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Chemical Polymerization of Diphenylamine and Characterization of the Obtained Polymer

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THE CHEMICAL polymerization of diphenylamine in DMF/water (50% v/v) using sodium dichromate as oxidant and HCl as dopant is performed. The effect of monomer, oxidant, HCl concentration and temperature on both initial and overall reaction rates is investigated. The data show that both the initial and overall reaction rates increase with the increasing of monomer, oxidant and HCl concentrations in the concentration range of study. Also, both the initial and overall reaction rates increase with increasing temperature. The reaction rate law is found to be:

$$R_i = k_2[\text{monomer}]^{0.723}[\text{oxidant}]^{0.854}[\text{HCl}]^{0.641}$$

The apparent activation energy Ea is found to be 15.299 kJ/mol. Also, ΔH^* and ΔS^*, were calculated and found to be 12.67 kJ/mol and -90.184 J/mol.K, respectively.

The obtained polymer sample prepared at the optimum conditions was characterized by IR, ^{1}HMMR, TGA, DTA and electron microscopy. Also, elemental analysis was carried out to confirm the suggested structure of obtained polymer. The mechanism of the polymerization reaction was discussed.

Keywords: Chemical polymerization, Initial and overall reaction rate, Monomer concentration, Oxidant concentration, Apparent activation energy and Characterization**.**

During the past two decades, the synthesis and characterization of electroactive polymers have become one of the most important areas of research in polymer and material science[1-4] . Among these polymers, polyanilines[5, 6] have been of particular interest due to their environmental stability[7-10], controllable electrical conductivity[11,12] and interesting redox properties associated with the chain nitrogen [13-15] .

The applications of polyaniline, however, have been limited because of its poor processability which is true for most conducting polymers. The alkyl substitution at phenylene carbon or nitrogen was reported to improve the solubility of polyaniline in an organic solvent[15-22] . The substitution, however

usually decreases the conductivity of the polymers. Also, in order to improve the process ability of polyaniline various approaches have been developed:

(i)   The utilization of a soluble "precursor" method, a processable precursor polymer is first prepared in an appropriate form and then chemically converted into the final conducting polymer [23-25],

(ii) Formation of conductive blends / composites [26-30],

(iii) Formation of PANI filled interpenetrating polymer networks [31-33] and,

(iv) The copolymerization method, in which graft, block or random conductive copolymers are formed [34-36].

It has been reported that mechanism of polymerization of diphenylamine (DPA) is different from the other N-substituted anilines. The polymerization of N-alkyl substituted aniline has been reported to proceed through N–C coupling, while the polymerization of DPA proceed through the 4,4-phenyl–phenyl coupling mechanism[37]. FT-IR spectrum of poly(diphenylamine) (PDPA) revealed the presence of benzidine band around $1607–1610$ cm^{-1}[38] and supported C–C coupling in the structure of PDPA. Due to the benzidine type of reaction during polymerization, an extraordinarily high rate has been reported for the polymerization of DPA. Many properties of PDPA, which include electrochemistry, conductivity and electrochromism[37], are found to be different from PANI and are not comparable with any other N-substituted aniline derivatives. Attempts have been made to introduce new properties into PDPA by grafting non conducting polymer onto the backbone [39,40]. Interestingly, PDPA has both poly (phenylene) as well as poly (aniline) type structures in the backbone[41,42]. The formation of such structure is expected to arise from intermediates of different origin than reported in polymerization of simple aniline/aniline derivatives. It is frequently assumed that reactive intermediates are formed in the initial stages of the electro oxidation of aniline or similar monomers. These highly reactive species subsequently react with solution species, yielding oligomers and polymers. Since the intermediate species are very reactive and leading to fast further reactions, it becomes difficult to detect them with usual techniques.

In the present study we intend to investigate the kinetics of the oxidative polymerization of N-phenylaniline in DMF-/water medium using sodium dichromate as oxidant in HCl medium. The obtained polymer is characterized by IR spectroscopy, ^{1}H-NMR spectroscopy, electron microscopy and thermal analysis.

Experimental

Materials

Diphenylamine provided by Merck Chemical Company (Germany), concentrated hydrochloric acid and ammonia solution (33%) were of chemically pure grade products provided by Prolabo-chemical Company (England). Double distilled water was used as a medium for the polymerization reactions during the

present work. Sodium dichromate was a product of Merck Chemical Company (Germany).

Polymerization of diphenylamine monomer

The chemical oxidative polymerization reactions were carried out in a well-stoppered conical flask of 250 ml capacity containing the amount of monomer in DMF followed by the addition of the required weight of sodium dichromate dissolved in aqueous hydrochloric acid solution under nitrogen atmosphere. The order of addition of substances was kept constant in all the performed experiments. The stoppered conical flasks were put in an automatically controlled thermostat at the required temperature. The flasks were shaken (15 shakings/10 sec/ every 15 min) for definite period of time by using automatic shaker. The reaction was stopped at will by the addition of ammonia solution (in equivalent amount to the acid) and cooling in ice bath. The polymer was then filtered using Buchner funnel, washed thoroughly with distilled water and methanol and finally dried in vacuum oven at 60^0C till constant weight. But, in case of the polymer samples prepared for characterization, the polymerization solutions after 4 hr were filtered without addition of ammonia solution, then washed with distilled water, air dried and finally under vacuum at room temperature till constant weight.

Infrared and ^{1}H-NMR spectroscopy

The infrared measurements were carried out using Shimatzu FTIR-430 Jasco Spectrophotometer (Japan) and KBr disk technique. The ^{1}HNMR spectra of the prepared polymer have been recorded in dimethyl-sulphoxide (DMSO) by using tetramethylsilane as internal reference.

Electron microscopy and thermal analysis

The electron microscopy analysis was carried out using JSM-T20 Scanning electron microscopy, JEOL, Japan.

The thermogravimetric analysis was carried as described in a previous publication [16].

