Oxidative copolymerization of aniline with *o*- and *p*-toluidine by ammonium per sulfate: Kinetic and pathway

M. RASHID and SUHAIL SABIR*

Polymer Research Laboratory, Department of Chemistry,
Aligarh Muslim University, Aligarh - 202 002 (India)

ABSTRACT

The kinetic study on the oxidation of aniline with *o*- and *p*-methylaniline by ammonium persulfate (APS) has been carried out. The course of copolymerization was investigated by UV-vis spectroscopic method. Structural characterization was studied by FT-IR spectral analysis. The electronic spectra of the copolymers poly(aniline-co-*p*-toluidine) and poly(aniline-co-*o*-toluidine) show hypsochromic shift. The shift has been observed in the bands corresponding to $\pi \rightarrow \pi^*$ transition as well as in the exciton transition. The increase in absorbance recorded during the reaction for different concentration of aniline, *o*- and *p*- toluidine at various times of intervals of polymerization reaction indicates a growth in the polymer formation. The degradation curve can be fitted reasonably well by an exponential decay of APS, suggesting first order kinetics. The resulting first-order rate constant was used to calculate the rate of copolymer formation using the rate equation $-d[A]/dt = kc^n$.

Key words: Copolymerization, degradation curve, electronic and vibrational spectra.

INTRODUCTION

Polyaniline nanomaterials have attracted a great deal of interest because of their potential applications in nanoelectronics and biomedical devices[1,2]. Among the organic conducting polymers, It has been named as a "smart" and 'living-polymer'. It has tremendous applications as fabricated nanoparticles for electronic devices with unique doped and de-doped properties, unique redox behavior, chemical and colloidal stability, high functionality and environmentally benign for numerous applications. There has been a growing interest in the field of research for conducting polymer nanostructures with different shapes and sizes create fascinating physiochemical properties in polymer[3-5]. Copolymers of aniline with *o*- and *p*-methylaniline have been studied extensively[6-12]. As an attempt to get more soluble polyanilines, we synthesized copolymers of aniline with *o*- and *p*-toluidines. The aim of this study is to investigate the effect of incorporation of *o*- and *p*-toluidine units in the polyaniline nanostructure backbone and the kinetic properties of the resulting copolymers. These copolymers were synthesized for 1:1, 1:2 and 1:3 molar ratios of the respective monomers using APS as an oxidant.

EXPERIMENTAL

Double distilled-water was used to prepare all the solutions. Aniline was purified by single distillation under reduced pressure when received from Aldrich. Toluidine from (Merck) was recrystallized with acetone-ethanol mixture. The ammonium persulfate is used as received from Merck Chemicals. Initially 1.0M of aniline dissolved in 0.5M of H_2SO_4 aqueous solution. 1.0M solution of *o*- and *p*-toluidine each mixed with aniline in a separate reaction. Ammonium persulfate (APS) was dissolved in 0.5M H_2SO_4 aqueous solution. The aqueous solution of ammonium persulfate was

introduced to start the polymerization. Macroscopic precipitation was prevented in dispersion polymerization carried out in presence of suitable steric stabilizer[13]. The reaction was carried out in 0.5M solution of H_2SO_4 under pseudo first-order conditions with a large [amines]: [ammonium per sulfate] ratio 10:1. The reaction mixture was thoroughly mixed with a magnetic stirrer for 5 minutes and kept in water-bath at desired temperature range 25-45°C. A sample of 2-3 ml was withdrawn from the solution at regular interval and its optical density or absorbance was noted at its λ_{max} in order to follow the course of copolymerization of the reaction with Thermo Spectronic Genesis 20 spectrophotometer. The electronic absorption spectra of the base form of the copolymer in DMSO were taken with Perkin-Elmer spectrometer. The structural characterization of these copolymers was studied by Fourier transform infrared spectra using InterSpec 2020 Spectrometer at resolution of 4 cm^{-1} in absorption mode, using 200 scans for different molar ratio of copolymers. The kinetics of the copolymerization of aromatic amines was studied under the verified Beer-Lambert's Law range.

