계면 활성제를 이용하여 가공성이 향상된 폴리아닐린과 이의 응용

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이창진*, 강영구

일반적인 전도성 고분자로는 폴리아세틸렌, 폴리피롤, 폴리아닐린, 폴리티오펜 등을 들 수 있으며 이들은 모두 공액 이중 결합을 가지므로 고분자 사슬이 딱딱하고 또한 도핑이 된 상태에서는 전하를 가진 사슬간의 상호 인력이 강하여 쉽게 용매에 녹지 않으며 용융 가공도 되지 않는다. 따라서 전도성 고분자의 실용적인 활용을 위해서는 가공성을 부여하는 것이 가장 큰 관건으로 되어 있다.

폴리아닐린은 염산 수용액에서 산화 중합하면 가공성이 없는 폴리에머랄딘 염이 얻어지나 이를 암모니아 수용액으로 처리하여 얻어진 폴리에머랄딘 염기는 NMP에 녹는다. 또한 이를 다시 산으로 처리하면 도핑이 되는 독특한 성질을 갖는다. 에머랄딘 염기를 도핑할 때, 계면활성제로 사용될 수 있는 dodecylbenzenesulfonic acid나 camphorsulfonic acid 같은 산으로 도핑을 하면 xylene, chloroform, dimethylsulfoxide, m-cresol 등에 녹는 폴리아닐린이 얻어진다. 이들을 코팅하거나 다른 고분자와 블렌딩하여 사용하는 것이 매우 유용한 방법으로 제시되고 있다.

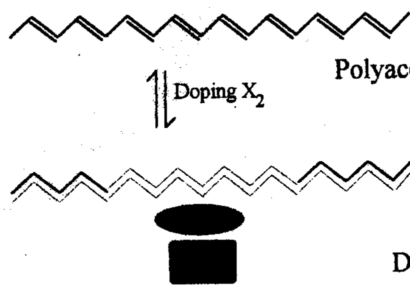
또한 여러 가지 계면활성제를 사용하여 emulsion polymerization을 통하여 폴리아닐린 에멀젼을 제조하는 것도 상당히 유용한 방법인데 최근에는 에멀젼 중합이 진행되면서 유기와 수용액 층이 분리되어 더 이상의 정제가 필요없이 유기 층만을 분리하여 사용할 수 있는 방법도 발표되었다.

일반적으로 산화 중합법으로 직접 제조된 폴리에머랄딘 염은 용매에 녹지 않고 분산도 잘되지 않으나 이들은 대부분 약 10 nm에서 150 nm 사이의 primary particle로 구성되어 있으며 이러한 primary particle이 모여서 사이즈가 큰 secondary particle이 형성된다. 따라서 폴리아닐린 그 자체는 organic nanometal이라고 생각될 수 있으며 이 경우 고분자 매트릭스에 분산시킬 경우 percolation에 의한 전기 전도도의 증가가 관측된다. 이러한 우수한 분산을 얻기 위해서는 폴리아닐린 제조시 미리 steric stabilizer 등을 이용하여 제조하거나 아니면 post polymerization treatment process를 거친다.

이러한 가공성이 있는 폴리아닐린을 이용하여 대전 방지용 코팅이나 전도성 코팅, 이차전지 전극 물질, 알루미늄 혹은 탄탈 고체전해콘덴서, 센서, 가스분리막, pervaporation membrane 등의 다양한 분야에 응용이 시도되고 있는 것을 최근 발표된 문헌을 통하여 알 수 있다.

INTRODUCTION

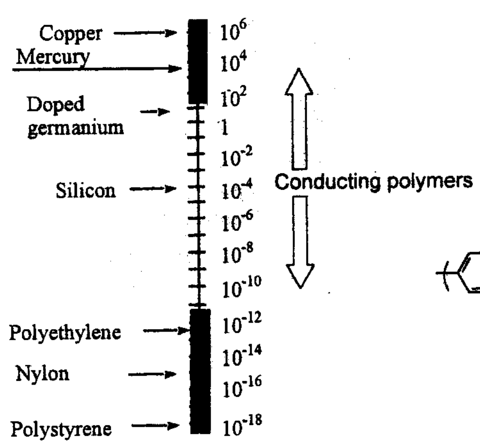
Discovery in 1977 by Shirakawa, Heeger, MacDirmaid and Park

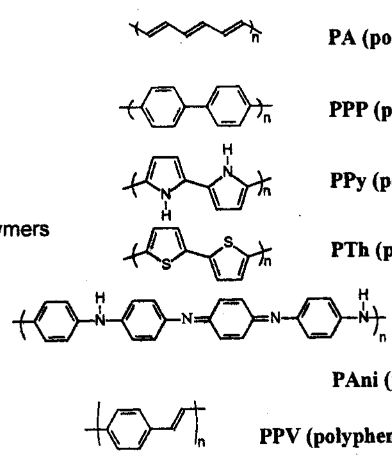


Polyacetylene (PA) **10^{-9} S/cm**

Doped PA **10^{3} S/cm**

Expectation that this conductive polymer possesses both the mechanical and processable properties of polymers and electrical and optical properties of metal brought many interests from academies and industries.





