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Chemical Oxidative Polymerization of 1,3-Phenylenediamine Dichloride in Aqueous Solution: Synthesis and Characterization

Feyza KOLCU[1,2*], İsmet KAYA[2]

Highlights:

- 1,3-phenylenediamine dichloride was oxidatively polymerized in water.
- The polymer exhibited green light emission.
- Quantum yield was calculated as 11.2%.
- The LOI value of 34.31for the polymer exhibited a low flammability with excellent thermal stability.

Keywords:

- Aromatic diamine
- Oxidative polymerization
- Green light emission
- LOI

ABSTRACT:

An aromatic diamine compound of 1,3-phenylenediamine dichloride (monomer), containing two polymerizable functional groups was submitted to selective polymerization in water via oxidative coupling polymerization with sodium hypochloride as the oxidant. Characterization of the synthesized polymer was performed utilizing UV-Vis, FT-IR, SEM, and photoluminescence techniques, identifying benzeneoid an quinoid units along the polymer chain. Based on the results of Gel Permeation Chromatography (GPC) analysis, the synthesized compound was identified as being in a polymeric form. The number of repeating units, as determined from M_w and M_n, was calculated as 151 and 86, respectively. Under visible light excitation, the polymer exhibited green light emission with a quantum yield of 11.2% in DMF. The monomer is oxidized via oxidative polymerization to a polymer with a higher electrochemical band gap. Scanning Electron Microscopy (SEM) revealed that the polymer particles with polyhedral and irregular sharp edges as well as spherical in the range from micro to nanometer in size were exhibited in the morphology of polymer.

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INTRODUCTION

Conjugated polymers (CPs) have been extensively investigated by numerous researchers [Deng, 211; Wen et al., 2019]. To date, this class of polymers has garnered significant attention due to its advantageous characteristics and broad applicability across various fields. Notably, the optical and electronic properties of these polymers can be readily modified through alterations in the organic precursors or synthetic methods, presenting a distinct advantage over inorganic materials [Baran and Saçak, 2017]. Given their favorable processability, conjugated polymers are widely utilized in the production of electronic materials, including accumulators, conductive coatings, solar cells, rechargeable batteries, photoreceptors, ion exchangers, photodiodes, sensors, electrochromic devices, and light-emitting diodes [Tatum and Luscombo, 2018; Zhuang et al., 2021].

Polyaniline (PANI) posesses a significant category of conjugated polymers, acclaimed for its outstanding optical and electronic properties, as well as its notable environmental stability and low coast (Shenashen et al., 2011). PANI has demonstrated a wide range of practical applications, including use in electrochromic devices, biosensors, light-emitting diodes, and battery electrodes (Gerard et al., 2002; Silva et al., 2005; Borole et al., 2006). PANI is an electrically conductive polymer that can be readily synthesized through the chemical oxidation of aniline, typically in aqueous medium (Stejskal et al., 1995).

Aromatic diamine conjugated polymers exhibit unique functionalities compared to polyanilines, including notable electroactivity, conductivity, and impressive electrochromic activity. Polyphenylene diamines have been investigated for applications in electrochromic devices, electrode materials, and sensors (Samantha et al., 2016). These polymers are π- conjugated polymers that enable conductivity through π-bond delocalization (Samantha et al., 2017). Aromatic diamines are highly susceptible to oxidative polymerization, which can involve the oxidation of one or both -NH_2 units, resulting in the formation of ladder poly(phenazine) or poly(aminoaniline) within the polymer chains (Zoromba, 2017; Zoromba & Abdel-Aziz, 2017). The synthesis of aromatic diamine polymers through the oxidation of one or both amino groups, resulting in structures with open rings or ladder structures (Samantha et al., 2017). Researchers have shown keen interest in the optoelectronic features of polypheneylene diamines, which are conducting polymers. These compounds have been studied in nanoscience and nanotechnology for applications such as polymer solar cells and polymer light-emitting transistors (da Rocha Rodrigues et al., 2020; Hwang et al., 2016). The polymer could be synthesized in one-step through C-C or C-N couplings by chemical oxidative polymerization route using NaOCl as the oxidant, resulting in cheap, easy, and one-pot synthesis of polymer.

The progress of low coast, convenient and eco-friendlier procedures for the synthesis of CPs is one of the goals followed by the researchers in this area. The efforts are to reduce the environmental impacts and toxic by-products, in line with the necessities of green chemistry (Marrocchi et al., 2016). To synthesize conjugated polymers through chemical oxidative polymerization to reach economic viability (Giraud et al., 2022), sustainable routes to conjugated polymers have been investigated by developing green polymer chemistry.

