導電性核殼型高分子材料的合成、分析與應用

王立義

國立台灣大學凝態科學研究中心

講 題 大 綱

- 導電性高分子簡介
- 導電性高分子之應用介紹
- 核殼型導電高分子之結構與特性
- 可撓式透明導電電極
- 製備與分析技術

Plastics

— Pliability

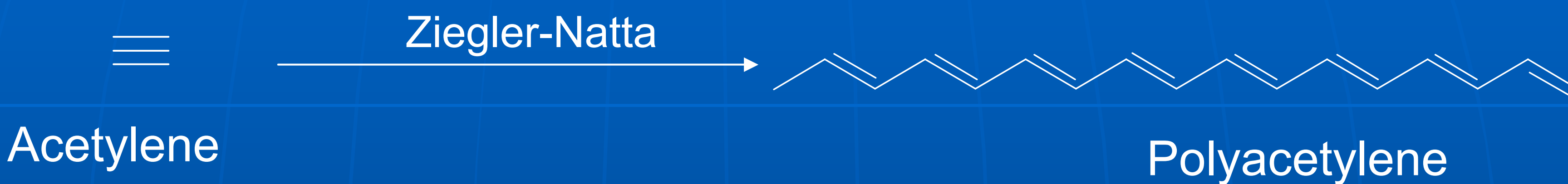
— Lightweight strength

— Cheap cost of production

— *Good electrical insulation*

→ Insulator in electricity cable

Hideki Shirakawa(日本筑波大學材料學院)



Tacticity-Control

100-fold excess of the Ziegler-Natta catalyst

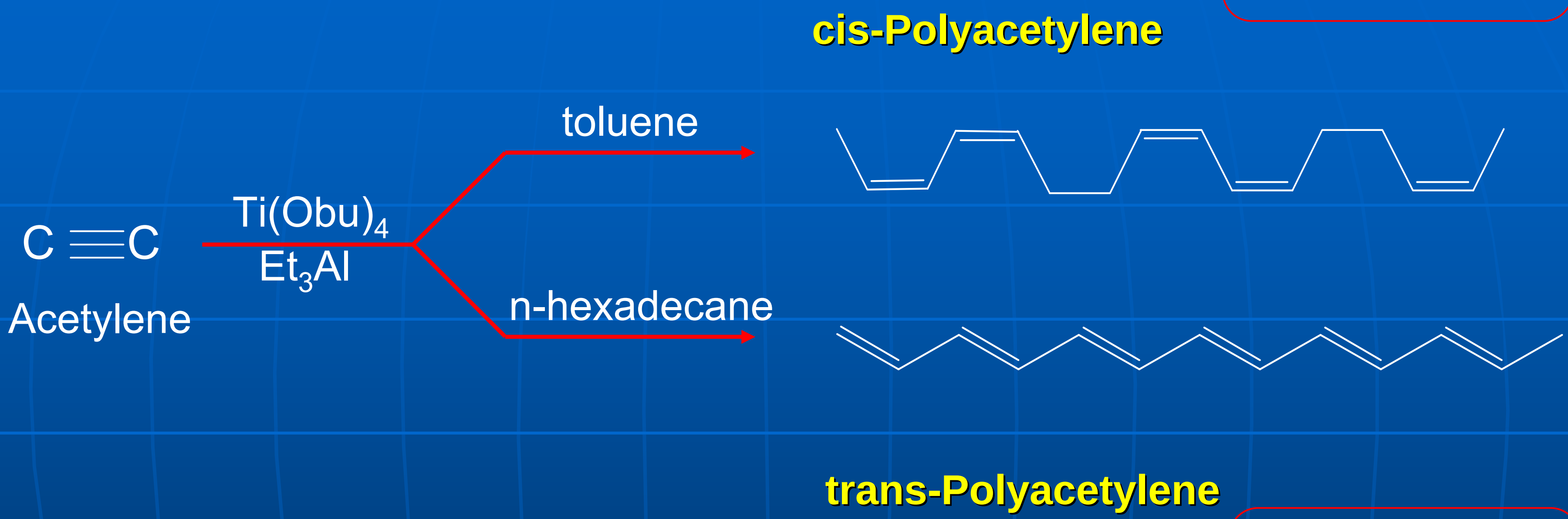
(By mistake)

→ Silvery trans-polyacetylene film

(Not a conductor)

Copper coloured

$10^{-10} \sim 10^{-9}$ Scm^{-1}



Silver coloured

$10^{-5} \sim 10^{-4}$ Scm^{-1}

T. Ito, H. Shirakawa and S. Ikeda, *J. Polym. Sci., Polym. Chem. Ed.* 12, 11-20 (1974)

Alan MacDiarmid, Alan Heeger

Explosive inorganic polymer: Poly(sulphur nitride)

Metal-Like

Semiconductor at low-T

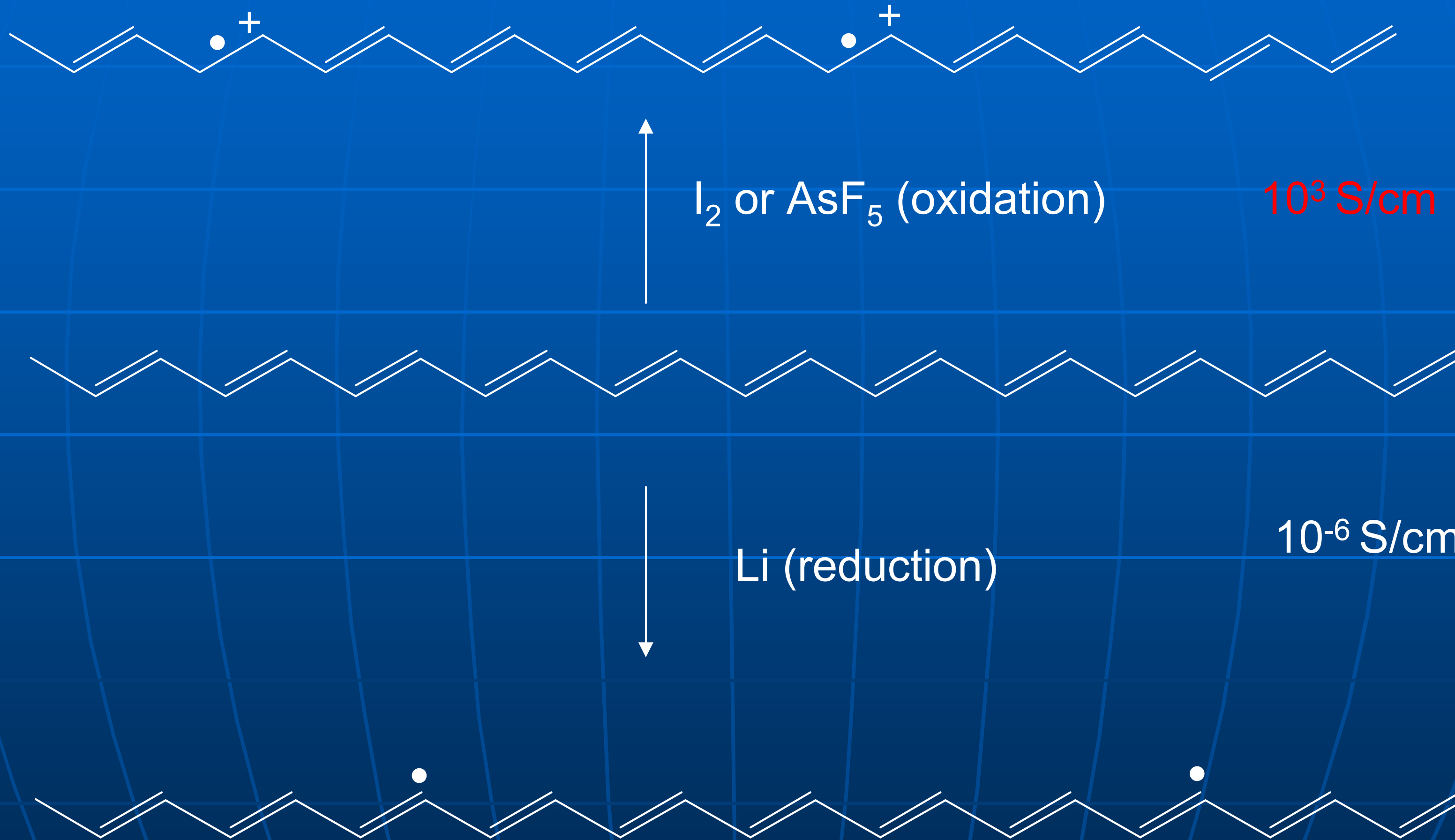
Polyacetylene

Ag、Cu

~10^6 S/cm

Teflon

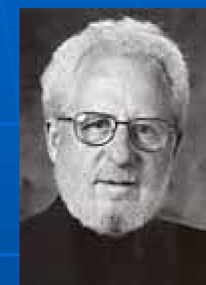
~10^{-16} S/cm



Phys. Rev. Lett., 39, 1098 (1977)

