

SYNTHESIS OF POLY ORTHO BROMO ANILINE AND STUDY ITS APPLICATION

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Abstract

After producing poly orthobromo aniline, FT-IR spectroscopy was used to investigate its structure. We examined the optical and electrical characteristics of poly-o-bromo aniline (o-BrAn) in this work. O-bromoaniline/Ag, an original polymer, has been combined. Several techniques, including FT-IR spectroscopy and UV-visible spectra, have been employed for analyzing the mixer. The nonlinear changes in voltage and current are demonstrated by the I-V characteristics. The conductivity values ranged from o-BrAnp is 5.6×10^{-8} S/cm, but at o-BrAn/Ag0.25 is 3.1×10^{-7} S/cm. Since the conductivity value of the material is in the range of semiconductor, it can be used in the field of organic semiconductors..

Keywords : Poly ortho bromo aniline ,Optical properties , I-V characteristics.

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Introduction

Because of the unique electrical properties that conjugated polymers display, researchers have focused a great deal of interest on studying these molecules and their composites [1, 2]. Miniaturized conducting polymers have become more and more popular recently, mainly due to their interesting features that find utility in nano electronics [3]. When confronted with external factors such oxidants, reductants, fluctuations in temperature, humidity, and acidity, conjugate polymers can change their electrical and optical characteristics [4-6]. Lithium-ion batteries may employ polymers with a semi-interpenetrating network structure as solution separator [7]. An ammonia sensor has been created and rendered possible through the use of polyaniline nanostructures [8]. Fluorine-doped polymers have demonstrated potential to enhance perovskite solar cell durability and efficiency as well as for use in polymer complexes for solar fuels [9-11]. One interesting approach to enhancing the characteristics and possible uses of conjugated polymers is the production of polymer composites with metal nanoparticle dispersion (hybrid materials), especially in the area of flexible semiconductors. Graphene-based polyaniline composites have been found useful in a number of applications, including lithium-ion batteries, fuel cells, solar cells, electrochromic devices, supercapacitors, and sensor platforms [12]. The proportions of metal nanoparticles comprised into the polymer matrix have an impact on the electrical properties of conducting polymer hybrid nanocomposites. Because of their remarkable electrical qualities, these nanostructures can be used to create a variety of devices, including capacitors and sensors. This is because of their remarkable optical and electrical characteristics, unique shape under controlled conditions, and outstanding catalytic activity [13]. The discovery of polyacetylene, polyaniline, and polypyrrole has led to a great deal of research interest in conjugated polymers [14]. Among them is the

conducting polymer polyaniline, which has tunable electrochemical and physical characteristics including oxidation and protonation [15–17]. Electronic gadgets, sensors, rechargeable batteries, conductive coatings, electromagnetic shielding, and separation membranes are just a few of the many uses for it [18, 19]. Both the chemical oxidation approach and the electrochemical method yield high conductivity when used to manufacture polyaniline. Polyaniline's poor solubility in different solvents, on the other hand, is a disadvantage that presents difficulties for industrial processing [20]. Numerous research projects have tried to increase the solubility of polyaniline by doping the polymer with protonic acids such as camphor sulfonic acid (CSA) [21] and dodecyl benzene sulfonic acid (DBSA) [22,23], as well as by copolymerizing aniline with other substituted aniline derivatives. For this reason, emulsion polymerization techniques have also been investigated [24]. The type of substituent group present, such as electron withdrawing or electron donating groups, or less significant groups like alkyl groups, affects the properties of poly(substituted aniline). Aniline's electron density is decreased by electron withdrawing groups and increased in the phenyl ring of aniline by electron giving groups. Surprisingly, in-situ doping polymerization of polyaniline and polypyrrole microtubes was achieved by employing β -naphthalene sulfonic acid as a surfactant and dopant [25]. Tubular PANI derivative synthesis was found to be a reliable process using the template-free method used in this investigation. The template-free approach forms nanostructures by a self-assembly process driven by molecular interactions such hydrogen bonding, π - π stacking, and Van der Waals forces, unlike the soft template method that uses a membrane template [26]. Recently, there have been notable electrical features demonstrated by nanostructured polymers that set them apart from their bulk counterparts. Surfactant-oriented template approaches have been used to synthesis a variety of conducting polyaniline nanostructures, including nanowires, nanotubes, nanoribbons, and nanospheres [27–31].

