Isomeric Effects on Structures and Properties of Polyaminophenols Synthesized in Basic Medium

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The oxidative chemical polymerizations of three isomers of aminophenol, *ortho, meta,* and *para* (PoAP, PmAP, PpAP) were performed in aqueous NaOH using ammonium persulfate (APS) as oxidant. Solubility tests for the synthesized polymers were performed in various solvents and it was found that all three polymers are soluble in DMSO and DMF. PpAP is soluble in aqueous strong acid, as well as in base, but PoAP is soluble in acid, whereas PmAP is soluble in base. The difference in their solubility is due to their structural difference, which can be supported by the proposed mechanisms of polymerizations. The film casting from the DMF or DMSO solution of PoAP and PpAP is difficult due to the presence of quinone impurity while casting of PmAP film from DMSO solution is possible. The intrinsic viscosities of the polymers were determined from the DMSO solution. The polymers were characterized by UV-VIS, FTIR and ^{1}H-NMR spectroscopy and elemental analyses. From structural analysis, it is found that PoAP and PpAP do not contain π-electron conjugation due to ether linkage in the backbone chain. So, PoAP and PpAP do not show any conductivity like sulfuric acid doped PmAP.

Keywords: Polymer of aminophenols, polyaminophenol, conducting polymer, polymer of aniline derivatives

1 Introduction

In the intrinsically conducting polymer family, polyaniline (PANI) (and its derivatives) is an important member due to its easy synthesizability, environmental stability and wide applicability. PANI shows better processaibility than other conducting polymers. Still the processing of polyaniline is a challenge (1–5). One of the ways to resolve this problem is polymerization of aniline having substituted groups (6–10). PANI and its derivatives were *in situ* doped with corresponding acid during synthesis of the polymer in acid medium. Generally, this doped form is not processable and thus many researchers characterized the material by making pellets of PANI or its derivatives (11–13). This problem can be resolved by the synthesis of undoped polymer in basic medium. However, most of the aniline derivatives are not soluble in basic medium and acid is necessary during the polymerization of the aniline derivatives (14). The aniline derivatives containing ortho, meta or para substituted –OH group (aminophenol) is soluble in acid as well as in base. Most recently, polymers have been synthesized chemically or electrochemically using *ortho, meta* or para

–OH group substituted anilines (15–24). Chemical polymerization of *ortho* and *meta* isomer in acid medium results ladder structures because of oxidation of both amine and hydroxyl substituents (15). Due to this ladder structure, polymers are insoluble in organic solvents resulting in both poor processability and conductivity (15). Salavagione *et al.* (17) reported that during the electropolymerization of oAP, quinone and phenoxazine byproducts were obtained. They also reported that the *p*-quinone product was obtained from a electrochemical reaction of pAP in aqueous acid medium while a complicated polymeric structure was explained by Taj et al.(24). There is very little reported in the literature on polymerization of aminophenol isomers in basic medium. Guenbourg et al. (25, 26) electropolymerized 2-aminophenol in alkaline hydroalcoholic medium and they got polyether having –NH$_2$ groups intact. In another study, *meta*-aminophenol was electropolymerized in both acidic (perchloric acid) and basic (potassium hydroxide) medium (27). It was reported that the polymer film synthesized from basic medium had less stability and reproducibility (27). We have already reported (28) that chemical polymerization of *m*-aminophenol (PmAP) is possible in the initial basic (NaOH) medium using ammonium persulfate (APS) as an oxidant. In that study, we have reported (28) the optimum condition for the synthesis of the poly(m-aminophenol) in NaOH medium and also the structure of the polymer obtained.

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In this work, the polymers of ortho and para isomers of aminophenol (oAP, pAP) were synthesized in initial aqueous NaOH using the optimized condition used for the synthesis of PmAP (28). We used APS as an oxidative initiator for polymerization from the monomers. All three polymers synthesized have different solubilities in various solvents. The difference in their solubility, film forming properties and conductivity is due to their structural difference, which could be explained by the proposed mechanism of synthesis.

2 Experimental

2.1 Materials

The crystalline synthesis grade ortho, meta and para aminophenol isomers (Merck, India.) were used as received. The sodium hydroxide pellets (Quest Chemicals, India), sulfuric acid (Merck, India), hydrochloric acid (S. D. Fine Chem., India), DMSO (Merck, India), DMF (Merck, India), acetone (Merck, India), liquor ammonia (Merck, India) were used without further purification. Deionized (D. I.) water was used for synthesis and washing purposes.