The 2000 Nobel Prize in Chemistry

The Royal Swedish Academy of Sciences has decided to award the Nobel Prize in Chemistry for 2000 jointly to



Alan J. Heeger
University of California at Santa Barbara, USA,

Alan G. MacDiarmid
University of Pennsylvania, Philadelphia, USA,

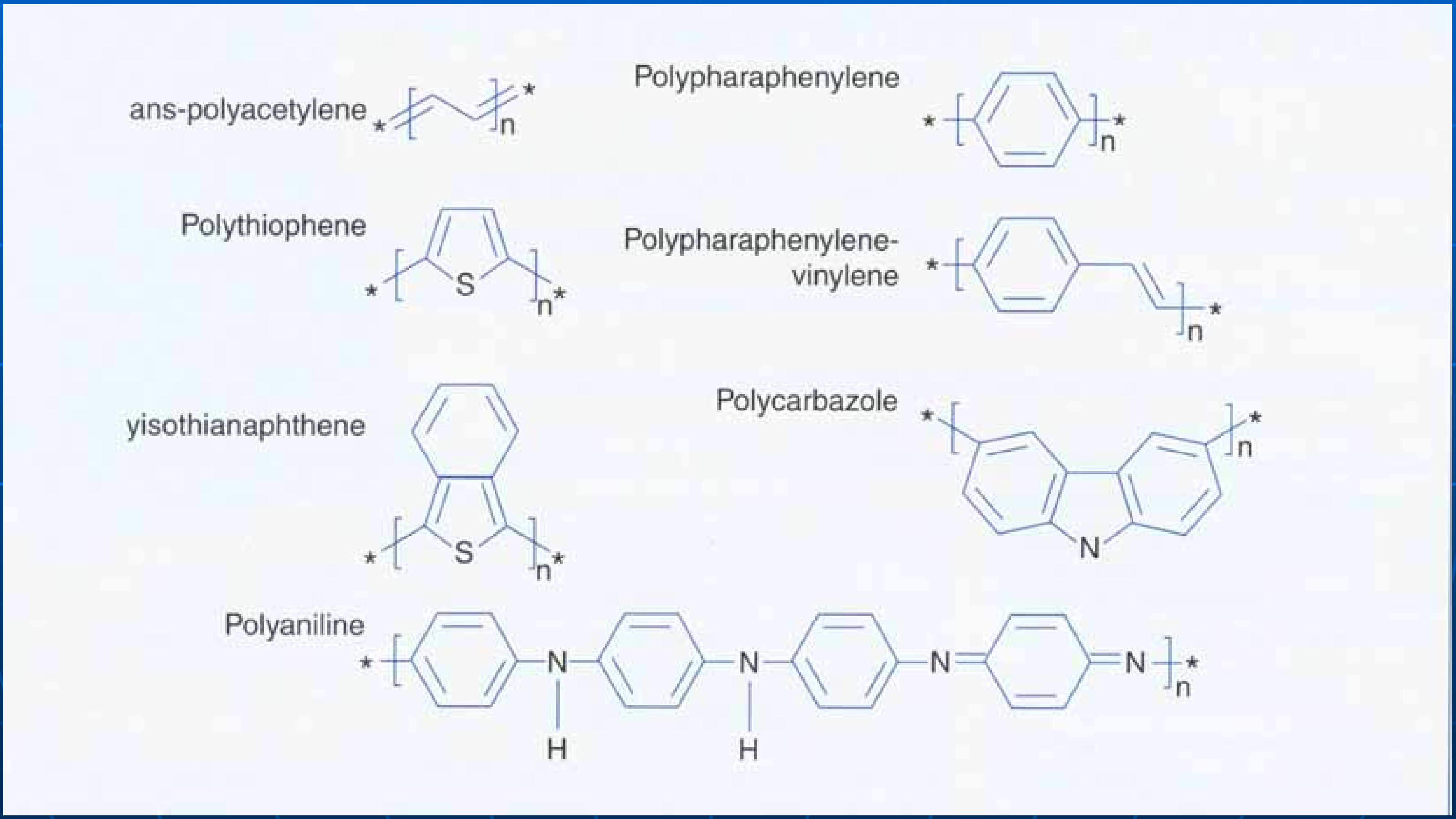
Hideki Shirakawa
University of Tsukuba, Japan

"for the discovery and development of conductive polymers"

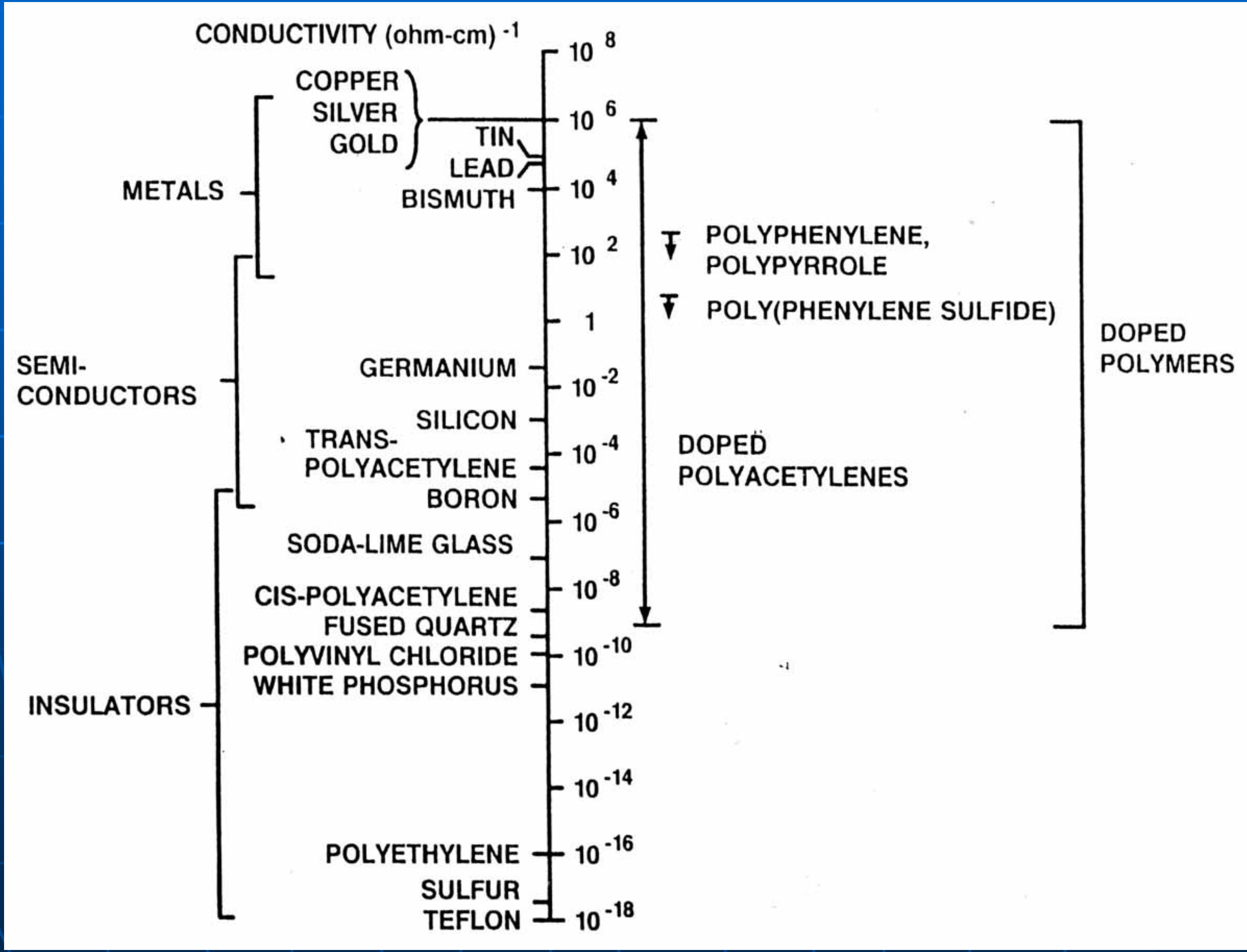
Advantages

- Light weight
- Flexible
- Easy Process
- Cheap
- Versatile

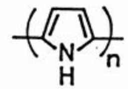
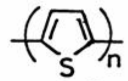
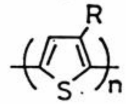
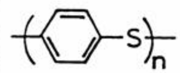
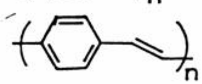
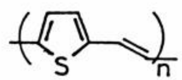
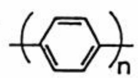
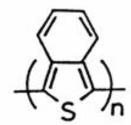
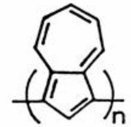
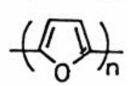
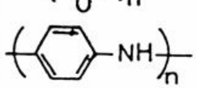
Examples of currently widely used types of conducting polymers



