

## **A novel tri-functional polyaren: synthesis and characterization**

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### **Abstract**

Conducting polymers containing different functional groups have received increasing attention in the last decade, due to wide application area including corrosion protection systems (Meneguzzi *et al.*, 2001), pH sensors (Xu *et al.*, 1995), or electrochromic devices (Schmitzand *et al.*, 1995). The characteristics of *polyarens* arise from the presence of three various functional groups (such as  $-\text{NH}_2$ ,  $-\text{OH}$  and  $-\text{SO}_3\text{H}$ ) in their structure. The chemical oxidative polymerization of these kinds of monomers has been scarcely reported up to now. In this study, we reported the facile and template-free oxidative synthesis of *6-amino-2-hydroxy-naphthalene-4-sulfonic acid* (a *tri-functional monomer*). The polymerization was performed in aqueous alkaline medium. We also aimed to investigate the kinetic parameters related to the solid state decomposition of the resulting polymer. In order to the calculation of the solid state degradation kinetics we used the TG-DTG and DTA data from ambient temperature to 1000 °C in nitrogen atmosphere. From TG-DTG curves it was clearly understood that the thermal decomposition occurred in one stages. CR (Coats *et al.*, 1964), HM (Horowitz *et al.*, 1963), MC (MacCallum *et al.*, 1970), vK (Van Krevelen, 1951), MKN (Madhusudanan *et al.*, 1993) and WHYC (WanJun *et al.*, 1993) methods based on single heating rates were used to investigate the thermal decomposition behavior of the resulting polymer. The kinetic parameters are the activation energy  $E$ , frequency factor  $A$ , reaction order  $n$ . We calculated the thermodynamic parameters such as entropy change  $\Delta H^\ddagger$ , enthalpy change  $\Delta S^\ddagger$  and Gibbs free energy  $\Delta G^\ddagger$ , related to the thermal decomposition. The activation energy values from so-called the methods were very close with each other. The mean activation energy of the thermal decomposition was found to be about 100 kJ/mol.

**Key words:** *activation energy; 6-amino-2-hydroxy-naphthalene-4-sulfonic acid; thermal decomposition.*

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**Introduction: Kinetic Theory**

Several methods have been used to calculate the kinetics and thermodynamic parameters of solid state degradation in the literature. Some of these can be expressed by following equations,

**1. The Coats-Redfern method**

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

**2. The Madhusudanan-Krishnan-Ninan method**

$$\ln\left[\frac{g(\alpha)}{T^{1.9206}}\right] = \ln\left(\frac{AE}{\beta R}\right) + 3.7678 - 1.9206 \ln E - 0.12040\left(\frac{E}{T}\right) \quad (2)$$

**3. The MacCallum-Tanner method**

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

**4. Wanjun-Yuwen-Hen-Cunxin method**

$$\ln\left[\frac{g(\alpha)}{T^{1.8946}}\right] = \left[\ln\left(\frac{AR}{\beta E}\right) + 3.6350 - 1.8946 \ln E\right] - 1.0014\left(\frac{E}{RT}\right) \quad (4)$$

**5. The van Krevelen method**

$$\ln g(\alpha) = \ln\left[\frac{A(0.368/T_m)^{\frac{E_a}{RT_m}}}{\beta\left(\frac{E_a}{RT_m} + 1\right)}\right] + \left(\frac{E_a}{RT_m} + 1\right)\ln T \quad (5)$$

**6. Horowitz-Metzger method**

By using  $\theta = T - T_m$

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

In the equations above,  $a$  is the degree of reaction.  $g(a)$  is the integral function of conversion.  $\beta$ ,  $T_m$ ,  $E$ ,  $A$ ,  $R$  are, the heating rate, DTG peak temperature, activation energy, pre-exponential factor 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 van Krevelen 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

All chemical compound used in this paper 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[6-amino-2-hydroxy-naphthalene-4-sulfonic acid]

