Futurum

Synthesis and Properties of Polyaminothiophene

Sae Kohroki, Hiromasa Goto*

Department of Materials Science, Institute of Pure and Applied Sciences, University of Tsukuba, Tsukuba, Ibaraki 305-8573, Japan

Abstract

Aminothiophene was synthesized from nitrothiophene using a one-pot reaction in an aqueous solution and subsequently oxidatively polymerized in the presence of iodine with ammonium peroxodisulphate. The resulting polymer exhibited electrical conductivity at room temperature. Resistivity measurements were conducted from liquid nitrogen temperature to 290 K. The presence of polarons, a type of charge carrier, was confirmed through electron spin resonance spectroscopy. The observed signal width was narrow (<1 mT), indicating that the polaron is delocalized. While polyaniline is typically composed of a benzene ring and secondary amines, no prior studies have reported on polyaminothiophenes (PATs) combining thiophene and nitrogen units. The synthesis of this polymer, along with its confirmed electrical conductivity and charge carrier properties, represents a new class of conductive polymer.

Keywords: conjugated polymers, conductivity, doping, ESR, polythiophene

1. Introduction

Conductive polymers are a class of doped conjugated polymers. Polyacetylene, a representative conducting polymer from a fundamental research perspective, has not seen practical development due to its low stability in air. In contrast, aromatic-type conjugated polymers such as polythiophene, polypyrrole, and polyaniline exhibit good electrical conductivity upon doping with electron acceptors and have been applied in practical uses, including sensors and capacitors. Among these, polyaniline (Figure 1a) has been extensively developed because it can be synthesized in water and maintains stable electrical conductivity in air. The synthesis and magnetic properties of polyaniline complexes with nickel have been investigated[1]. Composites with materials such as polyvinylidene fluoride/barium titanate[2], chitosan[3], ammonia-sensing magnesia[4], and gas-sensing polyaniline combined with Prussian blue[5] have been prepared. These composites have been utilized as anticorrosive materials, antistatic agents, base materials for solar cells, and electrodes for capacitors, contributing to advancements in the space industry. Furthermore, polyaniline composites with nanocarbons have also been developed[6]. Similarly, polythiophene (Figure 1b) is a significant conductive polymer applied in electronic devices, including materials for organic light-emitting diodes[7]. In addition, liquid polythiophenes have been synthesized[8], representing a form of liquid synthetic metals. The supramolecular assembly of anionic polythiophenes has also been studied[9]. Polyaniline[10] and polythiophene[11] have been utilized in energy storage materials. In this research, we have successfully synthesized polyaminothiophene (PAT), a novel polymer combining the advantages of polyaniline and polythiophene. PAT (Figure 1c) features a simple and unique structure and was prepared using aminothiophene as a highly reactive monomer, converted directly from nitrothiophene. This one-pot reaction approach circumvents the challenges typically associated with the synthesis of polyaminothiophene, including the difficulty of isolating and purifying the intermediate aminothiophene.

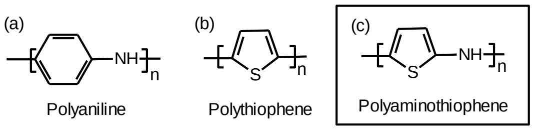


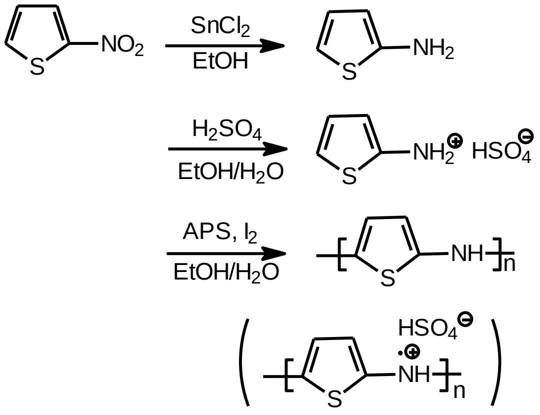
Figure 1. (a) Polyaniline, (b) polythiophene, and (c) polyaminothiophene.