Conductivity of various metallic, semiconductor, and insulting materials



Conductivities of conducting polymers vary widely

Polymer	Sructure	Doping matertals	Approxlmate conductivity (Siemens per cm)
Polyacetylene	$(CH)_n$	I_2, Br_2, Li, Na, AsF_5	10,000[a]
Polypyrrole		BF_4^-, ClO_4^-, tosylate[b]	500-7500
Polythiophene		BF_4^-, ClO_4^-, tosytate[b] $FeCl_4$	1000
Poly(3-alkylthio-phene)		BF_4^-, ClO_4^- $FeCl_4^-$	1000-10,000[a]
Polyphenylene sulfide		AsF_5	500
Polyphenylene-vinylene		AsF_5	10,000[a]
Polythienylene-vinylene		AsF_5	2700[a]
Polyhenylene		AsF_5, Li, K	1000
Polyisothiana-phthene		BF_4^-, ClO_4^-	50
Ployazulene		BF_4^-, ClO_4^-	1
Polyluran		BF_4^-, ClO_4^-	100
Polyaniline		HCl	200[a]

a Conductivity of oriented polymer b p-Methylphenylsulfonate.

Potential Industrial Applications for Conducting Polymers

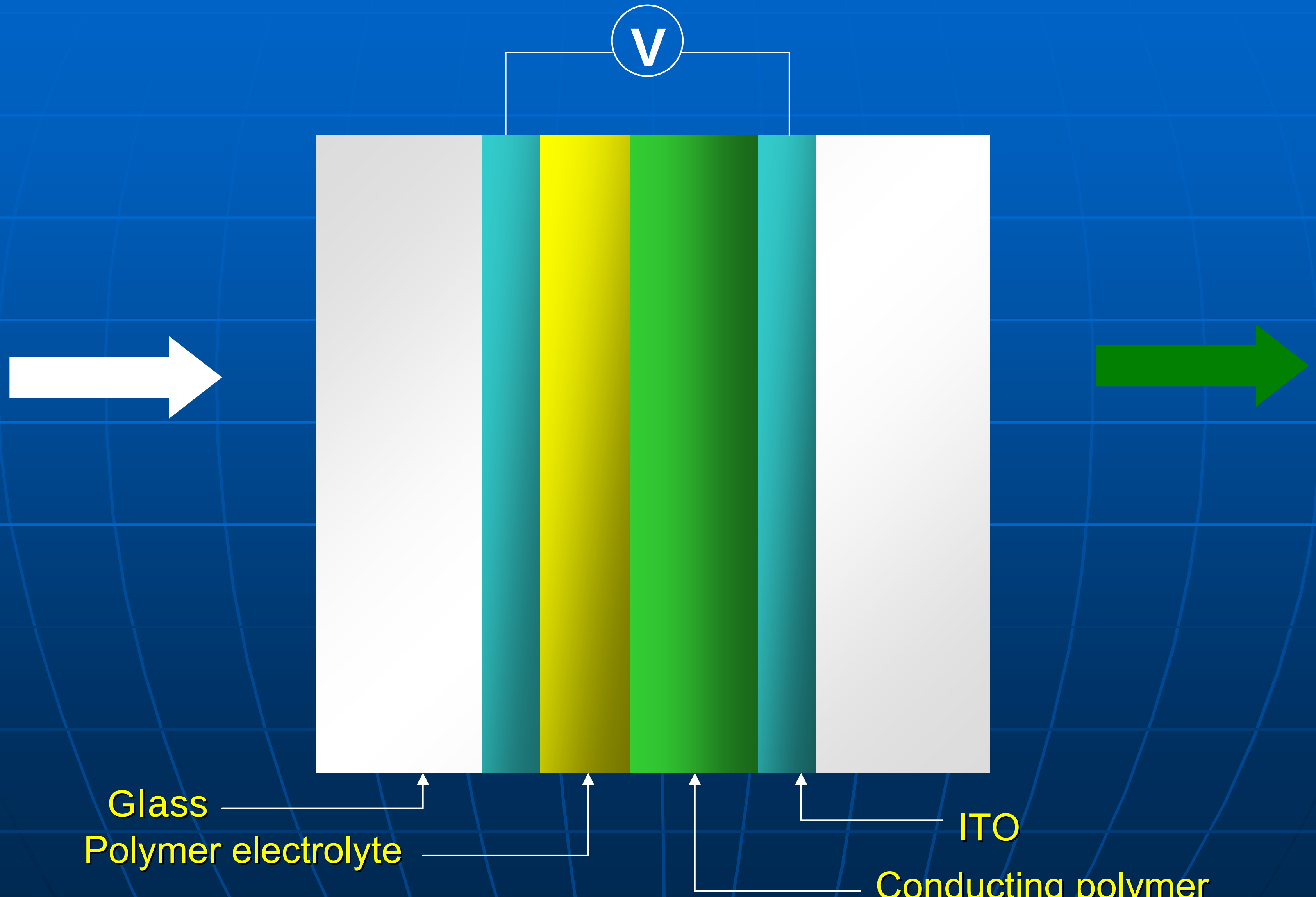
- Antistatic Coatings
- Cable Shielding
- Electrodes, Sensors
- Rechargeable Batteries
- Electrochromic Smart-Windows
- Flexible Light-Emitting Diodes
- Field-Effect Transistor
- Flexible Solar Cells