Results and Discussions

Effect of hydrochloric acid concentration

The polymerization of diphenylamine (0.05 M) in HCl solution which had different molarities in the range form 0.4 to 1.0 M was carried out by the addition of sodium dichromate solution (0.005 M) as oxidant under nitrogen atmosphere at 33 ^{0}C for different time intervals. The concentration of both monomer and oxidant are kept constant during the study of HCl effect on the polymerization reaction. The preparation methods were carried out as described in the experimental part (2.2) and the conversion-time curves for each acid concentration was calculated and the data are graphically represented in Fig. 1a. From which the initial rate of polymerization reactions are calculated. The HCl exponent is deduced from the slope of linear relationship of double logarithmic

plot of the initial rate versus HCl concentration (Fig. 1b). The HCl exponent   is found to be equal to 0.641.
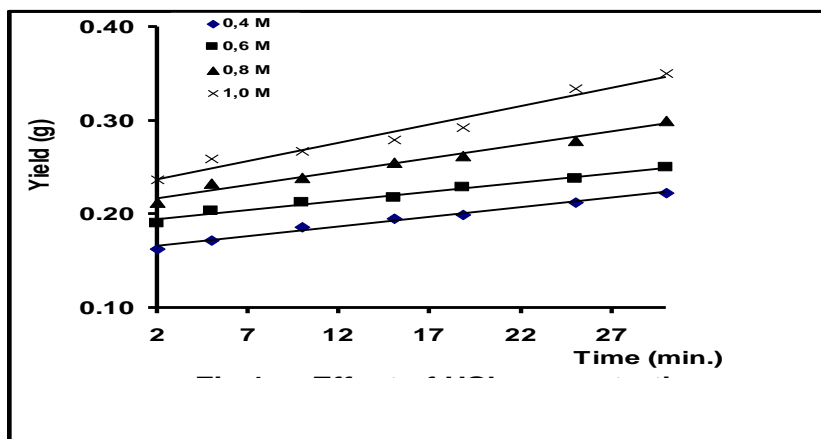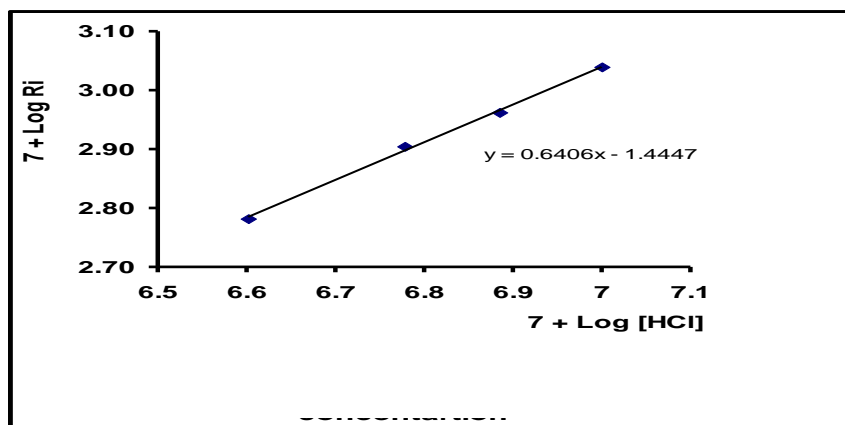

Fig. 1a. Effect of HCl concentration.

Fig. 1b. Double logarithmic plot of the initial rate of polymerization versus HCl concentration.

Effect of oxidant concentration

The polymerization of diphenylamine (0.05 M) in 1.0 molL^{-1} HCl solution using sodium dichromate solution as oxidant which had different molarities in the range form 0.00125 to 0.005 M was carried out under nitrogen atmosphere at 33 ^{0}C for different time intervals. The concentration of both HCl and monomer is kept constant during the study of oxidant effect on the polymerization reaction. The experiments were carried out as described in the experimental part (2.2) and the conversion-time curves for each oxidant concentration was calculated and the

data are graphically represented in Fig. 2a. From which the initial rate of polymerization reactions are calculated. The oxidant exponent is deduced from the slope of the linear relationship of double logarithmic plot of initial rate versus oxidant concentration (Fig. 2b). The oxidant exponent is found to be equal to 0.854.
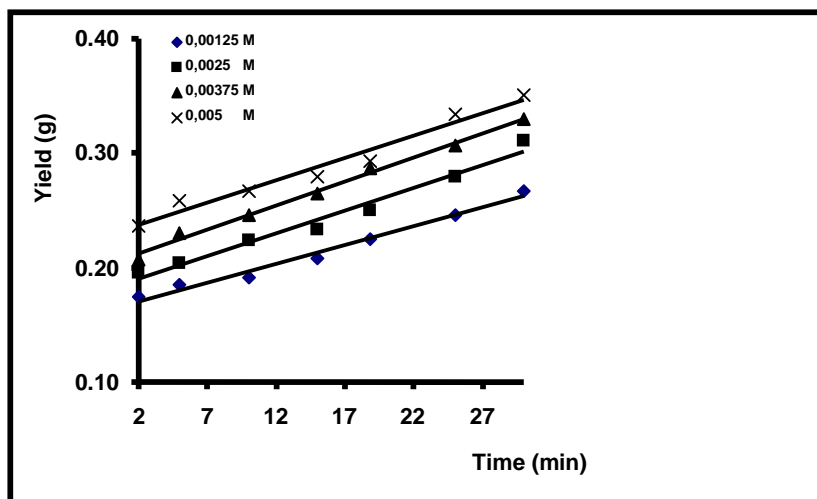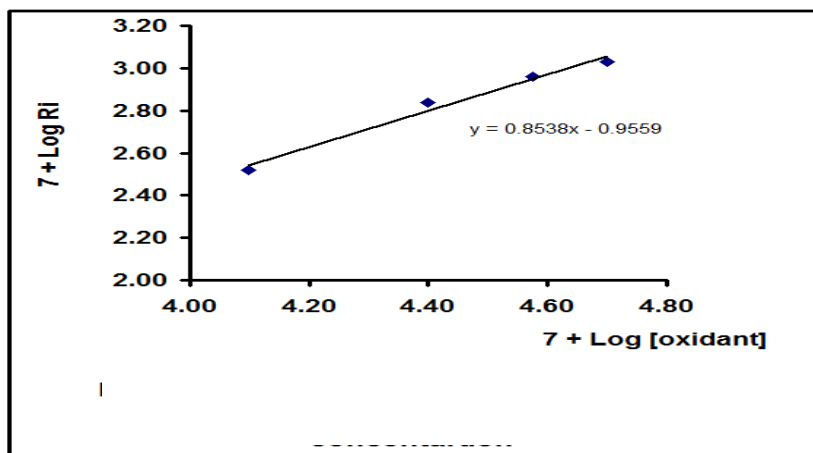

Fig. 2a. Effect of sodium dichromate concentration.