PA (polyacetylene)

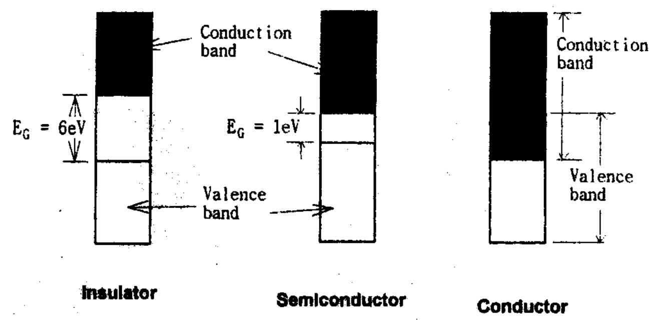
PPP (polyphenylene)

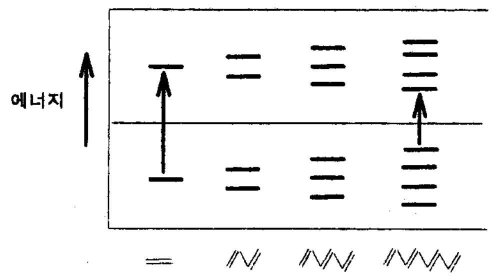
PPy (polypyrrole)

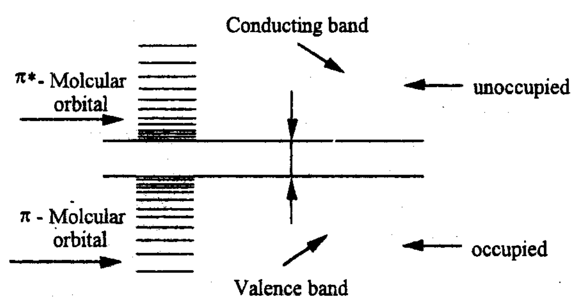
PTh (polythiophene)

PAni (polyaniline)

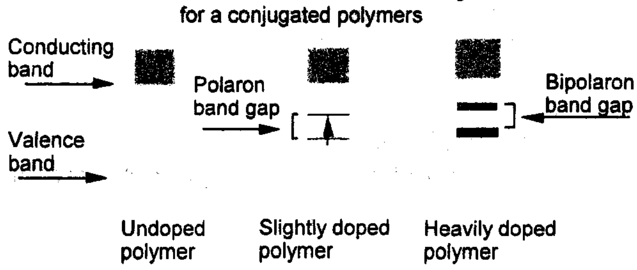
PPV (polyphenylene vinylene)







A schematic band structure and MO diagrams for a conjugated polymers



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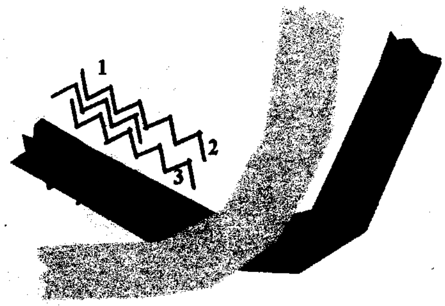

1 ↔ 2 intra-chain

2 ↔ 3 inter-chain

3 ↔ 4 inter-fiber

1 ↔ 4 superposition of above

Conductivity (σ) = n q μ

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Conjugated double bond
- **rod like, rigid back bone**
- **strong interchain interaction**

Doping for the conductivity
- **doped form contains charges**
- **strong interchain ionic interaction**

⇨ **Not soluble**
Not processable ⇨ **inhibit the applications**

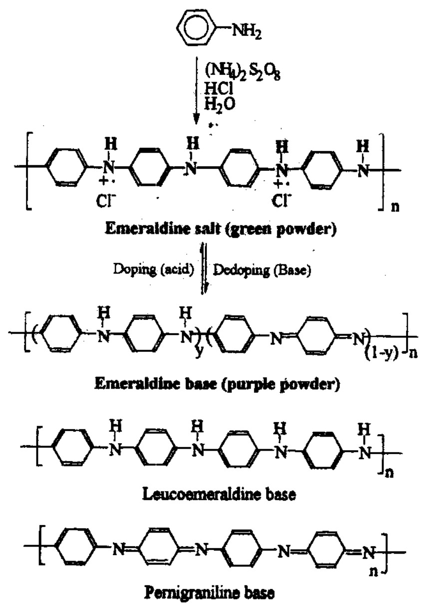
Conductivity
- **not high enough**
- **dependent on morphology, temperature and etc.**

POLYANILINE (PAni)

1. **Monomer is relatively inexpensive**
2. **The polymerization is straightforward**
3. **The polymerization proceeds with high yield**
4. **The conducting form has high stability (<200 ℃)**
5. **Extensively studied for the commercial application**
6. **Base form is soluble in NMP**

- **Low processability (but better than PPy and PTh)**
- **Acidic doping**

PREPARATION OF POLYANILINE



Oxidant : aniline mole ratio = 0.25
aniline: 0.39 - 0.42 M
HCl : 0.51 -0.53
at -7 ~ -14 ° C
LiCl to prevent freezing