2. Experiment

2.1. Synthesis of polyaminothiophene

Aminothiophene, a highly reactive monomer, presents challenges in separation and purification after synthesis. Conventional techniques such as recrystallization, solvent evaporation, and silica gel chromatography often lead to oligomerization or undesirable side reactions due to the high reactivity of aminothiophene. To address these issues, a one-pot reaction approach was adopted, combining monomer synthesis and polymerization (Scheme 1). The resulting polyaminothiophene (PAT) is insoluble and infusible, similar to polyaniline. Consequently, its characterization was carried out using infrared and UV-vis reflection spectroscopy.

In the synthesis procedure, 2-nitrothiophene (2.0 g, 15.5 mmol) and tin chloride (2.0 g, 0.0105 mol) were placed in a three-necked flask under an argon atmosphere. Ethanol (20 mL) was added, and the mixture was stirred[12]. After allowing the mixture to stand for 10 min, sulfuric acid (2.0 mL) was added. The oxidizing agent ammonium persulfate (APS, 2.0 g, 8.8 mmol) was dissolved in 20 mL of water, cooled, and then slowly added to the flask. Trace iodine (0.08 g) was introduced, and the mixture was stirred while being cooled in an ice bath. After 24 h, the product was filtered by suction and vacuum-dried to yield 1.846 g of brown powder.



Scheme 1. One-pot synthesis of polythiophene. APS: ammonium persulfate.

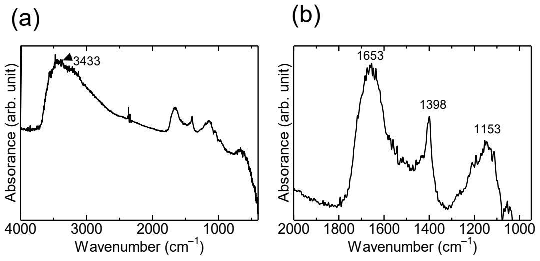


Figure 2. Infrared absorption spectra of polyaminothiophene. (a) Full scale. (b) 2000–900 cm^{-1}.

3. Results and discussion

3.1. Infrared spectroscopy

The infrared absorption spectra of the synthesized polymers are shown in Figure 2. The absorption band at approximately 3433 cm^{-1} corresponds to the NH stretching vibration (Figure 2a). A magnified view of the infrared absorption spectrum at low wavenumbers (Figure 2b) reveals characteristic peaks associated with the molecular structure of PAT. These include the aromatic absorption of the thiophene ring (1653 cm^{-1}), the C=C stretching vibration of the thiophene ring (1398 cm^{-1}), and the C–H out-of-plane vibrations of the thiophene ring (1153 cm^{-1}), confirming the presence of a polythiophene backbone and secondary amine structure.

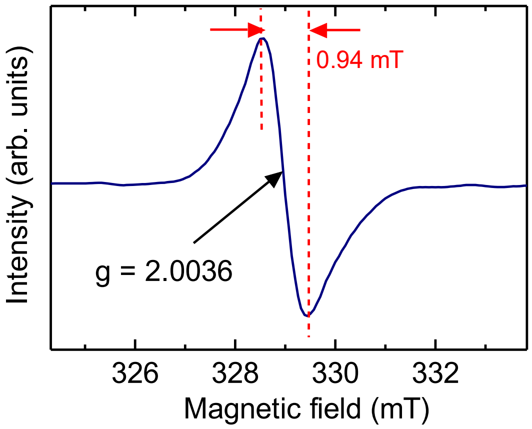


Figure 3. Electron spin resonance spectrum of as prepared polyaminothiophene.