Fig.2b. Double logarithmic plot of the initial rate of polymerization versus oxidant concentration.

Effect of monomer concentration

The polymerization of different concentration of diphenylamine ranged from 0.03 to 0.06 M in 1.0 M HCl solution using sodium dichromate solution (0.005 M) as oxidant was carried out under nitrogen atmosphere at 33 ^{0}C for different time intervals. The concentration of both HCl and oxidant is kept constant during the

study of monomer effect on the polymerization reaction. The conversion-time curves for each monomer concentration were calculated and the data are graphically represented in Fig. 3a. From which the initial rate of polymerization reactions is calculated. The monomer exponent is deduced from the slope of the linear relationship of double logarithmic plot of initial rate versus monomer concentration (Fig. 3b). The monomer exponent   is found to be equal to 0.723.
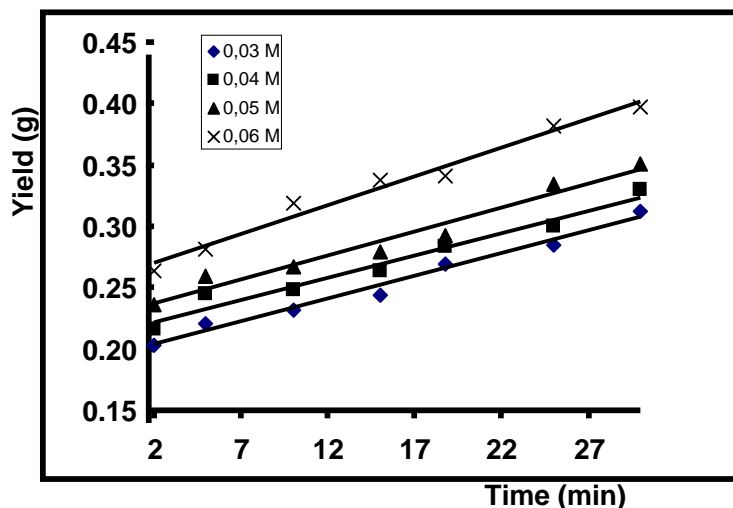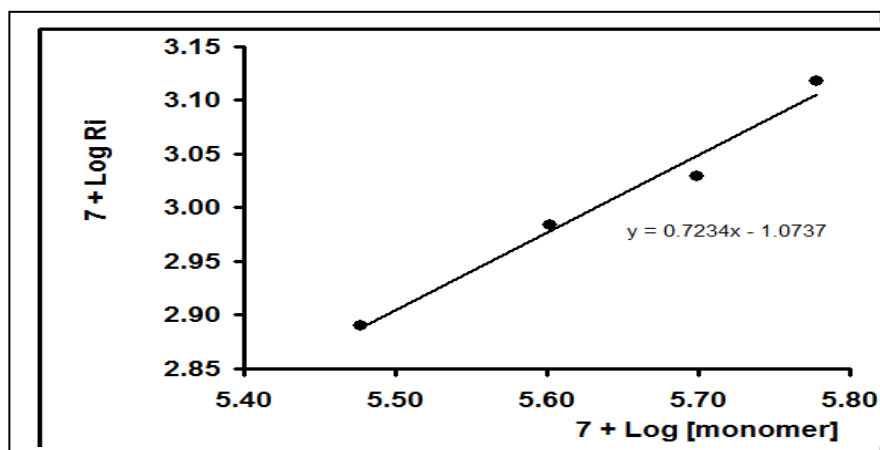

Fig. 3a. Effect of monomer concentration.

Fig. 3b. Double logarithmic plot of the initial rate of polymerization versus monomer concentration.

Deducing the rate expression for the homogeneous polymerization of diphenylamine

In the present study, the medium of polymerization was homogenous during the experimental conditions in which the kinetic results were obtained. This means that, the polymer formed in the first 30 min of polymerization reaction is soluble in DMF/water acidic medium. No autocatalytic effect in these conditions is present[43]. Figure 4 (a,b & c), represents the relations between R_i and $[HCl]^{0.641}$, $[oxidant]^{0.854}$ and $[monomer]^{0.723}$, which are linear and passing through the origin. These behaviours confirm the proposed kinetic equation:

$$R_i = k_2[monomer]^{0.723}[oxidant]^{0.854}[HCl]^{0.641}$$

Effect of reaction temperature

The polymerization of diphenylamine (0.05 M) in 1.0 M HCl solution using 0.005 M sodium dichromate solution as oxidant was carried out under nitrogen atmosphere at different reaction temperature (296, 301 and 306 K) for different time intervals. The concentration of HCl, oxidant and monomer is kept constant during studying the effect of temperature on the polymerization reaction. The conversion-time curves for each reaction temperature were calculated and the data are graphically represented in Fig. 5a. From which the initial rate of polymerization reactions is calculated.

The apparent activation energy (Ea) of the polymerization reaction of diphenylamine was calculated by plotting Log Ri against 1/T which gave straight line (*c.f.* Fig. 5b). From the slope and applying Arrhinus equation, it is found that the apparent activation energy 15.299 k J/mol.

