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# APPENDICES

**Appendix A** Synthesis of Poly *o*-anisidine

POA was synthesized via chemical oxidation polymerization (Mazrouaa *et al.*, 2012).

**Table A1** Poly *o*-anisidine synthesis conditions

| | Batch | Time (hours) | Temperature (°C) | Mole ratio of monomer/SDS | Yield (%) |
|---|---|---|---|---|---|
| Time / Temp. | POA-18-R-8.00 | 18 | Room temp | 8.00 | 19 |
| | POA-48-R-8.00 | 48 | Room temp | 8.00 | 17 |
| | POA-18-60-8.00 | 18 | 60 | 8.00 | N/A |
| | POA-18-3-8.00 | 18 | 3 | 8.00 | 57 |
| | POA-48-3-8.00** | 48 | 3 | 8.00 | 66 |
| | POA-72-3-8.00 | 72 | 3 | 8.00 | 65 |
| | POA-48-3-0.008 | 48 | 3 | 0.008 | 25 |
| SDS mole ratio | POA-48-3-0.12 | 48 | 3 | 0.12 | 30 |
| | POA-48-3-1.00 | 48 | 3 | 1.00 | 57 |
| | POA-48-3-4.00 | 48 | 3 | 4.00 | 60 |
| | POA-48-3-6.00 | 48 | 3 | 6.00 | 65 |
| | POA-48-3-8.00 | 48 | 3 | 8.00 | 66 |
| | POA-48-3-10.00 | 48 | 3 | 10.00 | 66 |
| | POA-48-3-12.00 | 48 | 3 | 12.00 | 74 |

**Appendix B** Surface Tension Measurement

Tensiometer (Kruss, Easydyne) was used to investigate the surface tension and critical micelles point (CMC) of SDS. The SDS was dissolved in DI-water at various concentrations from 0.5-16 mM. A solution was placed in a water bath to measure surface tension values (Umlong *et al.*, 2006). This figure shows that the critical micelle point of SDS at 24 °C and 6 °C is 6 mM (0.12 mole ratios of SDS/OA monomer).

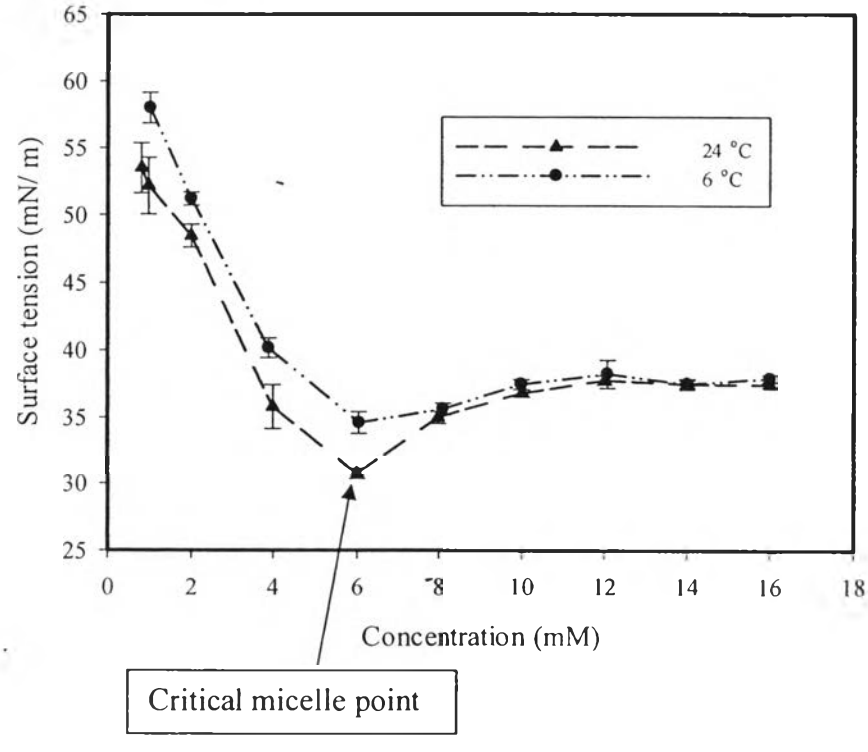



**Figure B1** Surface tension of SDS at different concentrations.

**Appendix C** FTIR Spectra of Poly *o*-anisidine

FT-IR spectrometer (Nicolet, Nexus 670) was used to characterize the functional groups of synthesized POA. The FT-IR absorption was taken for 64 scans at the wavenumber between 400-4000 $cm^{-1}$ with a resolution of 4 $cm^{-1}$. The sample was prepared by glided POA with potassium bromide (dried at 100 °C for 24 h) then compressed to a pellet and inserted in a sample holder (Mazrouaa *et al.*, 2012).

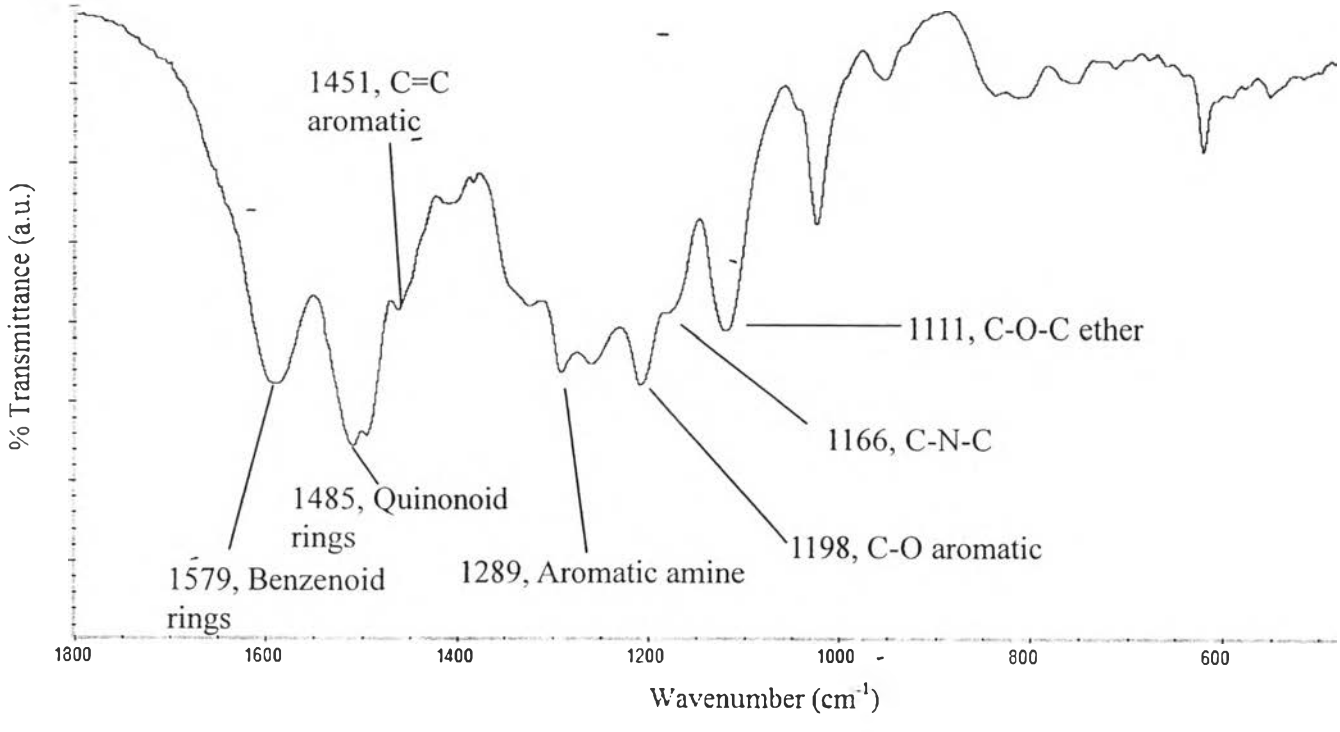
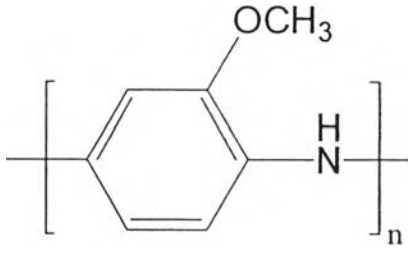