Based on the explanations above, this study focused on the synthesis and characterization of oxidatively polymerized compound derived from 1,3-phenylenediamine dichloride (PD) in an aqueous medium, thereby contributing to the field of chemistry. The polymer exhibiting C-N couplings was synthesized, and the product was readily isolated through chemical oxidative polymerization. Sodium hypochlorite (NaOCl) served as the oxidant in the oxidative polymerization reaction, facilitating a straightforward, cost-effective, and one-pot synthesis of polymer. The synthesized polymer exhibited green light emission upon visible light excitation. In the chemical oxidative polymerization of PD, the oxidation of phenylenediamine produces cationic radicals, leading to the formation of *ortho*-coupled or head-to-tail units via C-N linkage formation, culminating in a polymer. PL, TGA, UV-Vis, DSC, and CV techniques were conducted to evaluate the photoluminescence, thermal, and electrochemical features of the polymer.

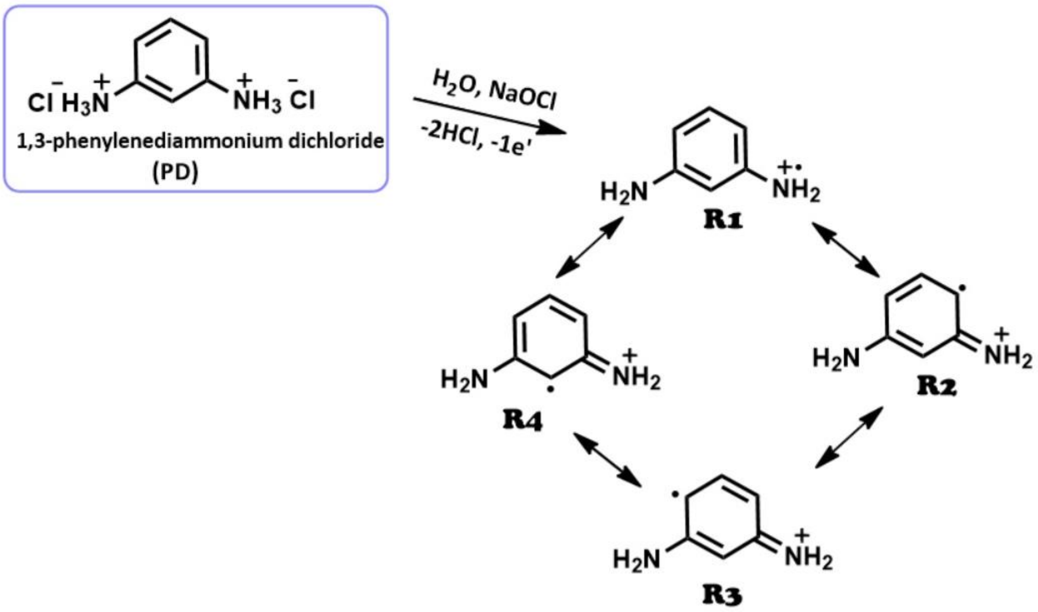
MATERIALS AND METHODS

Materials

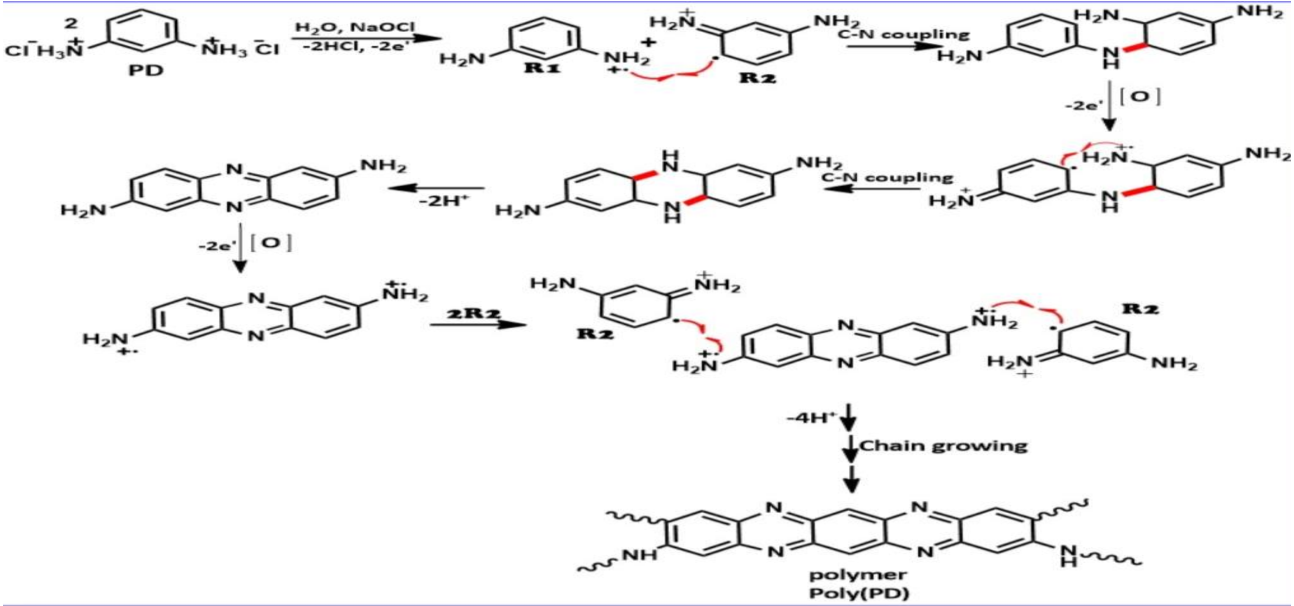
Merck Chemical Co. (Germany) supplied 1,3-phenylenediamine dichloride (PD; 99%), dimethyl sulfoxide (DMSO), acetonitrile (CH_3CN), tetrahydrofuran (THF), ethanol (EtOH), heptane, hexane, N,N-dimethylformamide (DMF), tetrabutylammoniumhexafluorophosphate ($TBAPF_6$), and 30% aqueous solution of sodium hypochloride (NaOCl), used as received.

Chemical oxidative polymerization of 1,3-phenylenediamine dichloride

Oxidative polycondensation was carried out using NaOCl as the oxidizing agent. The polymerization reaction was conducted in a 100 mL of three-necked round-bottom flask equipped with a thermometer, a condenser, and a magnetic stirrer. Approximately 0.905 g (5 mmol) of 1,3-phenylenediamine dichloride (PD) was dissolved in 30 mL of distilled water. To this solution, 1 mL of NaOCl was added dropwise over a period of 20 min. The reaction mixture was then refluxed at 50 ^{o}C for 15 h. The precipitated product was filtered to remove unreacted reactants, which were washed away with 100 mL distilled H_2O three times. A subsequent drying the polymer (poly(PD)) was performed in a vacuum oven at 45 °C, yielding 21%. The radical species formed through chemical oxidative polymerization and the proposed synthetic mechanism are outlined in Scheme 1 and Scheme 2.



