Indian Journal of Chemistry
Vol. 64, January 2025, pp. 38-42
DOI: 10.56042/ijc.v64i1.13995

Synthesis, characterization and fluorescence spectral studies of poly (diphenylamine-aminophenol) copolymers using a reactive surfactant

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Received 26 September 2024; accepted(revised) 27 December 2024

Poly (*para*-diphenylamine-co-*ortho*-aminophenol) copolymers have been synthesized through oxidative polymerization with sodium dodecylsulphate as the emulsifying agent. The synthesized copolymer has been characterized using UV-Visible spectroscopy, FT-IR, XRD, SEM and TG-DTA and DSC. The UV-Vis shows the peak at 273 nm due to the $\pi \rightarrow \pi^*$ transition which is related to the extent of conjugation between the adjacent phenylene rings in the polymeric chain. A broad peak that shows in the area of 3850 cm^{-1} is due to hydrogen-bonded –OH and $-NH_2$ groups. Two main peaks between 1564 and 1484 cm^{-1} refer to the ring stretching vibrations of the quinoid and benzenoid rings, respectively. The XRD studies confirm the polymer has semicrystalline nature. The SEM analysis of the copolymer exhibits cluster like arrangement on the rough surfaces and wide dispersion, without any regularity in shape. The TGA illustrate there exists three stages of weight loss. The polymer is found to be thermally stable till 518°C with the residual mass of 0.48%. The fluorescence spectroscopy data shows that synchronous scanning for both excitation and emission peaks at 399 nm.

Keywords: Diphenylamine, Aminophenol, Copolymer, TGA, Fluorescence

Intrinsically conducting polymers (ICPs) are organic materials that are characterized by the presence of π conjugated electronic system in their backbone. Polyaniline (PANI), and their derivatives have attracted the interest of researchers in multidisciplinary fields primarily for their unique structural and electronic properties[1]. Polymers with conjugated π-electron (*i.e.* system have C=C conjugated bonds) backbones display unusual electronic properties such as low energy optical transition, low ionization potentials, and high electron affinities. The result is a class of polymers that can be oxidized or reduced more easily and more reversibly than conventional polymers. The effect of this oxidation or reduction on polymer is called doping, *i.e.* convert an insulating polymer to conducting one[2]. Doping is the unique, central theme that distinguishes conductive polymers from all other types of polymers. Reversible doping of conductive polymer, associated with control of the electrical conductivity over the full range from insulator to metal (typically from 10^{-10} S/cm to 10^{5} S/cm), can be accomplished either by chemical or by electrochemical methods[3]. The doping and de-doping of the conducting polymers leads to a wide range of promising applications in the field of energy storage, electro-catalysis, organic electrochemistry, electro-analysis, sensors and corrosion protection[4]. In the present work, Poly Diphenylamine – Aminophenol (PDA-AP) copolymers were synthesized using a reactive surfactant and were characterized and the fluorescence studies were carried out.

Experimental Section

Diphenylamine, aminophenol, sodium dodecyl sulphate, ammonium persulphate were purchased as an analytical grade from *Nice* and used as received.

Synthesis of Poly DiphenylAmine- Co-AminoPhenol P(DPA-AP)

The copolymer of Poly DiphenylAmine-Co-AminoPhenol P(DPA-AP) was synthesized in emulsified systems using the reactive surfactant sodium dodecyl sulfate (SDS), as the emulsifying agent. For copolymerization, the molar ratio was 1.0:1.0:0.5 (DPA:AP:SDS). A typical experiment was conducted as follows: In a 500 ml round-bottomed flask, first, *para*-diphenylamine and *ortho*-aminophenol and monomers with equimolar ratio were dissolved in absolute ethanol separately through magnetic stirring. The reaction was carried out at

60°C. To start the polymerization reaction of ammonium persulfate, 0.25 M hydrochloric acid solution was added in a 1.0:1.0 molar ratio relative to the total amount of monomer. The polymerization reaction was carried out for six hours. The reaction mixture was left over night; ethanol was poured to stop the polymerization, then filtered and washed with water for several times. The product shows a black color[5,6].

