

Chemical synthesis of processable conducting polyaniline derivative with free amine functional groups

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Abstract. Processable conducting polyaniline derivative with free amine functional groups was successfully synthesized from the monomer o-phenylenediamine in aqueous hydrochloric acid medium using ammonium persulfate as an oxidative initiator. The synthesized poly(o-phenylenediamine) (PoPD) in critical condition was found to be completely soluble in common organic solvents like dimethyl sulfoxide, N,N-dimethyl formamide etc. From the intrinsic viscosity measurement, the optimum condition for the polymerization was established. The polymer was characterized by ultraviolet visible spectroscopy, Fourier transform infrared spectroscopy, proton magnetic resonance spectroscopy (¹HNMR) and thermogravimetric (TGA) analyses. The weight average molecular weights of the synthesized polymers were determined by the dynamic light scattering (DLS) method. From the spectroscopic analysis the structure was found to resemble that of polyaniline derivative with free amine functional groups attached to ortho/meta position in the phenyl ring. However, very little ladder unit was also present with in the polymer chain. The moderate thermal stability of the synthesized polymer could be found from the TGA analysis. The average DC conductivity of 2.8×10^{-4} S/cm was observed for the synthesized polymer pellet after doping with hydrochloric acid.

Keywords: polymer synthesis; molecular engineering; tailor-made polymers; smart polymers; conducting polymer; conjugated polymer

1. Introduction

Polyaniline (PANI) attracts much interest as intrinsically conducting polymer due to advantages like easy synthesizability, better doping ability, architecture flexibility, environmental stability, wide applicability etc. (Negi and Adhyapak 2002). Like other conducting polymers solution processability of PANI is also a great challenge due to its rigid rod like structure. Thus, much effort has been made to improve its processability by chemical and electrochemical polymerization of aniline with *ortho* and *meta*-substituted groups, viz., -OCH₃, -CH₂CH₃, -CH₃, -SO₃H, -Cl, -F, -I etc. Generally, polymers of *ortho* or *meta* substituted aniline give identical structure with better processability and they have some lower conductivity than that of PANI itself due to repulsion factor (Leclerc *et al.* 1989, Yue and Epstein 1990). However, *ortho*-isomer is preferred over the *meta*-isomer for polymer synthesis as the former gives better yield than the latter and the polymer obtained from *ortho*-isomer has higher conductivity than that of *meta*-isomer (Leclerc *et al.* 1989,

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Yue and Epstein 1990).

Recently, polymers have been synthesized chemically or electrochemically by using *ortho* or *meta* $-NH_2$ (phenylenediamine) and $-OH$ (aminophenol) substituted aniline (Levin *et al.* 2005, Rivas *et al.* 2002, Salavagione *et al.* 2004, Salavagione *et al.* 2005, Sayyah *et al.* 2002, Zhou *et al.* 2010, Huang *et al.* 2011, Pham *et al.* 2011, Huang *et al.* 2006). This is because synthesis of polyaniline derivatives containing free active functional groups (e.g., $-NH_2$, $-OH$ etc.) in the backbone chain that can offer better solution processability, better induce doping by metal nanoparticles and good sensitivity towards various chemicals. Unlike other derivatives of aniline, both the amine and hydroxyl substituents in these two monomers can be oxidized simultaneously with amine group of aniline. Thus the polymers have been reported to be insoluble in organic solvents resulting poor processability as well as conductivity. However, synthesis of polyaniline derivative with free $-OH$ or $-NH_2$ active groups may be help full for the processing, doping and sensing applications.