Scheme 1. Radical Species of PD Through Chemical Oxidation



Scheme 2. Proposed Mechanism for the Polymer Synthesis

Instruments

A solubility test was conducted with 1 mg of poly(PD), thoroughly dispersed in 1 mL of solvent. The functional groups of PD and poly(PD) were characterized using a PerkinElmer FT-IR Spectrum One, equipped with an ATR accessory, adjusting the spectral region to 4000-400 cm^{-1} and the spectral resolution was 4 cm^{-1}. The molecular weight distribution of the poly(PD) was determined by Gel Permeation Chromatography (GPC), which was equipped with Light Scattering and Refractive Index detectors (Malvern Viscotek GPC Dual 270 max). The GPC column was maintained at 55 ºC and calibrated with polystyrene standards (162 Da to 60.0000 Da, Polymer Laboratories). DMF containing 40 mM LiBr was used as the mobile phase. The optical features of PD and poly(PD) were assessed using an Analytikjena Specord 210 spectrometer over the range of 280-700 nm. Measurements were performed on sample solutions in a 1 cm quartz cell. Photoluminescence (PL) measurements were performed with a Shimadzu RF-5301PC spectrofluorophotometer with a slit width of 5 nm. Thermogravimetric-Differential Thermal Analysis (TG-DTA) was conducted using Perkin Elmer Diamond Thermal Analyzer in the temperature range of 25 °C to 1000 °C. Differential Scanning Calorimetry (DSC) analysis was carried out with a Perkin Elmer Sapphire Differential Scanning Calorimeter between 25 °C and 420 °C (nitrogen atmosphere, heating rate:10 °C min^{-1}). CHI 660C Electrochemical Analyzer was used to monitor cyclic voltammograms (CV) of the compounds. The scan rate was set to 25 mV s^{-1}. The supporting electrolyte solution consisted of 0.1 M $TBAPF_6$ in CH_3CN solution. CV measurements were conducted in argon atmosphere using a cell immersed in the sample, which was dissolved in the supporting electrolyte solution. The cell consisted of a silver reference electrode, a platinum auxiliary electrode, and a glassy carbon electrode (GCE) as the working electrode. The electrochemical band gap ($E_g^{'}$) between the electrochemical HOMO and LUMO levels was determined from the cyclic voltammograms (Cervini et al., 1997). Scanning Electron Microscopy (SEM) photographs were acquired to analyze the morphology of the polimeric particles.

