

Preparation of Poly(aniline-co-phenol) and Study Its Properties and Its Polymerization Kinetics Using Two Methods: UV-Vis and HPLC

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Summary: The co-polymerization of polyaniline is one of the most important methods used to improve the electrical activity and thermal stability of polyaniline. Previously, electrochemical co-polymerization of phenol and aniline was performed on 304 stainless steel anodes. In this study, we present the co-polymerization of aniline and phenol chemically at laboratory temperature in an acidic medium with ammonium pyrosulfate as an oxidant. The Scanning Electron Microscopy (SEM) analysis of poly(aniline-co-phenol) sample shows a rough (non-smooth) surface with crystalline particles with microscopic diameters. We characterized the prepared polymer with DSC, DTA, and thermogravimetric analysis (TGA). We found that the thermal decomposition of poly(aniline-co-phenol) was on six steps. The glass transition temperature of the co-polymer (T_g) was found at 863.89 °C and the melting transition temperature was observed at 877.80 °C. We studied the kinetics of Poly(aniline-co-phenol) using two methods: UV-Vis, HPLC. Then we determined the reaction order. It was found that the reaction was the zero-order reaction (n=0) in both previous two methods.

Keywords: Aniline, Phenol, Conducting Polymers, Polymerization Kinetics, Co-polymers, UV-Vis, HPLC.

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 for the manufacture of electronic devices, rechargeable batteries, and in the conversion of solar energy [2-3]. Looking at technological developments within the field of polymers, we note that the field has increased at an unprecedented speed [4].

Polyaniline is one of the most important materials because of its high conductivity [5-6-7], simple polymerization [7], good stability in aqueous solutions [8]. The synthesis of polyaniline does not require any special equipment [9]. Interest in polyaniline began after the discovery that polyacetylene had a mineral conductivity in 1977. PANI as a long-known chemical substance [10-11] has been used for diverse applications, such as biosensors, gas sensors, optoelectronics [12]. The polyaniline polymerization was carried out simply [13] as in Fig (1).

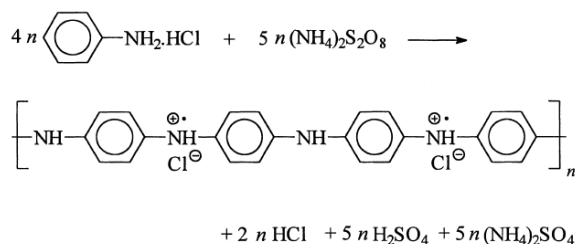


Fig. 1: Aniline polymerization reaction equation using ammonium peroxydisulfate.

Some methods aim to improve the electrical activity of polyaniline [14-17]. Co-polymerization is one of the most important of these methods, as it is possible to obtain polymers with specific desirable properties. Aniline co-polymers can be obtained using electrochemical or chemical co-polymerization [16-19]. In previous research, the electrochemical polymerization of poly(aniline-co-phenol) was accomplished on 304 stainless steel where the reasons for corrosion resistance enhancement with the addition of aniline in electropolymerization reaction were assumed [20]. In this work, we chemically prepared the co-polymer from aniline and phenol differently and simply, as it was at laboratory temperature and in the presence of ammonium pyrosulfate as an oxidizing substance. We studied its properties and the thermal stability of it using several techniques, as well as the kinetics of the polymerization reaction in two ways: UV-Vis, HPLC.

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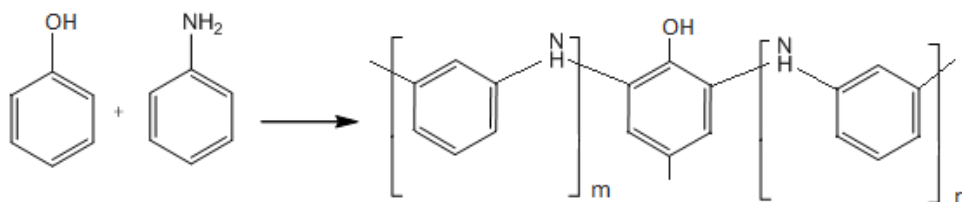


Fig. 2: Poly(aniline-co-phenol) Polymerization formula.