Aromatic amine polymers have attracted much interest of researchers due to their unique multifunctionality, involving variable conductivity, strong electroactivity, colorful electrochromism, good optical properties, magnetic activity, environmental stability and thermal stability (Li *et al.* 2002, Li *et al.* 2009). In the literature phenylenediamine as a monomer had been used very little to synthesize polymer in acidic medium by chemical or electrochemical methods (Premasiri and Euler 1995). Mostly, hydrochloric acid was used for the chemical synthesis of polymers with different oxidants, e.g., persulfate including Na^+ , K^+ , and NH_4^+ persulfates, iodine, H_2O_2 , ceric ammonium nitrate, cupric nitrate etc. (Levin *et al.* 2005, Rivas *et al.* 2002, Salavagione *et al.* 2004, Salavagione *et al.* 2005, Sayyah *et al.* 2002). It can be seen that, the structure, molecular weight and properties of polyphenylenediamine are changed with the chemical or electrochemical polymerization conditions (Li *et al.* 2002). The reports are available on the synthesis of polyphenylenediamine from phenylenediamine in acid medium with little or no importance to its processability and electrical conductivity (Zhou *et al.* 2010, Huang *et al.* 2011, Pham *et al.* 2011). In most cases the researchers are reported that the poly(*o*-phenylenediamine) (PoPD) are insoluble in organic solvents due to ladder structure. A few reports are also focused that the polymer having ladder and/or open ring structure, are slightly soluble in dimethyl sulfoxide (DMSO), *N,N*-dimethyl formamide (DMF), *N*-methyl pyrrolidone (NMP), tetrahydrofuran (THF) and acetone (Li *et al.* 2002). The soluble components of PoPD are assigned to low molecular weight fractions in the literature. On the basis of spectral evidence, the ladder type structure of PoPD is the more acceptable one (Li *et al.* 2002). This ladder PoPD exhibits a low yield, poor solubility, low molecular weight and brittle film forming properties, which hampers further study of the polymer structure and other properties. Copolymerization of *o*PD with other monomer remarkably enhances the solubility, and also leads to new modified copolymers. For example, processable copolymers of *o*PD with various monomers viz. aniline (Li *et al.* 2007), 2,3-xylidine (Li *et al.* 2001), 5-sulfonic-2-anisidine (Li *et al.* 2008), sulfonic phenylenediamine (Lu *et al.* 2007, Huang *et al.* 2012, Huang *et al.* 2013), *o*-phenetidine (Huang *et al.* 2005), etc. have demonstrated a great potentiality for different uses. However, up until now, solubility improvement through copolymerization modifies the original functionality with very low polymerization yield and is not very satisfactory. Therefore, the synthesis of processable polymer containing free $-NH_2$ functional groups from phenylenediamine monomer is important for stable doping or potential application purpose with the help of such type of polar functional groups, just like polyaminophenol (Kar *et al.* 2008, 2009, 2010, 2011).

After an extensive literature survey it appears that PoPD is not a well-established polymer and

there are controversies about polymerization mechanism, final structure and characteristics of the polymer (Li *et al.* 2002). Thus there is enough scope to investigate the structure and characteristics of the PoPD and its polymerization mechanism. In this communication we report the synthesis of PoPD by oxidative chemical polymerization using ammonium persulfate (APS) as an oxidative initiator in aqueous hydrochloric acid medium. The polymer is characterized by intrinsic viscosity measurement, ultraviolet visible spectroscopy, Fourier transform infrared spectroscopy, proton magnetic resonance spectroscopy and thermogravimetric analyses, DC-conductivity measurement.

2. Experimental

2.1 Materials

Crystalline synthesis grade *o*-phenylenediamine (Loba Chemicals, India.) was used as received. Hydrochloric acid (S. D. Fine Chemicals, India), DMSO (Merck, India), DMF (Merck, India), THF (Merck, India), NMP (Merck, India), acetone (Merck, India) were used without further purification. Deionised water was used for synthesis and washing purposes.

2.2 Synthesis of *o*PD mono-hydrochloride salt

*o*PD mono-hydrochloride salt was synthesized by treating the monomer *o*PD with calculated amount of hydrochloric acid. 1.08 g *o*PD was dissolved in 25 ml of exact 0.2 M dilute hydrochloric acid in a beaker at room temperature. The strength of the acid was confirmed after standardization by titration method. On cooling the mixture to 2°C using an ice bath the precipitate of *o*PD mono-hydrochloride salt was separated. However, 10 ml of cold methanol as non-solvent was added to the mixture for complete precipitation of the *o*PD mono-hydrochloride salt. Then, the precipitate was filtered using a Buchner funnel fitted with a water aspirator and it was washed with diethyl ether (approximately 100 ml) to remove unreacted monomer.