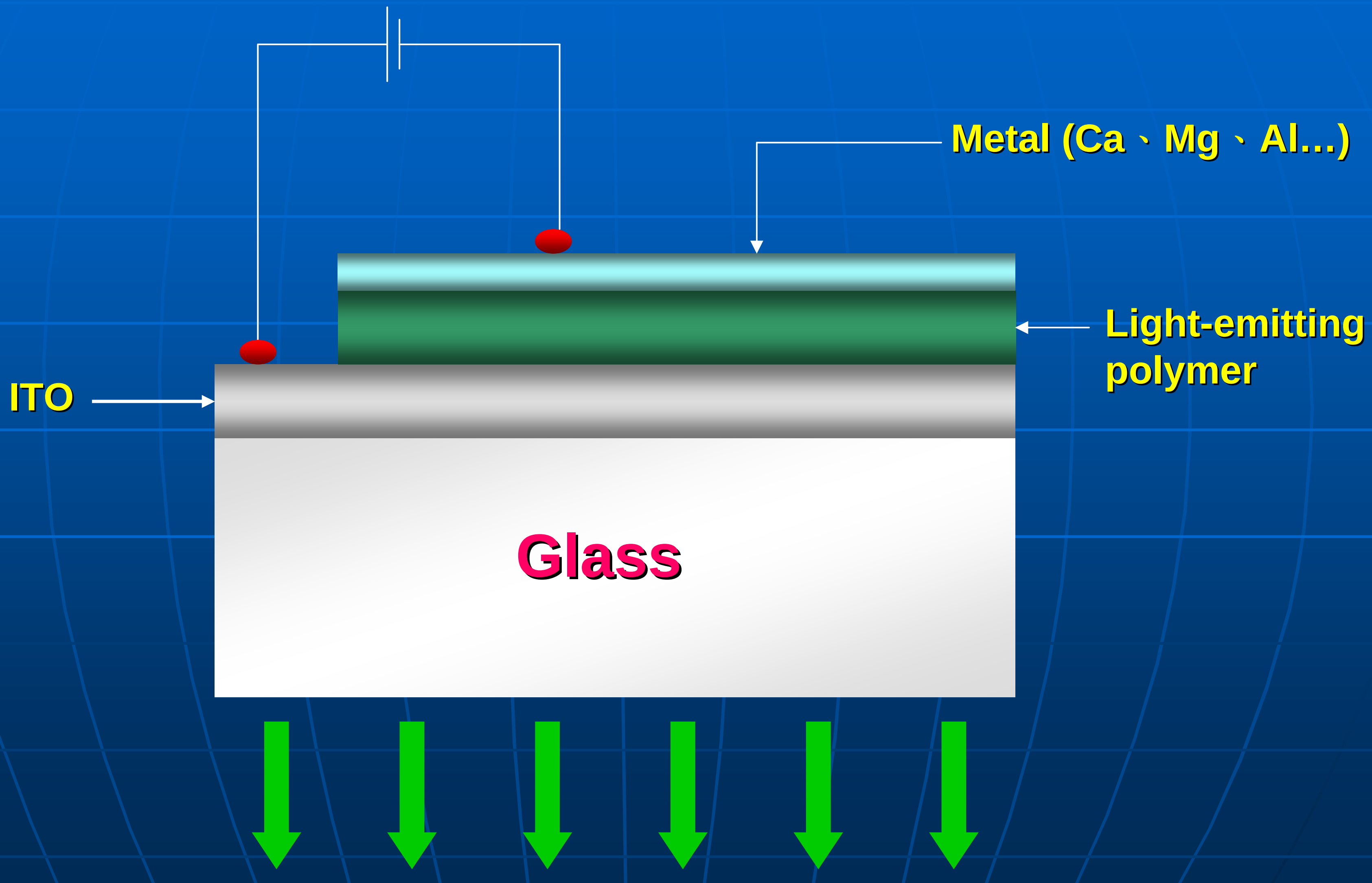
Polypyrrole-Coated Knitted Nylon Fabric

- Static Dissipation
- EMI Shielding
- Radar-absorption
- Highly efficient microwave absorption

Polymer	Color	
	Undoped	Doped
Polythiophene	red	blue
Polypyrrole	yellow-green	blue-black
Polyaniline	blue	green
Polyisothianaphthene	blue	light-yellow

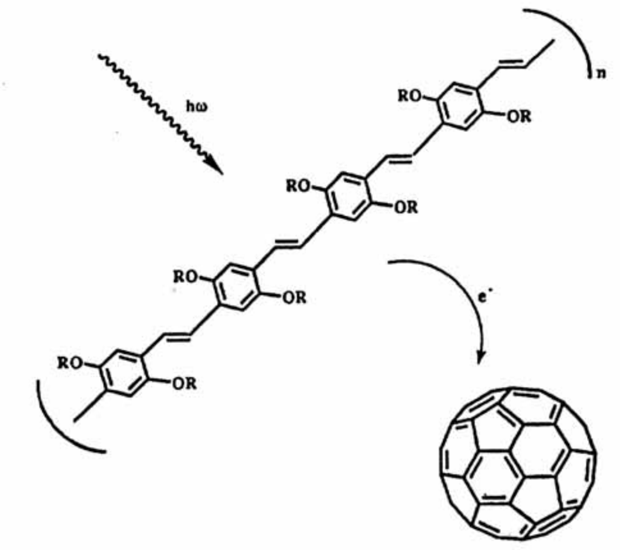
Electrochromic Window





Metal (Ca、Mg、Al…)
Light-emitting polymer
ITO
Glass

Ultrafast, Reversible, Metastable Photo-Induce e$^-$ Transfer



- Strong luminescence of MEH-PPV is quenched by a factor in excess of 10^3
- Luminescence decay time: τ_0: 550ps ⟶ $\ll$60ps
- ESR: triplet-triplet absorption signal (1.35 ev) ⟶ disappear