Calculation of the thermodynamic parameters

The enthalpy and entropy of activation for the polymerization reaction can be determined by calculation of k_2 from the following equation:

$$R_i = k_2[monomer]^{0.723}[oxidant]^{0.854}[HCl]^{0.641}$$

The values of k_2 at different temperatures were calculated, then both ΔH^* and ΔS^* of the activation associated with k_2 were calculated using Eyring equation:

$$K_2 = RT/Nh \, e^{\Delta S/R} . \, e^{-\Delta H/RT}$$

where:

K_2 is the rate constant

R is the universal gas constant

N is the Avogadro's number and

h is the Plank constant

By plotting Log.(k_2/T) versus 1/T (*c.f.* Fig. 5c), a linear relationship is obtained with slope = $- \Delta H/2.303$ R and intercept = Log (R/Nh) + $\Delta S/2.303$ R. From the slope and intercept, the values of both ΔH^* and ΔS^* were found to be 12.67 k J/mol. and -90.184 J/mol.K, respectively.
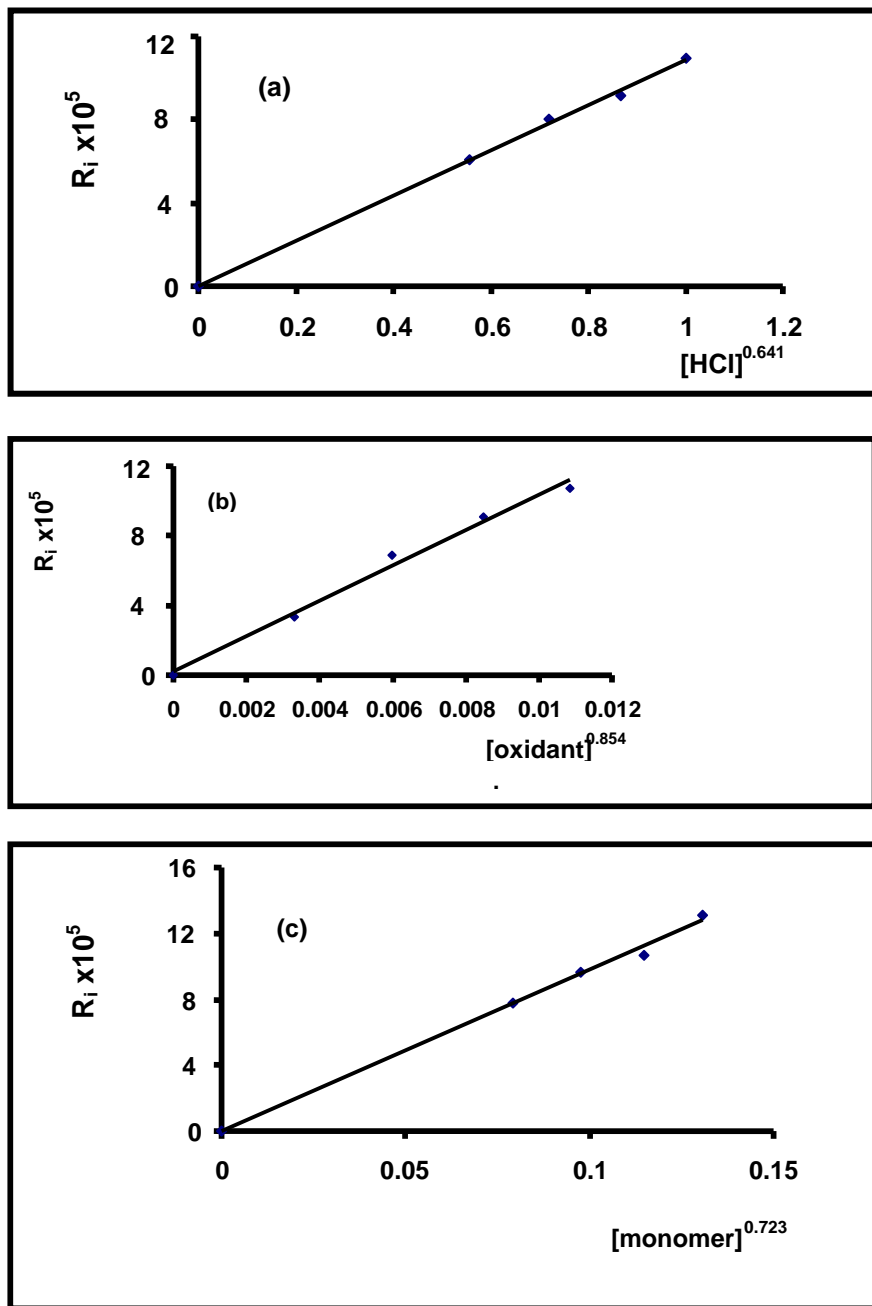
Fig. 4. The linear relationship between Ri and a-[HCl]$^{0.641}$, b-[oxidant]$^{0.854}$ and c-[monomer]$^{0.723}$.
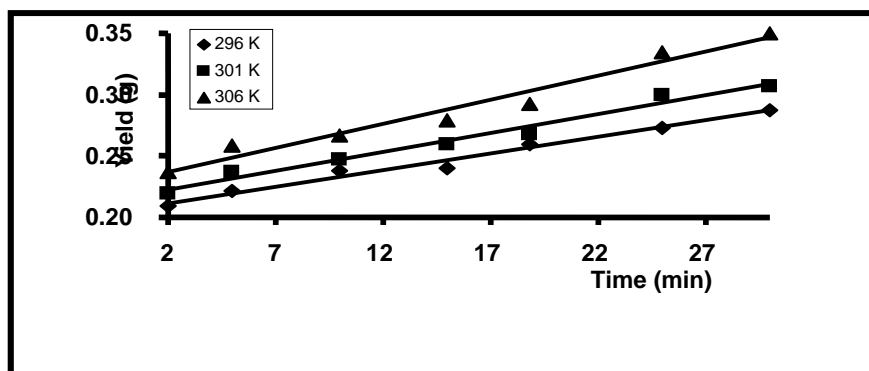
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Fig. 5a. Effect of temperature.

$$y = -799,31x + 5,639$$
$$E_a = 15,299 \text{ kJ/mol}$$

Fig.5b. The relation between 1/T (K^{-1}) and 7+ Log (k$_2$/T).

$$y = -661,97x + 5,6072$$
$$H^* = 12,67 \text{ kJ/mol}$$
$$S^* = -90,184 \text{ J/mol,K}$$
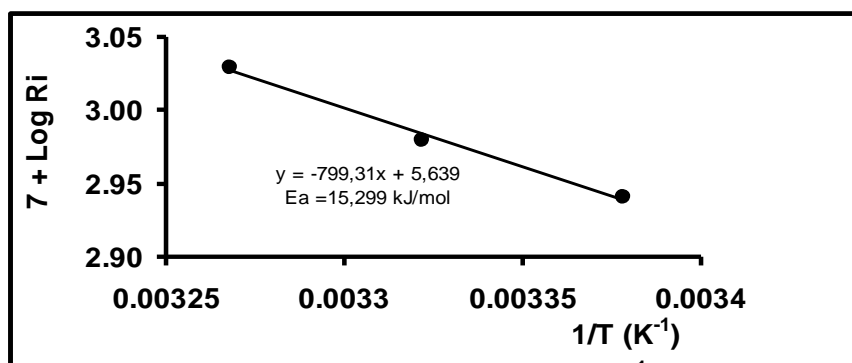
Fig.5c. The relation between 1/T (K^{-1}) and 7+ Log (k$_2$/T).