3.2. Electron spin resonance

Electron spin resonance spectrum is presented in Figure 3, showing a g value of 2.0036, indicative of polarons typical of conducting polymers. PAT was doped with sulfuric acid during polymerization. The signal exhibits a symmetrical Lorentzian shape, confirming the presence of polarons (radical cations) as charge carriers. The narrow peak-to-peak width ($\Delta H_{pp} <$ 1 mT) indicates that the polarons are delocalized along the main chain.

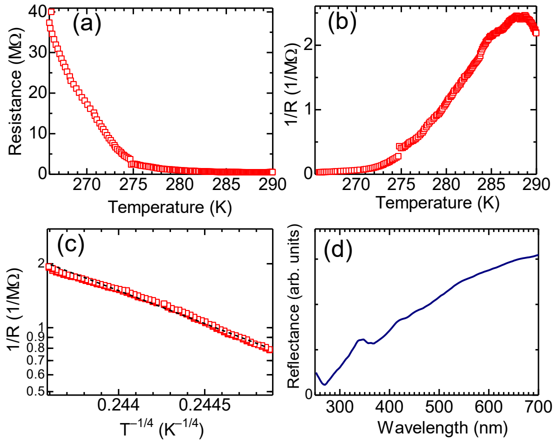


Figure 4. (a) Change in resistance of PAT with temperature. (b) 1/R (conductivity ∝ 1/R) vs. temperature. (c) 1/R vs. $T^{-1/4}$ plots. (d) Reflection spectrum of PAT.

3.3. Electrical conductivity

Figure 4 illustrates the electrical and optical properties of PAT. The change in resistance of PAT with temperature is shown in Figure 4a, with the inverse of resistance (conductivity ∝ 1/R) plotted against temperature in Figure 4b. Figure 4c presents the 1/R vs. $T^{-1/4}$ plot, indicative of the temperature-dependent behavior of conductivity. The reflection spectrum of PAT is shown in Figure 4d, further supporting the characterization of its electronic structure and confirming its properties as a conducting polymer.

3.4. Optical absorption

Figure 4(d) shows the UV-visible reflectance spectrum of PAT. The absorption band observed at 350 nm corresponds to the π–π* transition of the monomer repeating unit. The broad reflection bands in the visible range are attributed to the doping band. These results confirm that the synthesized PAT exhibits the characteristics of an organic semiconductor.

4. Possible structure

Polyaniline can exist in conducting (doped) and insulating (deprotonated) states, transitioning between these states through protonation and deprotonation. This complexity arises from the interaction between the nitrogen's lone electron pairs and the aromatic conjugated system, as seen in polyaniline. Similarly, PAT can form emeraldine salt (ES) and emeraldine base states. The plausible molecular structures of PAT in doped and dedoped (protonated and deprotonated) states are shown in Figure 5. The PAT synthesized in this study corresponds to sulfate-doped PAT-ES following polymerization.

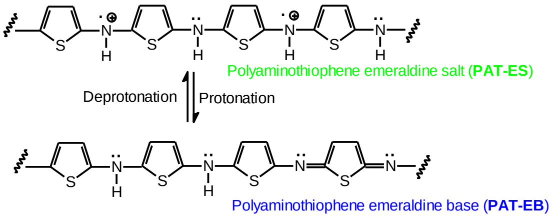


Figure 5. Plausible chemical structure of doped and dedoped (protonation-deprotonation) states of PAT.

5. Conclusions

PAT was synthesized through a convenient one-pot reaction. The synthesized PAT in its doped state corresponds to the emeraldine salt form of polyaniline. Infrared absorption spectroscopy confirmed its molecular structure, while temperature-dependent resistivity measurements and electron spin resonance confirmed the presence of charge carriers (polarons), affirming its semiconductor properties. The PAT obtained in this study exhibits characteristics of both polyaniline and polythiophene, making it a novel conductive polymer. These properties position PAT as a promising material for applications in sensors, conductors, and magnetic field shutters.

Corresponding Author

Hiromasa Goto
Department of Materials Science, Institute of Pure and Applied Sciences, University of Tsukuba, Tsukuba, Ibaraki 305-8573, Japan
Correspondence: gotoh@ims.tsukuba.ac.jp
ORCID: 0000-0003-4276-735X

All authors have read and agreed to the published version of the manuscript.