RESULTS AND DISCUSSION

Polymerization of aniline into polyaniline was found to take place very quickly as observed by the color change of the reaction from pale → bluish green → green within few minutes of the addition of the oxidant. The appearance of green color in the reaction mixture was taken as the indication of copolymerization. The copolymerization of aniline with *p*-toluidine was observed to be very slow process. At pH 3-4, the dispersed colloidal solution of the poly(aniline-co-toluidine) nanoparticles was green. The presence of methyl groups on *o*-toluidine and *p*-toluidine result in increase in the electron density in the phenyl ring and amino atoms which may not facilitate the polymerization. It can be seen that the rate of reaction decreases as the ratio of *p*-toluidine increases in the reaction mixture. Table 1 shows the values for rate of reaction and specific rate constant at different concentration of the aniline with *o*- and *p*-toluidine. It is the electron-donating group– CH_3 that retards the polymerization of aniline. The presence of methyl groups on the benzene rings explains the observed decrease in the rate of copolymerization. The steric effect is more pronounced during the polymerization of the aniline with *p*-toluidine.

In the reaction involving *p*-toluidine, the polymerization should take place by the coupling at *ortho* position to –NH_2 groups. The stable free radical is then produced at the *ortho*- position[6]. In the system containing *o*-toluidine, the coupling should be more favorable at *para* position to NH_2 groups,

Table 1: Values for reaction rate and specific rate constant for poly(aniline-co-p- toluidine) [APS]=1.25×10^{-2} M, [ANI]=1×10^{-2}M, [p-toluidine]=2×10^{-4}M, Temp=35°C

Time (min)	Absorbance	-d[A]/dt=kc^n×10^{-3}	k×10^{-3} (min^{-1})
05	0.030		
10	0.035	1.00	3.0
15	0.044	1.40	3.8
20	0.056	1.72	4.1
25	0.062	1.60	3.6
30	0.066	1.44	3.2
35	0.070	1.33	2.8
40	0.074	1.25	2.8
45	0.076	1.11	2.5
50	0.078	1.06	2.3
55	0.079	0.98	2.2

favoring the head-to-tail sequence. The kinetic parameters were also calculated and specific rate constant values were obtained from the integrated first-order kinetic equation. There is a decrease in the rate of reaction with increase in molar ratios of toluidine in the reaction mixture, thus, % yield decreases gradually. At the same time it also lowers the conducting efficiency of the polymers.

The specific rate constant k values were calculated from the first order-integrated rate equation k = (2.303/t) × log (Do/D), also D= ε *l* c, where ε is the molar extinction coefficient, *l* is the thickness of the absorbing medium and c is the molar concentration. A systematic approach has been considered to establish the dependencies of Rp on [APS], [ANI] and [toludines]. Since, the reaction has been carried out under pseudo-first order condition for different concentration of APS and ANI. The values are obtained for the rate of reaction and these are plotted against [APS] and [ANI]. It gives a straight line passing through origin, having positive slope of one. It indicates the first-order dependence on each of the reactant [APS] and [ANI]. The plot was obtained for absorbance vs time for the course of copolymerization of poly (aniline-co-toluidine) (fig 1.1). The reaction showed the time dependence of growth of absorbance at 330 nm.

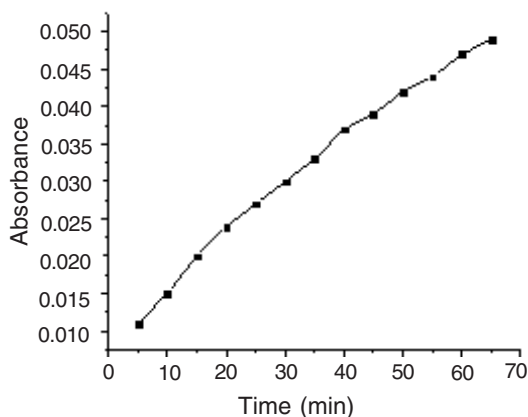The plot of log [A] versus time gives almost straight line with negative slope shown in (fig 1.2). The degradation curve can be fitted reasonably well by an exponentially decay curve, suggesting the first-order kinetics. The resulting first-order rate constant was used to calculate the rate using the formula.

$$Rp = -d\,[APS]/d\,t = kc^n$$
$$-d\,[A]/dt = kc^n$$

where A is the absorbance, k is the rate constant, c is the APS concentration.