Filtration, washing

NH_4OH for 72 h
Filtration, washing

High Mw upto 400,000 g/mol - below -30 ° C

Low Mw of EB prepared at high temp.
- poor solubility
- significant by products

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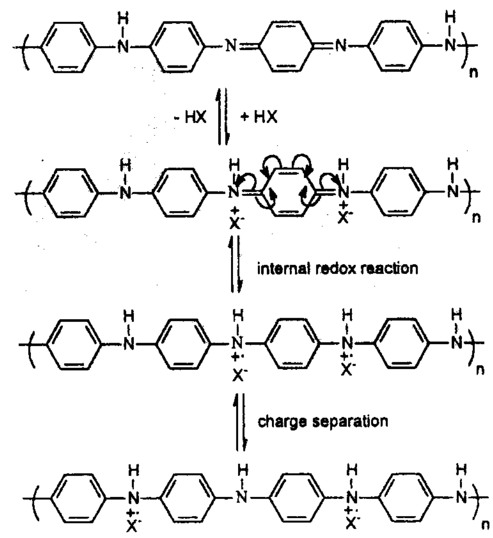
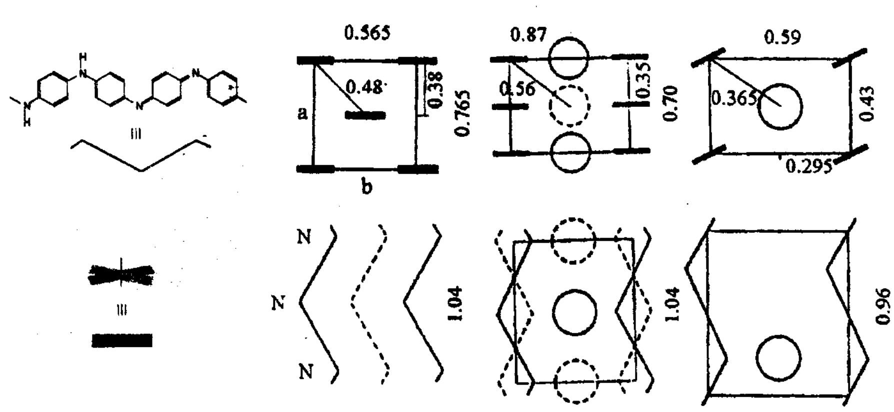
PROTON ACID DOPING OF EB



X-RAY STUDIES



EB-II (sovent cast film) **ES-II** (doping of EB-II) **ES-I** (pristine powder)

	EB	ES
Φ	30 °	0–10 °
δ	131 °	141 °

J.P. Pouget et al, *Macromolecules* **1991**, *24*, 779.

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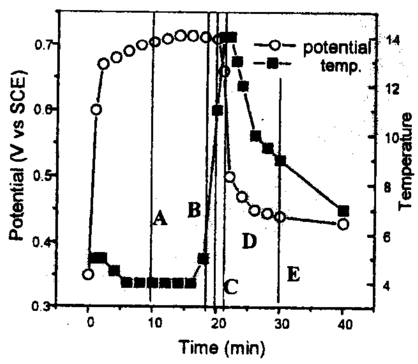
POLYMERZATION MECHANISM



Polymerization of aniline in 20vol% acetone

- Induction period
- Color of the reaction : blue during most of the reaction time
- Autoacceleration
- Addition of pernigraniline reduced the induction period

-d[AN]/ dt = k_1[AN][APS] + k_2[AN][P]

k_2 had value two or three orders of magnitude higher than k_1

A: light blue
B: deepening of color, some precipitation
C: temperature increase - autoacceleration
D: rapid decrease of potential
E: potential and temp were stabilized

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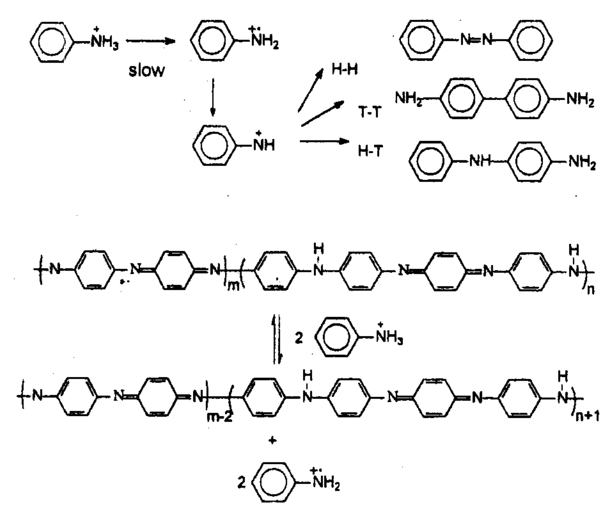
POLYMERZATION MECHANISM



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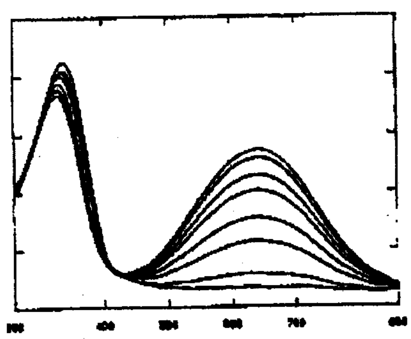
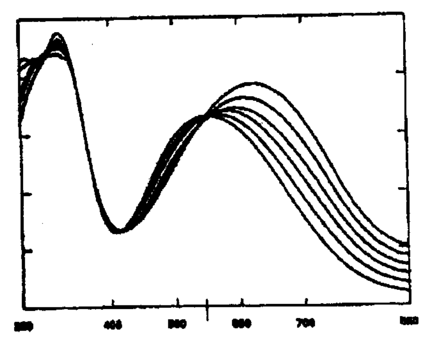
UV-VIS SPECTRA

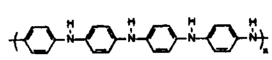


LEB → EB

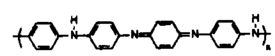


EB → PN

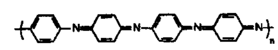
LEB :340 → EB : 340, 640 → PN : 330, 540



