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## Study the Properties of Poly(m-aminophenol) and its Polymerization Kinetics Using HPLC

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**Abstract** This study includes the preparation of poly(m-aminophenol) at laboratory temperature in an acidic medium with the presence of ammonium pyrosulfate as an oxidizer. The Scanning Electron Microscopy (SEM) analysis of the poly(m-aminophenol) sample showed a rough (non-smooth) surface with globular particles in microscopic dimensions. The poly(m-aminophenol) was characterized by thermogravimetric analysis (TGA), differential thermal analyzer (DTA), and differential scanning calorimetry (DSC). The kinetics of poly(m-aminophenol) were studied using HPLC. Then reaction order was determined and it was found that the reaction was zero-order reaction ( $n=0$ ).

**Keywords** m-aminophenol, Conducting Polymers, Polymerization Kinetics, TGA, HPLC

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### 1. Introduction

Polymers are important materials that are used in many electronic and electrical applications because of their typical properties such as strength, flexibility, and formability [1]. Since their discovery in 1977, conductive polymers have attracted researchers for their good conducting properties, corrosion resistance, and lightweight. They have been used in the manufacture of electronic devices, rechargeable batteries, and in the conversion of solar energy [2-3]. Looking at technological developments in the field of polymers, we note that the field has increased at an unprecedented speed [4]. A large part of these studies has been devoted to polyaniline formed by oxidative either electrochemically or chemically of aniline or its derivatives. Interest in polyaniline began after the discovery that polyacetylene had a mineral conductivity in 1977. PANI as a long-known chemical substance [5-6] has been used in diverse applications, such as bio-sensors, gas sensors, optoelectronics [7]. Aminophenols are interesting electrochemical that have two groups ( $-NH_2$  and  $-OH$ ) which can be oxidized unlike anilines and other substituted anilines, so it can exhibit electrochemical behavior similar to that of anilines and phenols. The declared electrochemical properties of each of the three positional isomers (o-, m- and p-) are completely different [8]. Although no research has been reported on the chemical polymerization of polyaniline derivatives in an alkaline medium [9,10], poly(m-aminophenol) was prepared electrically in an alkaline-aqueous medium [11] as well as in another study prepared in both acidic and basic medium [12]. Recently there have been a large number of studies on the polymerization of o-, m- and p-aminophenol [13-17]. However, the polymerization of m-aminophenol occurs like that of polyaniline, so it differs from ortho. In general, the chemical polymerization of m-aminophenol was

performed in a solution of NaOH or a solution of HCl in the presence of an oxidant such as ammonium pyrosulfate [18–20]. In this work, we chemically prepared poly (m-aminophenol) and studied some properties and formation reaction kinetics of the prepared polymer.

## 2. Materials and Methods

### 2.1. Used materials

Ammonium peroxydisulfate, m-aminophenol, sulfuric acid, hydrochloric acid, distilled water.

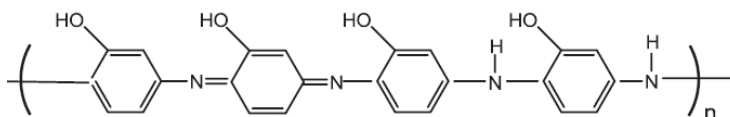
### 2.2. Used Equipment

- High-Performance Liquid Chromatography (HPLC).
- Electronic Scales (Sartorius Basic), Developed, manufactured, and tested by precise instruments Ltd. / Switzerland.
- Electric Heating of Magnetic Type, Made in England.
- Dryer, Model: Jsof-100, made in Korea.
- Numerous laboratory glassware, Made in England.

### 2.3. Used Method

#### Preparation of polym-aminophenol

We weighed (5 g) of m-aminophenol and (6.25 g) of ammonium peroxydisulfate dissolved in (80 ml) of prepared sulfuric acid (1M), where it was added drip for 15minutes. Then the reaction was left for 4 hours, stirring. The result was filtered and sodium hydroxide added to it (pH=12), then washed with distilled water and acetone in a ratio (1: 1).



Scheme 1: The structural representation of poly(m-aminophenol)

## 3. Results and Discussion

Poly(m-aminophenol) is a dark reddish-black powder. It melts at a high temperature (>300°C) with dissociation.