2.2 Synthesis of the Polymers

The polymers of *o*-aminophenol (oAP) and *p*-aminophenol (pAP) isomers were synthesized according to the process described in reference (28) for the polymerization of *m*-aminophenol (mAP). Monomers (30 mM) were dissolved separately in (50 ml) aqueous sodium hydroxide (0.6 M) in a two-necked round bottom (RB) flask containing a centigrade thermometer in one neck. APS (45 mM) solution in water (25 ml) was added to this monomer solution in one lot. The reaction was started at room temperature (30°C) and it was stirred continuously for 5–6 h. Temperature change and pH change was recorded with a particular time interval. A precipitate of the PmAP and PpAP was obtained, but PoAP remained in the solution. The PoAP was precipitated by adding excess dilute base, liquor ammonia. The precipitate of PmAP and PpAP was filtered and washed with 4 M HCl 4–5 times for removing the unreacted monomers or oligomers. The PoAP solution in reaction medium was treated with dilute ammonia solution to precipitate out the polymer. The precipitate of PoAP was filtered and washed with dilute ammonia solution to remove the unreacted monomers or oligomers. Then, all

the precipitates were further washed with D.I. water several times till the filtrate became neutral with respect to pH paper. The colored products were dried at 70—80°C in a vacuum oven for about 12 h.

2.3 Solubility Test and Film Casting of the Synthesized Polymer

The polymer powder was ground well by using a mortar and pestle. For solubility testing, this polymer powder (0.05–0.1 g) was taken in a test tube containing 5 ml experimental solvent. Then, the test tube was shaken well for 20–30 min continuously by using a mechanical shaker at room temperature (30°C).

The polymer film was cast by following the method described in our previous communication (28). About 0.7–0.8 g, PmAP was dissolved in 15–20 ml of the solvent and this solution was poured on a petridish of 10 cm diameter. Then the petridish was placed inside an oven maintained at 100°C for 7–8 h for the evaporation of the solvent.

2.4 Physical Characterizations

2.4.1. *Viscosity measurement*

The flow times of PmAP solutions of varying concentrations in DMSO were measured using an Ubbelohde Viscometer. The specific viscosity (η_{sp}) was calculated from the flow times by using the relation (29):

$$\eta_{sp} = \eta_r - 1 = (t - t_0)/t_0$$

and

$$\left[\frac{\eta_{sp}}{C}\right]_{C \to 0} = \eta$$

Where η_r is the relative viscosity, t and t_0 are the flow time for polymer solutions and pure solvent, respectively, η is the intrinsic viscosity of the polymer and C is the polymer solution concentration. Then, intrinsic viscosity [η] of the polymer was determined by extrapolating the straight line in η_{sp}/C vs. C plot to infinite dilution according to Huggins equation (29):

$$\eta_{sp}/C = \eta + K' [\eta]^2 C$$

Where K' is Huggins' constant.

2.4.2. *pH measurement*

The pH change of the reaction medium was measured by using a digital pH meter PH5652 (Electronic Corporation

Table 1. Synthesis of the polymers in aqueous NaOH medium

Name of the sample	Amount of monomer (mM)	NaOH (M)	Amount of APS taken (mM)	Crude polymer (%)	Intrinsic viscosity [η], (dL /g)
PoAP	30	0.6	45	80	0.100
PmAP	30	0.6	45	88	0.127
PpAP	30	0.6	45	90	0.096
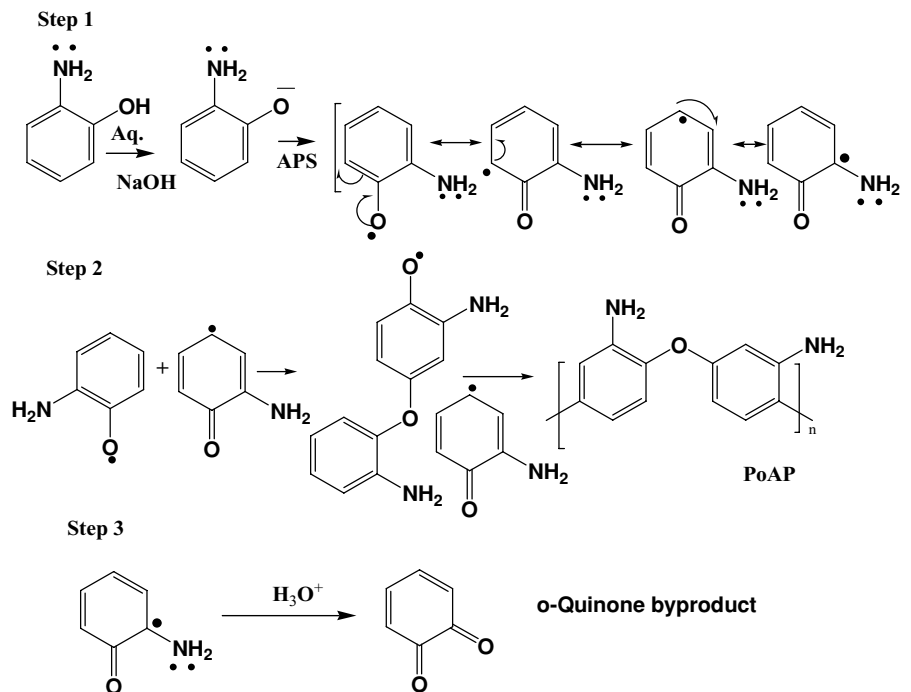
Scheme 1. Polymerization mechanism of oAP in initial NaOH medium.

of India Ltd.). The reading was taken by dipping the electrode into the reaction medium at the required time interval. Before taking a reading, the pH meter was standardized by using standard buffer solutions at the experimental room temperature (30°C).