  strong spin:1/2 signal

⬇

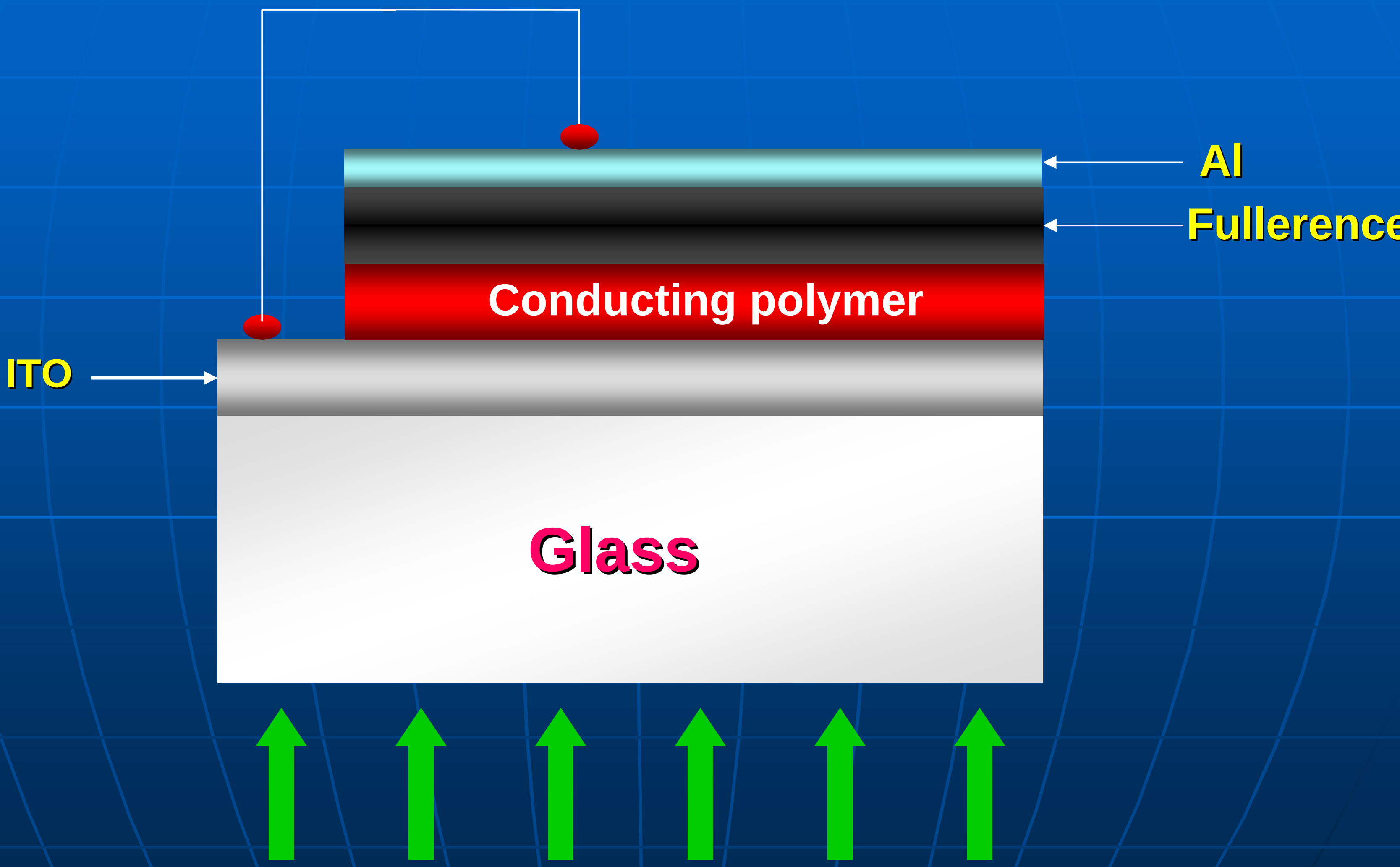
Enhance the charge carrier generation

Prevent charge recombination

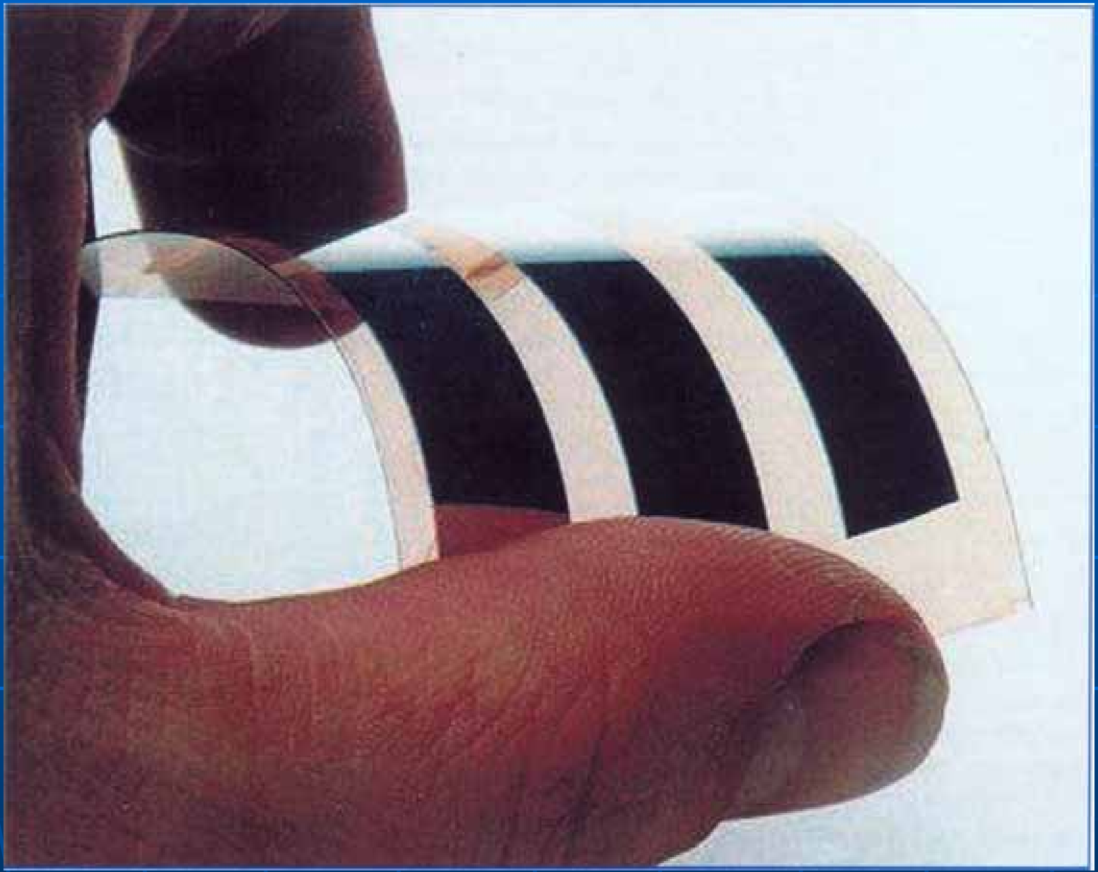
⬇

Quantum yield of photo-induced charge generation～100 ％

Photovoltaic Device



Flexible Solar Cell



PV elements on flexible ITO coated PET (6 × 6 cm)

MDMO-PPV/PCBM

Q~2%

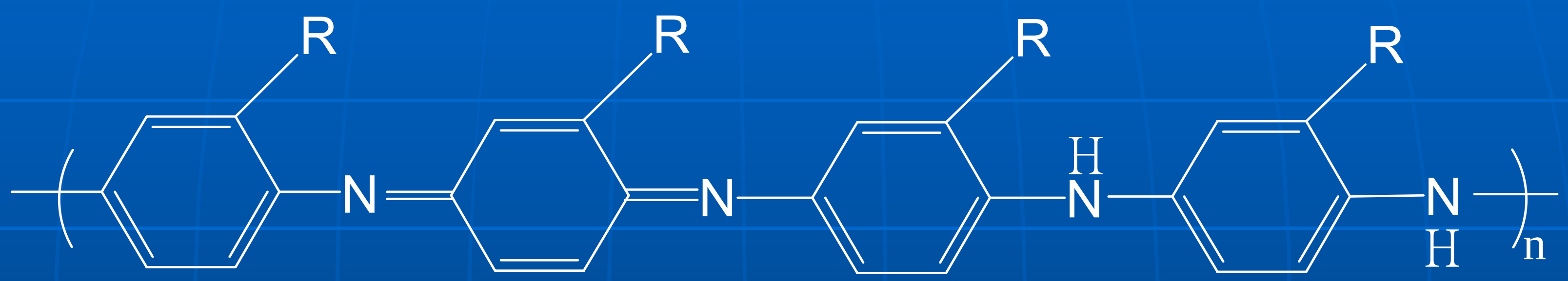
Disadvantages

- Rigid
- Infusible
- Insoluble

Improving Methods

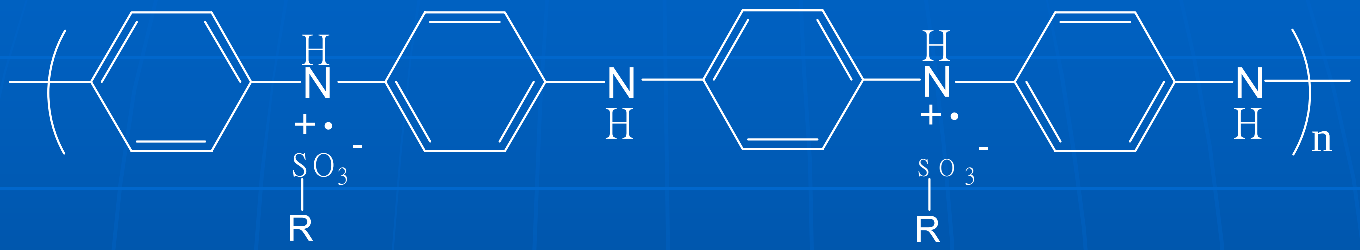
- Poly(alkyl-sbstituted aniline)
- Doped with long alkyl chain acids
- Blended with polymers

Poly(alkyl-substituted aniline)

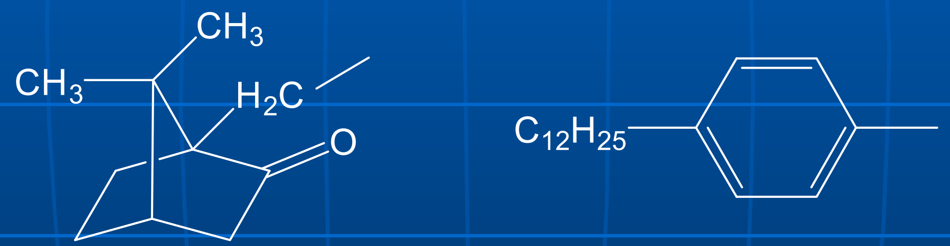


- Steric effect between side groups
- Nonplanar conformation
- Lower crystallinity
- Lower conductivity

Doped with Functionalized Protonic Acid



R =



- Soluble in a variety of common organic solvents, such as m-cresol, xylene, chloroform
- Good conductivity

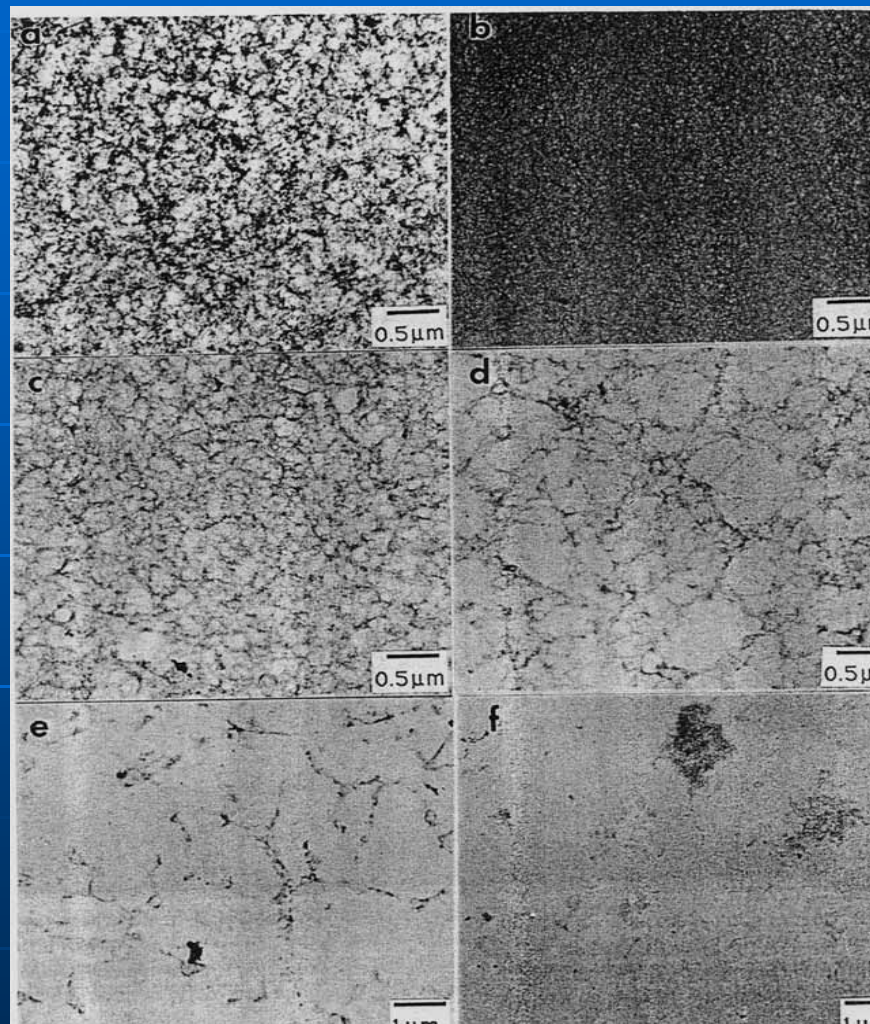
Y. Cao et al. Synthetic Metal 48, 91 (1992)

Electron micrographs of extracted PANI-CSA-PMMA polyblends films initially containing different concentration (in wt.%) of the PANI-CSA complex.