Leucoemeraldine base



Emeraldine base



Pernigraniline base

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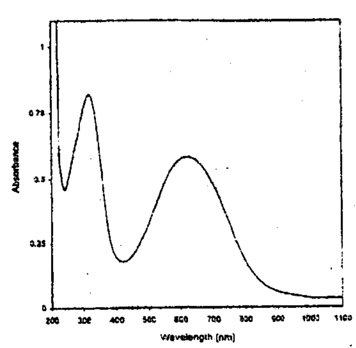
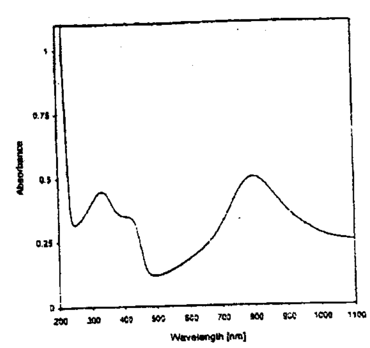
UV-VIS SPECTRA





Emeraldine base

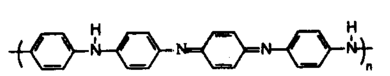
340 π–π* transition from benzenoid

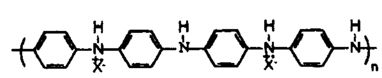
640 π–π* transition from quinoid

Emeraldine salts

340 π–π* transition from benzenoid

425, 840 nm transition from polaron





Processable forms of electrically conductive polyaniline

- **Doping of emeraldine base with surfactant like acids**
  - Soluble in xylene, chloroform and m-cresol
  - Melt processable
- **Emulsion polymerization**
  - Spontaneous phase separation
  - Synthesis in microemulsion
  - In the presence of SBS
- **Dispersible PAni**
  - Postpolymerization treatment of PAni
  - From the homogeneous aqueous suspension
  - Polymerization of aniline in the presence of latex or steric stabilizer

Doping of emeraldine base with surfactant like acids

Emeraldine base
+
Protonic acid — **Surfactant like protonic acid (Dodecylbenzenesulfonic acid Camphorsulfonic acid)**

(+)

Solvents — **xylene, chloroform, m-cresol**

PAni/DBSA - melt processable, soluble
PAni/CSA - soluble

Y. Cao, P. Smith and A. J. Heeger, **PCT International patent WO 92/22911**

SOLUTION PROCESSING

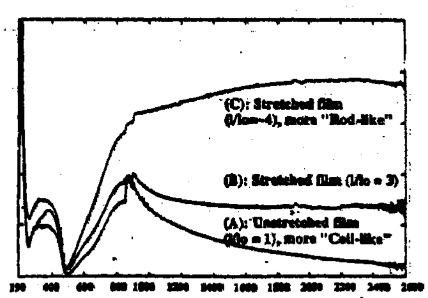
- PAni complex films can be prepared in a wide conductivity range by controlling dopants and solvents

Cast film	δ (s/cm)	Cast film	δ (s/cm)
PAni/DBSA in xylene	100-200 (200-400)[1]	PAni/DBSA in CH_3Cl	80
PAni/DBSA in m-cresol	41 (30)[2]	PAni/CSA in m-cresol	280 (400)[3]
PAni/CSA in DMSO	10^{-6}	PAni/CSA in CH_3Cl	0.1 (0.1)[2]

1. A. J. Heeger et al; 2. A. G. MacDiarmid et al; 3. R. H. Baughman et al

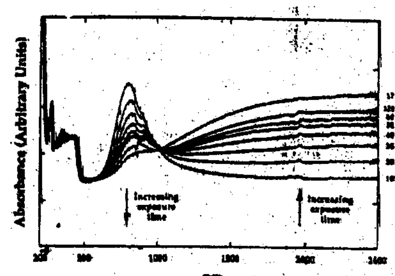
Enhancement of conductivity

Change of UV absorption on stretching



The absorption in NIR region increased as the PAni / PVC blend film was stretched.

Change of UV absorption on exposure to the m-cresol vapor



The absorption in NIR region increased when the cast film from PAni/CSA was exposed to the m-cresol vapor.

MacDirmid et al., *Synth. Met.*, 65 **(1994)** 103.

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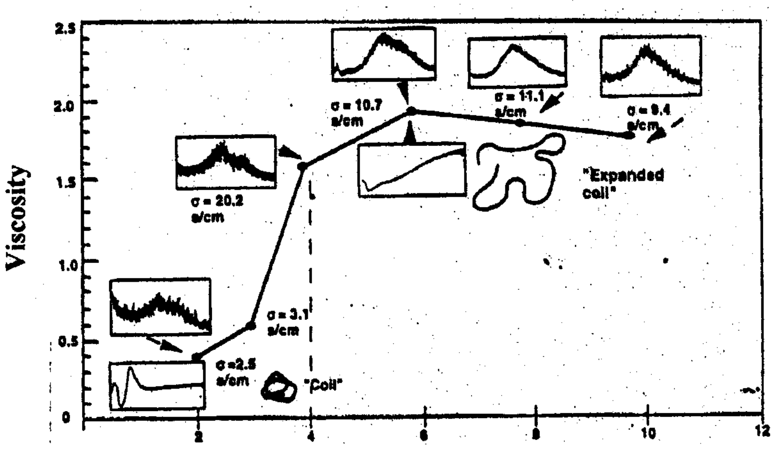
Dependence of crystallinity, viscosity, UV and conductivity on the dopant acid ratio



HDBSA/ EB tetramer molar ratio (in chloroform)

MacDirmid et al., *Synth. Met.*, 65 (**1994**) 103.