2.4.3. *UV-VIS spectra*

The UV-Vis spectra of the polymers were recorded using about 1% DMSO solution using Mikropack UV-VIS-NIR, DH 2000. The DMSO solvent was taken as a reference.
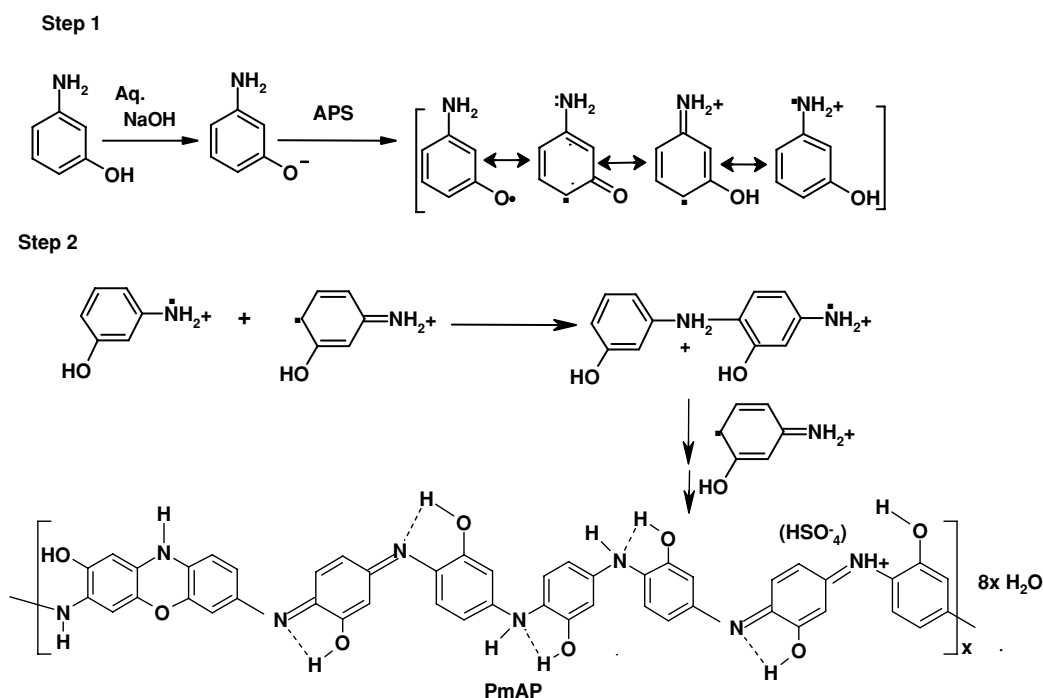
Scheme 2. Polymerization mechanism of mAP in initial NaOH medium.
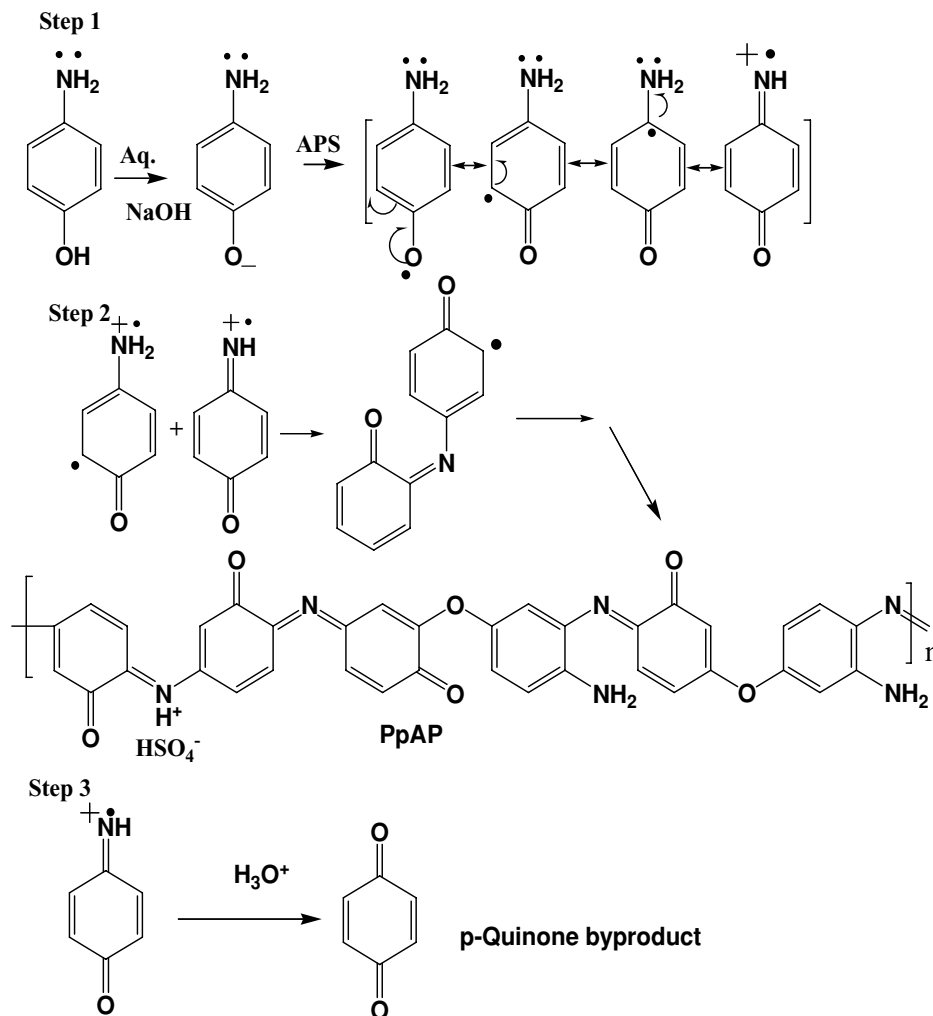
Scheme 3. Polymerization mechanism of pAP in initial NaOH medium.