**Figure C1** FTIR spectra of poly *o*-anisidine.




1579 $cm^{-1}$, Benzoid and quinoid rings
1451 $cm^{-1}$, C=C aromatic
1289 $cm^{-1}$, Aromatic amine
1198 $cm^{-1}$, C-O aromatic
1166 $cm^{-1}$, C-N-C
1111 $cm^{-1}$, C-O-C ether

The degree of oxidation (X) was calculated from the intensity of the quinonoid peak ($I_Q$) relative to the benzenoid peak ($I_B$) (Wang *et al.*, 2012) using the Eq (C1).

$$X+\{X/(I_Q / I_B)\} = 1 \qquad (C1)$$

**Table C1** Degree of oxidation of POA doped with different SDS mole ratio

| Mole ratio of SDS/monomer | $I_Q/I_B$ | Degree of Oxidation (%) |
|---|---|---|
| 0.008 | 0.71 | 41.64 |
| 0.12 | 0.68 | 40.58 |
| 1.00 | 0.51 | 33.99 |
| 4.00 | 0.59 | 37.46 |
| 6.00 | 0.50 | 33.69 |
| 8.00 | 0.58 | 36.80 |
| 10.00 | 0.57 | 36.50 |
| 12.00 | 0.52 | 34.04 |

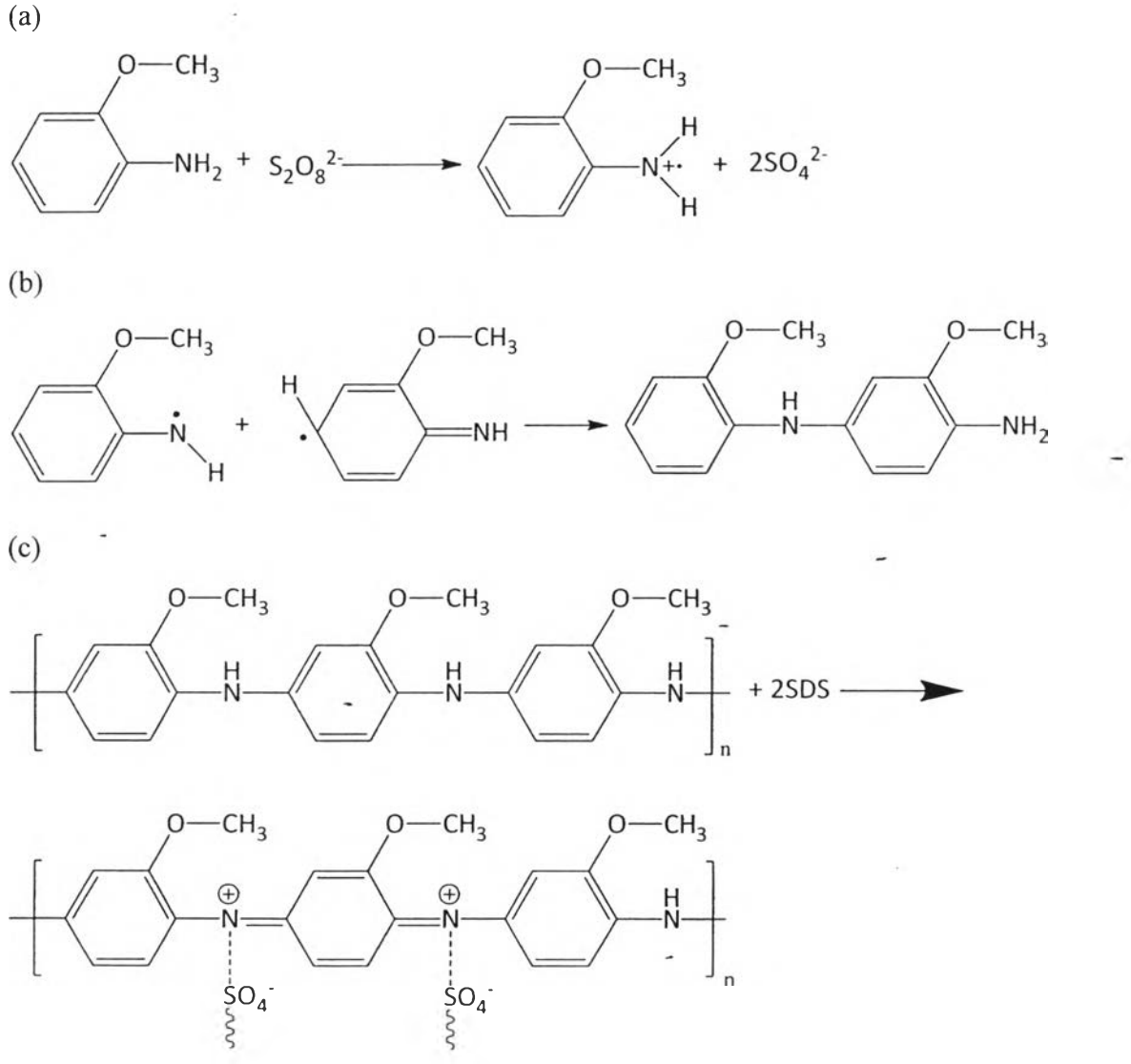



**Figure C2** Proposed polymerization mechanism of POA: (a) OA as monomer is oxidized by APS to a cation radical; (b) OA cation radicals form dimers that subsequently get deprotonated; and (c) POA polymer is doped and dodecyl sulfate ion acts as counter ion (Khan *et al.*, 2009).

**Appendix D** UV-vis Spectra of Poly *o*-anisidine

A UV-VIS spectrophotometer (UV-Tecan, Infinite M200) was used to determine the spectra peak of POA structure at wavelengths from 230 nm to 1200 nm. The absorption peaks of POA are at 330 and 600 nm. However, the peak at 600 nm was shifted to 700 nm depending on the doping level.