2.3 Synthesis of PoPD

PoPD was synthesized by direct aqueous chemical polymerization route from *o*PD mono-hydrochloride salt using ammonium persulfate (APS) oxidant. First 1.445 g *o*PD mono-hydrochloride salt was dissolved in 25 ml distilled water at room temperature with constant stirring. Separately prepared 3.42 g APS solution in 10 ml water was added in one lot into the above solution. In other set into the same solution of monomer salt in water 3.42 g APS solution in 10 ml aqueous (4.2 ml of 20-25% ammonia) ammonia was added at a time. The drop wise addition of oxidant solution is avoided as it leads to lower molecular weight of resulting polymer (Li *et al.* 2002). A deep brown precipitate of PmAP started separating during the initial period of polymerization for both the process. The mixtures were stirred continuously for 10 h at room temperature. The duration for the reactions was optimized after the product reached highest yield and viscosity. During the polymerization the pH change of the reactions medium with time was also measured by using a digital pH meter. The solid polymer mass was filtered the precipitated polymer was washed with water for several times till the filtrate became colorless from light brown color. Finally the deep brown colored polymers from both the batches were dried at 70-80°C in an oven for about 12 h.

2.4 Doping of PoPD

The synthesized PoPD powder was doped with very dilute hydrochloric acid (1 M) by solution doping technique. The PoPD powder was dipped in hydrochloric acid for 24 h at room temperature. Then the powder was filtered and washed with diethyl ether for 2-3 times. The PoPD doped with hydrochloric acid was dried in a vacuum desiccator for a day. The well dried hydrochloric acid doped PoPD powder was made into a thin pellet of thickness about 0.29-0.3 mm using a steel die having 1 cm diameter in a hydraulic press under a pressure of 5 tons.

2.5 Solubility test and film casting

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 2 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). For polymer film casting, about 0.7-0.8 g PmAP was dissolved in 15-20 ml of the solvent and this solution was poured on a Petri dish of diameter 10 cm. Then the Petri dish was placed inside an oven maintained at 100°C for 7-8 h for the evaporation of the solvent.

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2.7 Characterizations

2.7.1 pH Measurement

The pH change of both the reactions medium was measured by using a digital pH meter PH5652 (Electronic Corporation of India Ltd.). The reading was taken by dipping the electrode into the reactions medium at required time interval. Before measurement the pH meter was standardized by using standard buffer solutions.

2.7.2 Viscosity Measurement

The flow times of PoPD solutions in DMSO of varying concentrations were measured using an Ubbelohde Viscometer. The specific viscosity (η_{sp}) was calculated from the flow times by using the relation (Gowariker *et al.* 2005)

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

Where η_r is the relative viscosity, t and t_0 are the flow time for polymer solutions and pure solvent respectively. Then intrinsic viscosity $[\eta]$ of the polymer was determined by extrapolating the straight line in η_{sp}/C vs. C plot to infinite dilution as, according to Huggins equation (Gowariker *et al.* 2005);

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

Where K' is Huggins' constant.

2.7.3 Molecular weight determination by dynamic light scattering (DLS) method

The weight average molecular weights of the synthesized polymers were determined by the dynamic light scattering (DLS) method using Zetasizer Nano Series Nano-ZS, Malvern. Very dilute polymer suspension in DMSO was used after filtering through a Fluoropore filter (Millipore Corp.).

2.7.4 Ultraviolet visible (UV-vis) spectra

The UV-vis spectra of the polymers were recorded using about 0.1% DMSO solution using Mikropack UV-VIS-NIR, DH 2000. The DMSO solvent was taken as a reference.

2.7.5 Fourier transform infrared (FTIR) spectra

In order to get an idea about functional groups present, the FTIR spectra of synthesized polymers powder were recorded in Thermo Nicolet (model number Nexus 870) IR Spectrometer. The spectrum was recorded in the pellet form by mixing the dry powder material with KBr (Aldrich, 99%, FTIR grade) with in the region 400 cm^{-1} to 4000 cm^{-1} .