Characterization of synthesized P(DPA-PA)

The UV–Vis spectra of the synthesized P(DPA-AP) was recorded using a Systronics UV–Vis spectrophotometer, FTIR spectra was recorded by Jasco FT-IR at the range of 400- 4000cm^{-1}. The XRD studies of P(DPA-PA) are characterized by BRUKER AXS. The diffraction system based with Cu tube anode with voltage 40kV, current 35mA and wave length α 1 K = 1.5418 Å. The start angle (2θ) was 5° and the end angle was 80°. Bragg's Law ($n\lambda = 2d \sin\theta$) was used to compute the crystallographic spacing. The SEM images were recorded using JEOL JSM 5600 LV SEM and magnification rate of 1500 to 15000 units at 20 KeV. The thermal studies as TGA/DTA and DSC were carried out with NETZSCH DSC 204 F1PHOENIX build 101 at the heating rate of 10ºC min^{-1} at the temperature range of 30° - 1300°C under nitrogen atmosphere. The Fluorescence Spectroscopy were carried out with JY Fluorolog-3-11 by using Xenon lamp as the source, at the range 180-850 nm and the detector PMT for UV and Visible (180 to 850 nm) region.

Results and Discussion

UV–Vis spectra of P(DPA-AP)

The UV–Vis spectrum of the P(DPA-AP) is shown in Fig. 1a. The UV-Vis spectra of P(DPA-AP) shows strong absorption peak at 241 nm and 276 nm exhibiting π →π* transition, the peak at 347 nm is attributed to polaron band → π*and the peak at 594 nm is due to π* → polaron transition. These bands are due to the localized polaron band of doped P(DPA-AP) in its emeraldine salt form[7].

FT-IR spectra of P(DPA-AP)

The FT-IR spectra of P(DPA-AP) is given in Fig. 1b and the bands at 1882, 1728 and 1696 cm^{-1} region represent a series of weak combination and overtone bands and the pattern of the overtone bands reflects the substitution pattern of the benzene ring. Skeletal vibrations, representing C=C stretching, absorb in the 1484cm^{-1} range. The C–H bending bands are in the regions of 1221 cm^{-1} (in-plane bending) and 892 cm^{-1} (out-of plane bending). The