RESULTS AND DISCUSSION

1,3-phenylenediamine dichloride (PD) was oxidatively polymerized. The product yield of dark brown powder of polymer (poly(PD)) was 21%. Because the anilinium ion is a weak acid, it undergoes deprotonation, leading to the delocalization of the lone pair into the aromatic ring. Based on Scheme 1, the oxidation of PD was initiated by forming cation radicals generated in the monomer, which are then coupled via C-N bonds. Since -NH_2 group is an *ortho* and *para* director, the active sites in each polymerization route are available in the *ortho*- and *para*-positioned carbon atom to the amine groups of the radical cation. The polymeric structure of PD is formed between PD radical units, as seen in Scheme2. The anchored sites of anilinium groups on 1,3-phenylenediamine dichloride act as initiation centers for chain growth and the hydrogen atoms abstracted from the molecule during polymerization are released as protons ((Mohilner et al., 1962; Stilwell & Park, 1988). The most likely pathway for the chemical synthesis of poly(PD) involves the the coupling of R1 and R2 radicals. The dimerization of two PD units results in the chain growth of poly(PD). Within the polymer chain, the coupling of R1 and R2 radicals results in the formation of simultaneous double C-N-C bonds as a consequence of intramolecular cyclization (Scheme 2). The units are likely to be linked at the *ortho* positions, with the second amino group potentially participating in a reaction pathway analogues to the intramolecular oxidative cyclization of the units, leading to the formation of phenazine rings in a ladder-type poly(PD) (Ćirić-Marjanović, 2006, et al.; Stejskal, 2008).

Figure 1 presents the FT-IR spectra of PD and its oxidatively polymerized product (poly(PD). Due to the protonation on the nitrogen atoms, aniline HCl exhibited an amine salt stretch at 2797 cm^{-1}, a characteristic feature of primary amines in their salt form. The related stretching frequency is not observed in the spectrum of poly(PD). Additionally, aromatic C-H and aromatic C=C were observed at 2582 and 1525–1487 cm^{-1}, suggesting the presence of unpolymerized aniline (Li et al., 2021). The bands at 1251 and 1112 cm^{-1} were due to C-N stretching and C-H in-plane bending, respectively. The bands at 3325 and 3197 cm^{-1} observed in the spectrum of deprotonated poly(PD) are attributed to the N–H and aromatic C-H stretching vibrations, respectively. The peaks at 1612 and 1494 together with 1439 cm^{-1} can be ascribed to the characteristic absorption of C=N and C=C stretching modes for the quinoid and benzenoid rings, respectively. Notably, the peak observed at 1612 cm^{-1} in the spectrum of poly(PD) provides evidence for the formation of C=N bond, a feature that is absent in the spectrum of PD. This observation suggest that PD underwent polymerization into poly(PD), incorporating the phenazine unit, which contributed to the formation of the final poly(PD) and resulted in a polymer ladder structure (Zou & Huang, 2018). Two peaks centered at 1282 and 1209 cm^{-1} may be ascribed to the C-N stretching vibration in the benzenoid and quinonoid units, respectively (Li et al., 2003). The absence of C-H bending vibrations in the spectrum of poly(PD) provides evidence of cyclization between the aromatic rings, resulting in a reduction in the number of hydrogen atoms surrounding poly(PD) during polymerization.