2.7.6 Proton magnetic resonance (^1H NMR) spectra

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

2.7.7 Thermal analysis

The weight loss of the polymers powder was observed by thermogravimetric analysis (TGA) in a NETZSCH TG 209 F1 instrument under nitrogen atmosphere. The weight loss was recorded from room temperature (30°C) to 500°C at a heating rate of $10^\circ\text{C}/\text{min}$.

2.7.8 DC conductivity measurement

A standard four-point probe (Schroder 1990) system with a Keithley 2400 programmable current sourcemeter was used to measure the electrical conductivity of the doped PoPD pellet. Conducting silver paste adhesive was used at the contact point between the wires and polymer pellet. The voltage changes were measured against an applied current and then conductivity (σ) of the sample was calculated using the equation (Schroder 1990):

$$\sigma = [2\pi s (V/I)]^{-1}$$

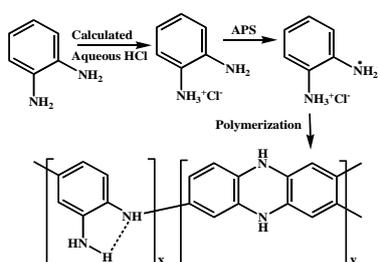
3. Results and discussions:

3.1 Synthesis of polymer

The mono-hydrochloride salt of oPD and the PoPD were synthesized following the procedure described in the previous section. In mono-hydrochloride salt of oPD the protonation occurs in one of the amine functional groups selectively and other remains free (Scheme 1), as calculated amount of hydrochloric acid is added. Similarly, in the aqueous solution of mono-hydrochloride salt only one of the $-\text{NH}_2$ functional groups remains protonated (Scheme 1). After addition of APS, the radical cation formation by an electron transfer from free $-\text{NH}_2$ functional group is

favorable than the electron transfer from the protonated $-\text{NH}_3^+$ functional group (Scheme 1), as oxidation potential steadily increases with increasing acidity (Yacynych and Mark 1976).

It has been reported that, two separate oxidation potential for oPD appears in pH higher than 3 and the separation of the oxidation potential is gradually increased with the increasing pH (Prasad *et al.* 1996). The starting pH of the reaction medium is 4.25 for both the reaction conditions (Fig. 1) and thus, it is expected that only one $-\text{NH}_2$ group is oxidized first selectively. Then, the reaction mediums became acidic within 2-3 min (Fig. 1) due to the formation of sulfuric acid from the



Scheme 1 Proposed scheme of polymerization and structure of the PoPD

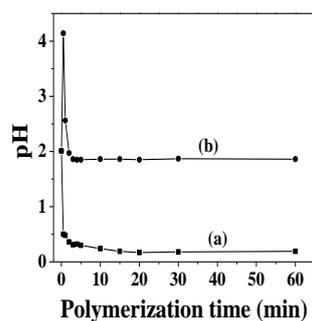


Fig. 1 Change of pH during the polymerization of oPD with time at different reaction conditions (a) using aqueous APS and (b) using aqueous ammoniacal APS oxidant

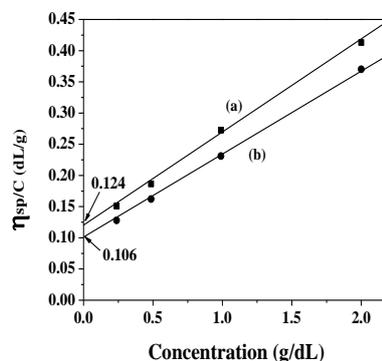


Fig. 2 Intrinsic Viscosity measurement for synthesized PoPD using (a) aqueous APS and (b) aqueous ammoniacal APS oxidant