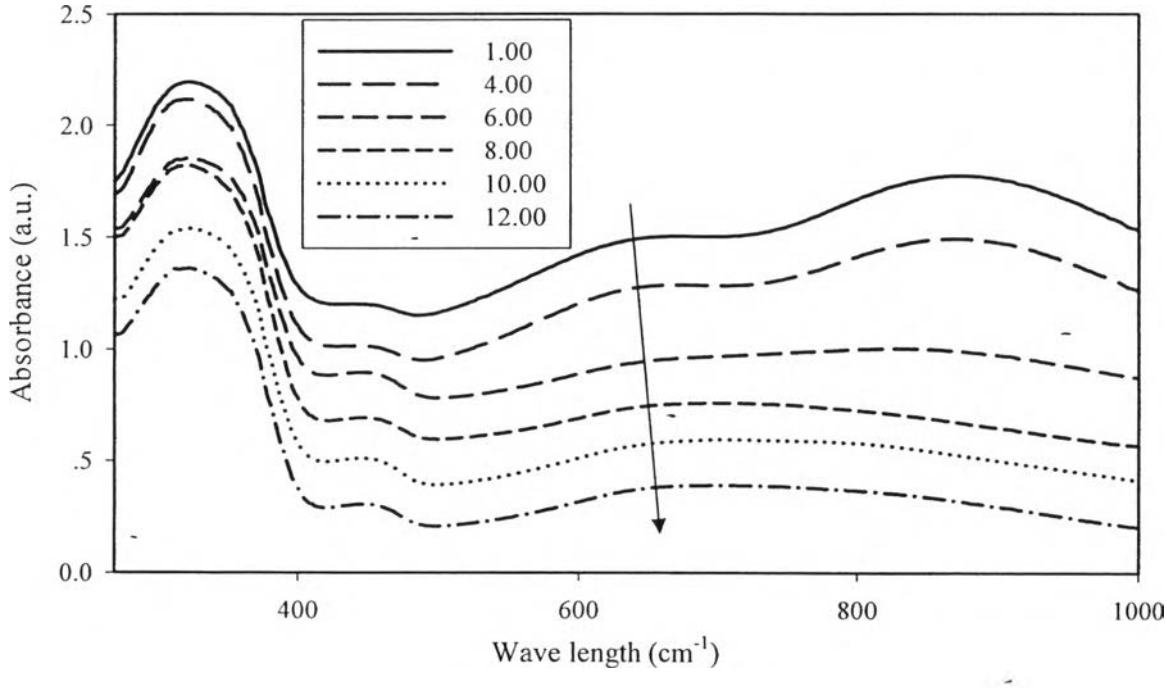
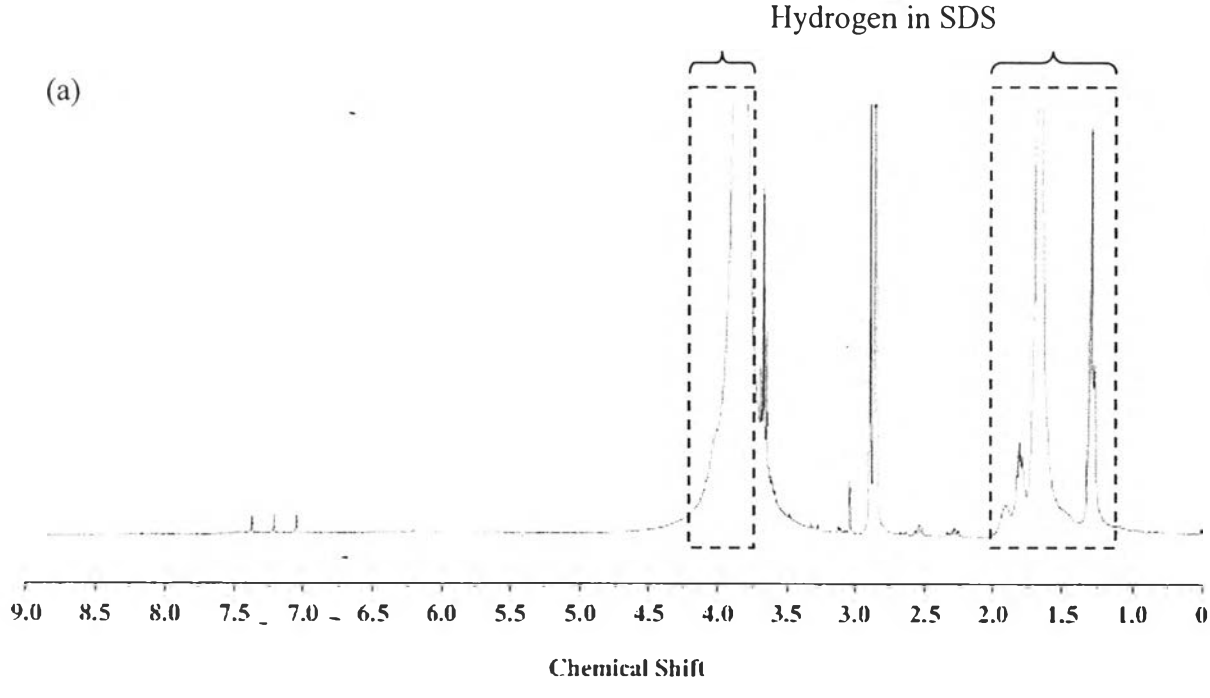



**Figure D1** UV-vis spectra of poly *o*-anisidine.

**Appendix E** $^{1}$H NMR Spectrum of Poly *o*-anisidine.

H-NMR (Bruker, Avance) was used to characterize the functional groups and determine the structure of POA. POA was dissolved in 1 ml of DMSO-$d_6$ and measured in 30 min to prevent the oxidation of the polymer structure. In Figure E1 (a), the signal in the range of δ=1.25-2.0 and δ=3.8-4.0 correspond to the interfere peak of sodium dodecyl sulfate. After washing sodium dodecyl sulfate, the real characteristic peak of POA is clearly obvious in Figure E1 (b). The signals in the range of δ=3.5-4.5 correspond to the hydrogen in methyl group (-$CH_3$). The signals in the range of δ=5.5-7.5 correspond to the hydrogen in aromatic carbon. The integration of area under two groups of peaks in spectrum (0.912 and 1.00 from 3H: 3H) indicates the structure of polymer in spectrum is POA (Wang *et al.*, 2010).