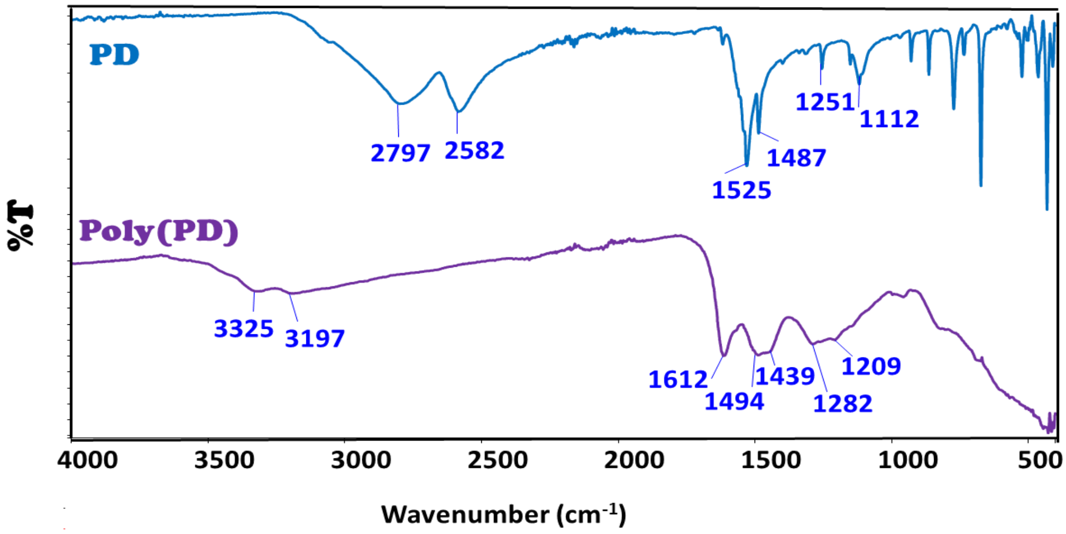


Figure 1. FT-IR Spectra of PD and Poly(PD)

UV-Vis spectral analyses were conducted for DMF solutions of PD and poly(PD) in the range of 260-800 nm, as illustrated in Figure 2. The maximum absorption wavelength corresponding to π→π* transitions induced by phenyl rings in PD and poly(PD) was observed at around 300 nm. Additionally, transitions associated with n→π* involving electron pairs on nitrogen atoms and imine bonds appeared between 350 and 465 nm region for poly(PD) (Yang & Mattes, 2002).

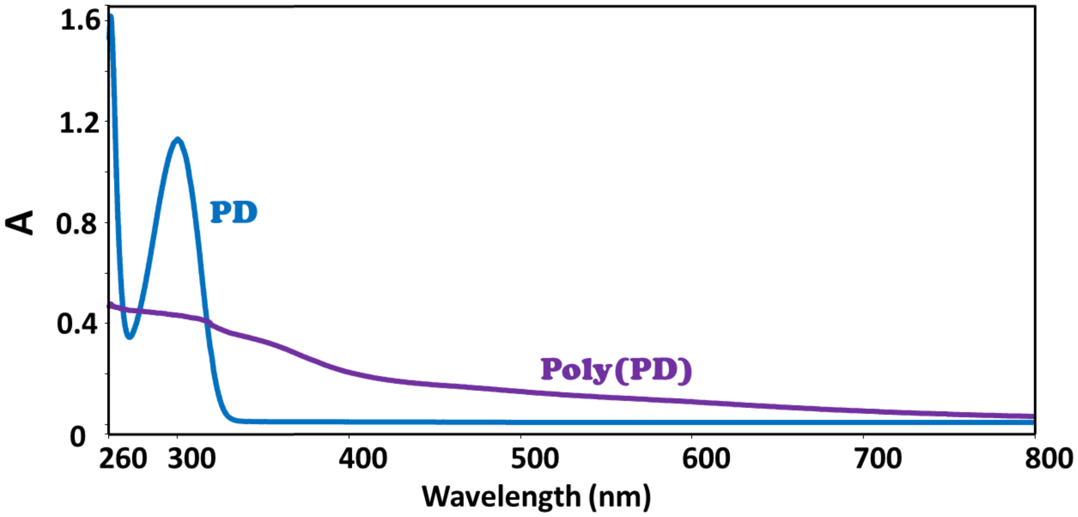


Figure 2. UV-vis Spectra of PD and Poly(PD)

A broad absorption of poly(PD) suggests the chemical complexity of the oxidation product, which is likely to include polymeric structures featuring secondary amine, imine linkages, and phenazine rings arranged within a network-like topology. It is hypothesized that the linkages between aromatic rings are primarily formed by secondary amine groups (Sulimenko et al., 2001). This extended tail phenomenon, as seen in Figure 2, is consistent with the delocalization of electrons within the quinodal structure, which is facilitated by the straightening of the polymer chain. The optical bandgap values (E_g) for PD and poly(PD) were calculated using the formula $E_g = 1242/\lambda_{onset}$, where the onset of the wavelength (λ_{onset}) can be identified by the tangent method (Cervini et al., 1997). The E_g values for PD and poly(PD) were calculated to be 3.86 eV and 2.95 eV, respectively. The synthesized poly(PD) exhibited a reduced band gap value in comparison to PD. A lower band gap facilitates easier electronic transitions between the HOMO and LUMO energy levels, resulting in higher electrical conductivity compared to the monomeric form of the polymer.