Effect of temperature on the reaction rate

The effect of changing temperature was examined in the range 25°-40°C. As the temperature increases, the rate of the reaction should increase according to Arrhenius equation. Fig. 1.3 for poly(aniline-co-*p*-toluidine) shows the Arrhenius plot of logarithmic rate of polymer formation versus 1/T. The apparent value of activation energies (E_a) as shown in table 2 for polymerization of aniline and with substituted anilines were determined to be 13.20, 28.51 and 81.30 respectively KJ/mol, which corresponds to an increase in the rate of reaction with an increase in the temperature

The plot of log k versus 1/T is nearly linear with negative slope of -4.33 poly(aniline-co-*p*-toluidine). This further confirms the first-order dependence in the reactants in the course of chemical oxidative copolymerization reaction.
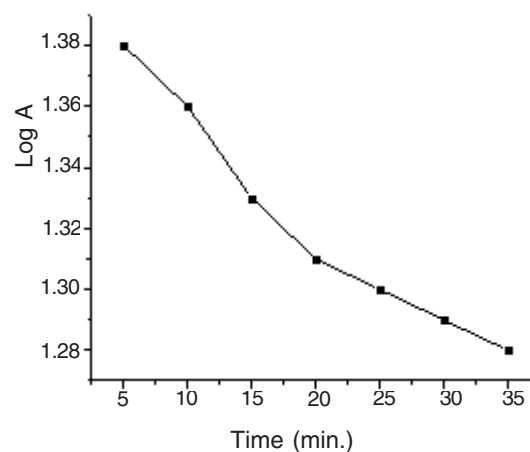

Fig. 1.1: Absorbance versus time plot indicates growth of polymer formation

Fig. 1.2: logA versus time plot indicates the decomposition of ammonium per sulfate

FTIR spectral studies

        The molecular structure of the copolymers nanostructure was studied by Fourier transform infrared (FTIR) spectroscopy. The FTIR spectra of PANI (curve A) and poly(aniline-co-*o*-toluidine) 1:1 (curve B) are shown in figure 1.4. The vibrational spectrum of polyaniline shows two major absorptions at 1589.5 cm^{-1} and 1492.4 cm^{-1} which are ascribed to the C=C vibrations of quinoid and benzenoid units respectively[13]. The relative intensity of quinoid to benzenoid band corresponds to the degree of the oxidation of the monomer unit into polymer chain[6]. It can be seen from the spectra of polyaniline that the number of quinoid units are almost equal to the number of benzenoid units. The band appeared at 1299 cm^{-1} is due to C-N stretching vibrations of benzenoid-qunoid-benzenoid sequence[14]. The weak band around at 810 cm^{-1} is ascribed to the C-H out of plane bending vibrations. A comparatively weak band at ~3300 cm^{-1} is due to N-H stretching vibrations and the band at ~3140 cm^{-1} is due to ring –C-H stretching vibrations. FTIR spectrum of poly(aniline-co-*o*-toluidine) 1:1 shows two major absorption peaks at 1583.4 cm^{-1} and 1515.3 cm^{-1} which are attributed to C=C vibration of benzenoid and quinoid units respectively[15].
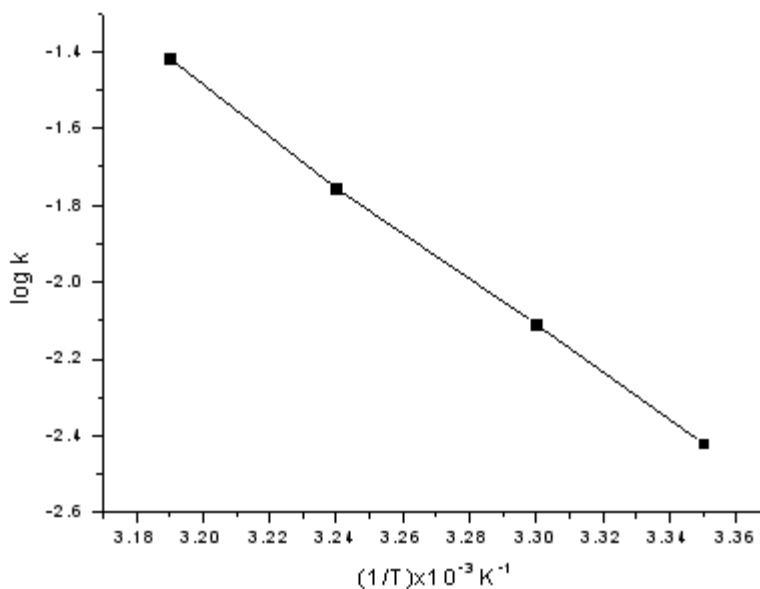