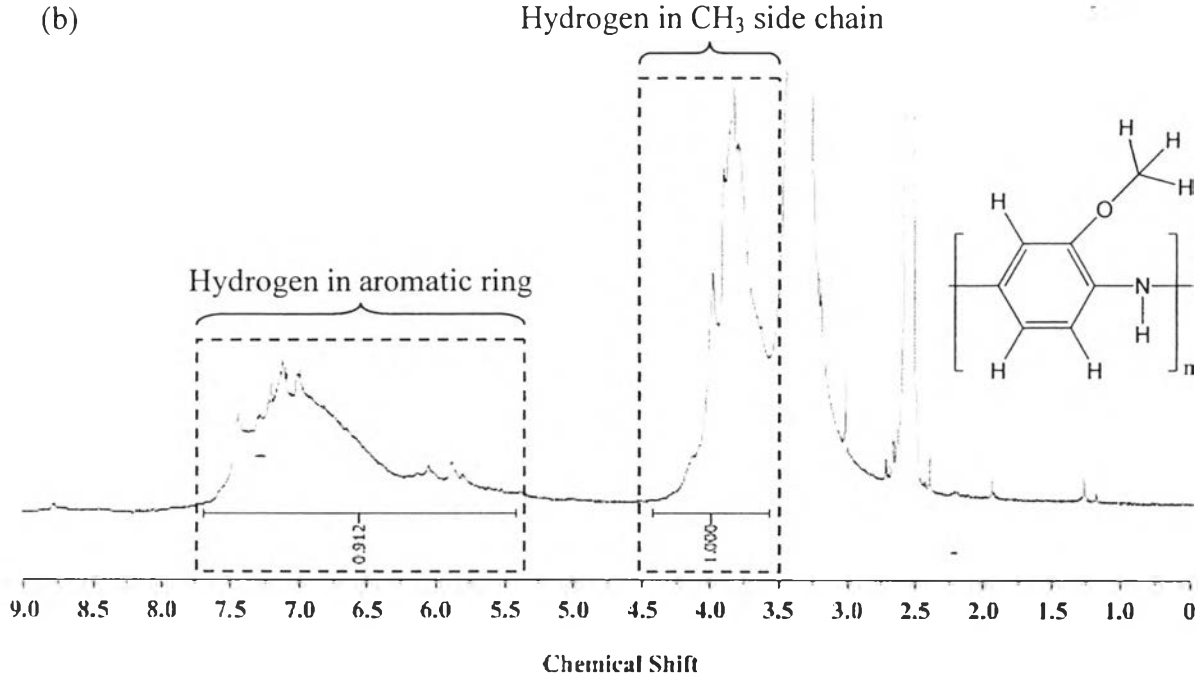



**Figure E1** $^1$H NMR spectrum of POA: (a) POA with SDS; (b) pure POA.

**Appendix F** TGA of Poly *o*-anisidine

Thermogravimetric (Perkin Elmer, Pyris Diamond) analyzer was used to investigate the weight losses of volatile molecules, the amount of residual water, and the degradation temperatures of POA. The samples were weighed in the range of 4-10 mg and loaded into an alumina pans. The thermograms of POA were performed with a temperature scan from 25 °C to 600 °C and with a heating rate 10 °C/min under nitrogen atmosphere. The thermal behavior of POA shows 2 steps of weight loss. First, the decomposition temperature of 370-500 °C corresponds to the decomposition of POA backbone (Mondal *et al.*, 2006). Second, the decomposition temperature of doped-POA also exhibits the degradation of dopant (SDS) at 180-250 °C (Kulkani *et al.*, 2006).

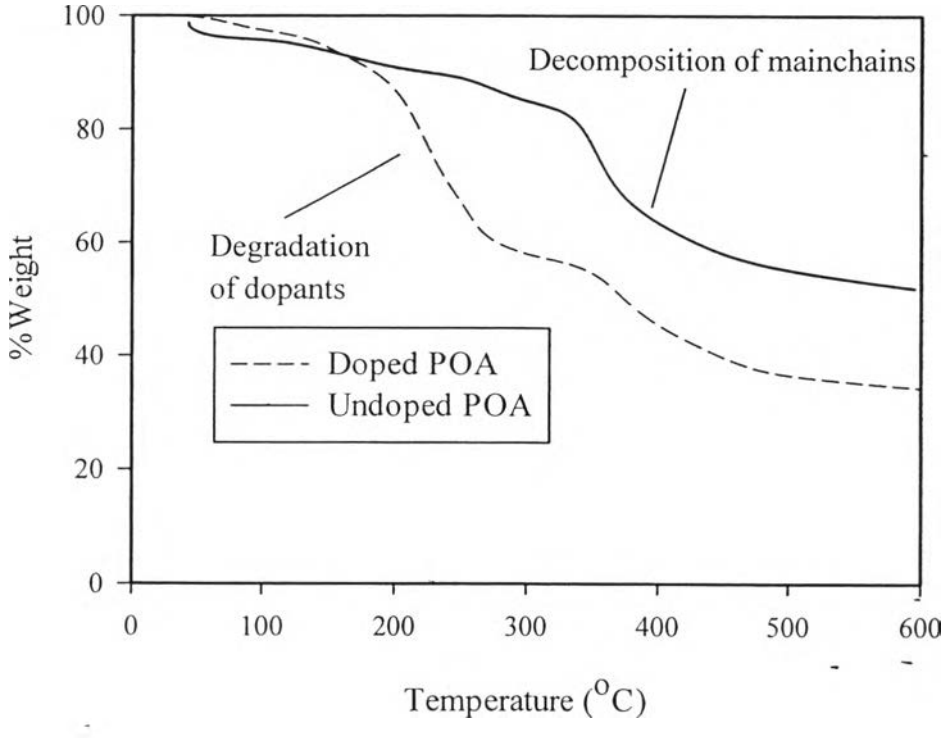



**Figure F1** Thermogram of poly *o*-anisidine.

**Appendix G** SEM Photographs and Electrical Conductivity

Electrical conductivity measurement

The two-point probe meter was used to measure the specific resistivity (ρ) of the material. The specific resistivity indicates the ability of material which resists electrical charge movement. This meter consists of two-point probe, the one probe was connected to a voltmeter for measuring the voltage and the other probe was connected to a constant current source. The specific conductivity (σ) was calculated from the specific resistivity by using Eq. (G1).

$$\sigma = 1/\rho = 1/(R_s t) = I/(KVt) \qquad (G1)$$

where σ is the specific conductivity (S/cm.), ρ is the specific resistivity (Ω.cm.), $R_s$ is the sheet resistivity (Ω), I is the applied current (A), K is the geometric correction factor, V is the voltage drop (V), and t is the film thickness (cm.). The sheet resistance ($R_s$) was obtained by introducing a current (I) through the outer two pins and determining the voltage drop (V) across the inner two pins.