Notes

The authors declare no competing financial interest.

References

[1] Jurča M., Vilčáková J., Kazantseva N. E., Prokeš J., Trchová M., Stejskal J.: Conducting and magnetic hybrid polyaniline/nickel composites. Synth. Met., **291**, 117165 (2022). https://doi.org/10.1016/j.synthmet.2022.117165.

[2] Atta M. M., Ahmed R. M., El Al S. A., El-Bayoumi A. S.: Radiation induced effect on structural and dielectric properties of polyaniline incorporation into polyvinylidene fluoride/barium titanate ternary composites. Synth. Met., 290, 117154 (2022). https://doi.org/10.1016/j.synthmet.2022.117154.

[3] Anisimov Y. A., Yang H., Kwon J., Cree D. E., Wilson, L. D.: Chitosan-polyaniline (bio)polymer hybrids by two pathways: A tale of two biocomposites. Polymers, **16**, 2663 (2024). https://doi.org/10.3390/polym16182663.

[4] Ganachari S. V., Shilar F. A., Patil V. B., Khan T. M. Y., Saleel C. A., Ali M. A.: Optimizing ammonia detection with a polyaniline−magnesia nano composite. Polymers, **16**, 2892 (2024). https://doi.org/10.3390/polym16202892.

[5] Da Luz Rodrigues I., Sousa Correia G., Costa Dos Santos C., Tadeu Boaes Mendonça L. A.: Novel prussian blue/polyaniline composite gas sensor for fast detection of ammonia. Mater. Lett., **358**, 135859 (2024). https://doi.org/10.1016/j.matlet.2023.135859.

[6] Luo R., Wu Y., Li Q., Du B., Zhou S., Li H.: Rational Synthesis and characterization of IL-CNTs-PANI microporous polymer electrolyte film. Synth. Met., 274, 116720 (2021). https://doi.org/10.1016/j.synthmet.2021.116720.

[7] Jaymand, M., Hatamzadeh M., Omidi Y.: Modification of polythiophene by the incorporation of processable polymeric chains: Recent progress in synthesis and applications. Prog. Polym. Sci., **47**, 26–69 (2015). https://doi.org/10.1016/j.progpolymsci.2014.11.004.

[8] Lu Y., Wang S., Xiong C., Hu G.-H.: Synthesis and characterization of a liquid-like polythiophene and its potential applications. Synth. Met., 270, 116603 (2020). https://doi.org/10.1016/j.synthmet.2020.116603.

[9] Wan W., Bedford M. S., Conrad C. A., Yang X., Smith R. C.: Influence of side - chain composition on polythiophene properties and supramolecular assembly of anionic polythiophene derivatives. J. Polym. Sci. Part Polym. Chem., 57, 1173–1179 (2019). https://doi.org/10.1002/pola.29371.

[10] Shindalkar S. S., Reddy M., Singh R., Nainar M. A. M., Kandasubramanian B.: Polythiophene blends and composites as potential energy storage materials. Synth. Met., 299, 117467 (2023). https://doi.org/10.1016/j.synthmet.2023.117467.

[11] Khan I., Shah A. U. H. A., Bilal S., Röse P.: Potentiostatic synthesis of polyaniline zinc and iron oxide composites for energy storage applications. Synth. Met., 310, 117784 (2025). https://doi.org/10.1016/j.synthmet.2024.117784.

[12] Barker J. M., Huddleston P. R., Wood M. L.: An easy synthesis of 3-amino- and 3-nitrothiophene. Synth. Commun., 25, 3729–3734 (1995). https://doi.org/10.1080/00397919508011446.

Accepted: 25 January, 2025

Citation: Kohroki, S.; Goto, H. Synthesis and Properties of Polyaminothiophene, *Futurum* 2025, **7**, 97−100.