In this document, we explored the characterization and conductive properties of PVA+Ag doped with poly(o-bromoaniline). Our aim is to examine how the arrangement of side chain molecules and the PVA+Ag dopant can impact the structural formation and electronic charge transport properties.

Methods

By oxidizing 2-bromoaniline with ammonium peroxy disulfate in the presence of sulfuric acid, Poly(2-bromoaniline) was created. An aqueous solution of sulfuric acid was present during the chemical polymerization of aniline. A suitable volume of 100 ml of H₂SO₄ acid is added to the appropriate amount of O-Bromo aniline (0.1 M) in the polymerization jar. After that, the tank was set up at 0°C on a magnetic stirrer. Using a dropping funnel, a (0.1M) aqueous solution of the (NH₄)₂S₂O₈ oxidant was gradually introduced to the reaction medium drop by drop for approximately 20 minutes. After the polymerization reaction was complete, the finished product was filtered, cleaned with diluted H₂SO₄ acid solutions, and vacuum-dried for 12 hours at 60 oC. Materials.

Experimental

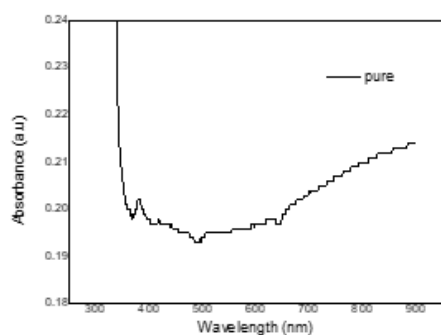
The PVA/Ag solution is used to prepare the o-Bromoaniline in this manner:

In 10 milliliters of distilled water, dissolve 0.03 grams of o-Bromo aniline and stir until well dissolved. In 50 milliliters of distilled water, dissolve 0.5 gram of PVA and stir until well dissolved. Submerge the silver electrodes in the o-Bromo aniline solution for 10 minutes at 20 volts.

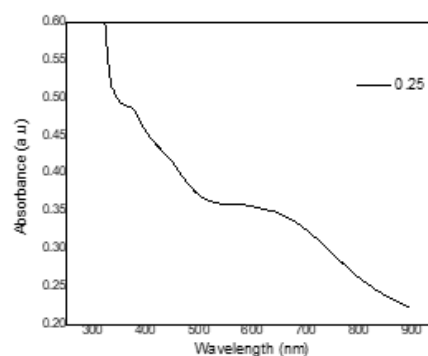
Consider the following ratios for the PVA/Ag solution and the o-Bromo aniline solution: (1:1), (1:0.25), and (1:0.50), respectively.

Result and Discussion

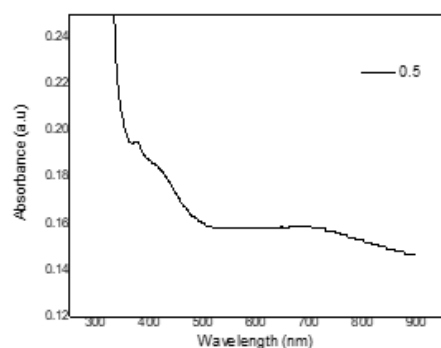
The understanding of the nature of the bonds, the quality of the internal structure of the polymer, and the expansion of potential application areas were all bolstered by the study of the optical properties of polymeric materials. After dissolving the poly-Bran sample in distilled water, the solution's electronic absorption spectra was recorded. The UV characteristics of poly o-BrAnp and poly o-BrAn/Ag are shown in Figure 1. The primary absorption peak of poly-o-BrAnp is located at 379 nm and is caused by the π - π^* transition. The functional groups that are connected to the benzene rings also have an impact on this absorption peak. Poly o-BrAn/Ag0.5 displays absorption peaks at 375, 517, and 681 nm, while poly o-BrAn/Ag0.25 has distinctive bands at 375, 668 nm. The peaks at 517, 668 nm, which are connected to the dispersion of silver in the polymer matrix, exhibit a shift in the absorption band maximum to a longer wavelength. This shift may be caused by the s-electrons spilling out, which could raise the conduction electrons' effective mass [32, 33].