Experimental

Used materials

Aniline MW: 93.129 g/mol- Sigma, Phenol MW: 94 g/mol- Sigma, ammonium pyrosulfate MW: 228.19 g/mol- Sigma, sulfuric acid Sigma, Hydrochloric acid Sigma 35.5%.

Used Equipment

- UV-Vis spectrometer, Model: Optizen, OUV322, Co Mecasys, made in England.
- High-Performance Liquid Chromatography (HPLC), Model: SHIMADZU, UFLC, SPD-M20A, made in Kyoto- Japan.
- Thermogravimetry (TG) & Differential Scanning Calorimetry (DSC), SDT Q600-TA Instruments, made in New Castle-England.
- Electronic Scales (Sartorius Basic), Developed, manufactured and tested by precise instruments Ltd., made in Switzerland.
- Electric Heating of Magnetic Type, made in England.
- Dryer, Model: Isof-100, made in Korea.
- Numerous laboratory glassware, made in England.

Used Method

Preparation of poly(aniline-co-phenol): 90% aniline, 10% phenol

We dissolved 6.25 g of ammonium pyrosulfite in 80ml of sulfuric acid 1M. We added 4.5 g of aniline and 0.5 g of phenol to it. Then we left the reaction for an hour, stirring. The resulting polymer was filtered and washed with KOH solution (pH = 12), then washed with distilled water and acetone in a ratio (1: 1). Finally, it was dried at 105°C for 48 hours. The preparation equation is shown in Fig (2).

Results and Discussion

Poly(aniline-co-phenol) is a dark greenish-black powder. It melts at a high temperature (>300°C) with dissociation.

Study of the solubility of poly(aniline-co-phenol) in different solvents

The solubility of poly(aniline-co-phenol) was tested in several different solvents. We noticed that the poly(aniline-co-phenol) was more soluble than polyaniline. The co-polymer dissolves in tetrahydrofuran THF, acetonitrile, formic acid, dimethylformamide DMF, and dimethyl sulfoxide DMS, unlike the polyaniline which does not dissolve in both THF and acetonitrile.

Study the solution viscosity of poly(aniline-co-phenol)

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 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 (g/100ml) and the passage time of the solvent (t₀). From the two quantities (t and t₀), we determined the intrinsic viscosity [η], reduced viscosity (η_{red}), specific viscosity (η_{sp}), as in the following equation [21], and table (1):

$$\eta_{rel} = \frac{t_1}{t_2}, \eta_{sp} = \frac{t_1 - t_2}{t_2}, \eta_{red} = \frac{\eta_{rel}}{C}$$

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

Scanning electron microscope (SEM)

The morphology of poly(aniline-co-phenol) was studied as shown in Fig (3). The poly(aniline-co-phenol) sample showed a rough (non-smooth) surface with crystalline particles with microscopic diameters.

Thermal Analysis

By thermogravimetric analyzer (TGA) and Differential thermal analyzer (DTA), the thermal stability of the polymer was analyzed as in Figs (4) and

(5). The thermal decomposition of the considered polymer was applied at a heating rate of 20 °C/min. The thermal decomposition of poly(aniline-co-phenol) was carried out in six steps. The first step is within the range of (30–100) °C. The second thermal step within the range of (125–225) °C. The third thermal step within (340–400) °C, the fourth (450–550) °C. The fifth thermal step within (575–800) °C and the last one within (820–950) °C, as shown in Fig (4).

Table-1: Viscosity of poly(aniline-co-phenol), the used solvent (Dimethyl sulfoxide).