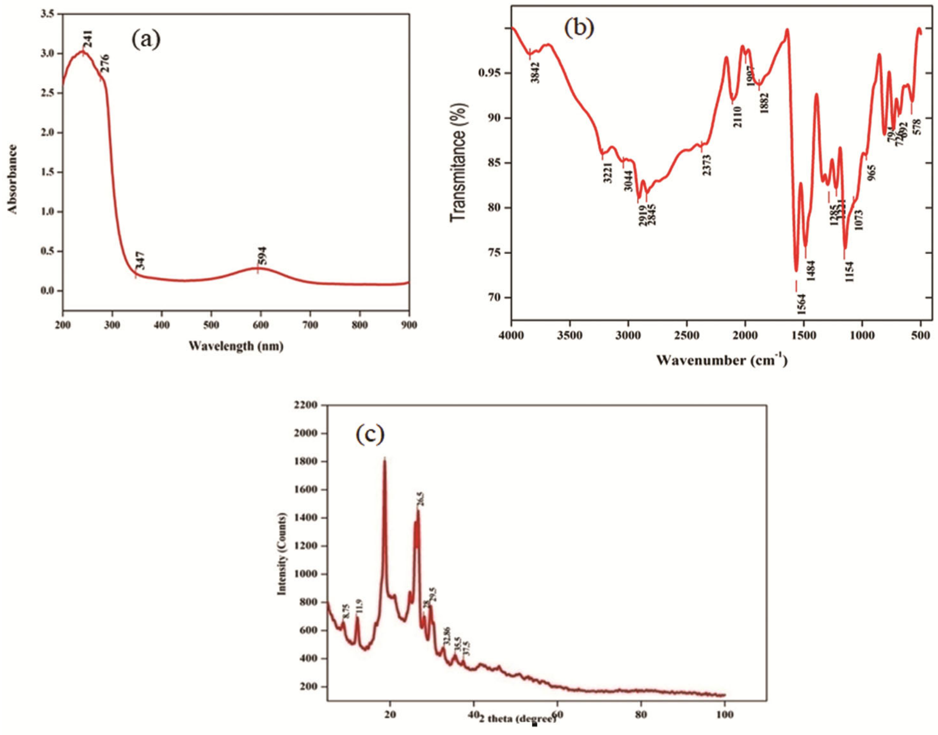

Fig. 1 — (a) UV-Vis spectra of P(DPA-AP) (b) FT-IR spectra of P(DPA-AP) (c) XRD of P(DPA-AP)

major IR absorption bands at 3221 cm^{-1} is for N–H bond. The presence of O-H band is confirmed by the band at 3842 cm^{-1}. The band at 1564 and 1484 cm^{-1} are the characteristic bands due to quinonoid–benzenoid rings C-C stretching of quinonoid rings and benzenoid rings, respectively, The band at 1440 cm^{-1} is assigned to N-H bending. The band at 1319 cm^{-1} corresponds to stretching of C–O. The band at 1221 and 965 cm^{-1} are attributed to the aromatic C–H in-plane bending and out-of-plane deformation of C–H in the substituted benzene ring[8].

XRD of P(DPA-AP)

The XRD patterns of P(DPA-AP) shown in Fig. 1c has six peaks with maximum intensity at 2θ: 8.75°, 11.9°,18.7°, 26.5°,28° and 29.5° and has a similar profile as reported in the literature for polyaniline. The peak at 26.5° of 2θ can be assigned to scattering from polyaniline chains at interplanar spacings[9] confirming that the P(DPA-AP) is semicrystalline nature. The ratio of half-width to height (HW/H) of an X-ray diffraction peak reflects the order of the polymer crystallinity. The crystallinity and orientation of conducting polymers have been of much interest, because more highly ordered systems can display a metallic conductive state and may influence the anticorrosion performance. However, the diffractive peaks of poly diphenylamine and aminophenol obtained using conventional polymerization have become weak, which indicates that the degree of crystallinity is decreased[10]. From the XRD data, the crystalline size can be determined using the Scherrer and shown in the Table 1. The crystalline sizes of P(DPA-AP) at different 2θ value were found to be 0.525 nm, 0.245 nm, 0.197 nm, 0.179 nm, 0.144 nm, 0.027 nm, 0.187 nm and 0.531nm, respectively[11]. The least crystalline size was found to be 0.027 nm at 28° of 2θ.

SEM of P(DPA-AP)

The SEM images of P(DPA-AP) are shown in the Fig. 2 at different magnification. P(DPA-AP) as the copolymer exhibited cluster like arrangement on the rough surfaces and wide dispersion, without any regularity in shape[12] with porous nature.

Thermo Gravimetric Analysis(TGA)of P(DPA-AP)

The thermal stability of the P(DPA-AP) was examined by TG/DTA and is shown in Fig. 3a. The

Table 1 — XRD data of P(DPA -PA)

Pos. [°2 θ]	Height [cts]	FWHM [°2 θ]	d-spacing [Å]	Rel. Int. [%]	Crystalline size (nm)
12.18	204.2	0.535	7.265	15.97	0.525
14.39	8.871	0.401	6.154	0.69	0.245
18.75	258.3	0.200	3.597	20.2	0.197
26.58	784. 9	0.200	3.416	61.39	0.179
29.67	917.2	0.200	3.341	71.73	0.144
28.13	176.6	0.401	3.171	13.82	0.027
35.52	75.99	0.401	2.526	5.94	0.187
37.47	47.28	0.535	2.401	3.7	0.531