2.4.4. *FTIR spectra*

To get an idea about functional groups present in the polymers, the Fourier transformed infrared (FTIR) spectra of synthesized polymers powder dispersed in KBr pellet were recorded in a Thermo Nicollet (model number Nexus 870) IR Sspectrometer. The spectrum was recorded from 400 cm^{-1} to 4000 cm^{-1}.

2.4.5. *^{1}H-NMR spectroscopy*

For structural analyses of the synthesized polymers, ^{1}H-NMR spectra of the samples were recorded in a BRUKER (400 MHz) instrument using d_6-DMSO as solvent.

2.4.6. *Elemental (CHNS/O) analyses*

The elemental analyses of polymers were performed by a combustion method. Carbon, nitrogen, hydrogen and sulfur were analyzed by a Perkin-Elmer C H N S/O Analyzer 2400. The theoretical calculation of the percentages of C, H, N and S were done based on the structural perception in the proposed schemes.
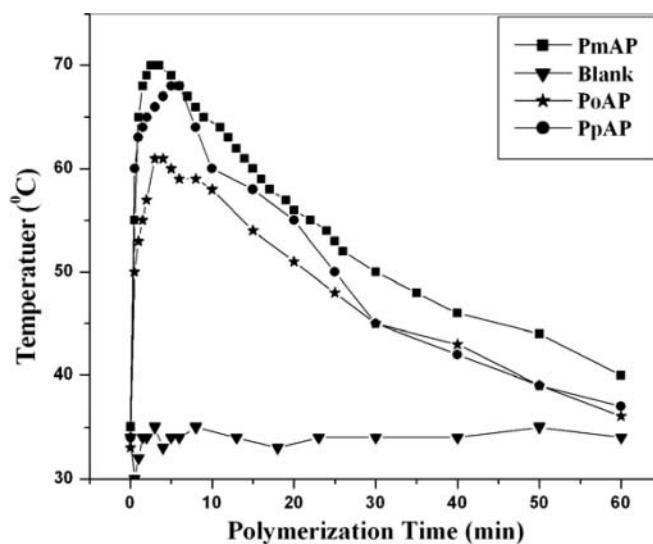

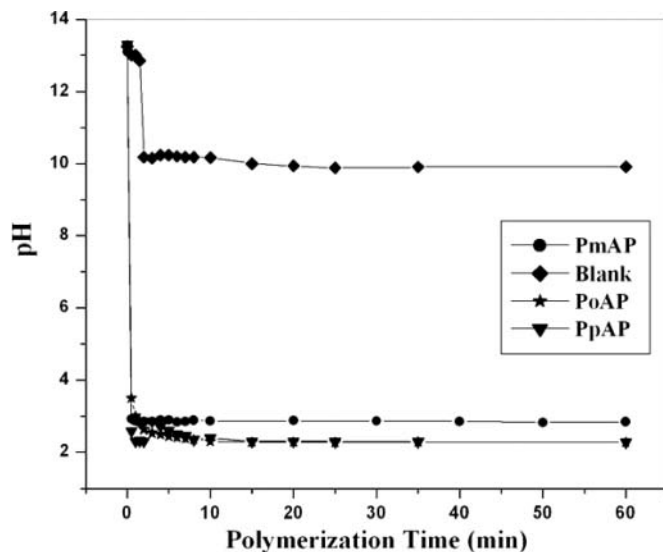**Figure 1.** Temperature change during the synthesis of the polymers.