vigorous reaction of APS and the monomer salt. After this step the pH of the medium is decreased to a steady value of 0.5 when aqueous APS is added as oxidant and 1.8 when aqueous ammoniacal APS is added as oxidant (Fig. 1). To prevent the protonation of other $-NH_2$ groups during polymerization, the ammoniacal APS oxidant is used to consume the byproduct sulfuric acid. Thus, pH of medium for synthesis of PoPD using aqueous APS is more acidic as compared to other one. But, as ammonia acts as a radical inhibitor for this type of polymerization, the yield (40 %) and intrinsic viscosity (0.106 dL/g) (Fig. 2) is decreased for the aqueous ammoniacal APS (Sayyah *et al.* 2002). The yield and intrinsic viscosity (Fig. 2) value for synthesized PoPD by using aqueous APS as oxidant is 58% and 0.124 dL/g respectively. However, all the polymers have shown straight line (Fig. 2) conforming to Huggins equation (Gowariker *et al.* 2005). Again using 1:2 (mole/mole) monomer:aqueous APS, the solid polymer separated in the polymerization medium with slightly higher yield (60%) but the isolated polymers became slightly soluble in organic solvents (DMSO, DMF). It can also be supported from the weight average molecular weight of 4000 Da for PoAP synthesized in ammoniacal APS medium and 7000 Da for PoPD synthesized in aqueous APS medium measured by DLS method. This happened because the excess APS oxidized the other $-NH_2$ groups also and ultimately ladder type structure containing very few free $-NH_2$ groups develops. Whereas, in the synthesized PoPD using mono-hydrochloride salt of oPD and 1:1.5 monomer:APS (mole/mole) in aqueous medium contains also few ladder units within the structure (Scheme 1) due to uncontrolled oxidation of both the functional groups in the higher acidic medium. However, the molecular weight of the synthesized polymers is only slightly increased than that of the reported molecular weight of the PoPD (Li *et al.* 2002).

3.2 Solution processability of the polymers

The synthesized polymer is found to be well soluble in strong acidic medium, DMSO, DMF, NMP and sparingly soluble in dilute acid, tetrahydrofuran. In the literature, the low molecular weight fractions of PoPD having ladder structure assigned as soluble components in dimethyl sulfoxide (DMSO), N,N-dimethyl formamide (DMF), N-methyl pyrrolidone (NMP), tetrahydrofuran (THF) and acetone (Li *et al.* 2002). As the synthesized polymer contains polar free $-NH_2$ functional groups with very few ladder units, it become soluble in strong acid and polar organic solvents, e.g., DMSO, DMF, NMP. However, the film casting of the synthesized polymers from the DMF or DMSO solution is difficult due to presence of quinone impurity, which can be confirmed from the spectral analysis. The polymer only gives brittle mechanically weak film from DMSO or DMF. So, from the characterization it can be said that although the solution processability of the synthesized polymer is improved but it gives brittle film due to low molecular weight product.

3.3 UV-vis

The UV-vis spectroscopy is a useful characterization to estimate the electronic structure of electrically conducting polymers. Both the synthesized polymers show only one absorption maxima at 429 nm in UV-VIS spectra, as shown in Fig. 3. The absorption band is attributed to a $\pi-\pi^*$ transition associated with the phenazine unit conjugated to long pairs of bridging nitrogens (Premasiri and Euler 1995). However, in UV-vis spectra other possible $\pi-\pi^*$ or $\pi-\sigma^*$ absorption for C=O group of quinone impurity having absorption maxima at around 300-400 nm (Fig. 3) is imposed with the above band (Kar *et al.* 2010). In the UV-vis spectra any other absorption band

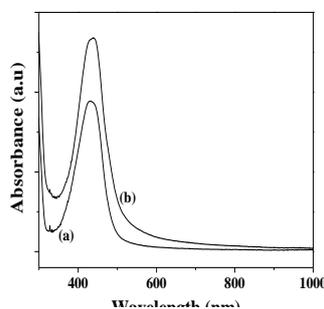


Fig. 3 UV-vis spectra of synthesized PoPD using (a) aqueous APS and (b) aqueous ammoniacal APS oxidant

like polaron absorption band is not observed, which is the characteristic band for in-situ acid doped polyaniline derivatives. The UV-vis spectra of the polymers confirm that the structure obtained for both the synthesized polymers are same and the synthesized polymers are not in-situ doped with used acid.