### 3.1. Study of the solubility of Poly(m-aminophenol) in different solvents

The solubility of poly(m-aminophenol) was tested in several different solvents. We noticed that the poly(m-aminophenol) was more soluble than polyaniline. The polymer dissolves in tetra hydro furan THF, acetonitrile, formic acid, dimethyl form amide DMF, and dimethyl sulfoxide DMS, unlike the polyaniline which does not dissolve in both THF and acetonitrile.

### 3.2. Study the solution viscosity of poly(m-aminophenol)

The concept of viscosity: It is one of the properties of a liquid that expresses the resistance experienced by the fluid particles, the fluid resistance scale for shear, the angular deformation, or the resistance that the particles encounter against each other as they move.

Capillary Tube Viscometer (Ostwald viscometer): Depending on the knowing the flow through a capillary tube length (L) and diameter (d) over time (t) according to the Ostwald scale, which is based on Poissier's Law on determining the flow rate between two lines surrounding the reservoir that contains the amount of fluid studied. Viscosity measurements are performed by comparing the flow time of the polymer solution (t) with a concentration of (gr/100ml) and the passage time of the solvent (t<sub>0</sub>). From the two quantities (t and t<sub>0</sub>), the relative viscosity (η<sub>rel</sub>), specific viscosity (η<sub>sp</sub>), reduced viscosity (η<sub>red</sub>), and the intrinsic viscosity [η], are determined as in the following equation [21], and table (1):



$$\eta_{rel} = \frac{t_1}{t_2}$$

$$\eta_{sp} = \frac{t_1 - t_2}{t_2}$$

$$\eta_{red} = \frac{\eta_{rel}}{C}$$

$$[\eta] = \frac{0.25(\eta_{rel} - 1) + (1.725 \text{Log} \eta_{rel})}{C}$$

**Table 1:** Viscosity of poly(m-aminophenol), the used solvent (Dimethyl sulfoxide)

C (g/50ml)	C (g/100ml)	t1 (sec)	t2 (sec)	$\eta_{rel}$	$\eta_{sp}$	$\eta_{red}$	$\eta$
0.1	0.05	163.666	161	1.016559	0.016559	0.33118	0.328869

### 3.3. Scanning Electron Microscope (SEM)

The Scanning Electron Microscopy (SEM) analysis was carried out to study the morphology of the polymer. Morphology is shown in figure (1). The poly(m-aminophenol) sample showed a rough (non-smooth) surface with globular particles in microscopic dimensions.

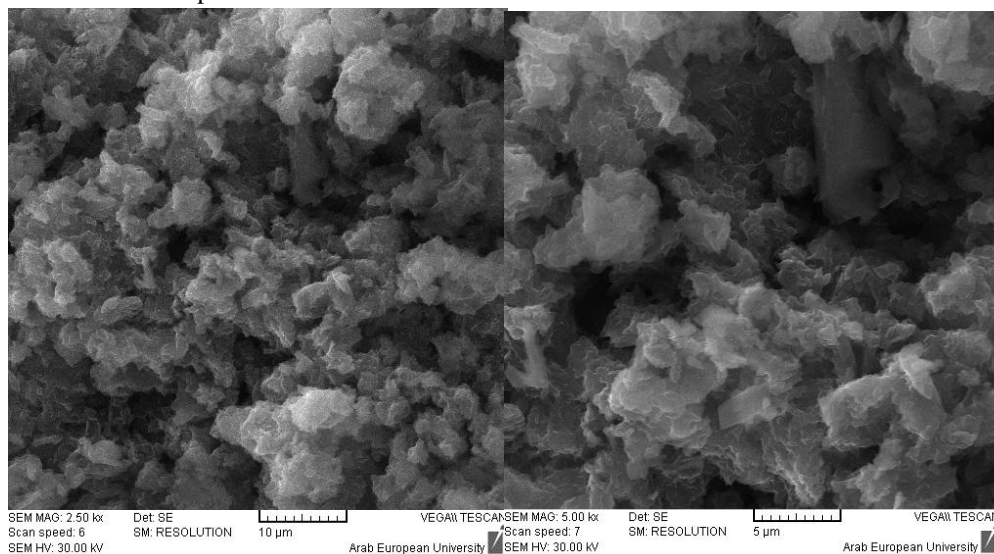


Figure 1: SEM images of Poly(m-aminophenol)

### 3.4. Thermal Analysis

The thermal stability of the polymer was analyzed by thermogravimetric analyzer (TGA) and Differential thermal analyzer (DTA). The thermal decomposition of the considered polymer was applied in the range of (30-1000) °C at a heating rate of 10 °C / min.

