

**BIOSURFACTANT MEDIATED SYNTHESIS OF CONDUCTIVE
POLYMERIC NANOPARTICLES**



Panisara Worakitsiri

A Thesis Submitted in Partial Fulfilment of the Requirements
for the Degree of Master of Science
The Petroleum and Petrochemical College, Chulalongkorn University
in Academic Partnership with
The University of Michigan, The University of Oklahoma,
Case Western Reserve University
2010

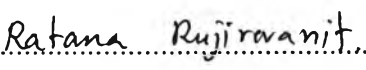
530043


Thesis Title: Biosurfactant Mediated Synthesis of Conductive Polymeric Nanoparticles
By: Panisara Worakitsiri
Program: Polymer Science
Thesis Advisors: Assoc. Prof. Ratana Rujiravanit
Assoc. Prof. Sumaeth Chavadej
Prof. Christoph Weder

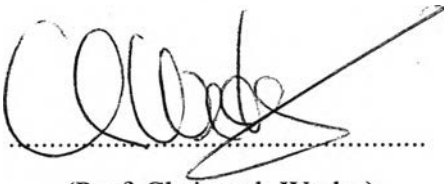
Accepted by the Petroleum and Petrochemical College, Chulalongkorn University, in partial fulfilment of the requirements for the Degree of Master of Science.

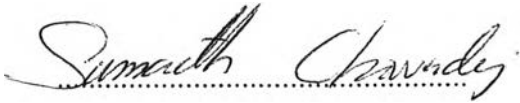

..... Dean
(Asst. Prof. Pomthong Malakul)

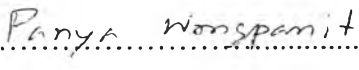
Thesis Committee:


.....
(Assoc. Prof. Ratana Rujiravanit)


.....
(Assoc. Prof. Anuvat Sirivat)


.....
(Prof. Christoph Weder)


.....
(Assoc. Prof. Sumaeth Chavadej)


.....
(Dr. Panya Wongpanit)

ABSTRACT

5172023063: Polymer Science Program

Panisara Worakitsiri: Biosurfactant Mediated Synthesis of
Conductive Polymeric Nanoparticles.

Thesis Advisors: Assoc. Prof. Ratana Rujiravanit,

Prof. Christoph Weder, and Assoc. Prof. Sumaeth Chavadej 127 pp.

Keywords: Biosurfactants/ Aniline/ *Pseudomonas aeruginosa*/ Conductive
polymer/ Nanoparticles

Polyaniline (PANI) nanofibers with the average diameter of several hundred nanometers were synthesized by oxidative polymerization using an ammoniumperoxydisulfate as an oxidant and a rhamnolipid biosurfactant as a template. The biosurfactant was produced by *Pseudomonas aeruginosa* SP4 isolated from petroleum-contaminated soil in Thailand. The biosurfactant reduced the surface tension of pure water to 30.1 mN/m with a critical micelle concentration (CMC) of 250 mg/L. The biosurfactant formed the vesicular structure at a concentration greater than its CMC. The entrapment ability of the biosurfactant vesicles suggested potential use as the template for aniline monomer accumulation and subsequent polymerization. The effects of aniline monomer and acid concentrations on the vesicle size were studied by the dynamic light scattering (DLS) technique. The PANI nanofibers showed the maximum electrical conductivity of 24.8 S/cm, which was consistent with the wide angle X-ray diffraction (WXR) results. The WXR results also indicated that the synthesized PANI nanofibers possessed a semi-crystalline structure. The UV-vis spectra revealed that the synthesized PANI existed in emeraldine salt forms. Moreover, the biosurfactant template caused only a change in the morphology of the synthesized PANI, but did not affect the chemical structure, the thermal property and the electronic state. However, the electrical conductivity and crystallinity of HCl-doped PANI was affected by the addition of biosurfactant template and the polymerization time.