3.4 FTIR spectra

In order to study the functional group present with in the structure of the synthesized FTIR analysis was performed. The characteristic vibrational bands obtained from FTIR spectra of both the polymers are exactly identical as shown in Fig. 4. So we can say that the structural change is not obtained for the polymers synthesized using aqueous APS or aqueous ammoniacal APS. A broad band appears in the region 3690 cm^{-1} to 2250 cm^{-1} is due to the stretching of aromatic C–H, hydrogen bonded –NH_2 , and –NH– groups. The –NH_2 group is hydrogen bonded with nearest nitrogen of –NH– group present in the polymer chain and so –NH_2 absorption band appears at about 3225 cm^{-1} as a broad peak. There are pair of bands at 1615, 1525 and at 1373, 1243 cm^{-1} due to stretching vibrations of quinoid C–C, benzenoid C–C and quinoid C–N, benzenoid C–N (Huang *et al.* 2001) bonds respectively. The band at 1691 cm^{-1} appears due to stretching C=O bond of quinone impurity, which is present in the synthesized polymers. The UV-vis spectra confirms the identical structure for both the synthesized polymer and the polymer contains most of the free –NH_2 functional groups in the structure, as shown in Scheme 1.

3.5 ^1H NMR spectrum

All the polymers showed identical ^1H NMR spectra like that of Fig. 5. In ^1H NMR (Fig. 5) spectrum of the polymer, chemical shift for three aromatic hydrogens appear at $6.8\ \delta$ (multiplet), $7.5\ \delta$ (multiplet) and $7.8\ \delta$ (multiplet). As the sample gives the signals of three aromatic hydrogens in ^1H NMR spectrum, the ladder structure having only two hydrogens is not formed or formed very little (Scheme 1). The terminal –NH_2 groups, give a broad peak at $5.6\ \delta$ as doublet and another broad doublet peak is observed at $5\ \delta$ due to the hydrogen bonded –NH_2 functional groups with in the polymer chain (Scheme 1). Other two strong singlet peaks are present at $6.23\ \delta$ and $6.9\ \delta$ for the –NH– groups of ladder units and –NH– groups holding benzene units with free –NH_2 functional groups, respectively (Scheme 1). Two other weak chemical shifts appear at $6.6\ \delta$ and $7\ \delta$ probably due to the aromatic CH (quinone) of o-quinone byproduct present with in the PoPD

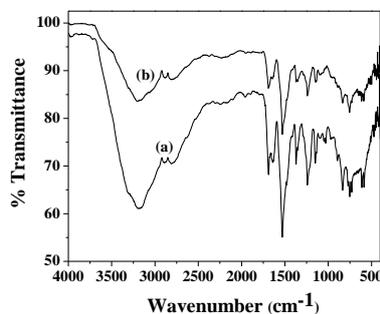


Fig. 4 FTIR spectra of synthesized PoPD using (a) aqueous APS and (b) aqueous ammoniacal APS oxidant

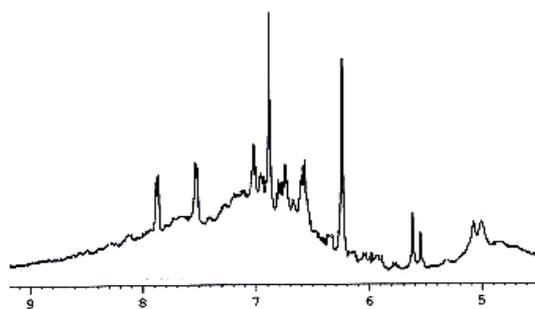


Fig. 5 ^1H NMR spectrum of synthesized PoPD

(Fig. 5) product as impurity. The weak signal for two aromatic hydrogens of ladder units is probably imposed on other aromatic hydrogen signals and so the signals are broad in nature.