Figure 2. pH change during the synthesis of the polymers.

Figure 3. Intrinsic Viscosity measurement for (a) PoAP, (b) PmAP and (c) PpAP.

3 Results and Discussions

3.1 Synthesis of the Polymers

Polymers were synthesized following the procedure described in the previous section. Polymerization conditions, yields and intrinsic viscosities are included in Table 1. The increase in polymerization temperature was recorded as shown in Figure 1. As can be seen from Figure 1, polymerization temperature increases with time and it reaches a maximum within 3–4 min in the case of synthesis of all the polymers. It was observed that the polymerization reaction was very fast and exothermic in nature. Polymerization of mAP is faster than that of pAP and oAP as maximum temperature increase was observed during the synthesis of PmAP. This is probably due to the formation of quinone byproduct from oAP and pAP (Schemes 1–3) (17) during the polymerization. These observations can also be explained from the pH change (Fig. 2) of the polymerization medium against time. For PmAP synthesis, the
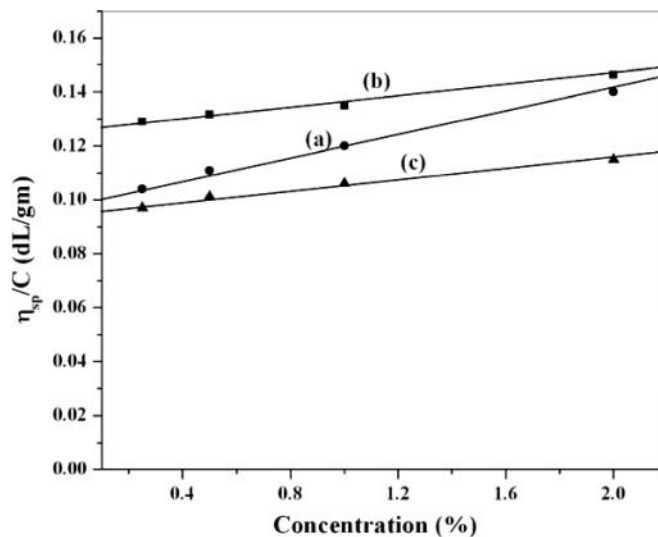
reaction medium becomes more acidic than that of PpAP and PoAP within 2–3 min due to the formation of sulfuric acid from the vigorous reaction of APS and phenoxide ion to the radical intermediate in basic medium. To compare the polymer chain growth, the intrinsic viscosity [η] of the polymers was obtained from a plot of specific viscosity/concentration (η_{sp}/C) vs. polymer concentration at infinite dilution (Fig. 3). All the polymers have shown straight line curves conforming to the Huggins equation (29). The intrinsic viscosity values for the polymers are comparable (Table 1) and so it can be said that the polymer chain growth is almost the same for all the polymers. Only the slight drop of intrinsic viscosity (Table 1) for PoAP and PpAP is probably due to the presence of quinone byproduct for both the case. However, the intrinsic viscosity values of all the polymers are less than that of the polyaniline. This is due to the steric effect of the substituted –OH groups (6). The solubility chart and the film forming properties of the polymers are shown in Table 2. All three polymers are soluble in

Table 2. Solubility chart for the synthesized polymers

Solvent	PoAP		PmAP		PpAP	
	Solubility	Film	Solubility	Film	Solubility	Film
DMSO	++	+	++	++	++	+
DMF	+	−	++	+	+	+
THF	−	−	+	−	−	−
Aq. NaOH	−	−	++	−	++	−
Aq. KOH	−	−	++	−	++	−
Aq. Ammonia	−	−	+	−	−	−
Aq. HCl	++	−	−	−	+	−
Con. HCl	++	−	−	−	+	−

++, excellent; +, good; −, not soluble

Table 3. UV-VIS spectral interpretation for synthesized polymers

Polymer	Absorption maxima (nm)	$\pi \rightarrow \pi^*$	$\pi \rightarrow \sigma^*$	Reason
PoAP	300	✓		Conjugated double bond
	480		✓	o-Quinine byproduct
PmAP	300	✓		Conjugated double bond
PpAP	300	✓		Conjugated double bond
	400		✓	p-Quinine byproduct

DMSO and DMF. PpAP is soluble in concentrated acid as well as in base, but PoAP is soluble in dilute acid, whereas PmAP is soluble in base. The film casting from the DMF or DMSO solution of PoAP and PpAP is difficult due to the presence of quinone impurity, while casting of PmAP film from DMF or DMSO solution is possible. All the above observations were well explained from the structural differences of the polymers, which were obtained due to the difference in the polymerization mechanism (Schemes 1–3).