**Table G1** Effect of time on poly *o*-anisidine synthesis

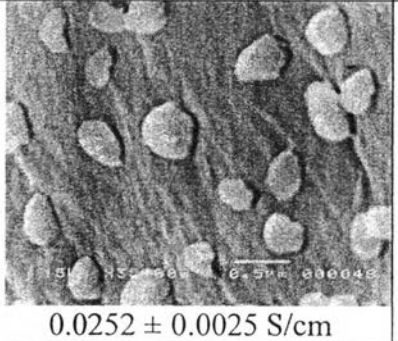
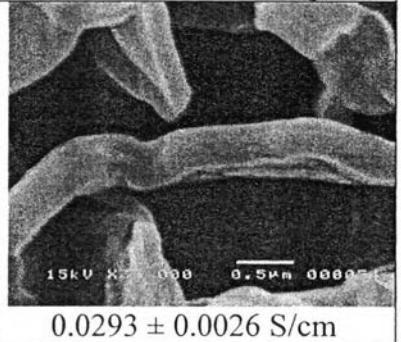
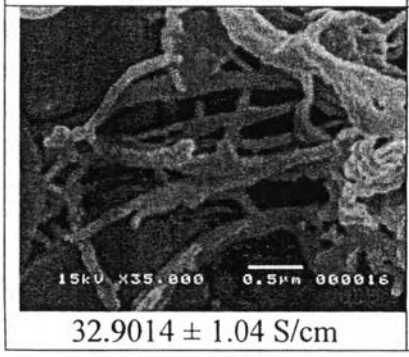
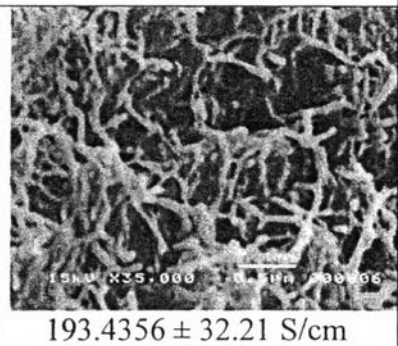
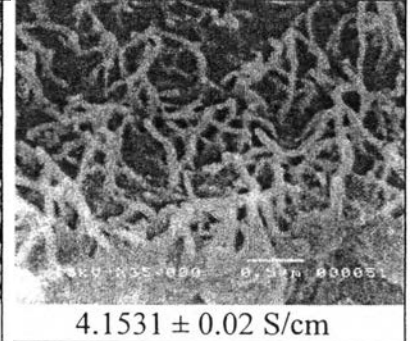
| 18 hrs. Room temp | 48 hrs. Room temp | |
|---|---|---|
|  |  | |
| 0.0252 ± 0.0025 S/cm | 0.0293 ± 0.0026 S/cm | |
| **18 hrs. 3 °C** | **48 hrs. 3 °C** | **72 hrs. 3 °C** |
|  |  |  |
| 32.9014 ± 1.04 S/cm | 193.4356 ± 32.21 S/cm | 4.1531 ± 0.02 S/cm |

**Table G2** Effect of SDS in synthesis at 48 hrs. 3 °C with various mole ratios

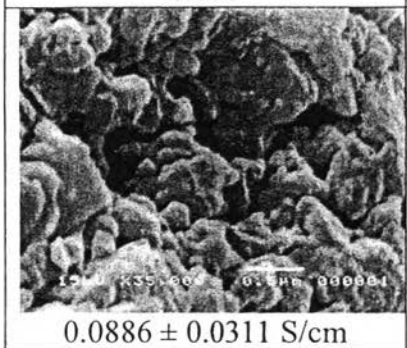
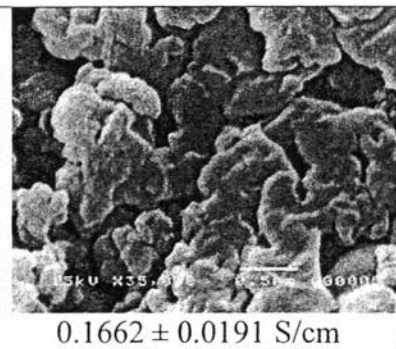
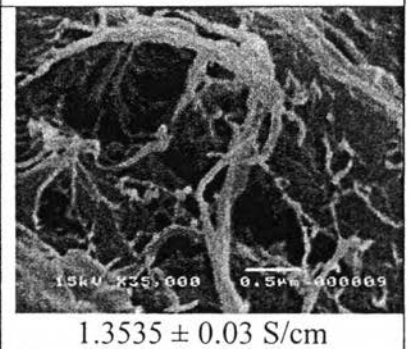
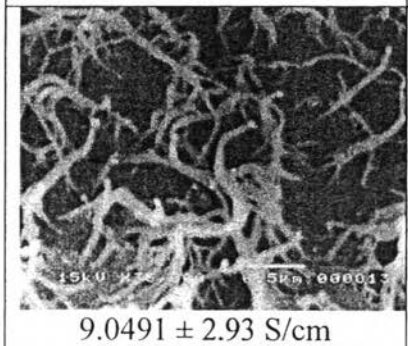
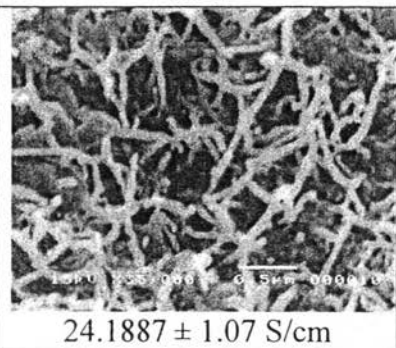
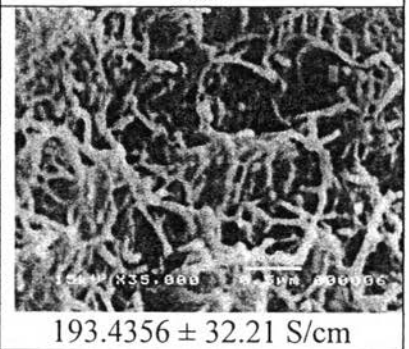
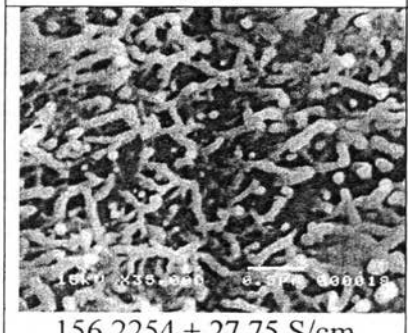
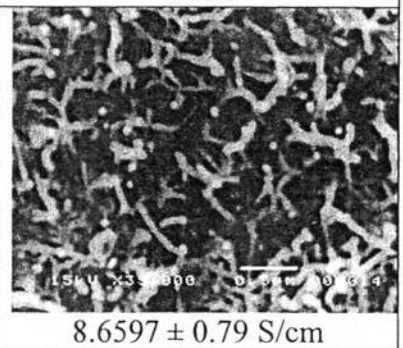
| 0.008 | 0.12 | 1.00 |
|---|---|---|
|  |  |  |
| 0.0886 ± 0.0311 S/cm | 0.1662 ± 0.0191 S/cm | 1.3535 ± 0.03 S/cm |
| **4.00** | **6.00** | **8.00** |
|  |  |  |
| 9.0491 ± 2.93 S/cm | 24.1887 ± 1.07 S/cm | 193.4356 ± 32.21 S/cm |
| **10.00** | **12.00** | |
|  |  | |
| 156.2254 ± 27.75 S/cm | 8.6597 ± 0.79 S/cm | |

**Table G3** Effect of SDS in POA fiber diameter

| Mole ratio of SDS/monomer | Diameter (nm) |
|---|---|
| 0.008 | 0 |
| 0.12 | 0 |
| 1.00 | 90 ± 17.9 |
| 4.00 | 73 ± 13.1 |
| 6.00 | 73 ± 13.5 |
| 8.00 | 65 ± 8.6 |
| 10.00 | 80 ± 13.7 |
| 12.00 | 60 ± 11.2 |