(a) (b)

(c) (d)

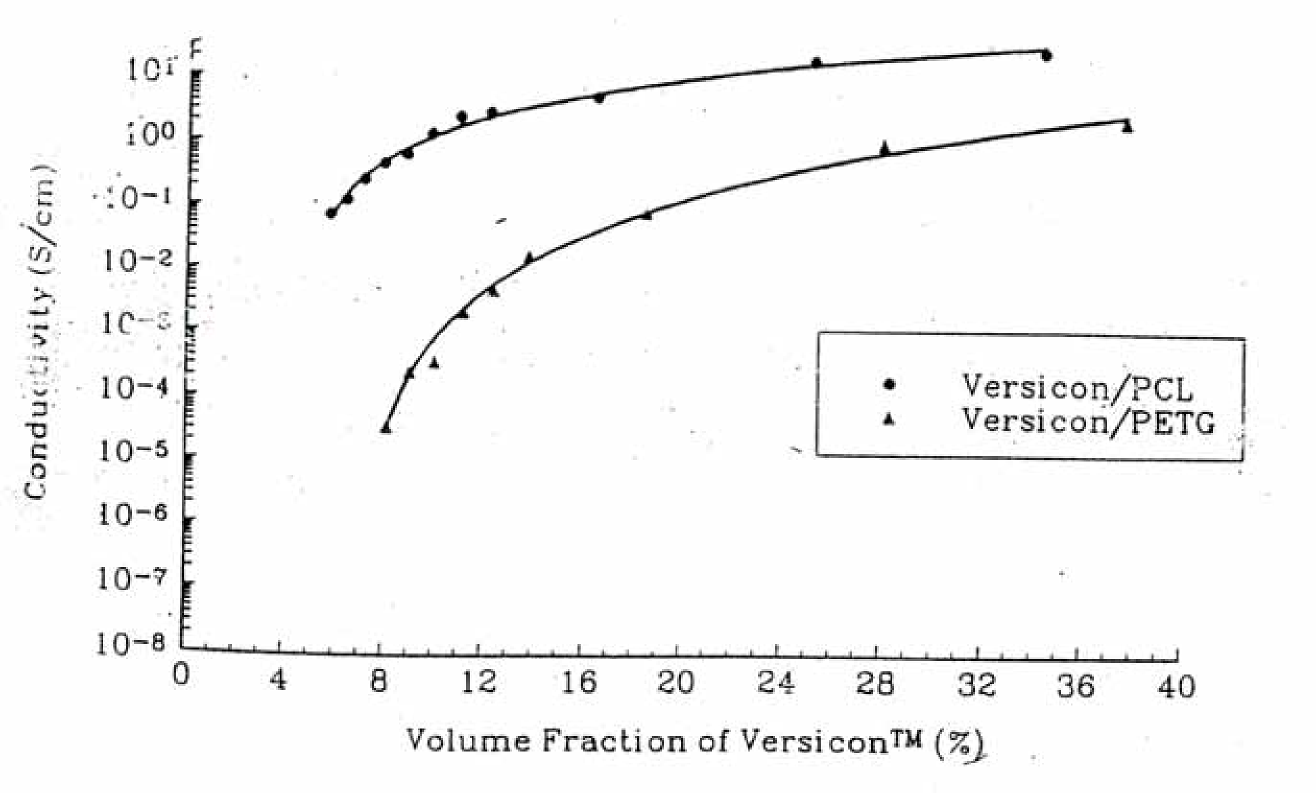
(e) (f)



(a) 28.0%, (b) 16.2%, (c) 3.7%, (d) 1.9%, (e) 0.96%, (f) 0.48% PANI-CSA

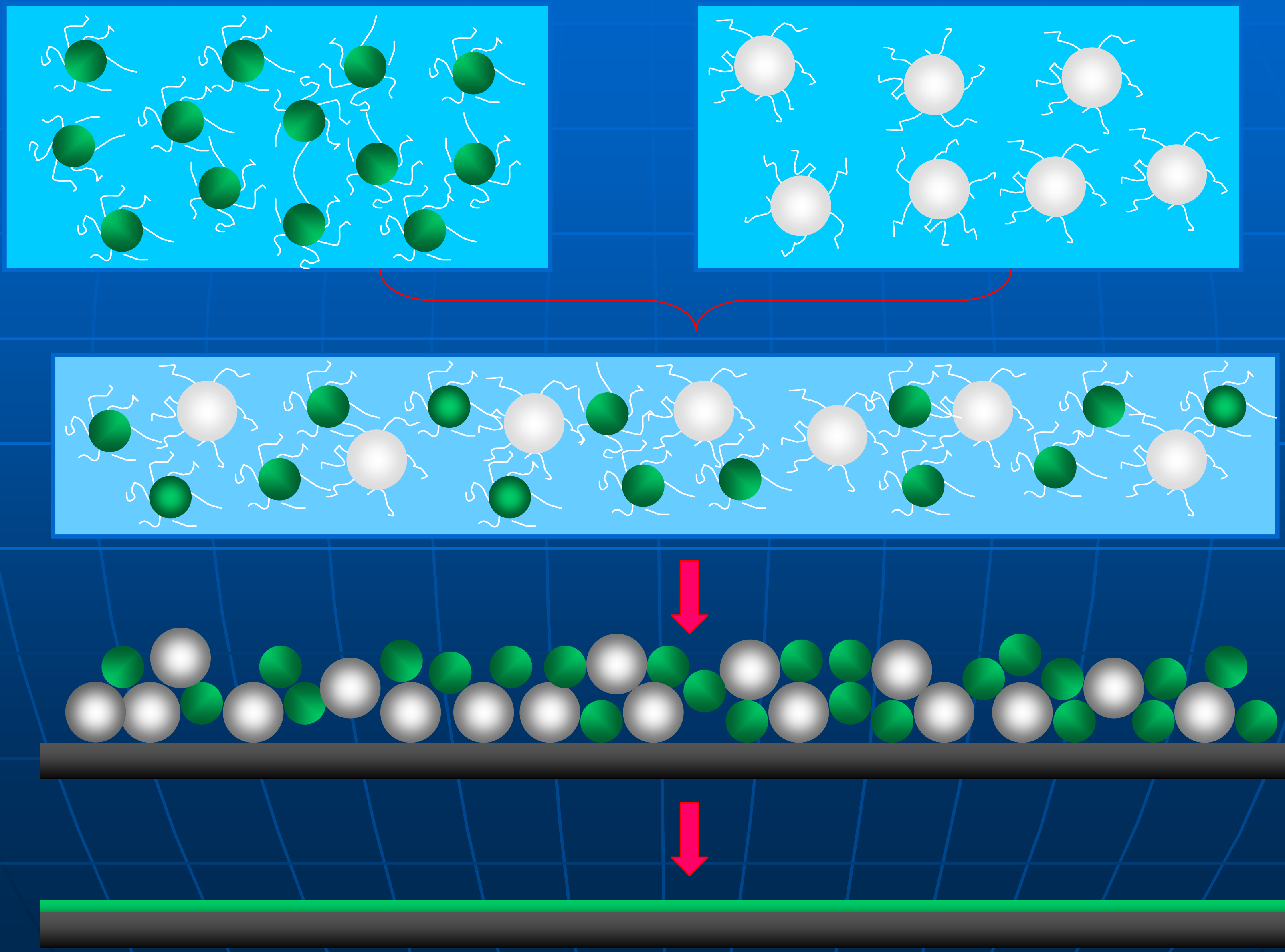
Polyaniline/Polycaprolactone(PCL)

Polyaniline/Poly(ethyleneterethphalate)