บทคัดย่อ

ปณิสรา วรกิจศิริ : การสังเคราะห์พอลิเมอร์นำไฟฟ้าซึ่งมีขนาดอนุภาคระดับนาโนโดยใช้สารลดแรงตึงผิวชีวภาพ (Biosurfactant Mediated Synthesis of Conductive Polymeric Nanoparticles) อ. ที่ปรึกษา : รองศาสตราจารย์ ดร. รัตนา รุจิรวนิช ศาสตราจารย์ ดร. คริสชอฟ เวเดอร์ และ รองศาสตราจารย์ ดร. สุเมธ ชวเดช 127 หน้า

งานวิจัยนี้ได้ทำการศึกษาการสังเคราะห์พอลิเมอร์ที่สามารถนำไฟฟ้าได้ อาทิเช่น พอลิอะนิลีนโดยใช้สารลดแรงตึงผิวชีวภาพเป็นเทมเพลต โดยสารลดแรงตึงผิวชีวภาพที่นำมาใช้ในกระบวนการศึกษาครั้งนี้ถูกผลิตขึ้นมาจากระบวนการเพาะเลี้ยงเชื้อแบคทีเรีย *Pseudomonas aeruginosa* สายพันธุ์ SP4 โดยมีน้ำมันปาล์มเป็นแหล่งของธาตุคาร์บอนให้กับแบคทีเรียในการผลิตสารลดแรงตึงผิวชีวภาพ ซึ่งสารลดแรงตึงผิวชีวภาพที่ใช้ในการวิจัยครั้งนี้มีคุณสมบัติลดแรงตึงผิวของน้ำจาก 72 mN/m ถึง 30 mN/m และมีค่าความสามารถในการจับกลุ่มรวมกัน (CMC) ที่ความเข้มข้นเท่ากับ 250 mg/L นอกจากนี้เมื่อความเข้มข้นของสารลดแรงตึงผิวชีวภาพมากเกินกว่าจุด CMC สารลดแรงตึงผิวชีวภาพสามารถเกิดการรวมตัวกันมีลักษณะเป็น vesicle ซึ่งสามารถนำมาใช้เป็นเทมเพลตสำหรับการสังเคราะห์พอลิอะนิลีนต่อไปได้ จากผลการทดลองพบว่าพอลิอะนิลีนที่สังเคราะห์ได้มีสถานะเป็นอิมเมอร์อลดีนซอลท์ (สถานะที่นำไฟฟ้าของพอลิอะนิลีน) และยังพบว่าขนาดและลักษณะทางกายภาพของพอลิอะนิลีนที่สังเคราะห์ได้ขึ้นอยู่กับอัตราส่วนโดยน้ำหนักระหว่างอะนิลีนต่อสารลดแรงตึงผิวชีวภาพ ระยะเวลาในการเกิดปฏิกิริยาพอลิเมอร์ไรเซชัน และความเข้มข้นของสารลดแรงตึงผิวชีวภาพ นอกจากนี้ยังพบว่าการใช้สารลดแรงตึงผิวชีวภาพร่วมในกระบวนการสังเคราะห์พอลิอะนิลีนไม่ส่งผลต่อโครงสร้างทางเคมี ระดับการเกิดออกซิเดชันและสมบัติทางความร้อนของพอลิอะนิลีนที่สังเคราะห์ได้ อย่างไรก็ตามความเป็นผลึกและค่าความสามารถในการนำไฟฟ้าเกิดการเปลี่ยนแปลงเมื่อใช้สารลดแรงตึงผิวชีวภาพร่วมในกระบวนการสังเคราะห์พอลิอะนิลีน

ACKNOWLEDGEMENTS

First of all I would like to sincerely thank Assoc. Prof. Ratana Rujiravanit and Assoc. Prof. Sumaeth Chavadej, and Professor Christoph Weder served as my thesis advisors, for their patient guidance, understanding and constant encouragement throughout the course of this research. Their positive attitude contributed significantly to inspiring and maintaining my enthusiasm in the field. I will always be proud to have been their student.

I would like to thank Assoc. Prof. Anuvat Sirivat for being the thesis committee. I also would like to thank all of my teachers at the Petroleum and Petrochemical College for their generous help.