The peaks for oxidation and reduction potentials of PD and poly(PD) are determined using Cyclic Voltammograms (CVs) from -1.6 V to +1.6 V, as presented in Figure 3. CV determines the oxidation (V_{ox}) and the reduction peak (V_{red}) potentials of PD and poly(PD). During oxidation, one electron is removed from the HOMO level of the compound. A radical cation, generated through CV oxidation, subsequently underwent a radical-radical coupling related to deprotonation, leading to the formationof a dimer (Yang et al., 1992). The anodic peaks can be ascribed to the oxidation of -NH_2 of the compound, forming a polaron structure ($^{\bullet+}NH_2$) through coupling with the parent molecule. The anodic and cathodic oxidation potentials were observed as 1236 mV and -1208 mV, respectively. For poly(PD), the anodic and cathodic oxidation potentials were noticed at 1210 mV and -896 mV, respectively. The E'_g values of PD and poly(PD) were calculated as 2.44 eV and 2.09 eV, respectively, reflecting a lower energy required for an electron to reach an excited energy level and poly(PD)'s enhanced suitability for semiconductor applications (Cervini et al., 1997).

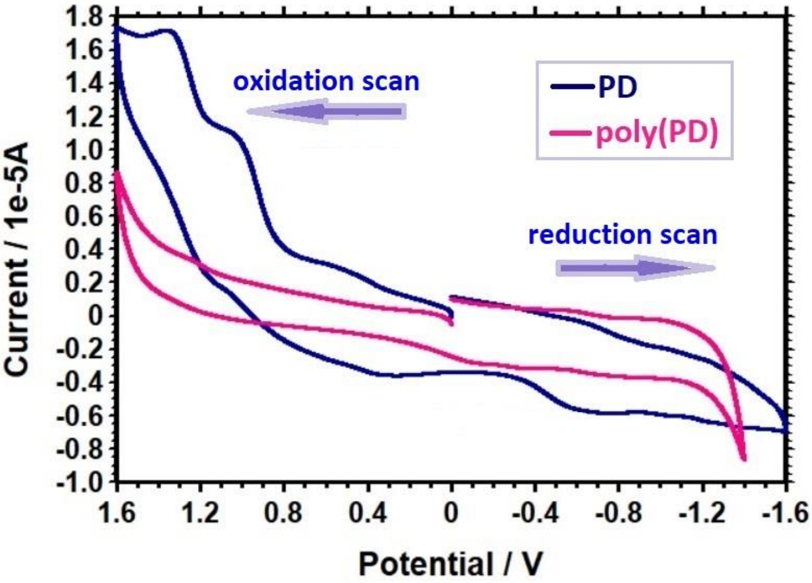


Figure 3. CVs of PD and Poly(PD)

The PL spectrum of the obtained polymer was recorded to study its pholuminescence property. Yellowish-green light emision was observed in DMF for the oxidatively synthesized polymer, as presented in Figure 4. The emission wavelength occurred at 482 nm, 502 nm and 514 nm corresponding to the emission of green light when excited by 400 nm, 430 nm, and 440 nm, respectively. The maximum PL emission intensity (I_{max}) was measured at 980 a.u. at the excitation wavelength of 430 nm. PL characteristic could be attributed to the contribution of quantum yield (QY) (Williams et al.; 1983). The polymer synthesized oxidatively exhibited a green PL emission QY of 11.2% in DMF. Notably, the polymer appears to be a promising candidate for future development in optoelectronic devices. The inset displays the time-dependent (0-3600 s) fluorescence measurement under 430 nm light excitation. No changes in fluorescence intensity were noticed within 3600 s under identical conditions, indicating that the oxidatively synthesized polymer exhibits excellent photostability when excited by 430 nm light. Consequently, the synthesized poly(PD) shows promising potential for use in display devices and light emitting diodes.