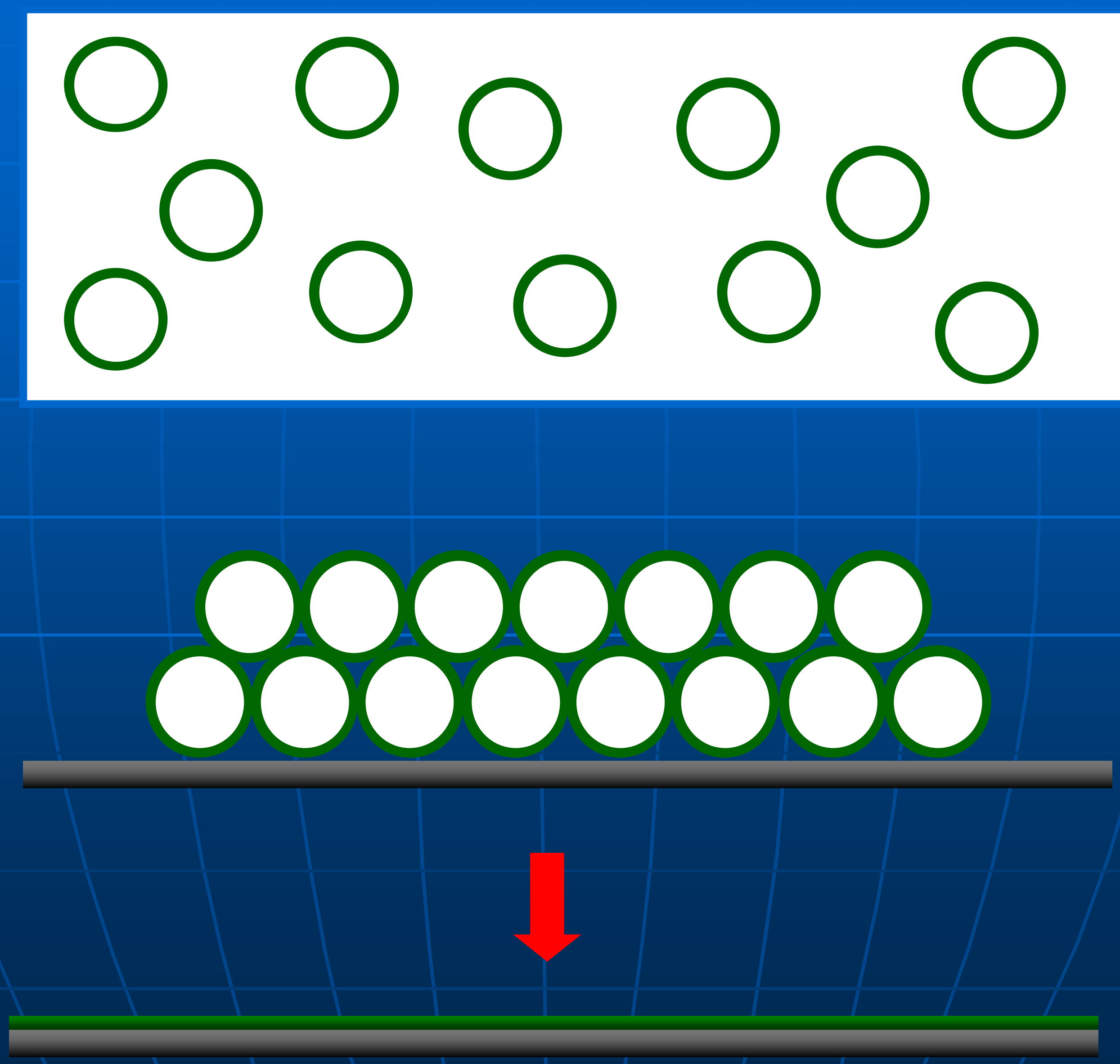


Shacklette et al. *Synthetic Metal*, 55, 3532(1993)

Polyaniline Colloids



Core-Shell Structure



Potential Applications

- Corrosion inhibitor
- Antistatic coating
- Conducting adhesive
- Flexible transparent conducting electrode

透明導電膜的主要用途

液晶顯示器
有機發光二極體
高分子發光二極體
電漿顯示器
電致發光體
有機太陽電池
電致變色材料
觸控面板
車用防霜加熱條
航空器窗戶防霧

透明導電膜種類

種類	導 電 材 質	實　例
無機材料	金屬薄膜	Cu、Ag、Au、Pd等
	複合膜	$TiO_2/Ag/TiO_2$ $Bi_2O_3/Au/Bi_2O_3$
	氧化物半導體薄膜	$In_2O_3(Sn)$、ZnO(Al)
有機材料	導電性高分子膜	Polypyrrole Polythiopene derivatives
	離子性複合膜	Polyethyleneglycol/$LiClO_4$
	無機填充高分子膜	In_2O_3/polyester resin

透明導電膜基本特性需求表

項目	試驗法	量測單位	典型值
透明性	分光光度計(波長@600 nm)	%	85
導電性	表面電阻計	Ω	300
耐熱性	150℃，3小時 表面電阻變化值	倍	1.0以下
耐磨耗性	摩擦100次 表面電阻變化值	倍	1.02
耐曲撓性	8mmΦ，收捲來回50次表面電阻變化值	倍	1.05
相位差值	相位差儀	nm	15以下
氣體透過率	氧氣、濕氣測定儀	cc/m^2-24hr-atm	0.5以下

Display 1, 58 (1995)

透明導電膜製作法

製法種類	方法
成膜法	網印印刷法
	塗佈法
	化學蒸著法
成長法	真空蒸著法
	Ion-plating
	濺鍍法

透明導電膜製作法比較

比較項目	成長法	塗佈法
儀器設備	複雜	簡單
成膜面積	小	大
原料利用率	低	高
塗佈時同時形成線路圖形	難	較易
薄膜性能	良好	較差

ITO透明導電膜規格

表面電阻	ITO膜厚 (nm)	透光率 (%@550nm)
5	310-350	75
7	230-270	80
14	150-190	85
25	90-130	82
30	70-90	80
80	40-60	83
150	20-30	86

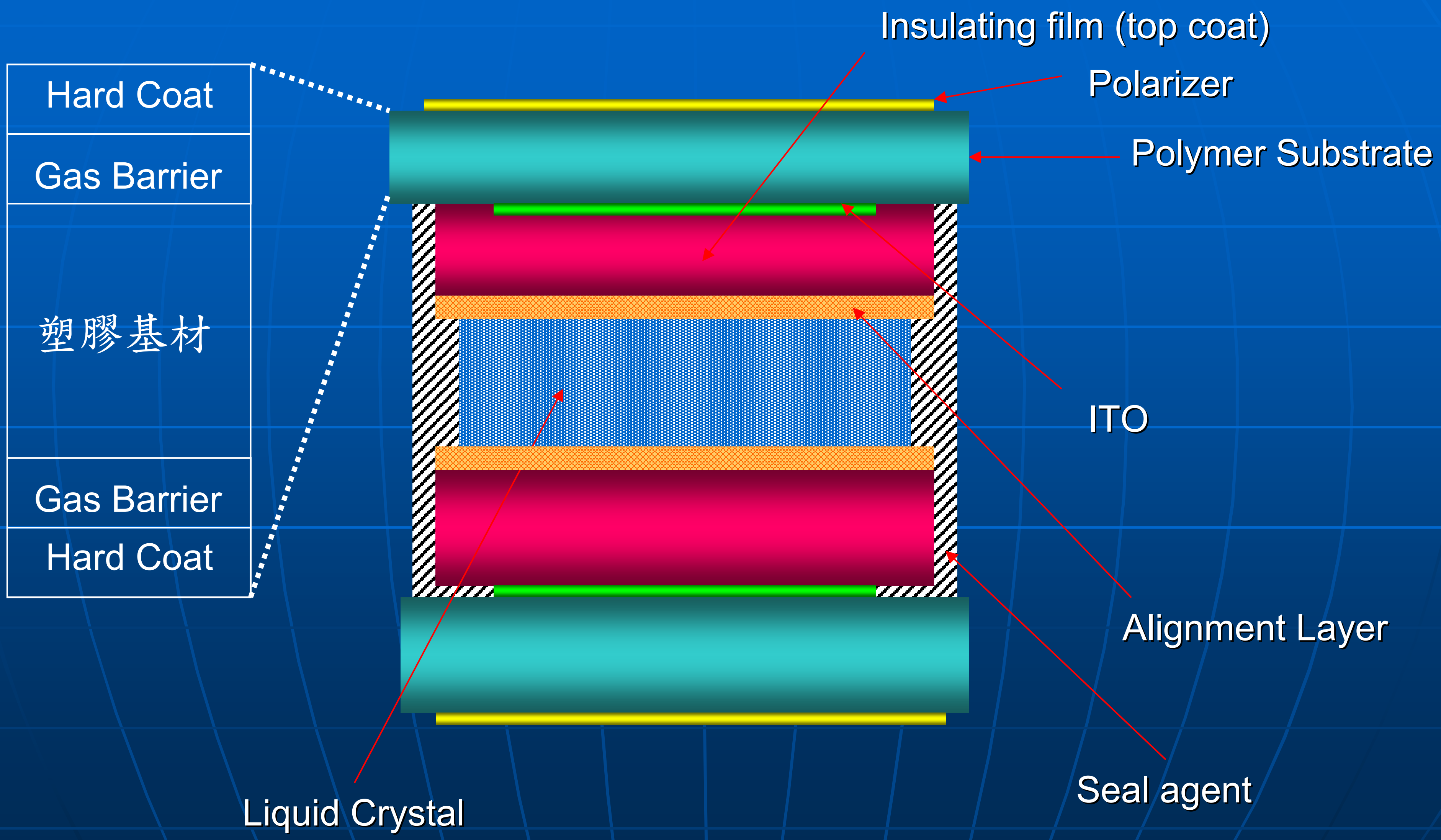
Display 1, 42 (1995)