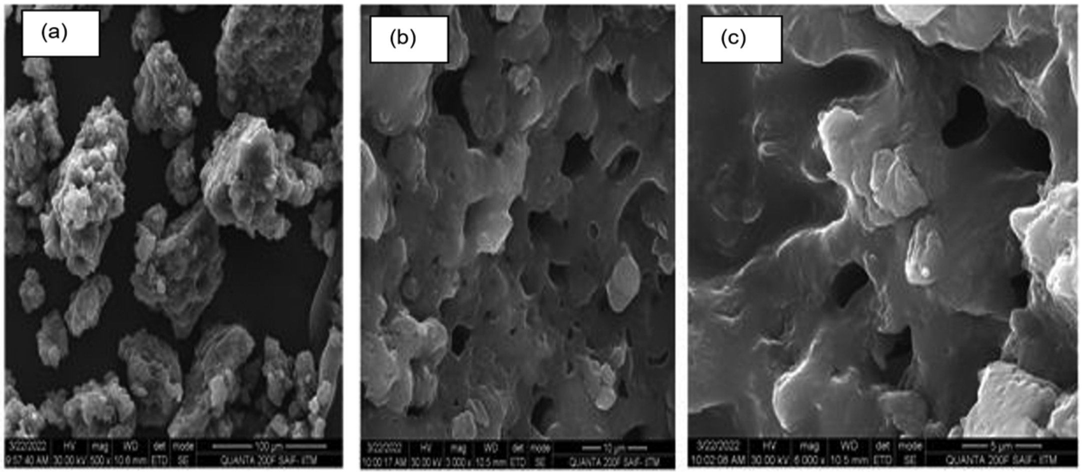

Fig. 2 — SEM images of P(DPA-AP) a 100µm, b.20 µm and c.5 µm at different magnification

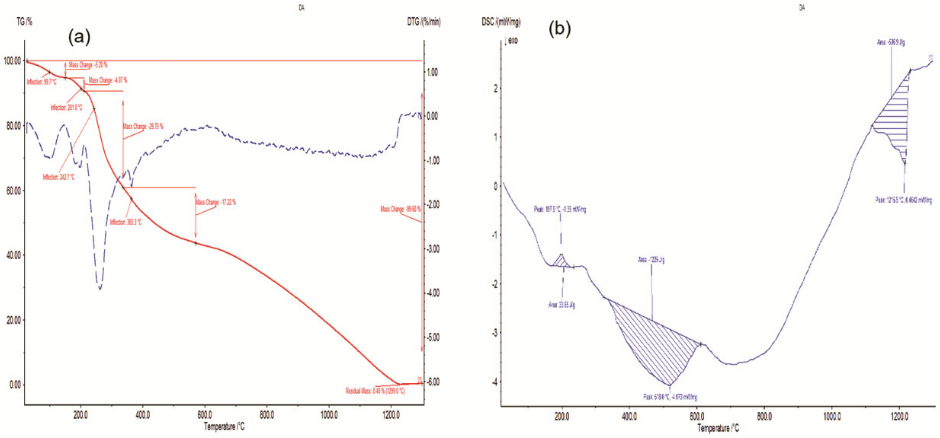

Fig. 3 — (a) TGA of P(DPA-AP) (red) and -DTA (blue) (b) DSC of P(DPA-AP)

P(DPA-AP) was compared to polydiphenylamine synthesized from sulphuric acid, H_2SO_4–tert-butanol mixture. However, magnitudes of steps corresponding to the initial weight loss turn out to be different. For the polymer synthesized through the interfacial polymerization, the initial weight loss is ~15% and while for polydiphenylamine prepared in the H_2SO_4–tert-butanol mixture, this value is as high as ~55%[13]. This difference is caused by different contents of low-molecular-mass oligomers in the polymers synthesized by various methods[14].