The thermal decomposition of poly(m-aminophenol) was carried out on five steps. The first step is within the range of (50–80) °C. The second thermal step within the range of (100–245) °C. The third thermal step within (250–450) °C, the fourth (490–800) °C, and the last one within (860–1000) °C, as shown in figure (2).

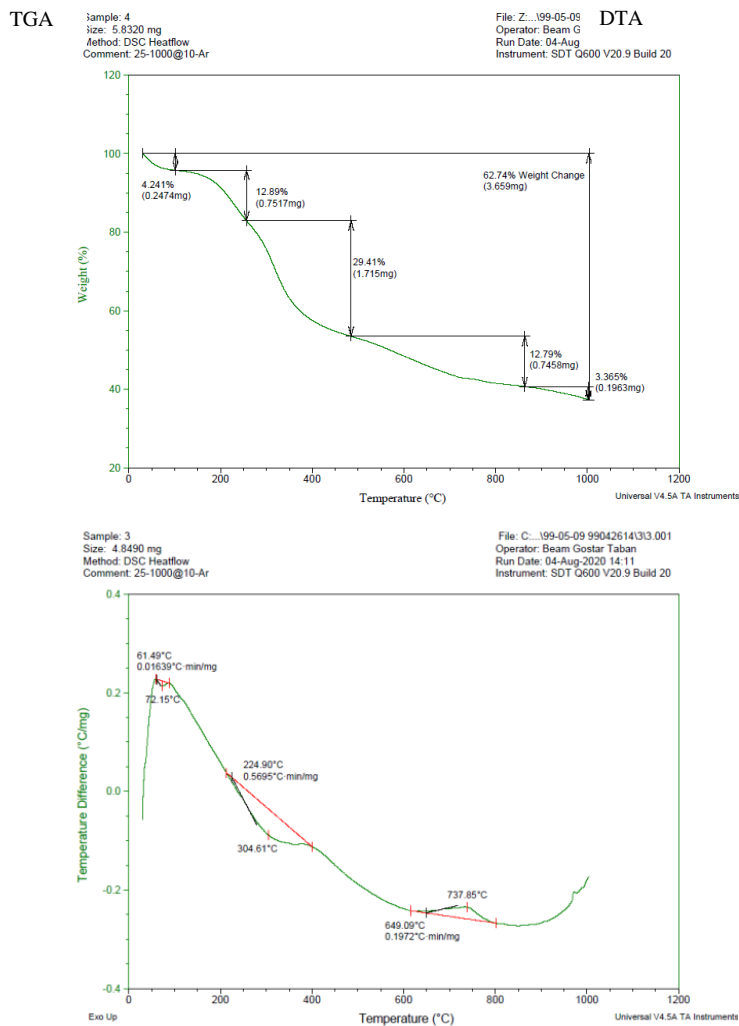


Figure 2: TGA-DTA of Poly(m-aminophenol)

### 3.5. Differential Scanning Calorimetry (DSC)

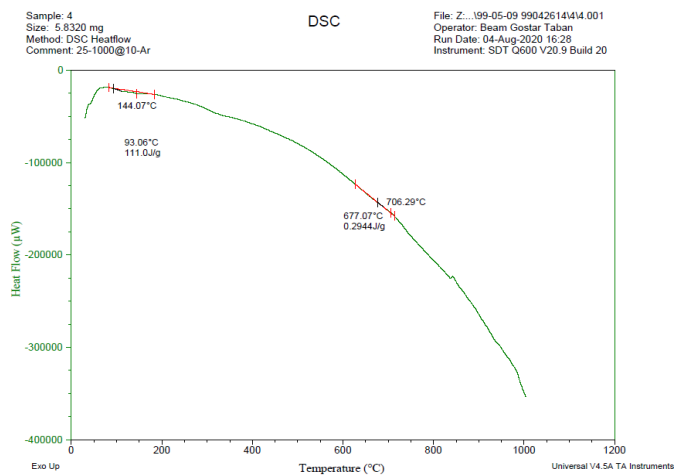


Figure 3: DSC of Poly(m-aminophenol)



The thermal transition of Poly(*m*-aminophenol) was measured with differential scanning calorimetry as shown in figure (3). The glass transition temperature ( $T_g$ ) was found to be 677.07 °C. The melting transition temperature of the polymer was observed in the temperature range of 706.29 °C.