From the derivation of the ^1H NMR peak we can also estimate the structure of the synthesized polymer. The proton ratio for terminal $-\text{NH}_2$ with hydrogen bonded $-\text{NH}_2$ with in the polymer chain is 0.24:3.6. As both the groups contain two hydrogens, the number of hydrogen bonded $-\text{NH}_2$ group is $(3.6/0.24) \times 2 = 30$ per two terminal $-\text{NH}_2$ groups, considering the groups in both end of single polymer chain. Considering the two terminal repeating unit with free $-\text{NH}_2$ the total number is $(30+2) 32$. The proton ratio for $-\text{NH}-$ holding benzene units with free $-\text{NH}_2$ functional groups and $-\text{NH}-$ of ladder units is 4.8:1. As two similar $-\text{NH}-$ groups are present per ladder unit so, we can said that in the polymer structure the ladder unit is repeated after around 10 ($4.8 \times 2 = 9.6$) benzene rings with free $-\text{NH}_2$ functional groups. Thus in a polymer chain of 32 structural repeating units, the calculated number of ladder units is approximately 3 ($32/10$).

3.6 TG analysis

The thermal stability of both the synthesized PoPD is explained in TGA traces. The thermal behaviors of both the polymers are exactly same, as shown in Fig. 6. The polymer shows an initial 1-2% weight loss up to 90°C due to the release of moisture present in the sample. In the TGA trace of the polymers a sudden weight fall is observed at around 270°C , which may be consider as degradation temperature for the polymers. The degradation temperature is some what lower than that of the reported polymers of phenylenediamine isomers (Li *et al.* 2002). The reason of weight

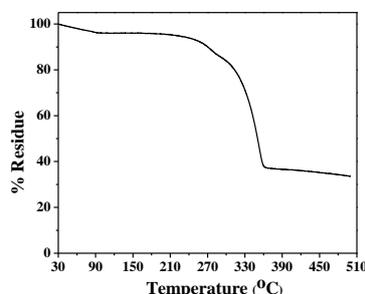


Fig. 6 TGA traces of synthesized PoPD

loss at that temperature might be due to the release of some decomposition products, possibly the substituted -NH_2 function groups of the polymers. From the TGA experiment it may be said that the synthesized polymer shows good thermal stability up to 270°C.

3.7 Doping and DC conductivity

The undoped polymer pellet shows an average conductivity $<10^{-11}$ S/cm. The hydrochloric acid doping is possible for the synthesized polymer following the same solution doping procedure like polyaniline and its derivatives. The average DC conductivity of hydrochloric acid doped PoPD pellet is 2.8×10^{-4} S cm^{-1} , which is better than the reported conductivity of in-situ doped polyphenylenediamines synthesized from acid medium (Li *et al.* 2002). However, we have already reported critical doping process for poly-m-aminophenol due to the presence of hydrogen bonded phenolic free -OH groups in the polymer. The structure of the synthesized PoPD is quite similar to that of our previous report poly-m-aminophenol (Kar *et al.* 2008, 2009) and here also the hydrogen bonding is present in the PoPD structure (Scheme 1). Still the doping process is simple like polyaniline and its derivative but not like poly-m-aminophenol (Kar *et al.* 2008, 2009), which is probably due to the protonation in the polar basic free functional -NH_2 groups of the polymers. This doping and electric conduction is a type of induced doping like sodium ion doping in poly-m-aminophenol (Kar *et al.* 2008, 2009). However, the further detail studies on the hydrochloric acid doped PoPD is needed before any concrete explanation, which is the future scope for the work.

4. Conclusions

In conclusion, processable PoPD was successfully synthesized from the corresponding oPD monomer. The yield and intrinsic viscosity of the synthesized PoPD was less for the aqueous ammoniacal APS oxidant than aqueous APS oxidant. The structure of the polymer, confirmed from the spectral analysis, was just like polyaniline derivative with free -NH_2 functional groups. However, some ladder unit was also present within the polymer backbone. Due to the presence of free polar -NH_2 functional group substitution the synthesized polymer was well soluble in polar organic solvent like DMSO and DMF. The synthesized PoPD had low molecular weight due to

presence of o-quinone by product as impurity. For same reason the PoPD gave brittle film form DMSO or DMF. The polymer showed only moderate thermal stability up to 270°C. The pellet of PoPD doped with hydrochloric acid was shown an improved conductivity (2.8×10^{-4} S/cm) than that of the reported polymer.

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