P[6A2HN4S] was synthesized by the oxidative polymerization reaction of corresponding monomer in water solution. In the polymerization reaction NaOCl was used as oxidant. The corresponding monomer (0.242 g, 0.001mol) was dissolved in an aqueous solution of KOH (10%, 0.056 g, 0.001mol) and NaOCl was added drop wise to this solution for about 20 min. The precipitated product was filtered and washed with hot water (3× 25 ml) and then dried in the oven at 110 °C (Kaya *et al.*, 2001; Tuncel *et al.*, 2008; Doğan *et al.*, 2007). Synthetic procedure for P[6A2HN4S] is given in Figure 1. The structure of the resulting polymer was verified by FT-IR spectrum. IR (KBr) ( $\lambda_{max}$ :  $cm^{-1}$ ): 3408 (-OH), 1643 (-C=N), 1405(-C=C-aromatic), 1284,1162, 1039, 815.

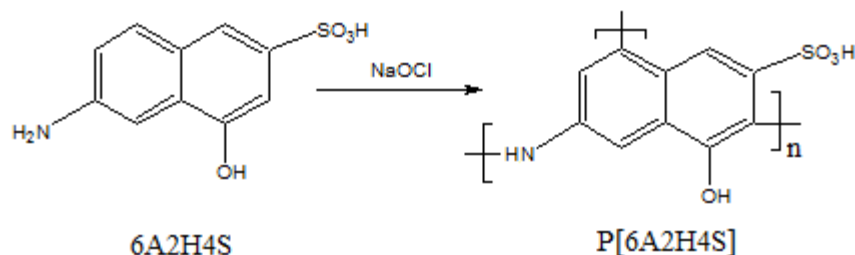


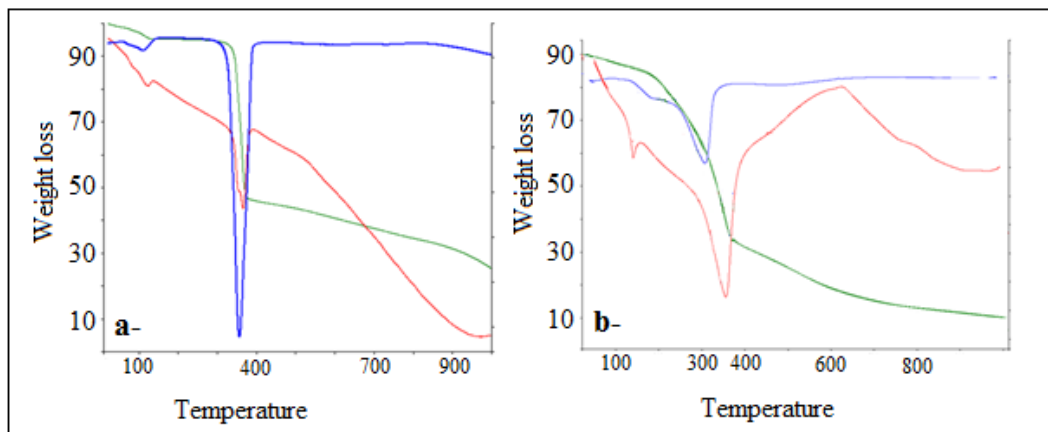
Figure 1. Synthetic procedure for P[6A2HN4S]

### Instrumental techniques

TG-DTA Perkin-Elmer Diamond system apparatus was used to investigate the kinetic parameters. The experiments were performed from the ambient temperature up to 1000 °C at heating rates of 5, 10, 15 and 20 °C /min. TG-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. Al<sub>2</sub>O<sub>3</sub> was used as a reference material.

## Result and Discussion

The kinetic parameters of resulting polymer were calculated by thermogravimetric analysis. Typical TG, DTG and DTA curves for the monomer and resulting polymer are shown in Figure 2.