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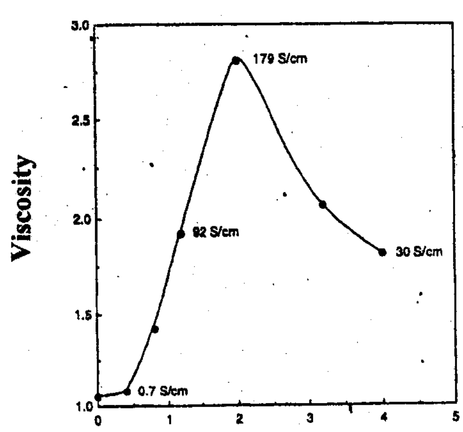
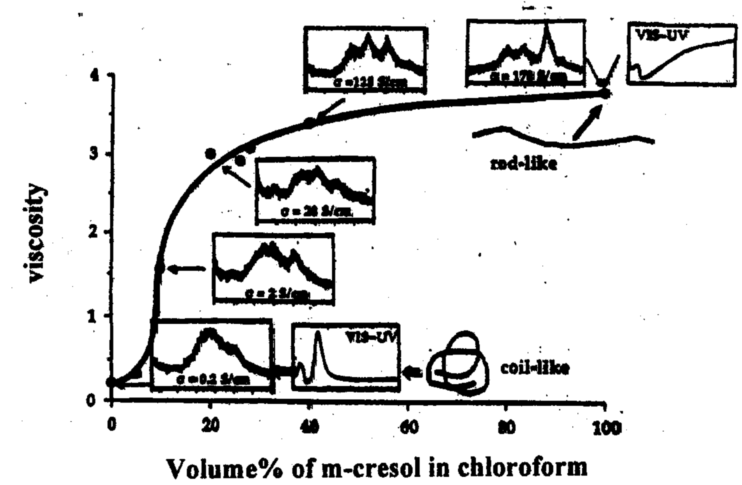
Effect of camphorsulfonic acid content on the conductivity and viscosity



HCSA/ EB tetramer molar ratio (in m-cresol)

MacDirmid et al., *Synth. Met.*, 65 (**1994**) 103.

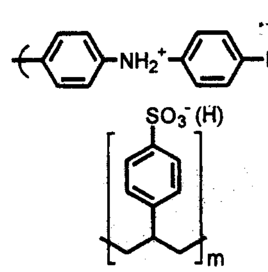
Effect of m-cresol content in solvent on crystallinity, UV, viscosity and conductivity of PAni/CSA



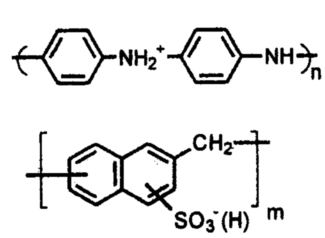
MacDirmid et al., *Synth. Met.*, 65 (1994) 103.

Water soluble PAni

Use of Polymeric Acids as a Steric Stabilizer



0.01 S/cm

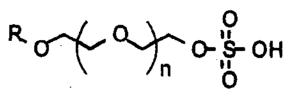


0.001 S/cm

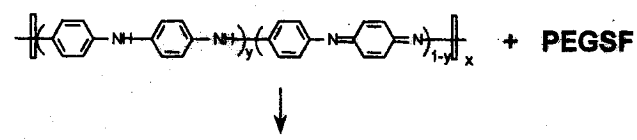
K. Shannon et al *J. Chem. Soc., Chem. Commun.* 643 (1994)   C. Lee et al **Kor. Pat. Appl.** 1995-13010

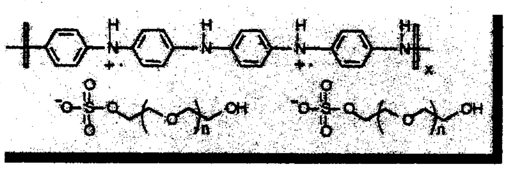
Disadvantages
- **Difficulties in isolation and purification**
- **Some of them are no longer soluble once purified.**

Water soluble PAni by hydrophilic dopant



R = H : PEGSF
Me : MeO-PEGSF
HSO_3 : PEGDSF

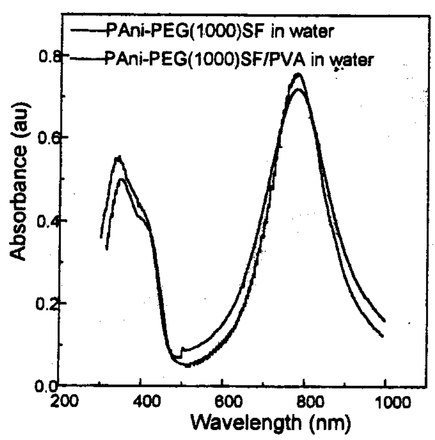




Pani/ PEGSF

1. Dependence of solubility on PEG molecular weight
   - need higher than 900
2. **MeO-PEGSF** and **PEGSF** did not produce water soluble polyaniline.