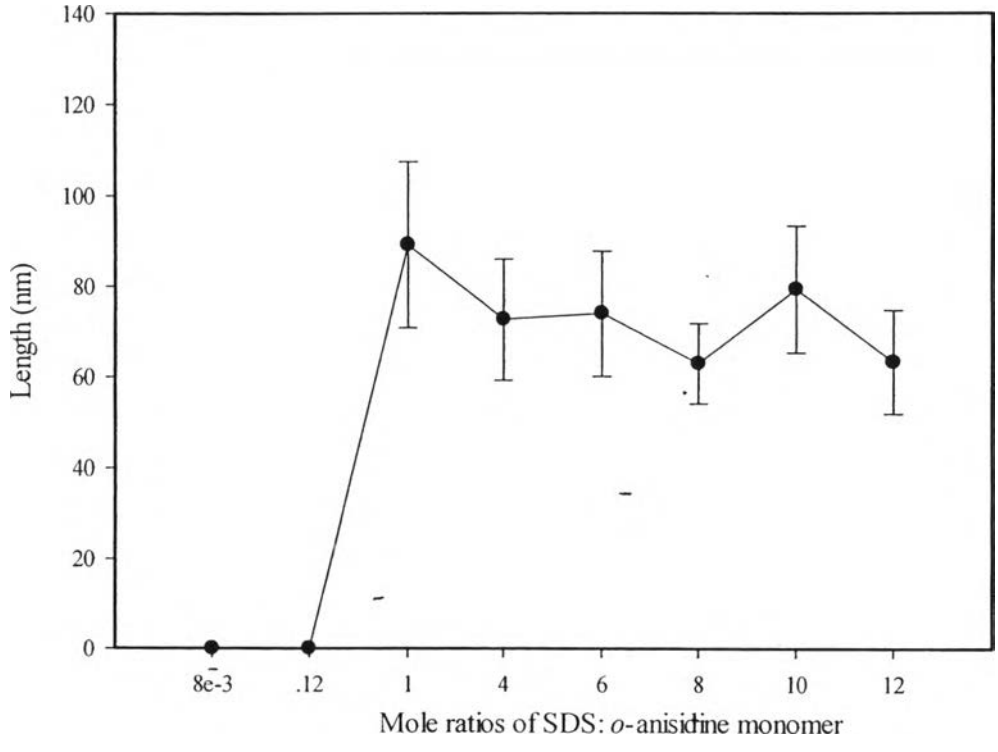



**Figure G1** Fiber diameter of poly *o*-anisidine at various mole ratios of SDS: *o*-anisidine monomer.

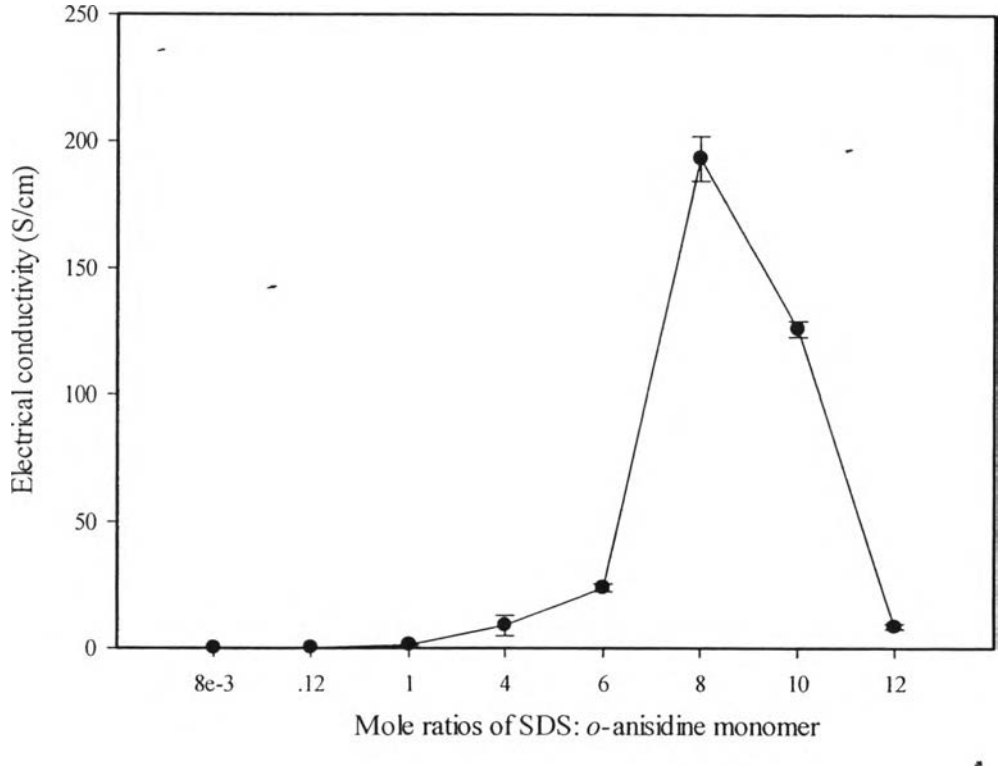



**Figure G2** Conductivity of poly *o*-anisidine at various mole ratios of SDS: *o*-anisidine monomer.

**Appendix H** Reproductivity of Poly *o*-anisidine in Condition of 48 hrs, 3 °C, and 8 mole ratio of SDS:*o*-anisidinemonomer