The TGA curve (Fig. 3a, blue curve) shows four stage weight loss. At first, the mass loss comes from the loss of water molecules and then it is increased due to the loss of oligomer. The first mass loss of 5.2% occurring in the range of 25 – 100°C may be attributed to the sublimation process removal of water molecules present in the polymeric chain[68]. The second stage is the removal of dopants and degradation of main chain mainly occurring in the temperature range of 100 - 200°C. The inflection was at 201°C with a mass change of 4.07% corresponding to removal of oligomeric portions with low molecular weight polymer or oligomer from the polymer matrix. P(DPA-AP), decompose at the temperature range of 200 - 600°C[15], and the inflection was at 363.3°C of 29.75% related to the weight loss corresponding to the decomposition of the P(DPA-AP) backbone. The final stage is from 600-1400°C, with the mass change of 99.6% and residual mass of 0.4% is attributed to the burning of elemental carbon formed in the second step. P(DPA-PA) exhibit four stages of weight loss. In the main processes of P(DPA-AP), degradation begin at 200-600°C that corresponds to temperature in the case of poly(p-phenylene) 250-500°C. At 560°C, P(DPA-AP), loses half of its initial weight, confirms that the P(DPA-AP), has high thermal stability when compared to other doped polyaniline[16].

DTA of P(DPA-PA)

The DTA curve is illustrated in the Fig. 3(a), blue curve. The first endothermic peak corresponds to the dehydration of the polymer. The second exothermic peak corresponds to the decomposition of the polymeric chain with the decarboxylation and the third endotherm corresponds to the crystallization process of the degraded polymeric chain[17].

DSC of P(DPA-AP)

The different phase temperature was observed from DSC curve represented in the Fig. 3b and the glass transition temperature T_g was at the range 99ºC, T_c was found to be at 197ºC. The P(DPA-AP), exhibit three exotherms in comparison with the both exotherms, the first exotherm was observed at around 197ºC and was attributed to the T_c value representing the decomposition of P(DPA-AP) content in the polymer. This exotherm showed a shift to a higher temperature region of 518ºC corresponding to the T_m in comparison with the decomposition nature[18]. The exothermic peak at 1215ºC is at the melting temperature T_m.

Fluorescence spectra of P(DPA- PA)

Fluorescence spectra of P(DPA- PA) shows (Fig. 4) both the excitation and emission peaks. The excitation is maximum at 399 nm, and only one single synchronous band at 399 nm was obtained.[19] The absorption band at 399 nm, with maximum is generally assigned to n→π* transitions mixed with π→π* transitions of the phenyl groups[20].

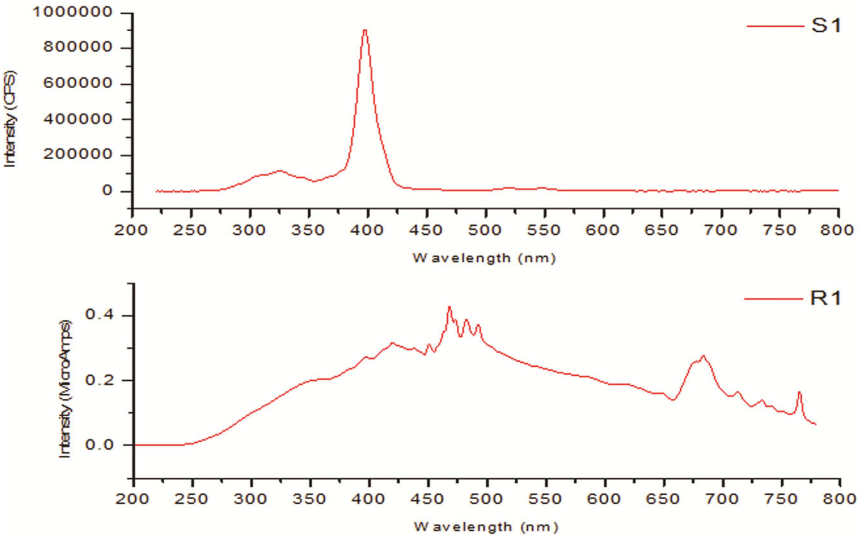

Fig. 4 — Fluorescence spectra of P(DPA-PA)