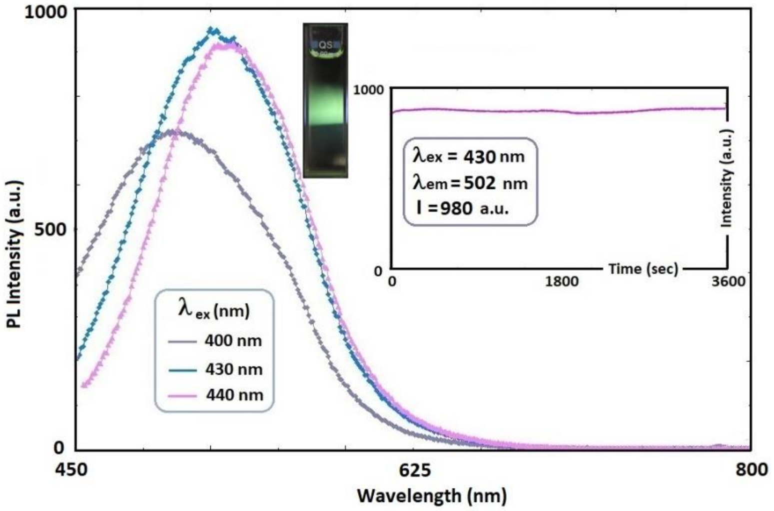


Figure 4. PL Emission Spectrum of Poly(PD). (Inset: Time-dependent PL spectrum of poly(PD)

Figure 5 presents the TGA-DTG curves of PD and poly(PD). While no solvent evaporation was detected in the monomer, it was evident in the synthesized poly(PD). This was indicated by an initial weight loss of 9.50% observed between 30 °C and 125°C, which can be attributed to moisture entrapped within the poly(PD) chain.

The degradation temperature (T_{on}) of PD and poly(PD) started at 215 °C and 195 °C, respectively. Maximum weight loss (T_{max}) occurred at 245 °C for PD. Two degradation steps for poly(PD) were observed with T_{max} at 300 °C and 732 °C for poly(PD). 20% weight loss (T_{20}) and 50% weight loss (T_{50}) temperatures were noticed at 219 °C and 238 °C; 369 °C and 885 °C for PD and poly(PD), respectively. The decomposition was fulfilled at 260 °C for PD, as seen in Figure 5A. For poly(PD), two decomposition stages were observed: the first ranged from 125 to 537 °C with a 29.80% weight loss, and the second stage ranged from 537 to 1000 °C with a 28.18% weight loss, as seen in Figure 5B. The char% was calculated to be 42.02% for poly(PD). This residual content is ascribed to the decomposition of polymer's rigid chain structure, which is organized into a structural order stabilized by phenazine units. Therefore, the synthesized polymer demonstrates potential for applications across diverse industrial sectors, including electrical applications necessitating high-temperature insulation, the production of aircraft components, weapon systems, and space vehicles (Konyushenko et al., 2006). 50% weight loss (T_{50}) temperature at 885 °C for poly(PD) could be attributed to the conjugation due to the presence of phenazine units, as depicted in Scheme 1. Consequently, the degradation of the phenazine-type structures within the polymer takes place at higher temperatures compared to monomer. The flame retardancy value of the polymer can be obtained using the TGA curve following the Van Krevelen's calculation, utilizing the percentage of residue at 1000 °C. The formation of carbon during thermal decomposition restricts the emission of organic volatile compounds. This carbonaceous layer, produced in the process, impedes the propagation of flammable gases by diminishing heat transfer to the material. In this regard, Van Krevelen proposed a formula of LOI = 17.5 + 0.4 (*s*) where LOI represents the limiting oxygen index and (s) denotes the percentage of residue in the polymer, respectively (van Krevelen, 1975). According to Van Krevelen's theory, an increase in residue formation correlates with the flammability of polymers. For polymers to be self-extinguishing, their LOI values must be at least 26 or higher (van Krevelen, 1975). The LOI value for poly(PD) was calculated as 34.31, indicating that the synthesized polymer exhibits a low flammability with excellent thermal stability.