Mechanism of the oxidative polymerization of diphenylamine

The pattern of the chemical oxidative polymerization develops in the following steps:

The initiation step

This step is the reaction between dichromate ion and hydrochloric acid which can be discussed as follows:

1. The orange red dichromate ions ($Cr_2O_7^{2-}$) are in equilibrium with the $HCrO_4^-$ in the range of pH-values between 2 and 6, but at pH below 1 the main species is H_2CrO_4. The equilibria are as follows:
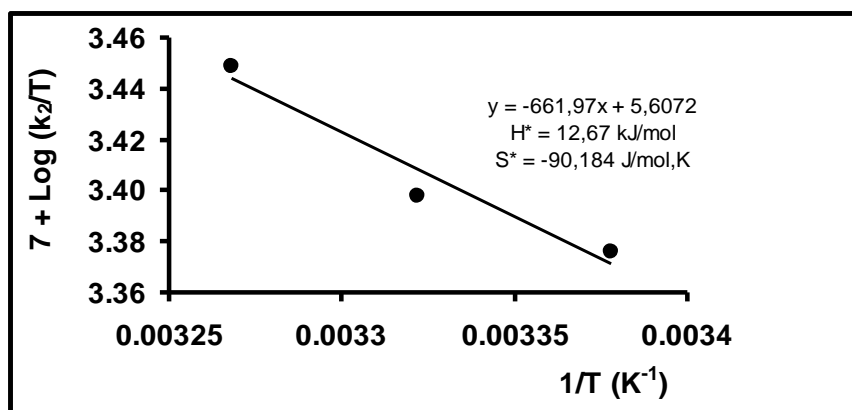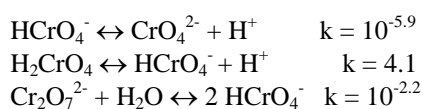
$$HCrO_4^- \leftrightarrow CrO_4^{2-} + H^+ \qquad k = 10^{-5.9}$$
$$H_2CrO_4 \leftrightarrow HCrO_4^- + H^+ \qquad k = 4.1$$
$$Cr_2O_7^{2-} + H_2O \leftrightarrow 2\,HCrO_4^- \quad k = 10^{-2.2}$$

Further, the species present depend on the nature of the acid used[44]. When HCl is used, there is essentially quantitative conversion into chloro chromate ion as follows:

$$CrO_3(OH)^- + H^+ + Cl^- \rightarrow CrO_3Cl^- + H_2O$$

2. The second step is the oxidation of diphenylamine by loss of electrons and conversion of the chromium ion to the lower oxidation state in simultaneous steps in Scheme 1:

$$CrO_3Cl^- + 6e + 14\,H^+ \rightarrow 2\,Cr^{3+} + 2HCl + 6H_2O$$
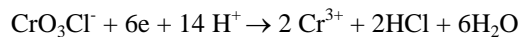
and
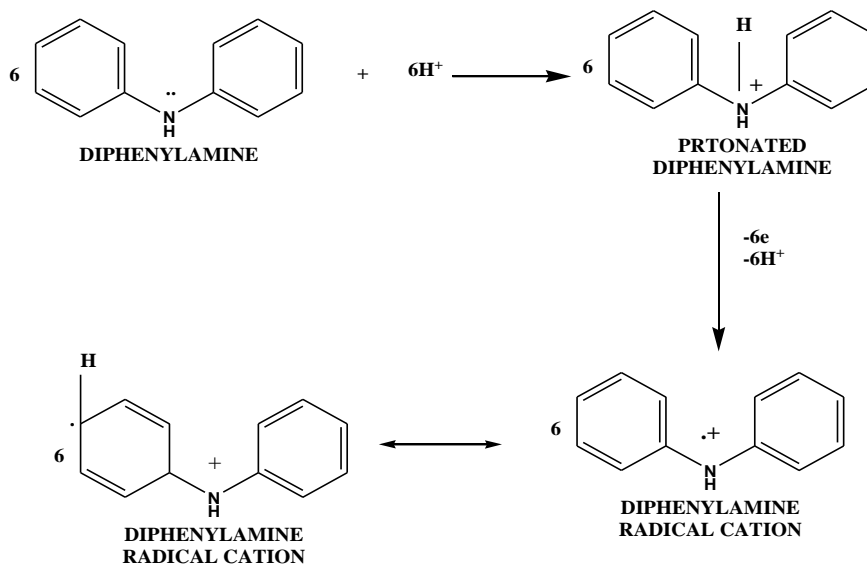
Propagation and polymer formation