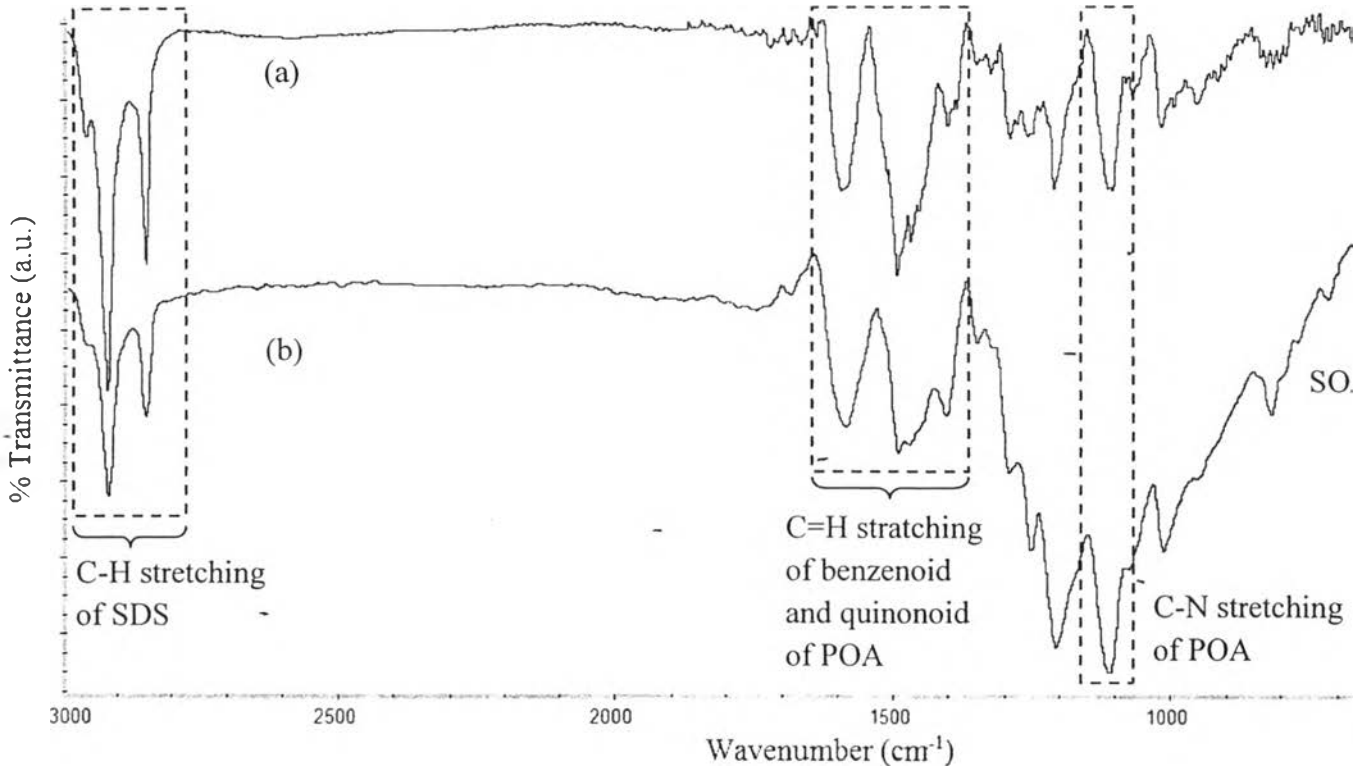



**Figure H3** FT-IR spectra of poly *o*-anisidine: (a) first batch; and (b) second batch.

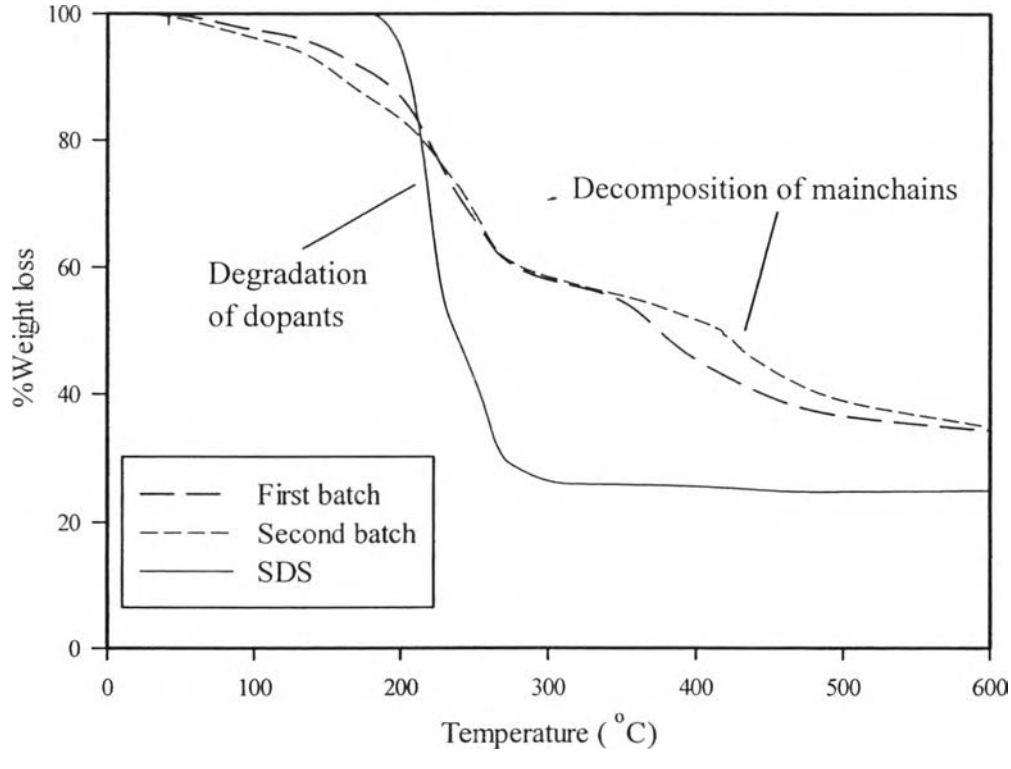



**Figure H1** Thermogram of poly *o*-anisidine.

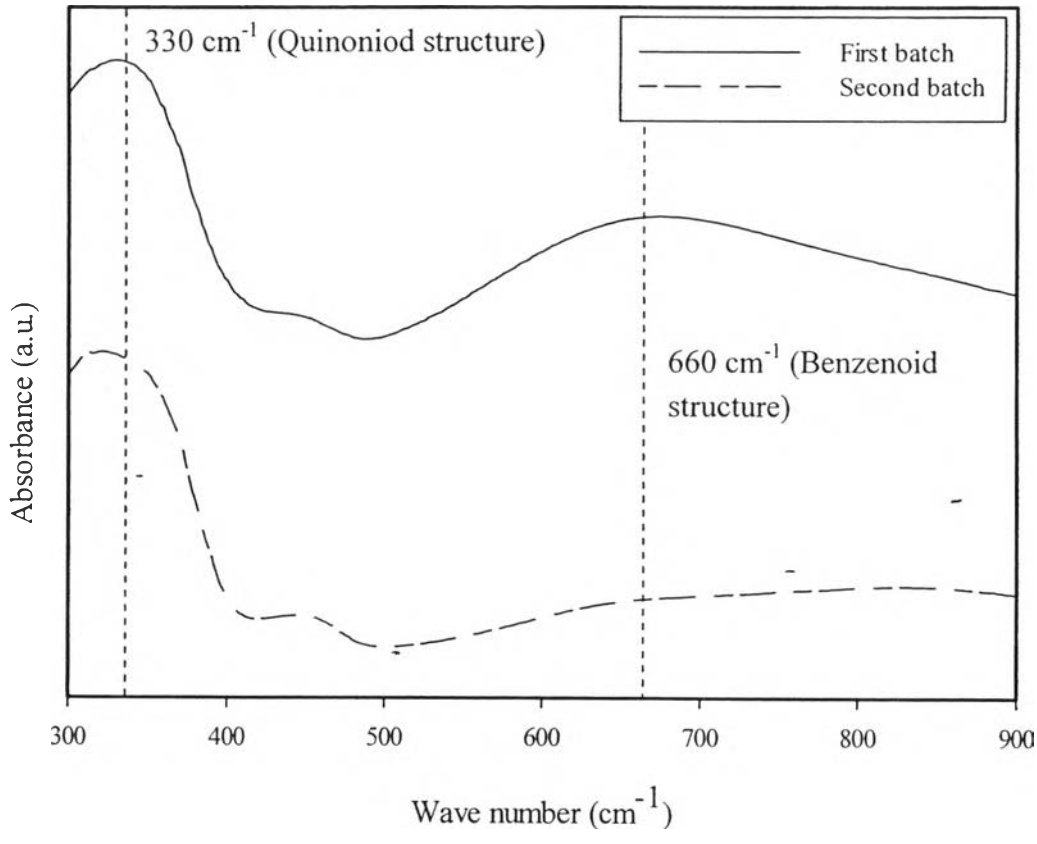



**Figure H4** UV-vis spectra of poly *o*-anisidine.

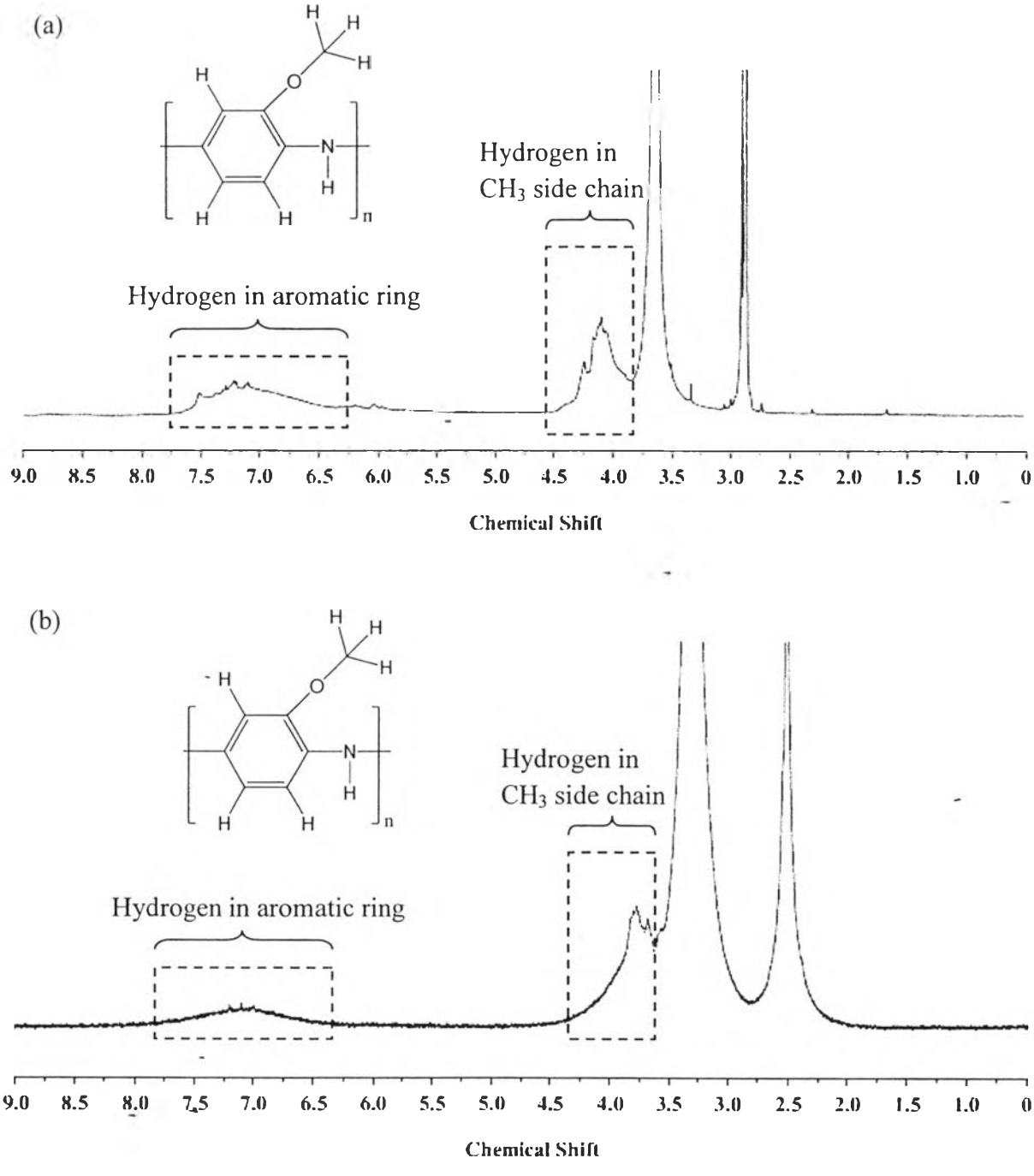
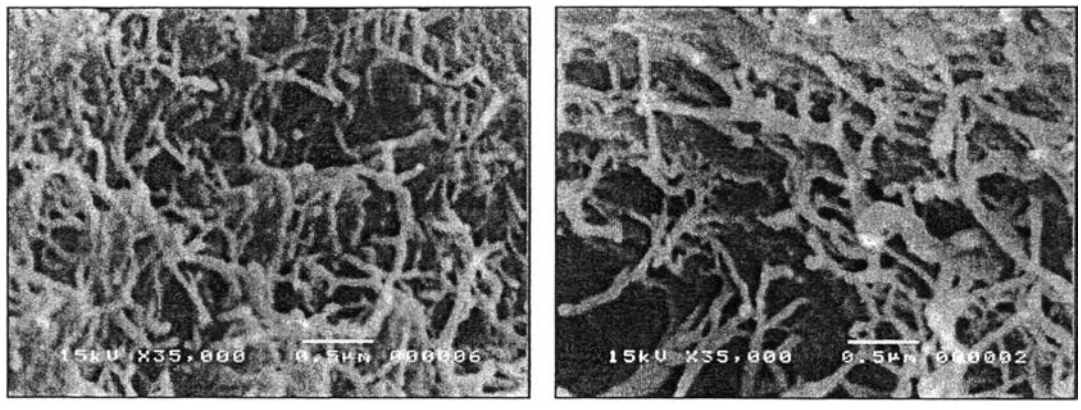



**Figure H5** $H^1$-NMR of poly *o*-anisidine: (a) first batch; and (b) second batch.




(a) (b)

**Figure H2** SEM image of poly *o*-anisidine: (a) first batch; and (b) second batch.

**Table H1** Electrical conductivity of poly *o*-anisidine

| Sample | First batch | Second Batch | |
|---|---|---|---|
| 1 | 184.43 | 96.08 | |
| 2 | 187.21 | 109.13 | |
| 3 | 208.65 | 228.25 | |
| Average | 193.43 | 144.47 | 168.96 |
| SD | 13.25 | 72.83 | 34.06 |

# CURRICULUM VITAE

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**Presentations:**

1. Khamngoen K.; and Sirivat, A. (2014, April 22) Chemical Oxidation Polymerization and Characterization of Poly *o*-anisidine Nanoparticles. Paper Presented at the 5th Research Symposium on Petrochemical and Materials Technology and the 20th PPC Symposium on Petroleum, Petrochemicals, and Polymers, Bangkok, Thailand.