This thesis work is funded by the Petroleum and Petrochemical College, and by the Nation Center of Excellence for Petroleum, Petrochemicals, and Advanced Materials, Thailand.

I would like to thank The Petroleum and Petrochemical College, Chulalongkorn University where I have gained the knowledge in the polymer science.

I gratefully acknowledge The Master Research Grant (TRF-MAG) from Thailand Research Fund and The 90th Anniversary of Chulalongkorn University Fund (Ratchadaphiseksomphot Endowment Fund) for financial support for this project.

I gratefully appreciates to thank the National Nanotechnology Center for their financial support and accommodation in dynamic light scattering characterization technique for this project.

Finally, I would like to thank my friends for their friendship, helpfulness, cheerfulness, suggestion, and encouragement. I am also greatly indebted my parents for their love, support, understanding, and encouragement during this pursuit.

TABLE OF CONTENTS

	PAGE
Title Page	i
Abstract (in English)	iii
Abstract (in Thai)	iv
Acknowledgement	v
List of Tables	x
List of Figures	xi
List of Schemes	xv
CHAPTER	
I INTRODUCTION	1
1.1 Theoretical Background	2
II LITERATURE REVIEW	18
2.1 Biosurfactant	18
2.2 Vesicle Formation	19
2.3 Biosurfactant Applications	20
2.4 Polyaniline	21
2.5 Factors Affecting the Morphology of PANI Nanoparticles	22
2.6 Factors Affecting the Electrical Properties of PANI	25
III EXPERIMENTAL	28
3.1 Materials	28
3.1.1 Bacterial Strain	28
3.1.2 Other Chemicals	28
3.2 Equipment	28
3.2.1 FTIR Spectrophotometer	28

CHAPTER	PAGE
3.2.2 UV/Visible Spectrophotometer	28
3.2.3 Thermogravimetric Analyzer	28
3.2.4 Scanning Electron Microscope	29
3.2.5 Transmission Electron Microscopy	29
3.2.6 Wide-angle X-Ray Diffractometer	29
3.2.7 Electrometer	29
3.2.8 Dynamic Light Scattering	29
3.2.10 Tensiometer	29
3.3 Methodology	30
3.3.1 Production and Extraction of Crude Biosurfactant	30
3.3.2 Surface Tension Measurement	30
3.3.3 Aggregation Behavior of Biosurfactant	30
3.3.4 Synthesis of Polyaniline in the Present of Biosurfactant	31
3.3.5 Dedoping and Doping of Polyaniline	31
3.3.6 Polyaniline Nanostructures Characterization	31
3.3.6.1 Structural Characterization	31
3.3.6.2 Morphology	31
3.3.6.3 Thermogravimetric Analysis	31
3.3.6.4 Crystalline Structure	32
3.3.6.5 Oxidation State	32
IV RESULTS AND DISCUSSION	33
4.1 Surface Activity of Produced Biosurfactant	33
4.2 Synthesis of Polyaniline Nanoparticles by Using the Biosurfactant as a Template	36

CHAPTER	PAGE
4.2.1 Effect of Acid Concentration	36
4.2.2 Effect of ANI:Biosurfactant Weight Ratio	38
4.2.3 Effect of Reaction Time	46
4.2.4 Effect of Biosurfactant Concentration	47
4.3 Yielding (%) of Synthesized Polyaniline	49
4.3.1 Effect of ANI:Biosurfactant Weight Ratio	49
4.3.2 Effect of Reaction Time	50
4.3.3 Effect of Biosurfactant Concentration	51
4.4 Characterization of Synthesized Polyaniline	52
4.4.1 FTIR Spectroscopy	52
4.4.2 UV-Vis Spectroscopy	55
4.4.3 Thermal Analysis	57
4.4.4 Wide Angle X-Ray Diffraction	61
4.4.5 Electrical Property	65
4.4.5.1 Effect of Degree of Doping	65
4.4.5.2 Effect of ANI:Biosurfactant Weight Ratio	66
4.4.5.3 Effect of Polymerization Time	68
V CONCLUSIONS	70
REFERENCES	71
APPENDICES	75
Appendix A Yielding (%) of Synthesized Polyaniline	75
Appendix B Determination of Ohmic Linear Regime	79