UV-vis spectra of PAni-PEG(1000)SF



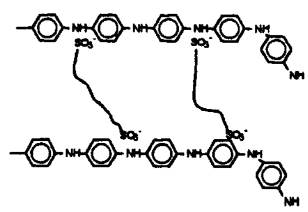
λ_{max} = 340nm, 420nm, 770 nm
Localized polaron structure of PAni-PEGSF
Conductivity : 10^{-3} S/cm

Blending with other water soluble polymers

PVA (polyvinyl alcohol) : homogeneous solution
PEO (polyethylene oxide) : homogenous solution
PAA (polyacrylic acid) : precipitation

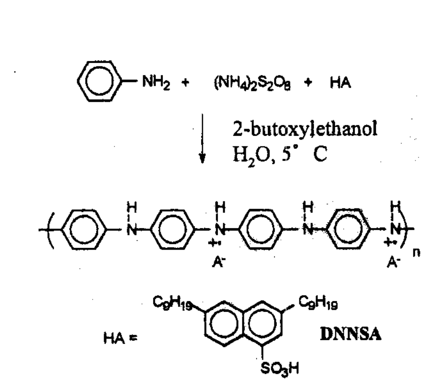
Depandence of solubility on PEG molecular weight
→ need PEG mw higher than 900

MeO-PEGSF and PEGDSF did not produce water soluble polyanile

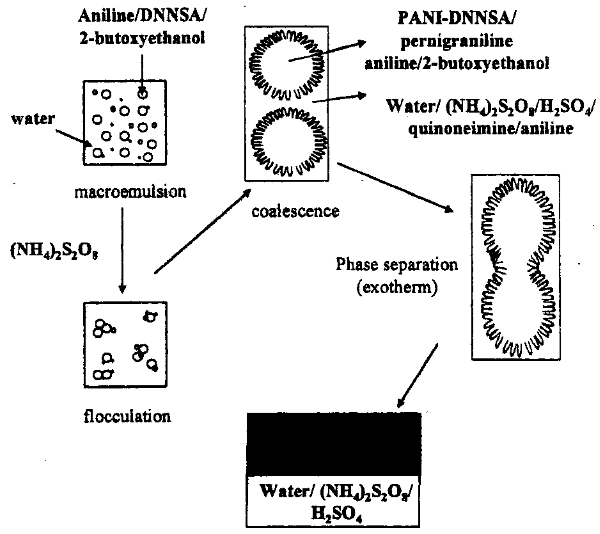


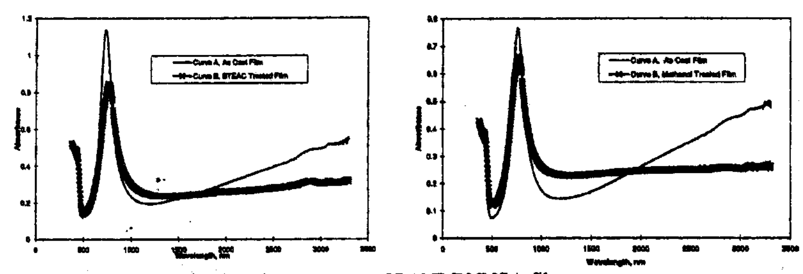
Soluble Polyaniline By Emulsion Polymerization

P.J. Kinlen et al *Macromolecules* **1998**, *31* 1735-1744.



Soluble emeraldine salt





UV/VIS/NIR spectra of PANI-DNNSA films

Effect of surfactant treatment on PANI-DNNSA conductivity

σ (x10[6] S/cm)

	0.05M BTEAC 22° C (30 s)	0.05M BTEAC 58° C (10 min)	0.5M BTEAC 22° C (30 s)	0.5M BTEAC 58° C (10 min)	17% 2A1 58° C (10 min)	5% 8339 58° C (10 min)	0.1M CAPS 58° C (10 min)	16% 2AO 58° C (10 min)
σ before treatment	6.5	12.0	8.1	63.0	18.0	12.0	9.0	29.0
σ after treatment and drying at 22° C	18000	130000	40000	610000	92000	71000	57000	300000
σ after treatment and drying at 70° C (10-50 mmHg)	320	160	1400	2500	35000	28000	31000	30000

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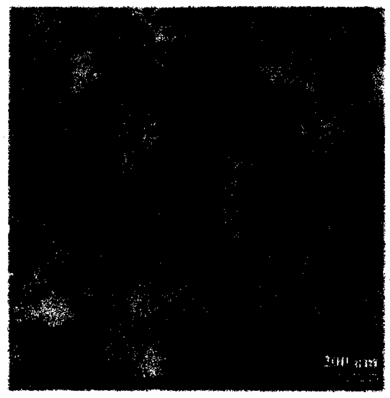

Bright-field TEM image of PANI-DNNSA film before and after treatment with 0.1M BTEAC for 2 min

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Emulsion polymerization of aninline with DNNSA

- A new emulsion process for the direct synthesis of the polyaniline salt of polyaniline soluble in organic solvents. - As the reaction proceeds, organically soluble polyaniline is formed directly by phase change from an emulsion to a two-phase system.
- Thin films of the polymer are readily cast from xylene and have relatively low conductivities due to aggregation of conducting domains.
- Treatment of thin films of PANI-DNNSA with quaternary ammonium salt solutions changes the morphology to one of multiply connected conducting pathways and results in a 3-4 order of magnitude increase in conductivity.
- Treatment of the films with acetone or methanol also results in an increase in conductivity; however, the mechanism is through densification and crystallization of the film by removal of excess dopant.
- The overall conductivity is still lower than the PANI-DBSA system