C (g/50ml)	C (g/100ml)	t1 (sec)	t2 (sec)	η_{rel}	η_{sp}	η_{red}	η
0.2	0.1	164.666	161	1.02277	0.02277	0.2277	0.2256

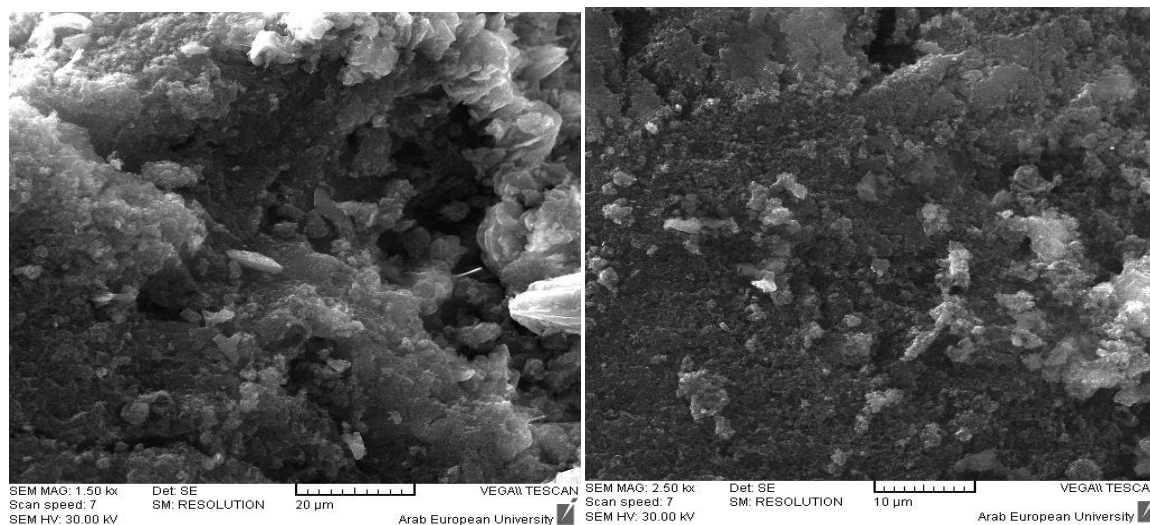


Fig. 3: SEM images of Poly(aniline-co-phenol).