CHAPTER	PAGE
Appendix C Determination of Geometric Correlation Factor (K) of Custom Built Two-Point Probe	82
Appendix D Conductivity Measurement	83
CURRICULUM VITAE	127

LIST OF TABLES

TABLE		PAGE
1.1	Major types of biosurfactants produce by microorganism	4
4.1	Yield (%) data of PANI nanomaterial as function of polymerization time	51
4.2	Yield (%) data of PANI nanomaterial as increase biosurfactant Concentration to 3,600 mg/L	51
4.3	WXRd data of HCl-doped PANI synthesized at different ANI:Biosurfactant weight ratio	62
4.4	Crystallinity of HCl-doped PANI which using 1800 mg/l biosurfactant concentration at ANI:HCl composition ratio of 1:100	63
4.5	Crystallinity of HCl-doped conventional PANI using various ANI:HCl composition ratio	63
4.6	WXRd data of HCl-doped PANI synthesized at different polymerization time (ANI:Biosurfactant weight ratio of 22.7:1)	64
4.7	Crystallinity of HCl-doped PANI which using 1800 mg/L biosurfactant concentration at different polymerization time	65
4.8	Electrical conductivities of pelletized HCl-doped PANI Samples at composition ratio of 1:100	67
4.9	Electrical conductivities as function of polymerization times of pelletized HCl-doped PANI samples	69

LIST OF FIGURES

FIGURE	PAGE
1.1 Schematic of (A) micelle and (B) inverse micelle structure.	3
1.2 Shows the four general chemical structures of rhamnolipids produced by certain species of <i>Pseudomonas</i> .	6
1.3 Trehalose dimycolate from <i>Rhodococcus erythropolis</i> .	7
1.4 Sophorolipid from <i>Torulopsis bombicola</i> in which dimeric sophorose is linked to a long-chain (C18) hydroxy fatty acid.	7
1.5 Structure of phosphatidylethanolamine produced by <i>Acinetobacter sp.</i>	8
1.6 Structure of cyclic lipopeptide surfactin produced by <i>Bacillus subtilis</i> .	9
1.7 Structure of emulsan, produced by <i>Acinetobacter calcoaceticus</i> .	9
1.8 The conductivity of a number of ICPs relative to copper and liquid Mercury.	11
1.9 Examples of conducting polymers.	12
1.10 The oxidation state of PANI.	13
1.11 Molecular structure of PANI in emeraldine base and emeraldine salt form.	14
4.1 Surface tension versus the culture supernatant concentration by <i>Pseudomonas aeruginosa</i> strain PS4.	34
4.2 Surface tension versus concentration of crude biosurfactant Produced by <i>Pseudomonas aeruginosa</i> strain PS4.	35
4.3 ANI+biosurfactant solution complex after left (a) 24 hr; (b) 48 hr; (c) 72 hr.	35

FIGURE	PAGE
4.4 SEM images of a) conventional PANI; b) before remove template of PANI 0.1M HCl; and PANI polymerized in the presence of various acid concentration at the ANI:Biosurfactant weight ratio equal to 22.7:1; c) 0.01M; d)0.1M; e) 0.5M; f) 1.0M.	38
4.5 SEM images of a) conventional PANI; and PANI polymerized In the present of different ANI:Biosurfactant weight ratio at constant 1800 mg/L biosurfactant; b) 28.3:1 c) 22.7:1; d) 19.3:1; and e) 11.3:1.	39
4.6 Transmission Electron Microscopy (TEM) images of PANI polymerized in the presence of different ANI:Biosurfactant weight ratio at constant 1800 mg/L biosurfactant a) 28.3:1; b) 22.7:1 and c) PANI before remove biosurfactant template.	40
4.7 Transmission Electron Microscopy (TEM) and Dynamic light scattering measurement (DLS) of a) 1,800 mg/L biosurfactant in distillation water; b) biosurfactant solution + aniline; c) biosurfactant solution + aniline + 0.1M HCl; d) biosurfactant solution + APS complexes and e) 3,600 mg/L biosurfactant in distillation water.	42
4.8 SEM images of PANI polymerized at the different reaction time in the presence of ANI:Biosurfactant weight ratio equal to 22.7:1 at 1800 mg/L biosurfactant b) 4 h; c) 6 h; d) 8 h.	47