Macromolecules **1998**, *31* 1735-1744

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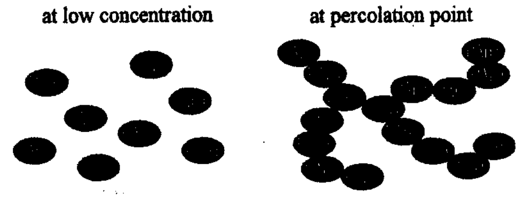
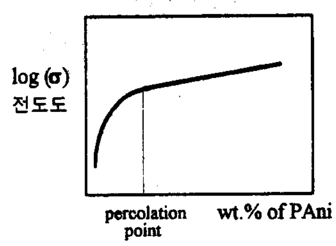
DISPERSION OF POLYANILINE





Dispersion polymerization of aniline in the presence of steric stabilizer

- **PANI-HCl modified with PVME (polyvinyl methyl ether) (σ=4.9 s/cm)**
- **Centrifugation and redispersion**
- **Dispersing submicron particle by solution blend with PVC, PMMA, PS, PVAc, PVA**
- **PVA/ PANI-HCl at 4 wt% σ=0.5 s/cm**
  at 0.007 wt% $\sigma=1.12\times10^{-5}$ s/cm

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APPLICATIONS

As Passive Materials

- Antistatic
- EMI/RFI
- Conductive coating
- Corrosion protecting
- Electrolytic condensors
- Gas separating membranes
- Pervaporation membrane

As Active Materials

- Rechargeable batteries
- Electrochromic devices
- Sensors
- Light emitting diodes
- Transistors
- Solar cells
- Actuators

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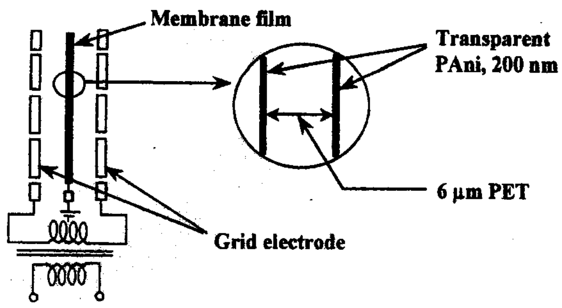
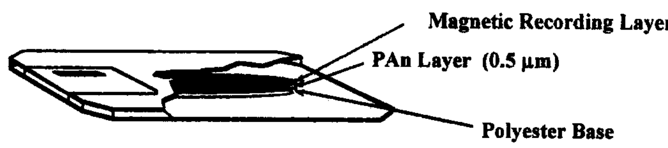
Electrostatic Loud speaker



4 MB floppy disk utilizing polyanilne coating as antistatic layer



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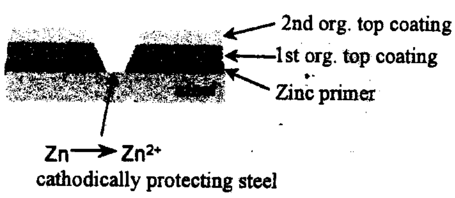
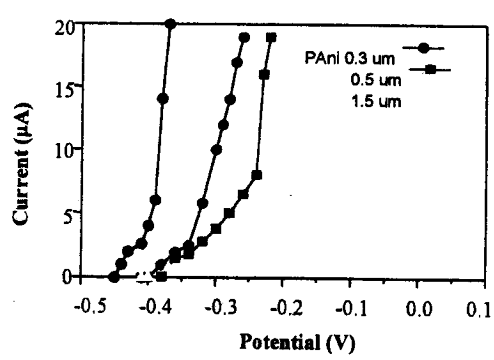
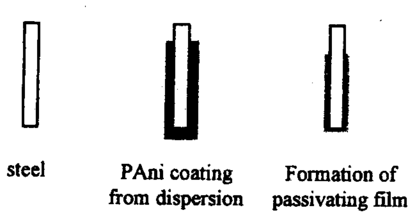
CORROSION PROTECTION





Corrosion pretecting of metals by passivation



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CONDUCTIVE TRANSPARENT COATING

ITO glass (Indium Tin Oxide)

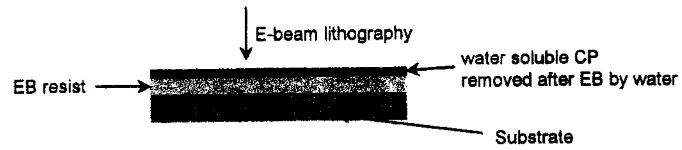
surface resistivity : ~ 10 ohm/sq LCD, EL, touchpanel
~ 200 ohm/sq LCD, EL,touchpanel
~ 1000 ohm/sq Antistatic

Conducting polymer coating ?
1 x 10^3 to 1 x 10^9 ohm/sq (transparency 40-70%)
by the use of Versicon