### 3.6. Kinetic study of the formation of poly(*m*-aminophenol)

HPLC has been used to determine reaction kinetics [22-23]. By tracking the concentrations of the reactants, we determined the reaction order for *m*-aminophenol, using the differential method by taking several concentrations of the monomer (*m*-aminophenol) and with an invariable concentration of the oxidant (ammonium pyrosulfate), as in Table 2.

**Table 2:** *m*-aminophenol concentrations change with time during the polymerization reaction Where: [A]0: Monomer concentration (g/l), [B]0: Oxidant concentration (g/l).

[A]0 M	0.25	0.2	0.15	0.1	0.05					
[B]0 M	0.25	0.25	0.25	0.25	0.25					
ln[A0]	-1.386294361	-1.609437912	-1.897119985	-2.302585093	-2.995732274					
-dA/dt	0.000815116	0.000423622	0.000113778	0.000108913	3.51353E-05					
ln (-dA/dt)	-7.112180614	-7.766668538	-9.081262548	-9.124965444	-10.25630349					
t (min)	Area 1	[C1]	Area 2	[C2]	Area 3	[C3]	Area 4	[C4]	Area 5	[C5]
0	21216080	0.2121608	18352117	0.18352117	12577553	0.12577553	4668762	0.04668762	3671535	0.03246667
5	20260637	0.20260637	18283503	0.18283503	12453261	0.12453261	4157688	0.04157688	3527363	0.03119179
10	20101549	0.20101549	18169815	0.18169815	12429974	0.12429974	4039473	0.04039473	3492513	0.03088361
15	19887265	0.19887265	18141115	0.18141115	12426173	0.12426173	4029443	0.04029443	3491856	0.0308778
20	19474663	0.19474663	17808536	0.17808536	12425940	0.1242594	4021521	0.04021521	3473707	0.03071732
25	19086226	0.19086226	17710583	0.17710583	12286211	0.12286211	4018901	0.04018901	3470323	0.03068739
30	18543893	0.18543893	17220998	0.17220998	12259032	0.12259032	4008888	0.04008888	3463032	0.03062292
35	18000538	0.18000538	16903647	0.16903647	12220123	0.12220123	3999832	0.03999832	3454101	0.03054394
40	17776875	0.17776875	16791884	0.16791884	12019534	0.12019534	3988238	0.03988238	3448606	0.03049535

To know the order of the polymerization reaction for *m*-aminophenol, we drew  $\ln(-dA/dt)$  with  $\ln[A]_0$ . It was found that the reaction order was zero, as in Figure (4).

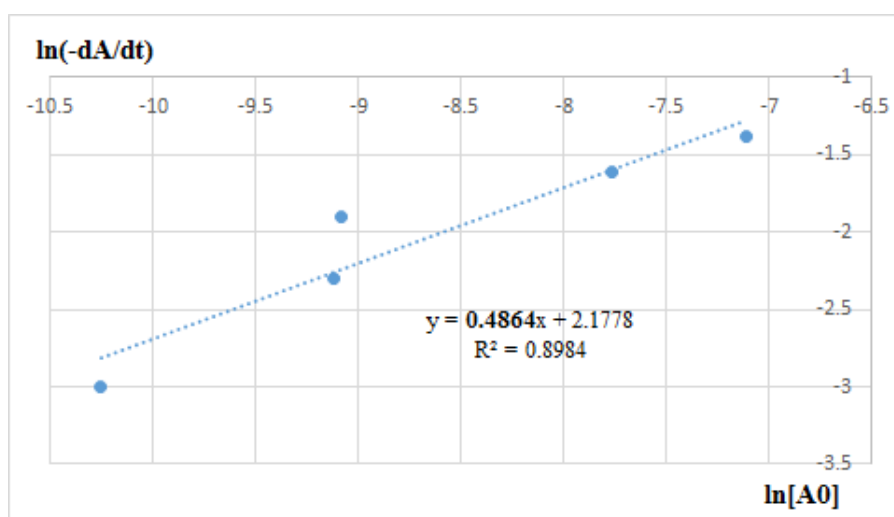


Figure 4: The curve determining the order of the polymerization reaction

The reaction order for *m*-aminophenol was also determined using the integrative method by taking invariable concentrations of the monomer and the oxidant, as in Table (3) and figure (5).