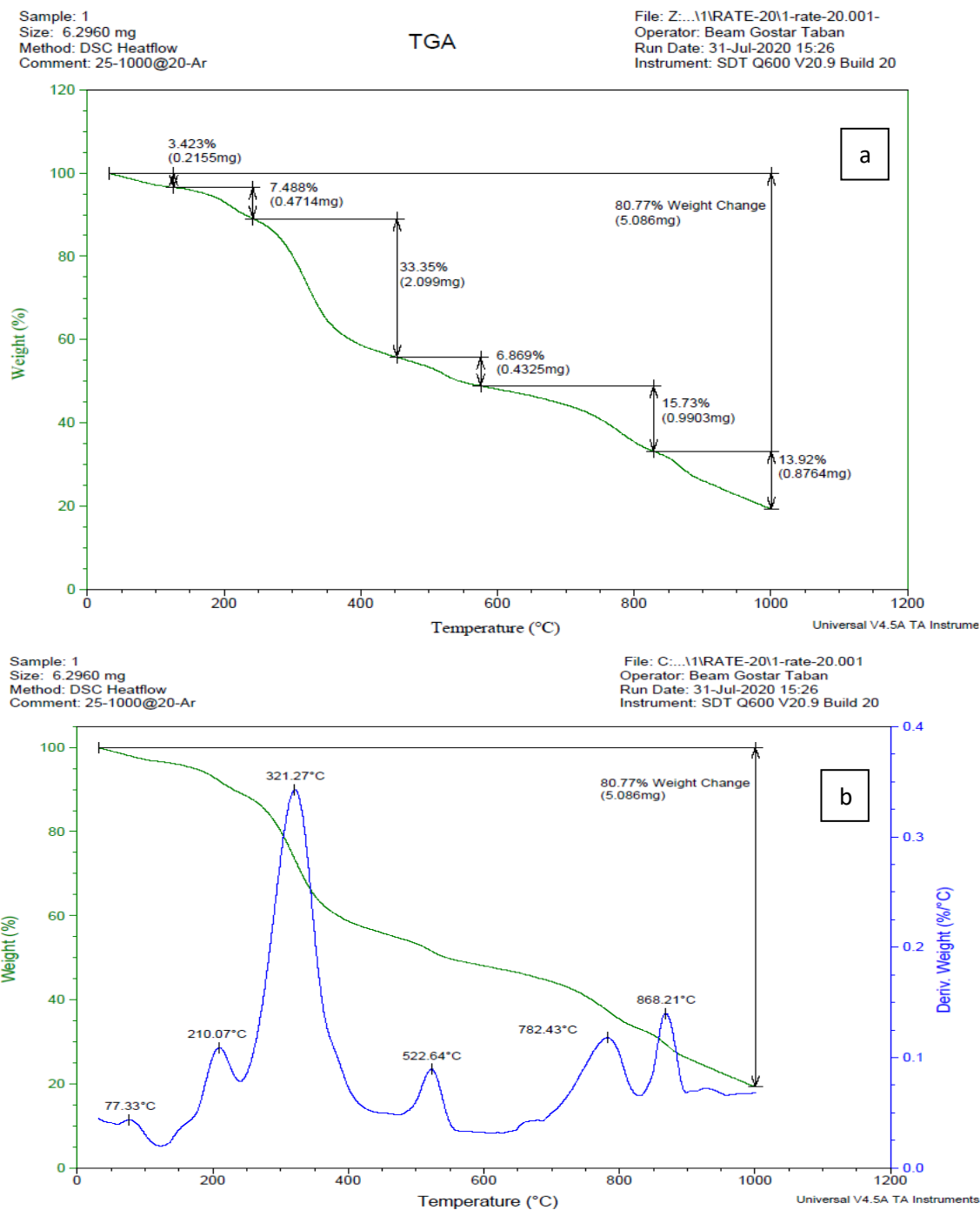


Fig. 4: a) TGA, b) DTG of Poly(aniline-co-phenol).

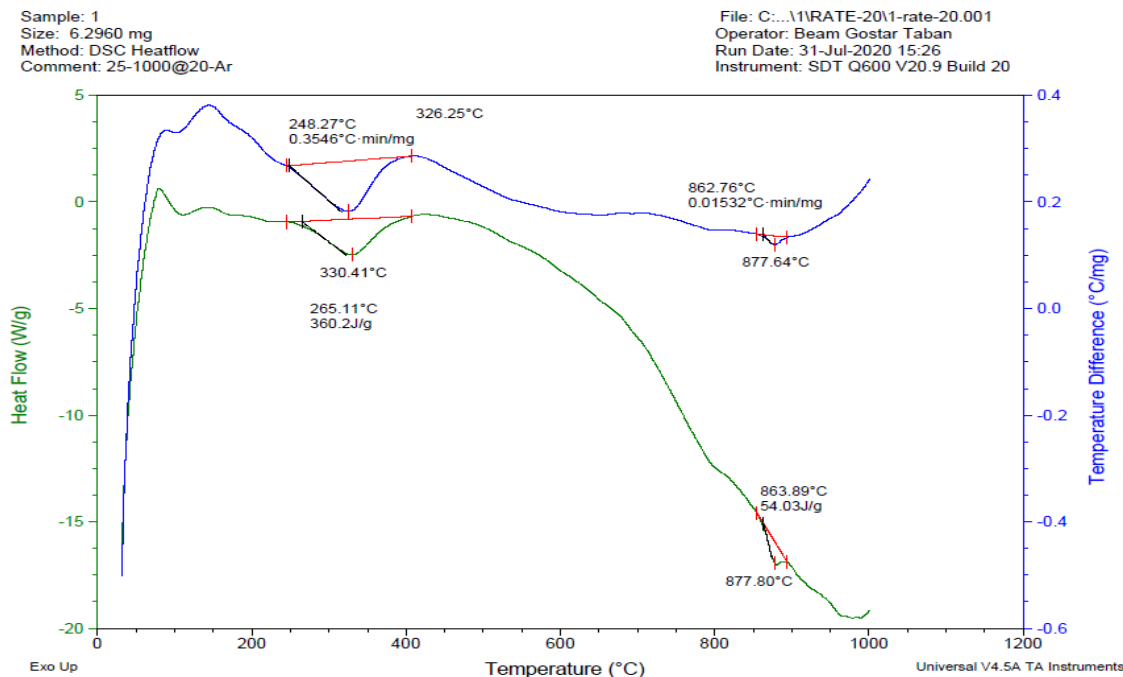


Fig. 5: DSC-DTA of Poly(aniline-co-phenol).