V. Kulkarni at Americhem, *Synth. Met.*, 1993, *55-57*, 3780.

EB lithography, SEM discharging layer

M. Angelopoulos et. al, *Polym. Eng. Sci.*, 1992, *32*, 1535.



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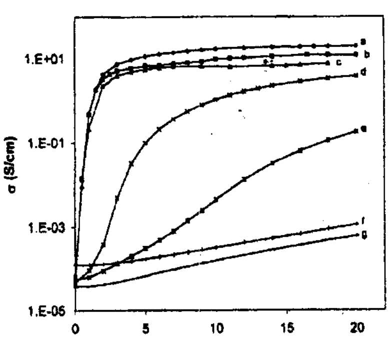
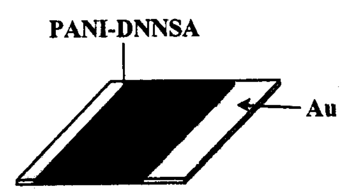
CONDUCTOMETRIC SENSORS BASED ON POLYANILINE FILMS

Svetlicic et al, *Chem. Mater.* **1998**, *10*, 3305-3307

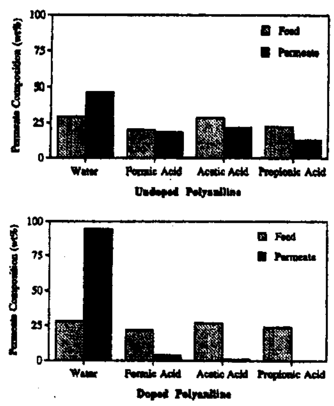


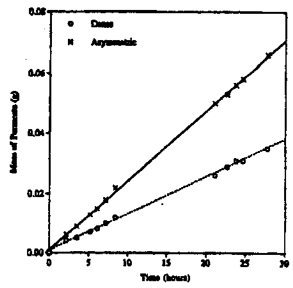
Conductivity of 50 μm PANI films exposed to the vapor above various ethanol/water mixtures (% by volume of ethanol).
A, 100%; B, 50%; C, 33%; D, 12.5%; E, 6.6%; F, 1.3%; G, 0%.



10^5 Fold increase of conductivity when exposed to ethanol within 1 min.
- lighter beer $\Delta\sigma$=60S/cm
- higher alcohol content $\Delta\sigma$=1260S/cm

PERVAPORATION MEMBRANE



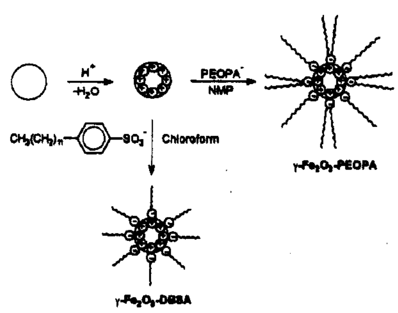


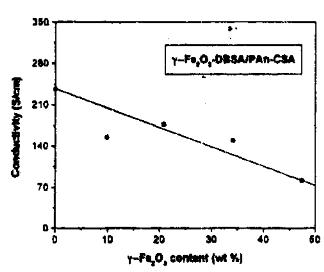
The relative low permeation can be improved by forming asymmetric film and increasing the feed temperature without any detectable loss of selectivity

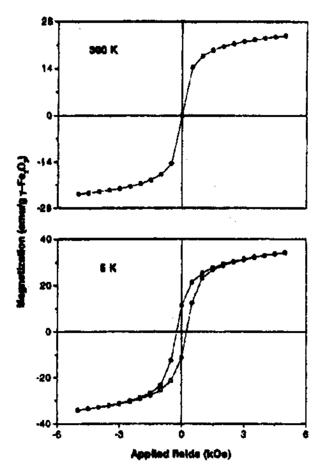
Size and polarity of acid affect the permeability
Undoped film showed poor selectivity
Fully HCl doped film selectively permeate water over acetic acid.
- Separation factor > 1300 which is the most selective membrane reported.

NANOCOMPOSITE OF MAGNETIC PARTICLES AND POLYANILINE

B. Z. Tang et al, *Chem. Mater.* **1999**, *11*, 1581-1589

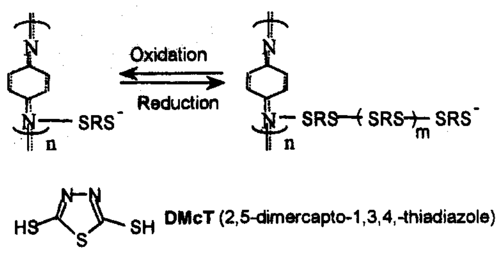


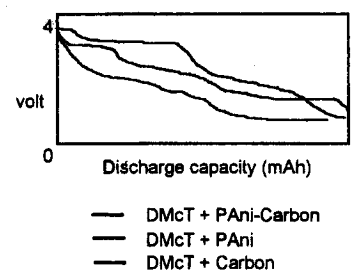




LITHIUM SECONDARY BATTERY ELECTRODE

- The addition of DMcT to the solution of EB in NMP produced thick paste which can be cast into thick film.
- The PAni-DMcT composite electrode showed high charge due to the electrochemical redox of disulfide.
- The low conductivity of film was improved with the addition of carbon powder.





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SUMMARY

1. Many forms of processable polyanilines are available.
   - EB soluble in NMP, DMSO, m-cresol, etc.
   - Conductive form is soluble in xylene, chloroform and m-cresol.
   - Emulsion also produced dispersible powder and solution.

2. Hydrogen bonding of EB in NMP significantly affects the properties of solution and film cast from the solution.
   - Gelation, LiCl pseudo doping
   - Crystallinity, conductivity

3. Various applications were proposed for the use of conductive polyaniline
   - Sensors, corrosion protection, battery, membrane, antistatic and conductive coating, etc

4. More research are needed for the improvement of conductivity and stability for the practical applications