**Table 3:** m-aminophenol concentrations change with time during the polymerization reaction where:  $[A]_0=0.1$  M (monomer),  $[B]_0=0.1$  M (oxidant)

t (min)	Area	[C]	ln [C]	1/[C]
0	3481633	0.042868437	-3.149619454	23.32718583
5	3480069	0.04284918	-3.15006877	23.33766945
10	3470856	0.042735743	-3.152719642	23.39961669
15	3470697	0.042733785	-3.152765453	23.40068868
20	3456817	0.042562884	-3.156772668	23.4946484
25	3457161	0.04256712	-3.156673159	23.4923106
30	3443115	0.042394175	-3.160744306	23.5881462

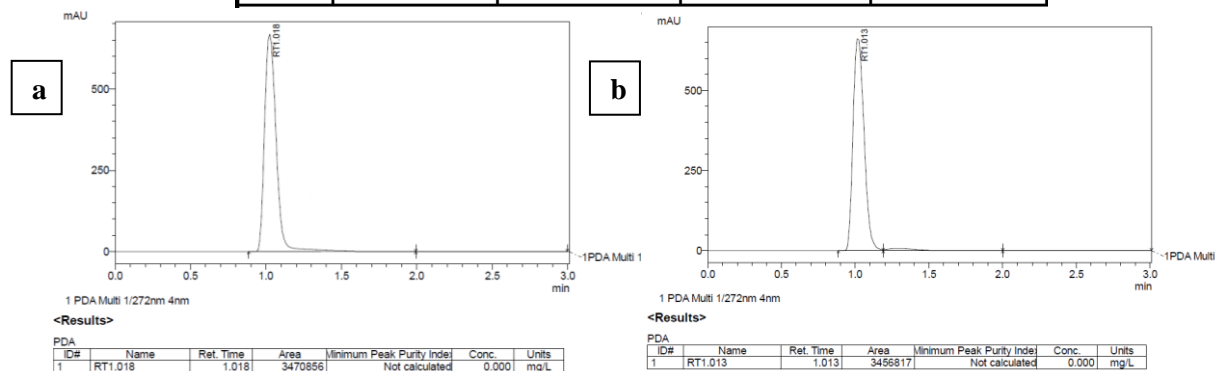


Figure 5: Chromatogram expressing the concentration of (m-aminophenol) during the polymerization reaction when  $[A]_0=0.1$  M,  $[B]_0=0.1$  M at: a)-  $t = 10$  min, b)-  $t=20$  min

To know the order of the polymerization reaction for m-aminophenol, we drew  $[C]$  with time,  $1/[C]$  with time, and  $\ln[C]$  with time, so it was found that the reaction order was zero, as in Figure (6).

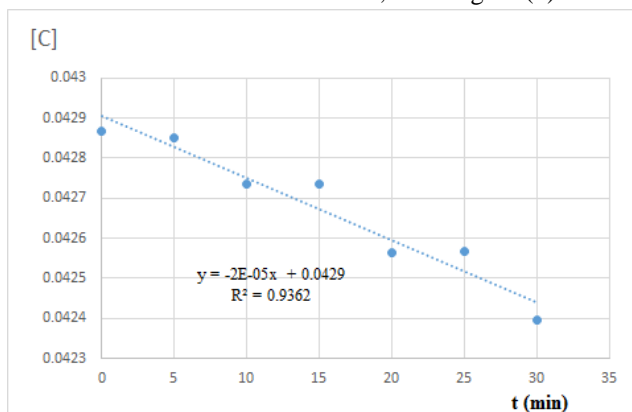


Figure 6: m-aminophenol concentration change  $[C]$  with time ( $t$ ) during the polymerization at  $n=0$

#### 4. Conclusions

We have successfully prepared poly(m-aminophenol) at laboratory temperature in an acidic medium with the presence of ammonium pyrosulfate as an oxidizer. The poly(m-aminophenol) sample showed a rough (non-smooth) surface with globular particles in microscopic diameters. The thermal stability of the polymer was analyzed by thermogravimetric analyzer (TGA) and Differential thermal analyzer (DTA) and it found that the thermal decomposition of poly(m-aminophenol) was carried out on five steps. The thermal transition of the obtained polymer was measured with differential scanning calorimetry (DSC), the glass transition temperature ( $T_g$ ) was found to be  $677.07$  °C and the melting transition temperature was observed in the range of  $706.29$  °C. On the other



hand, we studied the polymer formation kinetics using HPLC. It was found that the reaction of the polymer formation was a zero-order reaction.

### Data Availability

The data used to support the findings of this study are available from the corresponding authors upon request.

### Conflicts of Interest

The authors declare that there is no conflict of interest regarding the publication of this paper.

### Acknowledgments

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