3.2 Proposed Polymerization Mechanism

The polymerization mechanism for mAP in initial basic medium is already reported in our previous communication (28). Like mAP (28), the first free radical was generated on phenoxide anion of oAP and pAP (Schemes 1–3) in an initial NaOH solution due to the addition of APS. After this step, polymerizations proceed in acid medium (28) as reaction medium becomes acidic due to sulfuric acid liberation from reduction of APS. So, pH of the reaction medium decreased (Fig. 2). For oAP, the delocalization of free radical on phenoxide is shown in Scheme 1/Step 1. The polymerization occurs through the –O- group resulting in a structure of the PoAP just like a polyphenol type (Scheme 1/Step 2) containing a –NH$_2$ group intact.

Due to this free –NH$_2$ group, the PoAP was well soluble in aqueous acid medium. From the acid hydrolysis of one of the delocalized intermediates, an o-benzoquinone byproduct is obtained from oAP (Scheme 1/Step 3) during the polymerization. In the case of mAP, the free radical delocalized over –NH$_2$ group and ultimately polymerization occurs through the –NH- group (Scheme 2/Step 1). So, the structure obtained for PmAP (Scheme 2/Step 2) is like polyaniline containing –OH group intact. This free –OH group makes the polymer soluble in aqueous base. In this case, very little ladder unit may also incorporate in the polymer chain (28). As the –OH and –NH$_2$ groups are in para position with respect to each other, the delocalization of free radical (Scheme 1) on phenoxide is extended over the –NH$_2$ group (Scheme 1/Step1). In addition, the combination of intermediate as shown in Scheme 3/Step 2 results in a polymer having random –N= as well as –O- linkage within the polymer backbone. In PpAP, the –OH group was oxidized to =O because of more stable o-quinone like aromatic structure and in basic medium. the polymer is soluble due to the formation of –O$^-$Na$^+$ ion. Again, the polymer is also soluble in strong acid medium due to the presence of free –NH$_2$ groups containing a polyphenol-like unit in the polymer back bone. Like PoAP synthesis,
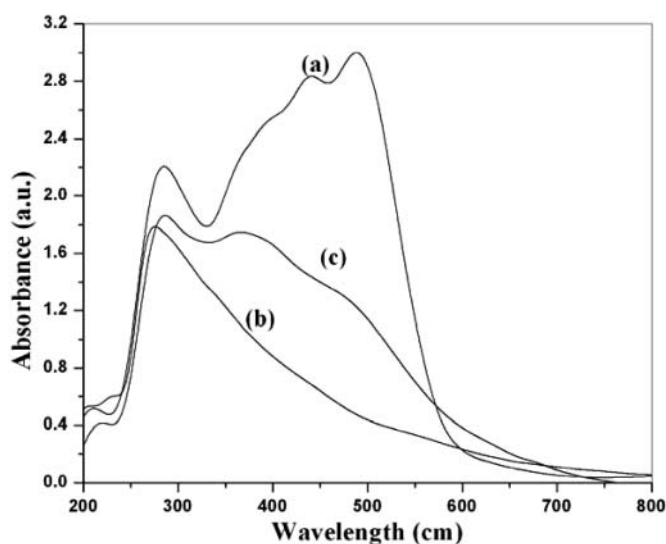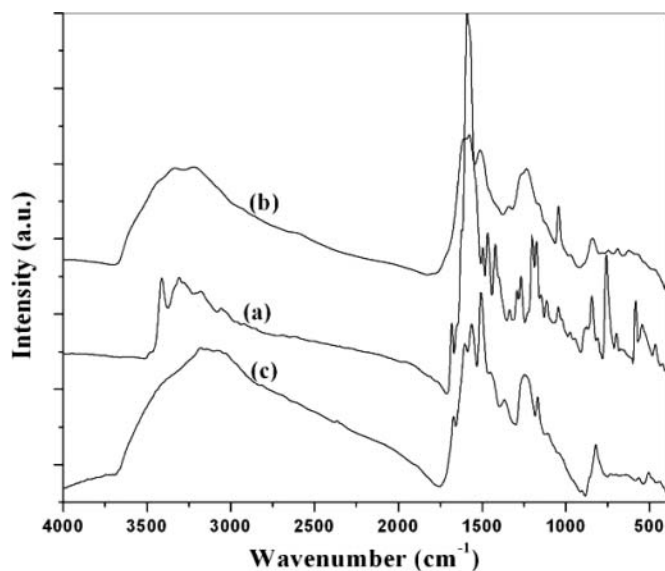

Figure 4. UV-VIS spectra of (a) PoAP, (b) PmAP and (c) PpAP.