(a)



(b)



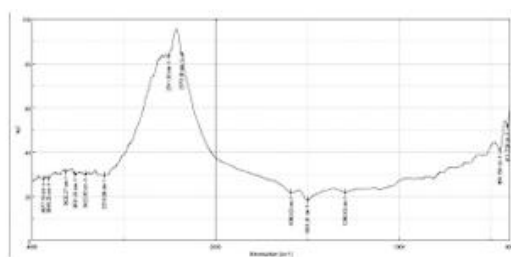
(c)

Figure 1: shows the spectrum of (a) o-BrAn_p, (b) BrAn/Ag^{0.25}, (c) BrAn/Ag^{0.5}.

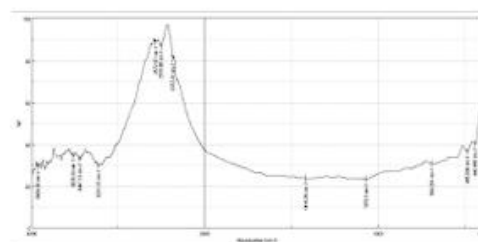
FT-IR spectroscopy

The FT-IR spectra of o-BrAn_p, o-BrAn / Ag^{0.25}, and o-BrAn Ag^{0.5} are shown in Figures 2a, 2b, and 2c, respectively. The FT-IR spectra display the distinctive peaks of o-BrAn pure; the peaks at 1590 and 1501 cm⁻¹, respectively, are ascribed to the C=C bonds found in quinoid and benzenoid rings, respectively[34]. The combination of C-N stretching of the secondary aromatic amine is indicated by the peak at 1295 cm⁻¹.

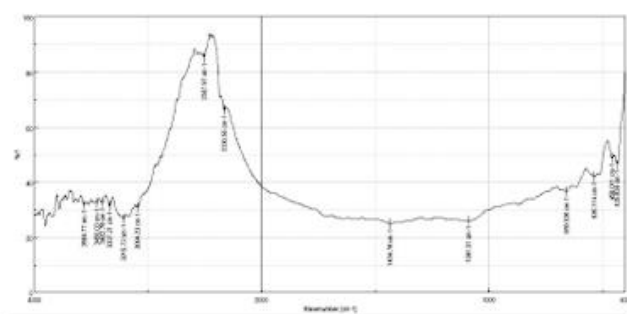
Figure 2b displays the distinctive peaks of o-BrAn/ Ag^{0.25}. Although in fig. 2c the peak around 1434 cm⁻¹ is due to C=C bond, 1091 cm⁻¹ attributed to the aromatic C-H in-plane deformation in the substituted benzene rings, the peak at 659 cm⁻¹ confirms the presence of C-Br stretching in the o-BrAn / Ag^{0.5}. The peak at 1419 cm⁻¹ is due to the C=C bond. The peak at 1070 cm⁻¹ may be attributed to the aromatic C-H in-plane deformation in the substituted benzene rings.



(a)



(b)



(c)

The current-voltage characteristics of o-BrAn and o-BrAn/Ag0.25,0.5 blends at room temperature are shown in Fig. 3(a-c). For every concentration, the electric conductivity was ascertained. According to the data, electrical conductivity rises at o-BrAn/Ag0.25 and falls at o-BrAn/Ag0.5. Remarkably, at 0.25 weight percent Ag/PVA, the conductivity achieves its maximum value. The conductivity values varied between 5.6×10^{-8} S/cm at o-BrAn and 3.1×10^{-7} S/cm at o-BrAn/Ag0.25.