This step involves the interaction between the formed radical cations and the monomer to form dimmer radical cation (I and / or II) as follows:
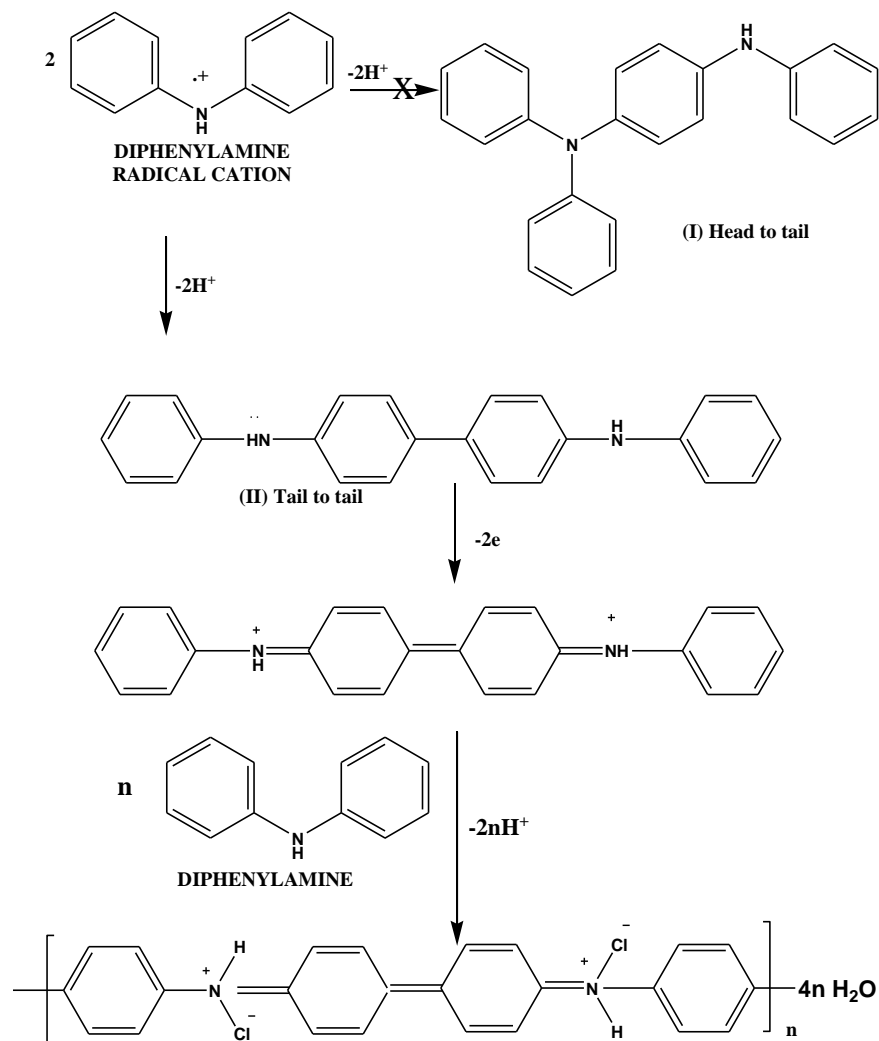
The Formed Poly (Diphenylamine) .

The formation of dimmer structure (I) is more difficult than (II) due to the MOPAC-COMPUTE PROPERTIES–AM1 calculations give indication that, structure (I) needs more energy of formation than (II) and less stable one (*c.f.* Table 1) which confirms the suggested mechanism illustrated in my pervious works[16-22] .

TABLE 1. Some compute properties of dimmer structure (I) and (II).

Property	Heat of formation (kcal/mole)	Steric energy summary (kcal/mole)	Total dipole moment (Debye)
Structure (I)	265.7147	89.14871	0.032
Structure (II)	123.42379	-5.25319	0.034

Elemental and spectroscopic analysis

The elemental analysis of the obtained polymer sample (*at 33^0C in 1.0 M HCl (DMF/water) medium using 0.005 M $K_2Cr_2O_7$ as oxidant and 0.05 M monomer concentration*) was carried out in the Micro Analytical Laboratory at Cairo University. The C%, H%,N% and Cl% are found to be in good agreement with the calculated one for the suggested structure of the formed polymer. The elemental analytical data are given in Table 2.

TABLE 2. Elemental analysis of poly(diphenylamine).

The element	C%	H%	N%	Cl%
Calculated %	60.38	5.45	5.87	14.88
Found%	60.80	6.10	6.30	13.90

The infrared spectrum is present in Fig.6 and the absorption bands and their assignments are summarized in Table 3. Form the figure and table the strong band appears at 692 cm^{-1} may be attributed to the torsional oscillation of NH_3^+ group. The three strong absorption bands appear at 747, 821 and 877 cm^{-1} are attributed to the out of plane C-H deformation showing 1,4-disubstitution in benzene ring. The appearance of different bands in the region of 939 to 1315 cm^{-1} are for CN stretching vibration or in plane deformation of CH aromatic or OH deformation (coupled) or NH deformation. The three strong absorption bands appear at 1504, 1594 and 1671 cm^{-1} may be attributed to the stretching vibration of benzidine structure C=C and/or in C=N in the suggested polymer structure. The stretching vibrations aromatic CH and NH appear at 3025 and 3387 cm^{-1}, respectively. The stretching vibrations of the free OH group appear at 3651 and 3675 cm^{-1} as weak bands.
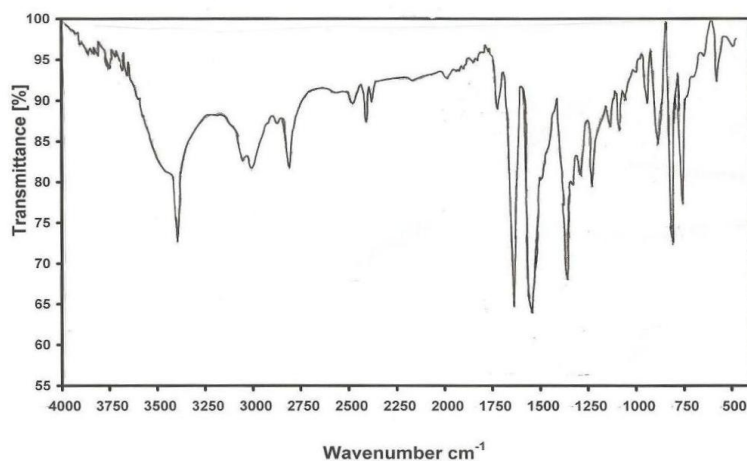
Fig. 6. The IR spectrum of the prepared polymer sample.

TABLE 3. Assignment of bands in the IR spectrum of the polymer.

Wave number (cm^{-1})	Assignment [45]
692^{S}	Torsional oscillation of NH$_3^+$ group
747^{S}	Out of plane C-H deformation showing 1,4-disubstitution in benzene ring
821^{S}	
877^{m}	
939^{w}	CN stretching vibration or in plane deformation CH aromatic or OH deformation (coupled) or NH deformation.
993^{w}	
1024^{w}	
1075^{w}	
1171^{m}	
1235^{w}	
1276^{sh}	
1315^{s}	
1504^{S}	Stretching vibration of C=C and/or C=N in the suggested polymer structure.
1594^{S}	
1671^{m}	
2340^{w}	C-N str.vibration (overtone) or combination band of the asymmetric bending and torsional oscillation of the protonated amine group.
2367^{w}	
2439^{w}	
2781^{m}	
2982^{w}	
3025^{w}	The stretching vibrations of aromatic CH
3387^{S}	The stretching vibrations of NH or strong H-bonded OH groups
3651^{w}	The stretching vibrations of the free OH group.
3675^{w}	

(s = strong, m = medium, sh = shoulder and w = weak) .