Differential Scanning Calorimetry (DSC)

The thermal transition of poly(aniline-co-phenol) was measured with differential scanning calorimetry as shown in Fig (5). The glass transition temperature (T_g) was found to be 863.89 °C. The melting transition temperature of poly(aniline-co-phenol) was observed at 877.80 °C

Kinetic study of the formation of poly(aniline-co-phenol) by UV-Vis

In 1993 the optical absorption spectra of PANI were reported in visible regions [22]. We studied the kinetics of the polymer formation with a UV device by preparing (0.1 M) of the prepared mixture of (aniline 90%-phenol 10%) and (0.1 M) of ammonium pyrosulfate and placing them in an equal amount in the measurement cell with mixing, then we studied the kinetics of the device for (20 min) at every minute, as shown in (6).

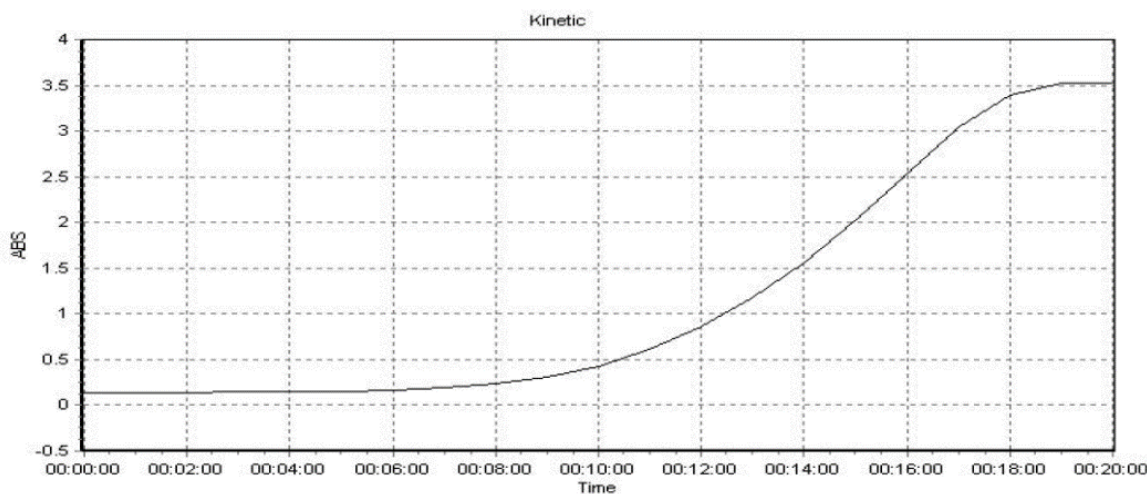


Fig. 6: Kinetic of Poly(aniline-co-phenol) by UV-Vis.

The relationship of $(A_{\infty}-A_t)$ with time, and the relationship of $\ln(A_{\infty}-A_t)$ with time, as well as the relationship between $1/(A_{\infty}-A_t)$ with time, was drawn by selecting several times of the total time studied, as in Table (2) and Fig(7).

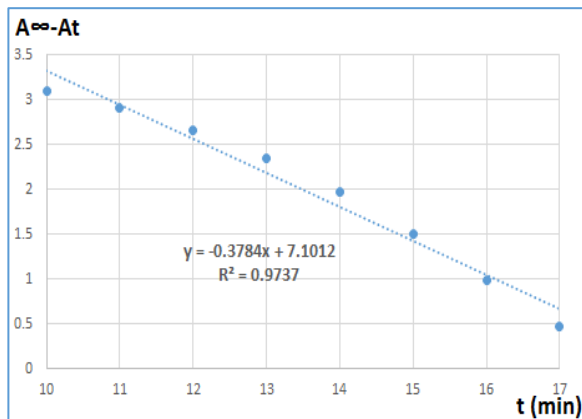


Fig. 7: $(A_{\infty}-A_t)$ with time of Poly(aniline-co-phenol); $n=0$.