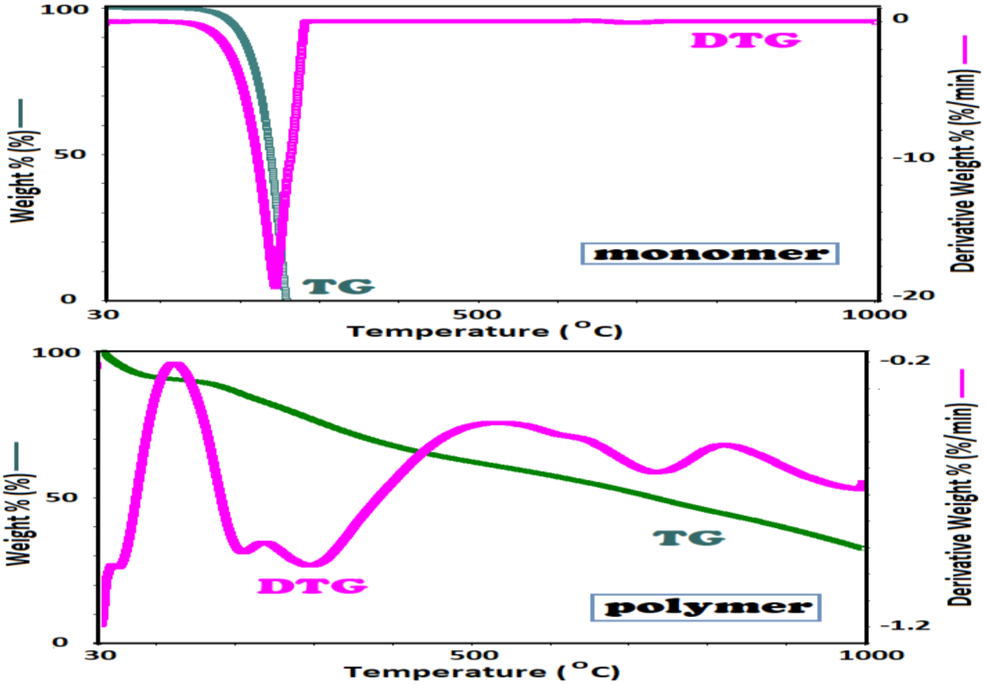


Figure 5. TG and DTG Curves of (A) PD and (B) poly(PD)

The sample was sprinkled onto the stub and subsequently subjected to a sputter coating with a 5 nm layer of gold. Morphological properties of poly(PD) were examined using SEM at different magnifications, as illustrated in Figure 6. The polymer particles with polyhedral and irregular sharp edges as well as spherical in the range from micro to nanometer in size were exhibited in the morphology of poly(PD). However, the bulk particle features are fused together rather than being discrete particles, producing larger particle sizes and greater rigidity (Chao et al., 2005).

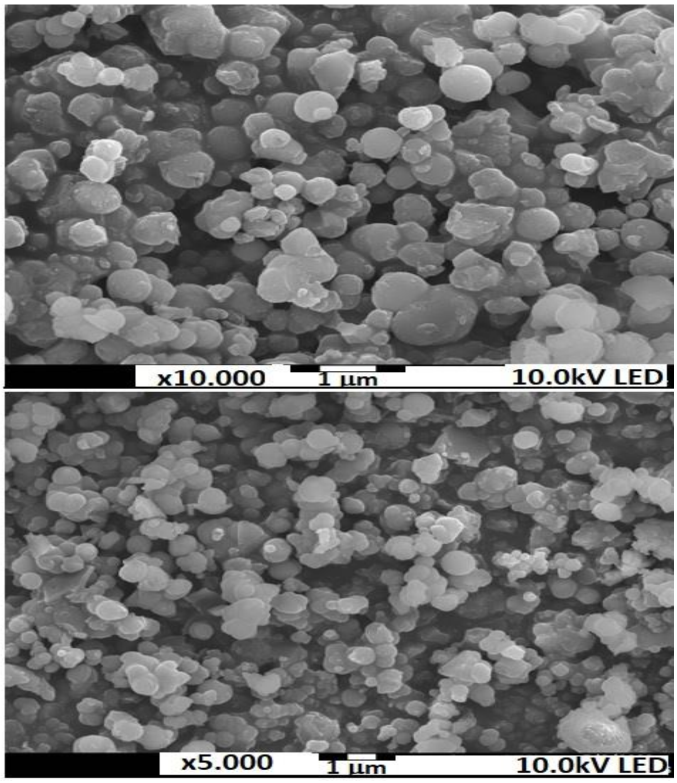


Figure 6. SEM images of Poly(PD

CONCLUSION

The chemical oxidation of 1,3-phenylenediamine dichloride resulted in an oxidatively coupled polymer poly(PD). An extended tail upto 800 nm observed in UV-Vis analysis, is consistent with the delocalization of electrons within the quinodal structure, which is facilitated by the straightening of the polymer chain. Due to its potential as a green light emitter with quantum yield of 11.2%, the oxidatively synthesized polymer can be a promising compound for the fabrication of display appliances and in bioscience applications. Additionally, the exceptional thermal stability of the polymer suggested to be used in the manufacture of electrical appliances requiring high- temperature insulation. These attributes highlighted the advantages of the chemically oxidative synthetic process, which provides simplicity in synthesis, environmental compatibility, chemical stability, and notable thermal and photophysical features. Analyzing and characterizing macromolecules synthesized through various catalysts and oxidative polymerization techniques applied to the monomer investigated in this study will provide valuable insights for future research.

Conflict of Interest

The article authors declare that there is no conflict of interest between them

Author's Contributions

The authors declare that they have contributed equally to the article.

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