The ^{1}H-NMR spectrum of the prepared polymer sample is represented in Fig.7. The figure shows two singlet signals at δ=2.50 and δ=3.35 ppm, which are due to the solvent protons. The singlet signal appearing at δ = 6.83 ppm may be due to the NH in ph-NH. The signals appear at δ = 6.83, 7.10, 7.23 and 7.49 ppm may be due to the phenyl ring protons. The singlet signal at δ = 8.26 ppm could be attributed to the protonated amino group. These signals are in agreement with the theoretical ^{1}H-NMR signals illustrated in Fig.8.

Fig . 7. ^{1}H-NMR spectrum of the prepared polymer sample.

Fig. 8. The theoretical and experimental (Bold and Italic) ^{1}H-NMR signals of the repeated poly(diphenylamine) unit.

Electron microscopy analysis

The electron microscopy picture of the prepared polymer shows a crystalline material with elongated particles. Their size ranged from 4 x 10^{-4} mm to 28.5 x 10^{3} mm as shown in Fig. 9.
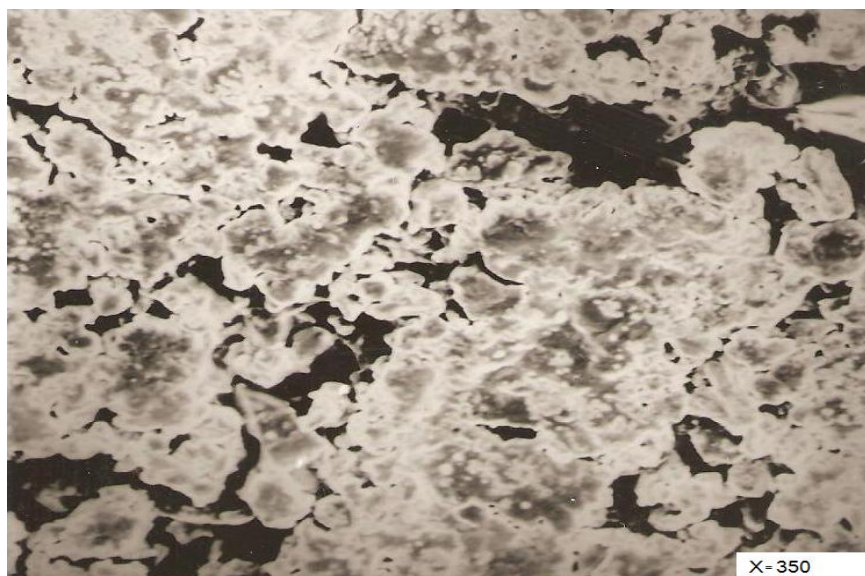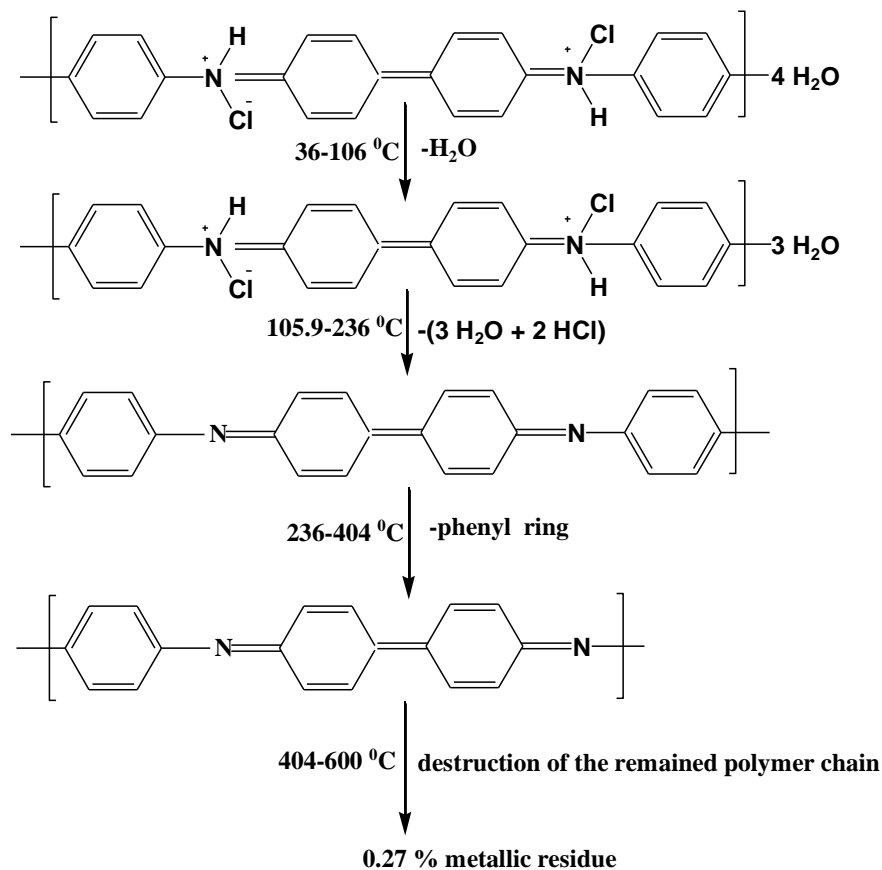

Fig. 9. Electron microscope picture of the prepared polymer.