Conclusion

The present research work comprises of the synthesis and characterization of Poly Diphenylamine–Co-Aminophenol (PDPA-PA) by chemical oxidative polymerization. The UV–Vis spectra reveal the presence of both benzenoid and quinonoid transitions responsible for conducting polymers. The FT-IR spectra confirms the presence of secondary –NH stretching. The XRD data substantiate the semicrystalline nature. The crystalline size was calculated using the Debye – Scherrer formula. The SEM images of (PDPA-PA) had cluster like arrangement. The polymer was found to be thermally stable till 518°C with the residual mass of 0.48%. From fluorescence spectra, the excited and the emission peaks confirms that the synthesized polymer can be widely used in the field of electrochromic sensors.

Acknowledgement

The author acknowledges the instrument facilities provided by the SAIF, IIT-Madras and NRC, SRMIST Chennai.

References

1 Zhang H, Li X, Zhao C, Fu T, Shi Y & Na H, *J Mem Sci,* 308 (2008) 66.
2 Niu Z, Bruckman M A, Li S, Lee L A, Lee B, Pingali S V, Thiyagarajan P & Wang Q, *Langmuir*, 23 (2007) 6719.
3 Ziadan K M, Haykaz K A & Abudalla A Q, *Energy Procedia*, 18 (2012) 1059.
4 Grubbs R B, *J Poly Sci Part A: Poly Chem*, 43 (2005) 4323.
5 Zoromba M S, Abdel-Aziz M H, Bassyouni M, Attar A & Al-Hossainy A F, *J Mol Struct,* 1225 (2021) 129131.
6 Slimane A B, Al-Hossainy A F & Zoromba M S, *J Mat Sci Mat Elec*, 29 (2018) 8431.
7 Jana T & Nandi A K, *Langmuir*, 16 (2000) 3141.
8 Guay J & Dao L H, *J Elec Chem Interfac Electrochem,* 274 (1989) 135.
9 Abdiryim T, Xiao-Gang Z & Jamal R, *Mater Chem Phys,* 90 (2005) 367.
10 Kim Y, Lee J, Kang H, Kim G, Kim N & Lee K, *Sol Energy Mat Sol Cells*, 98 (2012) 39.
11 Zaragoza-Contreras E A, Hernández-Escobar C A, Estrada-Monje A & Kobayashi T, *Syn Met*, 214 (2016) 5.
12 Kim M H, Bae D H, Choi H J & Seo Y, *Poly J*, 119 (2017) 40.
13 Ozkan S Z, Karpacheva G P, Orlov A V & Dzyubina M A, *Poly Sci Ser B,* 49 (2007) 36.
14 Orlov A V, Ozkan S Z, Bondarenko G N & Karpacheva G P, *Poly Sci Ser B*, 48 (2006) 5.
15 Showkat A M, Cao X T, Kim D W, Islam M R & Lim K T, *Mat Sci Eng*, 77 (2015) 012007.
16 Veerakumar P, Madhu R, Chen S M, Veeramani V, Hung C T, Tang P H & Liu S, *J Mater Chem A*, 2 (2014) 16015.
17 Raj, Michael Ruby, et al. *Int J Poly Mat,* 62 (2013) 23.
18 Waware U S, Hamouda A M S & Majumdar D, *Poly Bull*, 76 (2019) 5603.
19 Barbero C, Silber J J & Sereno L, *J Electroanal Chem Interfac Electrochem,* 263 (1989) 333.
20 Mu S, *J l Electroanal Chem*, 743 (2015) 31.