Fig.1.3: Plot of log k versus 1/T, the effect of temperature on reaction rate for copolymerization of aniline with *p*- toluidine

Table 2 :Values of rate constants for polymerization aniline with *o,* and *p*-toluidine

Solvent 0.5 M H$_2$SO$_4$: pH 3-4, k x10^{-2} (l.mol^{-1} min^{-1})				
Amine	25°	30°	35°	40°	E$_a$ KJ/mol
Aniline	2.23	2.4	2.67	2.8	13.20
o-toliudine	0.32	0.37	0.42	0.55	28.51
p -toluidine	0.9	1.4 1	2.53	3.90	81.30

Electronic spectral studies

UV-vis absorption spectra of the base form of poly(aniline-co-*p*-toluidine) 1:1 and poly(aniline-co-*p*-toluidine) 1:2 in DMSO are shown in figure 1.5. It is clear that both the copolymers show two major absorptions corresponding $\pi \rightarrow \pi^*$ transition and benzenoid to quinoid exciton transitions[16-17]. A hypsochromic shift (blue shift) is found both in the bands corresponding to $\pi \rightarrow \pi^*$ transition and in the exciton transition for the copolymers as compared to that in polyaniline. The shift is more prominent in poly(aniline-co-*p*-toluidine) 1:1. As can be seen from figure. Poly (aniline-co-*p*-toluidine) 1:2 shows the $\pi \rightarrow \pi^*$ transition at 291 nm and the benzenoid to quinoid transition band at 570nm. It is clear that, the blue shift increases as the ratio of the *p*-toluidine unit increases in the copolymers derived from aniline and *p*-toluidine.
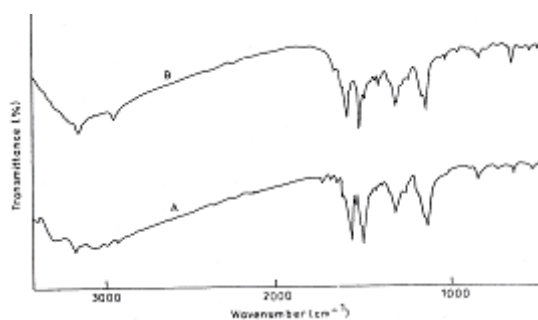

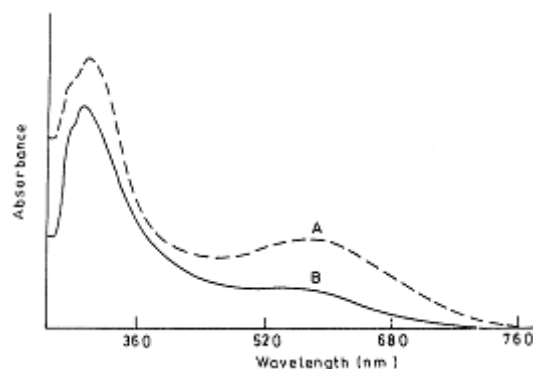**Fig. 1.4: FTIR Spectra of (A) Polyaniline, (B) poly(aniline-co-*o*-toluidine) 1:1**