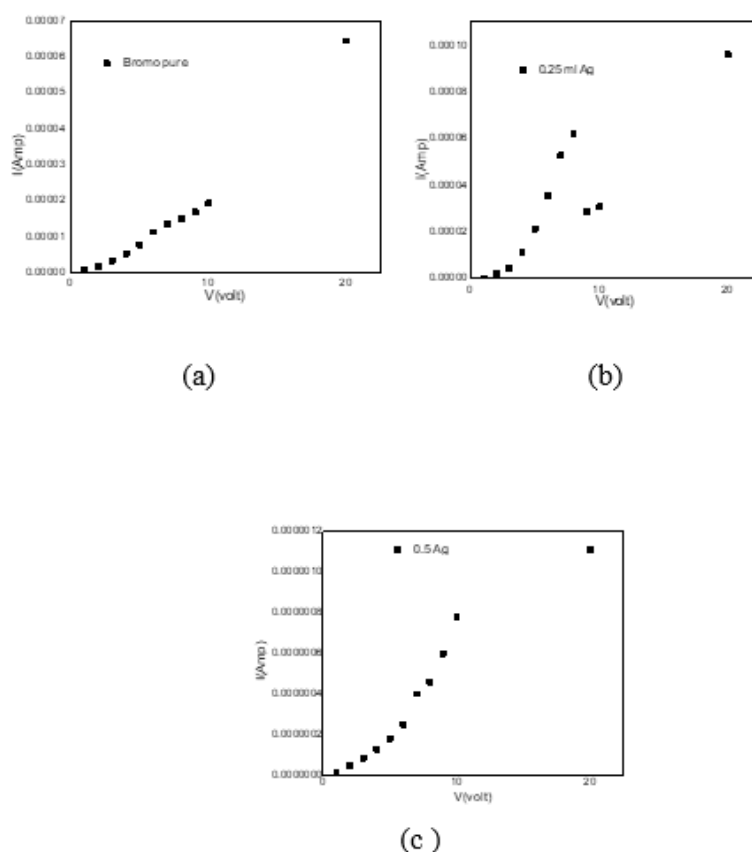


Fig.3: I-V characteristic of BrAn_p and BrAn/Ag in different concentration.

Conclusion

The chemical approach was used to produce the poly0-BrAn. The coast method was used to deposit the poly 0- BrAn thin films. The optical and electrical characteristics of Poly o-bromo aniline (o-BrAn) and a novel polymer (o-bromo aniline/ Ag) mixer were investigated. Numerous methods, including FT-IR spectroscopy and UV-visible spectra, have been used to characterize the mixer. The nonlinear changes in voltage and current are demonstrated by the I-V characteristics. The conductivity values varied between 5.6×10^{-8} S/cm at o-BrAnp and 3.1×10^{-7} S/cm at o-BrAn/ Ag0.25..

References

- [1]. NALWA H.S., Handbook of Conducting Polymers, Wiley, New York, 1986.
- [2]. [2] FINCH C.M., SSRICHANTAROPAS S., MAILEY S.W., GRACE I.M., GARCIA-SUAREZ V.M., LAMBERT C.J., J. Phys-Condens. Mat., 20 (2008), 22203.
- [3]. GUENZA M.G., J Phys-Condens. Mat., 20 (2008), 33101.
- [4]. KUMAR D., Synth. Met., 114(2000), 369.
- [5]. MAHUDESWARAN A., MANOHARAN D., CHANDRASEKARAN J., VIVEKANANDAN J., VIJAYANAND P.S., Mater. Res., 18 (2015), 482.
- [6]. MAHUDESWARAN A., VIVEKANANDAN J., VIJAYANANDAN P.S., Asian J. Chem., 27 (2015), 4501.
- [7]. NAIR J.R., DESTRO M., BELLA F., APPETECCHI G.B., GERBALDI C., J. Power Sources, 306 (2016), 258.
- [8]. DOBROCZYNSKA J.I., GRABAS K., Mater. Sci.-Poland, 31(2013), 95.