Table-2: Absorption values of the copolymerization reaction of aniline and phenol with time.

t (min)	ABS	A	$A_{\infty}-A_t$	$\ln(A_{\infty}-A_t)$	$1/(A_{\infty}-A_t)$
10	0.431	0.291	3.092	1.12881813	0.323415265
11	0.613	0.473	2.91	1.06815308	0.343642612
12	0.862	0.722	2.661	0.97870199	0.375798572
13	1.177	1.037	2.346	0.85271175	0.42625746
14	1.553	1.413	1.97	0.67803354	0.507614213
15	2.022	1.882	1.501	0.40613155	0.666222518
16	2.538	2.398	0.985	-0.01511364	1.015228426
17	3.046	2.906	0.477	-0.74023879	2.096436059

By studying the kinetics of the reaction and the graphical representation, it was found that the reaction order was Zero ($n=0$).

Kinetic study of the formation of poly aniline-phenol by HPLC

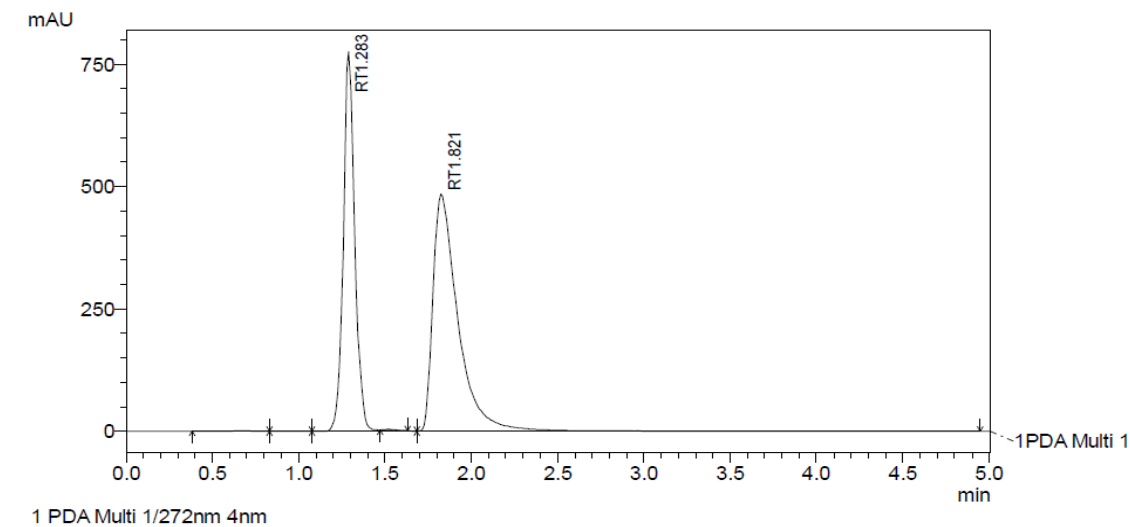
Previously, HPLC has been used to determine reaction kinetics [23-24]. In this work, we determined the reaction order for aniline and phenol by tracking the concentrations of the reactants. Initially, we did a survey of aniline and phenol (separately) in the HPLC to find out where their peaks appeared in the chromatogram.

We performed the polymerization reaction by adding oxidized ammonium pyrosulfite (0.1 M) to a mixture of aniline and phenol (90% aniline, 10% phenol) (0.1 M) and let the reaction run for about an hour until the color of the solution darkened to black. We drew the chromatogram every 5 minutes. We noticed the change in the concentration of both aniline and phenol, as the first peak that appeared in the chromatogram was for aniline, and the second was for phenol, as in Table (3) and Fig (8).

To know the reaction order for aniline and phenol, we drew $[C]$ with time, $1/[C]$ with time, and $\ln[C]$ with time, so it was found that the reaction order was zero, for both aniline and phenol, as in Figs (9) and (10). In a similar case, previously, when the kinetic of poly(m-aminophenol) was studied, it was found that the polymerization reaction order was zero [25].