The TGA and DTA analysis

The thermogravimetric analysis (TGA) and differential thermal analysis (DTA) for the prepared polymer sample is investigated and the obtained curves are presented in Fig. 10 (a & b). The first stage includes the loss of one molecule of water of the hydration in the temperature range 36 to 106 ^{0}C (mid point = 52.4^{0}C). The estimated weight loss for this stage is found to be 4.46% but the calculated one is 3.77%. In DTA curve, this stage gives endothermic peak at 56.4^{0}C which indicate the removal of water of hydration. The second stage of the TGA curve is the loss of the remained water of hydration (3 H_2O) and 2 molecules of doping HCl. This stage in the temperature range 105.9 to 2.36^{0}C. The found weight loss is 25.4% but the calculated is 26.62%. From TGA curve in the temperature range between 236 and 404^{0}C (mid points 240 and 325.59^{0}C) the weight loss is found to be 12.5% which could be attributed to the loss of phenyl ring. The calculated weight loss for this stage is 15.93%. On DTA curve an endothermic peak is present at 235.97^{0}C which indicate the decomposition of main polymer bonds. In the temperature range 404 to 600^{0}C (mid point 546.4^{0}C) the remained polymer (ph-N-ph-ph-N-) is destructed. The calculated weight loss for this stage is 53.697%, the found weight loss from TGA curve is 57.37%. The exothermic peak on DTA curve at 547.94^{0}C confirms the oxidation of the

polymer. The thermal degradation mechanism of the prepared polymer was suggested in the following scheme.

The thermal degaradtion mechanism of the prepared polymer.

Conclusion

A smooth kinetics was noticed for the polymerization of diphenylamine in DMF/water hydrochloric acid medium. The rate of polymerization showed 0.854 exponent dependence on sodium dichromate as oxidant and 0.641 exponent dependence on HCl. The monomer exponent was found to be 0.723. Mechanisms for the polymerization of diphenylamine were proposed. Kinetic expression was deduced for the rate of polymerization reaction and used to evaluate the rate constant (k_2) at different temperatures, then both ΔH^* and ΔS^* of the activation associated with k_2 were calculated using Eyring equation. The obtained polymer sample was characterized by IR, H-NMR, TGA, DTA, elemental analysis and electron microscopy.
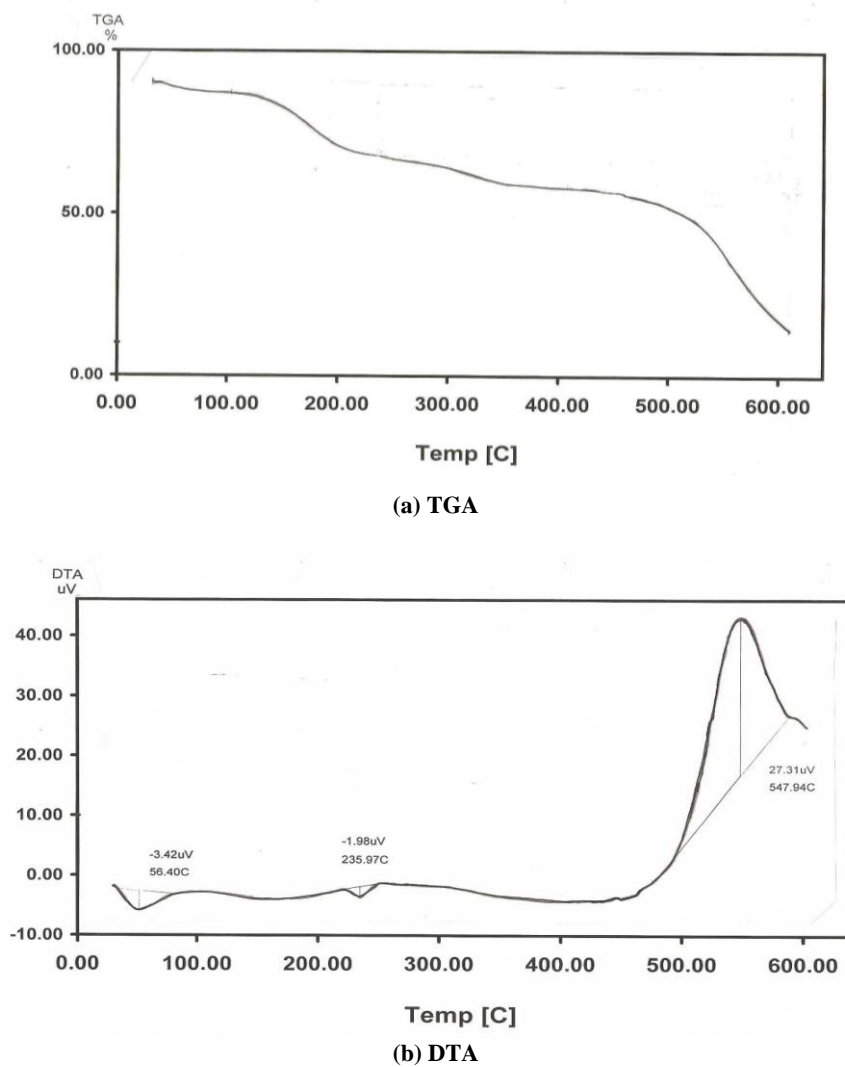
(a) TGA

(b) DTA

Fig. 10. The thermogravimetric analysis (a) and differential thermal analysis (b) of the prepared polymer.

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البلمرة الكيميائية لثنائي فينيل الامين ودراسة البوليمير الناتج

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تم دراسة بلمرة ثنائى فينيل الامين في وسط مائى ل DMF بنسبة ٥٠ ٪ حجما وذلك باستخدام ثانى كرومات الصوديوم كعامل مؤكسد وفي وجود محلول حمضي للهيدروكلوريك، كما تم دراسة تاثير درجة الحرارة وتركيز المونيمير والحمض علي عملية البلمرة وقد ادت هذة الدراسة الى اشتقاق معادلة معدل هذا التفاعل لتكون :

$$R_i = k [monomer]^{\cdot,\vee\Upsilon\Upsilon} [oxidant]^{\cdot,\wedge\circ\xi} [HCl]^{\cdot,\Upsilon\xi\Upsilon}$$

وقد تم حساب كل طاقة التنشيط الظاهرية والمحتوي الحرارى وكذلك الانتروبى٠ التركيب الكيميائى للبوليمير الناتج تم فحصة بالتحاليل IR, HNMR, TGA, DTA, وكذلك الميكروسكوب الالكتروني ووضع ميكانيكية للبلمرة .