Figure 5. FTIR spectra of (a) PoAP, (b) PmAP and (c) PpAP.

Table 4. FTIR spectral interpretation for synthesized polymers

| Responding groups | Absorption peaks ($\bar{v}$, cm^{-1}) | | | Mode of vibration |
	PoAP	PmAP	PpAP	
O—H (hydrogen bonded)	3418 (broad)	3426 (broad)	3190	Stretching
N—H (aromatic ring)	3300	3238 (broad)	3127	Stretching
C—H (aromatic)	3050 (broad)	2920 (broad)	3030 (broad)	Stretching
C=N (polymer chain)	–	1625	1611	Stretching
C=O (quinone)	1690	–	1680	Stretching
C—O—C (ether linkage)	1270, 1050	–	1258, 1050	Stretching
C—O/C—N	1370	1251	1306	Stretching

here also a p-quinone byproduct is obtained from pAP by acid hydrolysis of one of the delocalized intermediates (Scheme 3/Step 3) during the polymerization. Due to the presence of respective quinone byproduct in PoAP and PpAP, the film forming property of the polymer is poor (Table 2). The structures of the polymers are explained from the spectral characterization of the polymers and the elemental analysis data.

3.3 UV-VIS Spectra

The UV-VIS spectra of all the polymers are shown in Figure 4 and the data obtained from the figure is shown in Table 3. In the UV-VIS spectra of PoAP, PmAP and PpAP the $\pi - \pi^*$ absorption maxima is observed (Fig. 4) around 300 nm (Table 3). The intensity of the $\pi - \pi^*$ absorption maxima is comparable for all the polymers (Fig. 4). However, the $\pi - \pi^*$ transition is also possible for the quinone impurity present in PoAP and PpAP. The intensity of these absorption maxima in PmAP is less than that of PoAP or PpAP probably due to this reason. In the case of PmAP, no other band is noted, but in UV-VIS spectrum of PoAP (Fig. 4) another broad absorption maxima at 480 nm is found (Table 3). Similarly, in UV-VIS spectrum PpAP (Fig. 4),

Table 5. ^{1}H-NMR spectra of the synthesized polymers

| Responding proton | Chemical shift (δ) | | |
	PoAP	PmAP	PpAP
NH$_2$ (Terminal)	5.49, 6.04	5.8	5.53, 6.03
CH (Aromatic)	6.66	6.77	6.83
CH (Aromatic)	6.96	7.02	7.20
CH (Aromatic)	7.47	7.32	7.68
C-H (quinone)	6.36, 7.82	–	6.88
>NH (Polymer chain)	–	9.07	–
OH (Aromatic H-bonded)	–	9.20	–

the second absorption appears showing maxima at 400 nm (Table 3). For PoAP and PpAP the second absorption in UV-VIS spectra is due to the $\pi - \sigma^*$ absorption of quinine (Table 3) byproduct with the conjugated auxochrome C=O present in the polymer structure.

3.4 FTIR Spectra

The vibration bands obtained from FTIR spectra of the polymers (Fig. 5) are summarized in Table 4. For all the polymers, a broad peak appeared in the 3800–2000
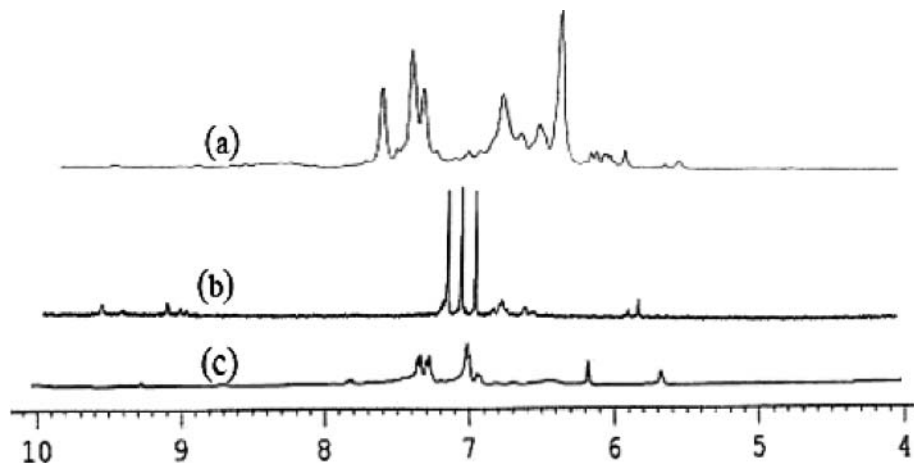

Figure 6. ^{1}H-NMR spectra of (a) PoAP, (b) PmAP and (c) PpAP.