- [9]. BELLA F., GRIFFINI G., CORREA-BAENA J., SARACCO G., GRATZEL M., HAGFELDT A., TURRI S., GERBALDI G., *Science*, 354 (2016), 203.
- [10]. PINTOSI D., IANNACCONE G., COLOMBO A., BELLA F., VALIMAKI M., VAISANEN K., JAST J., LEVI M., GERBALDI C., DRAGONETTI G., TURRI S., GRIFFINI G., *Adv. Electron. Mater.*, 2 (2016), 1600288. 534 A. MAHUESWARAN et al.
- [11]. BERARDI S., FRANCAS L., NEUDECK S., MAJI S., BUCHHOLZ J.B., MEYER F., LLOBET A., *Chem. Sus. Chem.*, 8 (2015), 3088.
- [12]. WANG L., LU X., LEI S., SONG Y., *J. Mater Chem.*, 2 (2014), 4491.
- [13]. MA Y., LI N., YANG C., YANG X., *Colloid Surfaces A*, 269 (2005), 1.
- [14]. S. Bhadra, D. Khastgir, N.K. Singha, J.H. Lee, *Progress in preparation, processing and applications of polyaniline*, *Prog. Polym. Sci.* 34 (2009) 783–810.
- [15]. J.L. Bredas, R. Silbey, *Conjugate Polymers*, Kluwer Academic Publishers, London, 1991.
- [16]. J.Z. Chen, B. Li, J.F. Zheng, J.H. Zhao, *Controllable assembly of polyaniline nanostructures and improving their electrochemical performance by high gravity*, *J. Phys. Chem. C* 115 (2011) 23198–23203.
- [17]. I. Kulszewicz-Bajer, J. Sobczak, M. Hasik, J. Pretula, *Spectroscopic studies of polyaniline protonation with poly(alkylene phosphates)*, *Polymer* 37 (1996) 25–30.
- [18]. A. Sakhri, F.X. Perrin, A. Benaboura, E. Aragon, S. Lamouri, *Corrosion protection of steel by sulfo-doped polyaniline-pigmented coating*, *Prog. Org. Coat.* 72(2011) 473–479.
- [19]. J. Yun, J.S. Im, H.I. Kim, Y.S. Lee, *Effect of oxyfluorination on electromagnetic interference shielding of polyaniline-coated multi-walled carbon nanotubes*, *Colloid Polym. Sci.* 289 (2011) 1749–1755.
- [20]. J. Vivekanandan, V. Ponnusamy, A. Mahudeswaran, P.S. Vijayanand, *Synthesis, characterization and conductivity study of polyaniline by chemical oxidative and electrochemical methods*, *Arch. Appl. Sci. Res.* 3 (2011) 147–153.
- [21]. D. Verma, V. Dutta, *Role of novel microstructure of polyaniline-CSA thin film in ammonia sensing at room temperature*, *Sens. Actuat. B: Chem.* 134 (2008) 373–376.
- [22]. A. Shakoor, T.Z. Rizvi, M. Sulaiman, M. Nasir, M. Ishtiaq, *Electronic properties of polyaniline doped with dodecylbenzenesulphonic acid (PANI-DBSA) and poly(methyl methacrylate) (PMMA) blends in the presence of hydroquinone*, *J. Mater. Sci.: Mater. Electron.* 21 (2010) 603–607.
- [23]. S.S. Im, M.G. Han, S.K. Cho, S.G. Oh, *Preparation and characterization of polyaniline nanoparticles synthesized from DBSA micellar solution*, *Synth. Met.* 126(2002) 53–60.
- [24]. P.J. Kinlen, J.L.Y. Ding, C.R. Graham, E.E. Remsen, *Emulsion polymerization process for organically soluble and electrically conducting polyaniline*, *Macro-molecules* 31 (1998) 1735–1744.
- [25]. Wan MX, Shen YQ, Huang J (1998) Chinese patent no. 98109916.5.
- [26]. M. Wan, *Conducting Polymers with Micro or Nanometer Structure*, Springer & Tsinghua University Press, Beijing, 2008.
- [27]. Y. Haba, E. Segal, M. Narkis, G.I. Titelman, A. Siegmann, *Polyaniline-DBSA/polymer blends prepared via aqueous dispersions*, *Synth. Met.* 110(2000) 189–193.
- [28]. X.Jing, Y.Wang, D.Wu, " Sonochemical synthesis of polyaniline nanofibers" *J. Qiang, Ultrasonic. Sonochem.* 14 No.1, 75(2007).

- [29]. I. Sapurina, J. Stejskal, The mechanism of oxidative polymerization of aniline and the formation of supramolecular polyaniline structures, *Polym. Int.* 57(2008) 1295–1325.
- [30]. J.E. Osterholm, Y. Cao, F. Klavetter, P. Smith, Emulsion polymerization of aniline, *Polymer* 35 (1994) 2902–2906.
- [31]. Y. Jiping, D. Yan, Z. Jingkun, Uniform rice-like nanostructured polyanilines with highly crystallinity prepared in dodecylbenzene sulfonic acid micelles, *Mater. Chem. Phys.* 112 (2008) 322–324.
- [32]. B. Hsieh, H. Chuang, L. Chao, Y. Li, Formation mechanism of a nanotubular polyanilines prepared by an emulsion polymerization without organic solvent, *Polymer* 49 (2008) 4218–4225.
- [33]. CHOUDHURY A., *Sensor Actuat. B-Chem.*, 138 (2009), 318.
- [34]. COCHET M., LOURAN G., QUILLARD S., BUISSON, J.P., LEFRANT S., *J. Raman Spectrosc.*, 31 (2000), 1041.
- [35]. A. MAHULESWARAN¹, A. JEEVA², J. CHANDRASEKARAN³, P.S. VIJAYANAND², Structural and electrical properties of new core-shell silver poly(m-toluidine-co-2-bromoaniline) nanocomposites, *Materials Science-Poland*, 37(4), 2019, pp. 526-534.