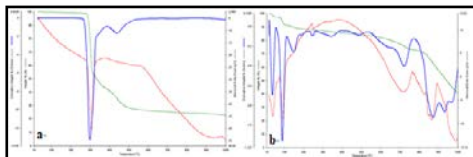


Figure 3. Typical TG, DTG and DTA curves for monomer (a) and resulting polymer (b)

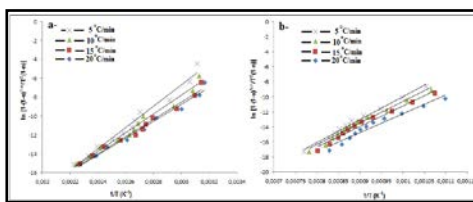


Figure 4. Coats-Redfern plots of the dehydration and decomposition steps

Where h , T and A are the planck constant, temperature at the maximum rate of weight loss, pre-exponential factor. The thermodynamic parameters calculated were reported in Tables 2 and 3.

Heating rate methods	n	E (kJ/mol)	ln A [†]	ΔH [†] (kJ/mol)	ΔS [†] (J/mol.K)	ΔG [†] (kJ/mol)	Calculation of R ²
9	WHYC	1.4	1001.9	12.6	-149.9	-127.9	0.9996
	HM	1.4	1001.9	12.6	-149.9	-127.9	0.9996
	MC	1.4	1001.9	12.6	-149.9	-127.9	0.9996
10	WHYC	1.4	1001.9	12.6	-149.9	-127.9	0.9996
	HM	1.4	1001.9	12.6	-149.9	-127.9	0.9996
	MC	1.4	1001.9	12.6	-149.9	-127.9	0.9996
11	WHYC	1.8	108.9	18.6	-131.2	-148.7	0.9991
	HM	1.8	108.9	18.6	-131.2	-148.7	0.9991
	MC	1.8	108.9	18.6	-131.2	-148.7	0.9991
20	WHYC	1.8	108.9	18.6	-131.2	-148.7	0.9991
	HM	1.8	108.9	18.6	-131.2	-148.7	0.9991
	MC	1.8	108.9	18.6	-131.2	-148.7	0.9991

Table 2. The Kinetic data on the decomposition step of the resulting polymer

Heating rate methods	n	E (kJ/mol)	ln A [†]	ΔH [†] (kJ/mol)	ΔS [†] (J/mol.K)	ΔG [†] (kJ/mol)	Calculation of R ²
9	WHYC	2.1	214.4	-21.5	-487.5	-481.5	0.9979
	HM	2.1	214.4	-21.5	-487.5	-481.5	0.9979
	MC	2.1	214.4	-21.5	-487.5	-481.5	0.9979
10	WHYC	2.1	214.4	-21.5	-487.5	-481.5	0.9979
	HM	2.1	214.4	-21.5	-487.5	-481.5	0.9979
	MC	2.1	214.4	-21.5	-487.5	-481.5	0.9979
14	WHYC	2.1	214.4	-21.5	-487.5	-481.5	0.9979
	HM	2.1	214.4	-21.5	-487.5	-481.5	0.9979
	MC	2.1	214.4	-21.5	-487.5	-481.5	0.9979
20	WHYC	2.1	214.4	-21.5	-487.5	-481.5	0.9979
	HM	2.1	214.4	-21.5	-487.5	-481.5	0.9979
	MC	2.1	214.4	-21.5	-487.5	-481.5	0.9979

Conclusion

***A study on the thermal dehydration and decomposition steps of polymer, P[1A2HN4S] was carried out by using the methods based on a single heating rate.**

***The activation energy, pre-exponential factor, the entropy change, enthalpy change and Gibbs free energy change related to the dehydration and decomposition kinetics was obtained by the dynamic thermogravimetric data. It was found that the mean activation energies of polymer were 103.11 kJmol⁻¹ for the dehydration step and 114.70 kJmol⁻¹ for decomposition step.**

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