**Figure 2. Typical TG, DTG and DTA curves for monomer (a) and resulting polymer (b)**

From TG curves (Figure 2a), monomer exhibited one step decomposition process over the temperature range 362-389 °C with a mass loss 72.1 % in weight. Also, endothermic thermal effect at 367 °C in DTA profile corresponded to the decomposition point of monomer. From the TG curve for resulting polymer (Figure 2b), it appeared that the sample decomposed in one stages over the temperature range 210-383 °C. This decomposition stage occurred with a mass loss 90.2 % in mass due to thermal decomposition. From the corresponding DTA profiles, two endothermic peaks for resulting polymer were displayed. First endothermic peak observed at 113 °C were attributed to the melting point of resulting polymer. Second one at 384 °C was related to the decomposition stage. In addition to the thermal stability, the several methods based on a single heating rate were used to calculate the kinetic parameters related to the solid state decomposition of resulting polymer. The linearization curves of the decomposition step of the resulting polymer were obtained by using the least squares method. By the linearization curves, the reaction order,  $n$ , activation energy,  $E$  and pre-exponential factor,  $A$ , were determined (Doğan, 2006). The kinetic parameters obtained by all the methods using in this study was presented in Table 1. The results are in good agreement with the values obtained from all of them. As can be seen in Table 1, the value of correlation coefficients of linearization curves for decomposition step is

approximately 1.00 and the activation energy of decomposition step is about 100 kJ/mol. Also the reaction order is found to be approximately 3.1. Moreover this value increased with increasing heating rate. The thermodynamic parameters such as the entropy change  $\Delta H^\ddagger$ , enthalpy change  $\Delta S^\ddagger$  and Gibbs free energy  $\Delta G$ , related to the decomposition step can be calculated by following relations,

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

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 Table 1.

**Table 1. The Kinetic data on the decomposition step of resulting polymer**

Heating rate	methods	$n$	$E$ kJ/mol	$\ln A$ 1/s	$\Delta S^\ddagger$ J/molK	$\Delta H^\ddagger$ kJ/mol	$\Delta G^\ddagger$ kJ/mol	Correlation, $r$
5	CR	3,1	104,8	-22,8	-440,3	-440,0	-199,1	0,99747
	WHYC	3,1	104,2	-22,8	-439,7	-439,6	-199,3	0,99686
	MKN	3,1	104,4	-22,7	-438,9	-439,2	-199,4	0,99345
	MC	3,3	97,2	-14,5	-437,2	-370,6	-131,4	0,99345
	HM	3,6	90,1	10,9	-436,4	-159,0	79,5	0,99251
	vK	3,5	116,8	331,8	-435,0	2509,8	2747,9	0,99076
10	CR	3,3	105,7	-21,9	-433,3	-432,9	-195,8	0,99777
	WHYC	3,3	105,1	-21,9	-432,9	-432,4	-195,6	0,99774
	MKN	3,4	105,2	-21,8	-432,5	-432,0	-195,4	0,99774
	MC	3,4	97,9	-13,6	-475,7	-363,3	-103,1	0,99602
	HM	3,7	93,6	11,6	-153,2	-152,7	-68,9	0,99463
	vK	3,8	117,9	330,8	2500,2	2501,0	1133,4	0,99298
15	CR	3,3	106,8	-21,6	-430,6	-430,0	-194,5	0,99835
	WHYC	3,4	106,2	-21,6	-430,2	-429,6	-194,3	0,99632
	MKN	3,4	106,4	-21,5	-429,8	-429,2	-194,1	0,99433
	MC	3,6	99,0	-13,2	-360,9	-360,3	-162,9	0,99268
	HM	3,8	93,4	11,9	-151,6	-151,0	-68,0	0,99009
	VK	3,8	120,1	332,2	2511,3	2512,4	1138,7	0,98537
20	CR	3,4	106,6	-21,1	-426,6	-425,9	-192,5	0,99726
	WHYC	3,5	106,0	-21,1	-426,1	-425,4	-192,3	0,99723
	MKN	3,5	106,1	-21,0	-425,7	-425,0	-192,1	0,99624
	MC	3,7	98,7	-12,7	-356,7	-356,0	-160,8	0,99458
	HM	4,1	95,0	9,75	-150,5	-168,8	-86,5	0,99420
	VK	3,9	120,9	329,9	2492,1	2493,4	1130,2	0,99239

## Conclusions

In this paper, a novel *tri-functional polyarene* was synthesized by an oxidizing agent in aqueous basic solution and the kinetic parameters related to the solid state decomposition of the resulting polymer was calculated by using the methods based on a single heating rate. It was found that the mean activation energy related to the

solid state decomposition of the resulting polymer was determined to be approximately 100 kJ/mol

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