Fig. 1.5: UV-VIS spectra of base form of the copolymer in DMSO, (A) poly (aniline -co-*p*-toluidine) 1:1, (B) poly (aniline-co -*p*-toluidine) 1:2

The band corresponding to $\pi \rightarrow \pi^*$ transition is measure of the extent of conjugation between the adjacent phenyl rings of the polymer. When methyl groups are present on the phenyl rings, they substantially alter the planarity of the system and influence the p-orbital overlap resulting in a shift in the $\pi \rightarrow \pi^*$ transition band. Thus the blue shift observed in the copolymers is due to the presence of methyl group present in the phenyl rings, which ultimately results in the increase of band gap of the polymers[18].

REFERENCES

1. Ajayan, P.M., "Handbook of Nanostructured Materials and Nanotechnology", vol. 5 ed. H. S. Nalwa, Academic Press San Diego, 99.
2. Lei, J., Menon, V.P., Martin, C.R., *Polym. Adv. Technol.* **4**: 124 (1992).
3. Sailor, M.J., Curtis, C.L., *Adv. Mater.* **6**: 688 (1994).
4. Wallace, G.G., Innis, P.C., L.A.P. Kane-Maguire. *In Encyclopedia of Nanoscience and Nanotechnology*, H.S. Nalwa ed. American Scientific Publishers, Los Angels **4**: 113 (2004).

5.   Everaldo, C., Venancio, Pen-Cheng Wang, A.G. MacDiarmid, *Synthetic Metals.* **156**: 357 (2006).

6.   Kumar, D., Dhawan, S.K., Ram, K.K., Sharma, R.C., Malhotra, B.D, Chanda, S., *Ind. J. Chem.* **36**A: 290 (1997).

7.   Gupta, M.C., Warhadpande, S.V., Umare, S.S, *Ind. J. Chem.* **32**A: 298 (1993).

8.   Genies, E.M., Noe, P., *J. Electroanal. Chem.* **296**: 473 (1990).

9.   Wei, Y., Focke, W.W., Wnek, G.E., Ray, A., MacDiarmid, A.G., *J. Phy. Chem.* **93**: 495 (1989) .

10.   Misra, R.A., Dubey, S., Prasad, B.M., Singh, D., *Ind. J. Chem.* **38**A: 141 (1999).

11.   Bidan, G., Genies, E.M., Penneaw, J.F., *J. Electroanal. Chem.* **27**: 59 (1989).

12.   Gok, A., Sari, B*., J. Appl. Polym. Sci.* **84**: 1993

(2002).

13.   Challier, T., Slade, R.C.T., *J. Mat. Chem.* **4**(3): 367 (1994).

14.   Bacon, J., Adams, R., *J. Am. Chem. Soc.* **90**: 6596 (1969).

15.   Roy, B.C., Gupta, M.D., Ray, J.K, *Macromolecules.* **28**(6): 1727 (1995).

16.   MacDiarmid, A.G., Chiang, J.C., Halpern, M., Huang, W.S., Mu, S.L., Somastri, N.L.D., Wu, W., Yaniger, S.I, *Mol. Cryst. Liq.* **121**: 173 (1985).

17.   Yu,, A. Wang, Z.H., Cromaek, K.R., Epstein, A.J., MacDiarmid, A.G., *J. Am. Chem. Soc.* **113**: 2665 (1991).

18.   Zagorska,M., Adam Pron, S. Lefrant, "Handbook of Organic Conductive Molecules and Polymer", Vol.3, Ed. H.S. Nalwa, John Wiley & Sons 194 (1997).