FIGURE	PAGE
4.9 SEM images of a) PANI before remove biosurfactant template; and PANI polymerized in the presence of different ANI:Biosurfactant weight ratio at 3600 mg/L biosurfactant: b) 14.2:1; c) 11.4:1; and d) 9.6:1.	48
4.10 Yielding (%) of synthesized PANI at different biosurfactant concentration.	50
4.11 FTIR spectra of PANI synthesized using different HCl acid concentration a) 1.0M; b) 0.5M; c) 0.1M; and d) 0.01M; e) crude biosurfactant.	52
4.12 FTIR spectra of PANI synthesized at different ANI:Biosurfactant weight ratio, a) 11.3:1; b) 19.3:1; c) 28.3:1; d) 22.7:1; e) conventional PANI; f) undoped state of PANI (PANI EB); g) crude biosurfactant.	54
4.13 FTIR spectra of a) Rhamnolipid biosurfactant; b) conventional PANI; PANI synthesized at different ANI:Biosurfactant weight ratio using biosurfactant as a template, c) 14.2:1; d) 11.4:1; e) 9.6:1.	55
4.14 UV-vis spectra of synthesized polyaniline as a function of weigh ratio ANI:Biosurfactant a) PANI EB b) 11.3:1 c) 19.3:1 d) 22.7:1 e) 28.3:1 f) conventional PANI.	56
4.15 TGA thermograms of a) biosurfactant; PANI synthesized using various acid concentration b) 0.5M, c) 0.01M HCl; d) aniline monomer.	58
4.16 TGA thermograms of PANI synthesized using 1800 mg/L biosurfactant as a template at difference ANI:Biosurfactant weight ratio; a) 11.34, b) 19.28, c) 22.7, d)28.36, e) conventional PANI, and f) biosurfactant.	59

FIGURE	PAGE
4.17 TGA thermograms of PANI synthesized at different polymerization time: a) 4 hr, b) 6 hr and c) 8 hr. (ANI:Biosurfactant weight ratio of 22.7).	60
4.18 TGA thermograms of PANI synthesized using 3600 mg/L biosurfactant as a template at difference ANI:Biosurfactant weight ratio; a) 9.6, b) 11.4, c) 14.2, d) conventional PANI, and e) biosurfactant.	60
4.19 WXRd patterns of HCl-doped resulting PANI with the ANI:HCl composition ratio of 1:100 at different ANI:Biosurfactant weight ratio of a) 11.3:1; b) 19.3:1; c) 22.7:1; d) 28.3:1; and WXRd patterns of PANI synthesized by conventional approach at different ANI:HCl composition ratio of e) 1:100; f) 1:25.	61
4.20 WXRd patterns of HCl-doped PANI at different polymerization time; a) 4 hr; b) 6 hr; C) 8 hr (using the ANI:biosurfactant weight ratio of 22.7:1).	64
4.21 Room temperature conductivities versus the mole ratios of aniline units in PANI to the mole ratios of hydrochloric acid unit.	66
4.22 Specific conductivity of dedope PANI as a function of ANI:Biosurfactant weight ratio.	68
4.23 Specific conductivity of HCl-doped PANI as a function of ANI:Biosurfactant weight ratio.	68

LIST OF SCHEMES

SCHEME	PAGE
1. Chemical structure of rhamnolipid biosurfactant.	33
2. Proposed formation mechanism for PANI nanostructured using a biosurfactant as a template.	44
3. H-bond formed between amine group of aniline and carboxylic group of biosurfactant.	45
4. Electrostatic interaction between amine group of aniline and carboxylate group of biosurfactant.	46