Table 6. Elemental analyses of the polymers

	% Elements									
	Carbon		*Hydrogen*		*Nitrogen*		*Sulfur*		*Oxygen*	
Sample	Ex	Th	Ex	Th	Ex	Th	Ex	Th	Ex	Th
PoAP	68.60	69.55	5.55	5.35	13.0	13.52	–	–	12.85	11.58
PmAP	51.71	52.70	5.44	4.85	9.90	10.25	2.83	2.93	29.92	29.27
PpAP	59.90	59.01	4.56	3.28	11.30	11.47	1.59	4.37	22.85	21.87

Ex: Experimentally determined; Th: Theoretical value.

cm^{-1} region. These absorption bands in FTIR spectra of the polymers (Table 4) are due to the stretching of aromatic C-H (and also stretching of C-H bond present in the quinone byproduct), –NH$_2$ stretching, -OH stretching (where applicable), etc. The stretching C=N group appeared at around 1611 cm^{-1} for PpAP and PmAP. A distinct –NH$_2$ stretching absorption band appears in FTIR spectrum of PoAP at around 3300 cm^{-1}. The PoAP also shows two peaks at 1050 cm^{-1} and 1270 cm^{-1} due to the characteristic stretching absorption of C-O-C linkage (15). For a p-quinone byproduct, and also the group present in PpAP, a C=O stretching peak appears at 1680 cm^{-1} in the FTIR spectrum of the polymer, while a small C=O stretching peak is noted at 1690 cm^{-1} in the FTIR spectrum of PoAP due to the presence of o-quinone byproduct. Other peaks for all the three polymers in FTIR spectra are obtained as described in the Table 4.

3.5 ^{1}H-NMR Spectra

The ^{1}H-NMR spectra of the synthesized polymers are shown in Figure 6 and the data obtained from the figure is shown in Table 5. In the ^{1}H-NMR spectra of PoAP, PmAP and PpAP, the chemical shift is observed for three aromatic hydrogen atoms in the region 6–8 δ (Table 5). So, in all the polymers, three positions of the benzene ring are engaged due to substitution and the other three positions are free. Two other chemical shifts appear at 6.36 δ and 7.82 δ due to the CH (quinone) of o-quinone byproduct are present in the PoAP, but in ^{1}H-NMR spectrum of PpAP, only one chemical shift appears for CH (quinone) of p-quinone byproduct at 6.88 δ (Fig. 6). In ^{1}H-NMR spectrum of PoAP, the strong chemical shift appears at 5.49 δ due to the free –NH$_2$ group present in the polymer (Fig. 6). However, a weak chemical shift appears at 5.53 δ in ^{1}H-NMR spectrum of PpAP due to the terminal –NH$_2$ group (Fig. 6). Two chemical shifts appear for OH (hydrogen bonded) and >NH (with in the chain) in the ^{1}H-NMR spectrum of PmAP (Fig. 6) (28).

3.6 Elemental Analyses

The theoretical, as well as the experimental elemental analysis data for all the polymers are given in Table 6. The theoretical percentages of elements for polymers were cal-culated from the structures shown in the Schemes 1–3. The theoretical and experimental data are comparable with each other. In the PmAP and PpAP, some S incorporates due to the salt formation of liberated sulfuric acid from the reduction of oxidant APS with >N- present within the chain (28). In the case of PmAP, some water molecule is also hydrogen bonded with the –OH group present in the polymer (28). For the quinone byproducts in PoAP and PpAP, the elemental analysis value is almost the same with the polymers. In the case of PpAP, the experimental data for S is so low compared to the theoretical one due to the reason that the quinone impurity was not taken into account in the calculation.

3.7 Remarks on DC-conductivity of the Synthesized Polymers

We have already reported that PmAP doped with sulfuric acid shows a conductivity 4.8 × 10^{-4} S/cm (28, 30), this is due to the hydroxyl derivative of polyaniline-like π-conjugated structure of PmAP. From structural analysis, it is found that PoAP and PpAP do not contain π-electron conjugation due to ether linkage in the backbone (Schemes 2–3). We have tried to measure the conductivity of undoped pellets of PoAP and PpAP. The polymers show a conductivity in >10^{-12} S/cm. Therefore, we can say that the use of PoAP or PpAP, as a conducting polymer is not possible like doped PmAP.

4 Conclusions

In this work, we have tried to synthesize processable conducting polymers for oAP and pAP like mAP in aqueous basic medium by chemical oxidative polymerization, but the polymer synthesized from oAP and pAP was not conducting due to the presence of ether linkage in the polymer backbone. The film casting from the DMF or DMSO solution of PoAP and PpAP is difficult due to the presence of quinone impurity while casting of PmAP film from DMSO solution is possible. The difference in their properties is due to their structural difference, which is explained from the proposed mechanisms for polymerization. We can conclude that PoAP and PpAP synthesized from basic

medium cannot be used as conducting polymers like doped PmAP.

Acknowledgement

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