Table-3: Aniline and phenol concentrations change with time during the copolymerization reaction.

t (min)	Area Aniline	Area Phenol	[C1] Aniline	$\ln [C]$ Aniline	$1/[C]$ Aniline	[C2] Phenol	$\ln [C]$ Phenol	$1/[C]$ Phenol
0	3591072	4972861	0.0252428	-3.67921348	39.6152235	0.0234471	-3.75300822	42.6491873
5	3576312	4939584	0.0251391	-3.68333214	39.7787218	0.0232902	-3.75972243	42.9365064
10	3502069	4908616	0.0246172	-3.70431031	40.6220209	0.0231442	-3.76601152	43.2073888
15	3445753	4883688	0.0242213	-3.72052178	41.2859308	0.0230267	-3.77110287	43.427934
20	3393725	4860781	0.0238556	-3.7357361	41.9188709	0.0229186	-3.77580442	43.6325932
25	3345593	4829538	0.0235173	-3.75002028	42.5219445	0.0227713	-3.78225274	43.9148589
30	3280120	4816880	0.023057	-3.76978424	43.3707059	0.0227117	-3.78487713	44.0302603
35	3218704	4785834	0.0226253	-3.78868545	44.1982612	0.0225653	-3.79134324	44.3158873
40	3127250	4731852	0.0219825	-3.81751022	45.490805	0.0223107	-3.80268688	44.8214526
45	3057659	4706421	0.0214933	-3.84001465	46.5261561	0.0221908	-3.8080758	45.0636439
50	2954825	4665151	0.0207704	-3.87422481	48.1453622	0.0219962	-3.81688334	45.4622969



<Results>

PDA

ID#	Name	Ret. Time	Area	Minimum Peak Purity Index	Conc.	Units
1	RT1.283	1.283	3576312	Not calculated	0.000	mg/L
2	RT1.821	1.821	4939584	Not calculated	0.000	mg/L

Fig. 8: Chromatogram expressing the concentration of both aniline and phenol during the copolymerization reaction at $t = 5$ min.

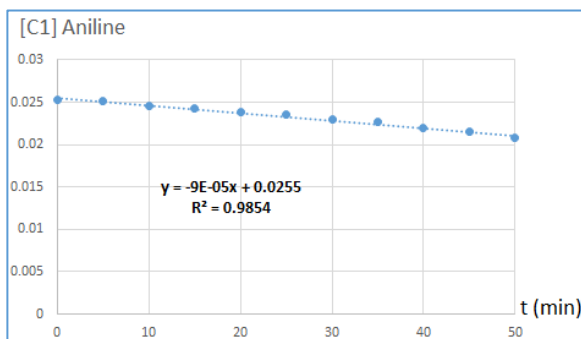


Fig. 9: Aniline concentration change [C] with time during the copolymerization at $n=0$.

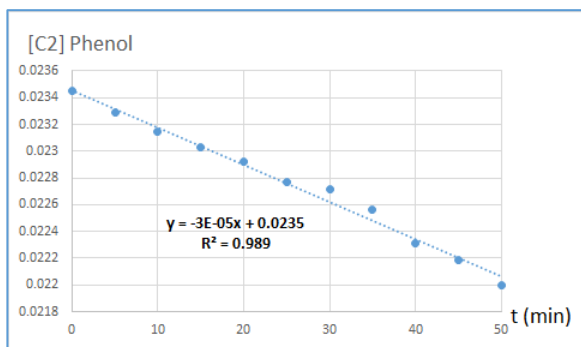


Fig. 10: Phenol concentration change [C2] with time during the copolymerization at $n=0$.

Conclusions

We have successfully prepared Poly(aniline-co-phenol) chemically at laboratory temperature in an acidic medium in the presence of ammonium pyrosulfite as an oxidizer. The Poly(aniline-co-phenol) sample showed a rough (non-smooth) surface with crystalline particles with microscopic diameters. The thermal stability of the polymer was analyzed by thermogravimetric analyzer (TGA) and DTA. We found that the thermal decomposition of poly(aniline-co-phenol) was carried out in six steps. The thermal transition of the obtained polymer was measured with (DSC), the glass transition temperature of poly(aniline-co-phenol) (T_g) was found at 863.89°C and the melting transition temperature was observed at 877.80°C . On the other hand, we studied the copolymer formation kinetics by two methods: UV-Vis and HPLC. It was found that the reaction of the copolymer formation was a zero-order reaction in both previous two methods.

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