玻璃及塑膠面板性質比較

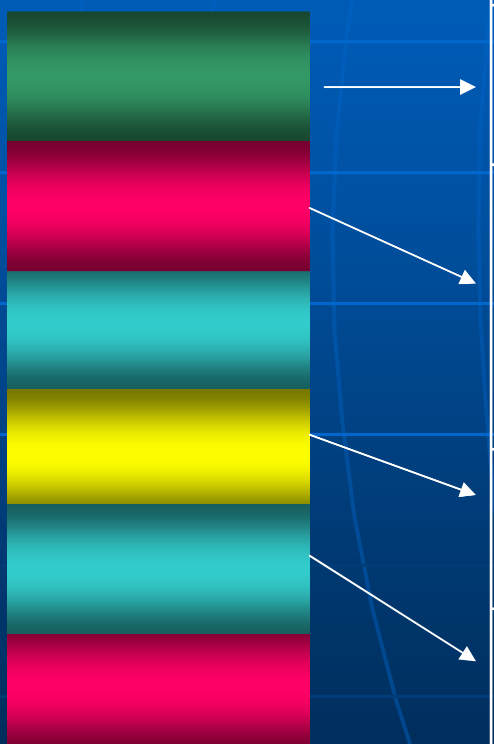
		玻璃面板		塑膠面板	
厚度	Cell	1.95mm	1.35mm	1.35mm	0.95mm
	基板	0.7mm	0.4mm	0.4mm	0.2mm
重量	Cell	4.6g	3.7g	2.1g	1.6g
	基板	4.3g	3.4g	1.8g	1.3g
對比		8:1		8:1	
反應時間		250ms		250ms	
可靠性		在40 ℃, 95%RH下 1000個小時		在40 ℃, 95%RH下 1000個小時	
作業溫度範圍		-20~70℃		-20~70 ℃	
儲存溫度範圍		-30~80 ℃		-30~80 ℃	
耐衝擊力(相對)		1		10	

工研院材料所資料

塑膠液晶顯示器構造圖


Hard Coat
Gas Barrier
塑膠基材
Gas Barrier
Hard Coat
Insulating film (top coat)
Polarizer
Polymer Substrate
ITO
Alignment Layer
Seal agent
Liquid Crystal

LCD用塑膠基材基本結構圖



層別	厚度 (μm)	功能	製法
透明導電層	0.05-0.1	導電層	Sputtering Sol-gel
Hard Coat	5-10	抗濕層 耐傷性 ITO密著性 耐溶劑性	Wet Coat / UV (nano tech)
Plastic	200-400	Support	Extrusion Flow-casting
Gas Barrier	2.5	阻氣性	Sputtering / EB PVD Sol-gel / nano tech.

可撓式LCD對基材特性的需求

	Unit	Hard Coat
Thickness	μm	100-200
Water Absorption	%	≤ 0.2
Water Vapor Permeability	g/m^2-day	< 0.15
O_2 Permeability	cc/m^2-day	< 0.1
Refractive Index		~ 1.5
Retardation	nm	< 15
Birefringence	nm	< 10
Haze	%	< 0.5
Total Light Transmittance (at 550nm)	%	≥ 90
Glass Transition Temp.	℃	> 150
Coefficient of Linear Expansion	ppm/K	≤ 50
Pencil Hardness		≥ 3H
Surface Roughness	nm	≤ 10
Chemical Resistance	Methanol	○
	Ethanol	○
	Acetone	○
	MEK	○
	Toluene	○

可撓式基材特性比較

項目	單位	要求水準	基版基材		
			PC	PAR	PES
連續使用溫度	℃	150	130	160	180
熱膨脹係數	ppm/K	≤ 50	65	60	50
熱收縮率	ppm/溫度	< Pixel size/20	100/130	100/150	100/200
表面平整性	Nm	≤10	< 10	< 10	< 10
透光率	%	> 90	90	90	87
相位差值	nm	< 15	< 15	< 15	10
透氧度	cc/m^2-atm-day	15	15	15	-
透溼度	g/m^2-day	0.1	0.1	0.1	0.1
耐藥性	Alkaline	○	○	○	○
	Acid	○	△	△	○
	Acetone	○	△	◇	△
	Butylacetate	○	△	◇	△
	Alcohol	○	○	○	○

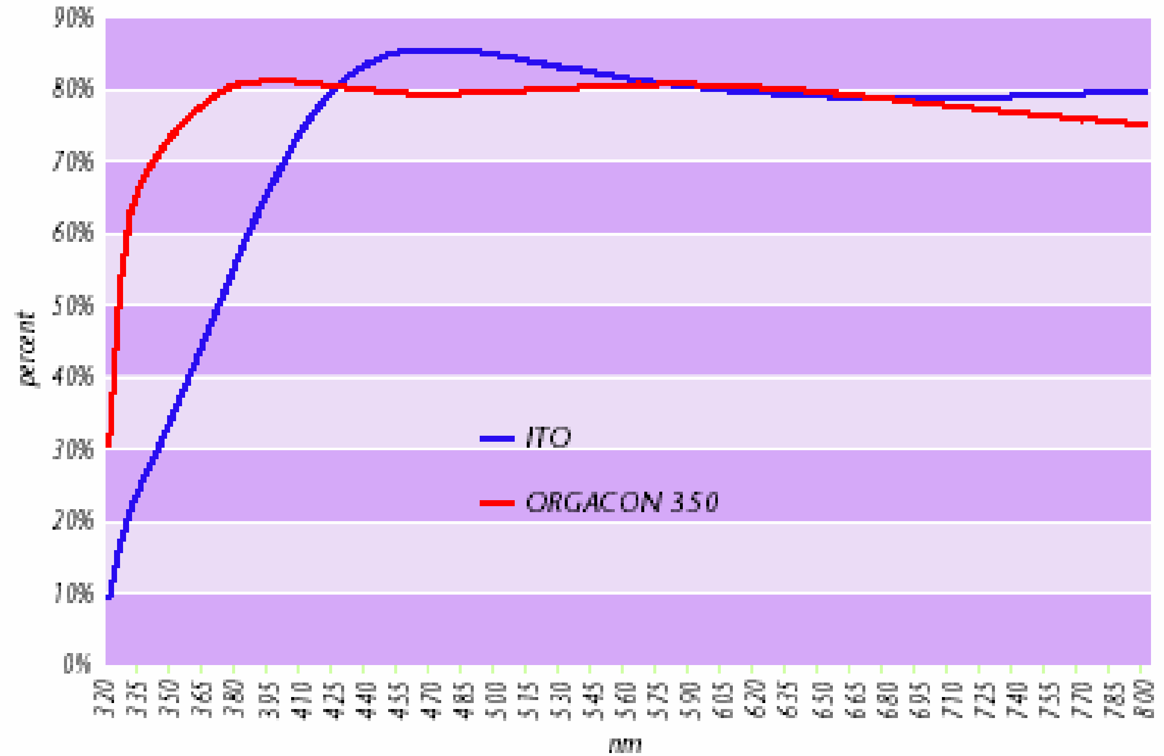
○ = good , △ = poor , ◇ = only contact

AGFA's Orgacon™與ITO透明導電膜比較

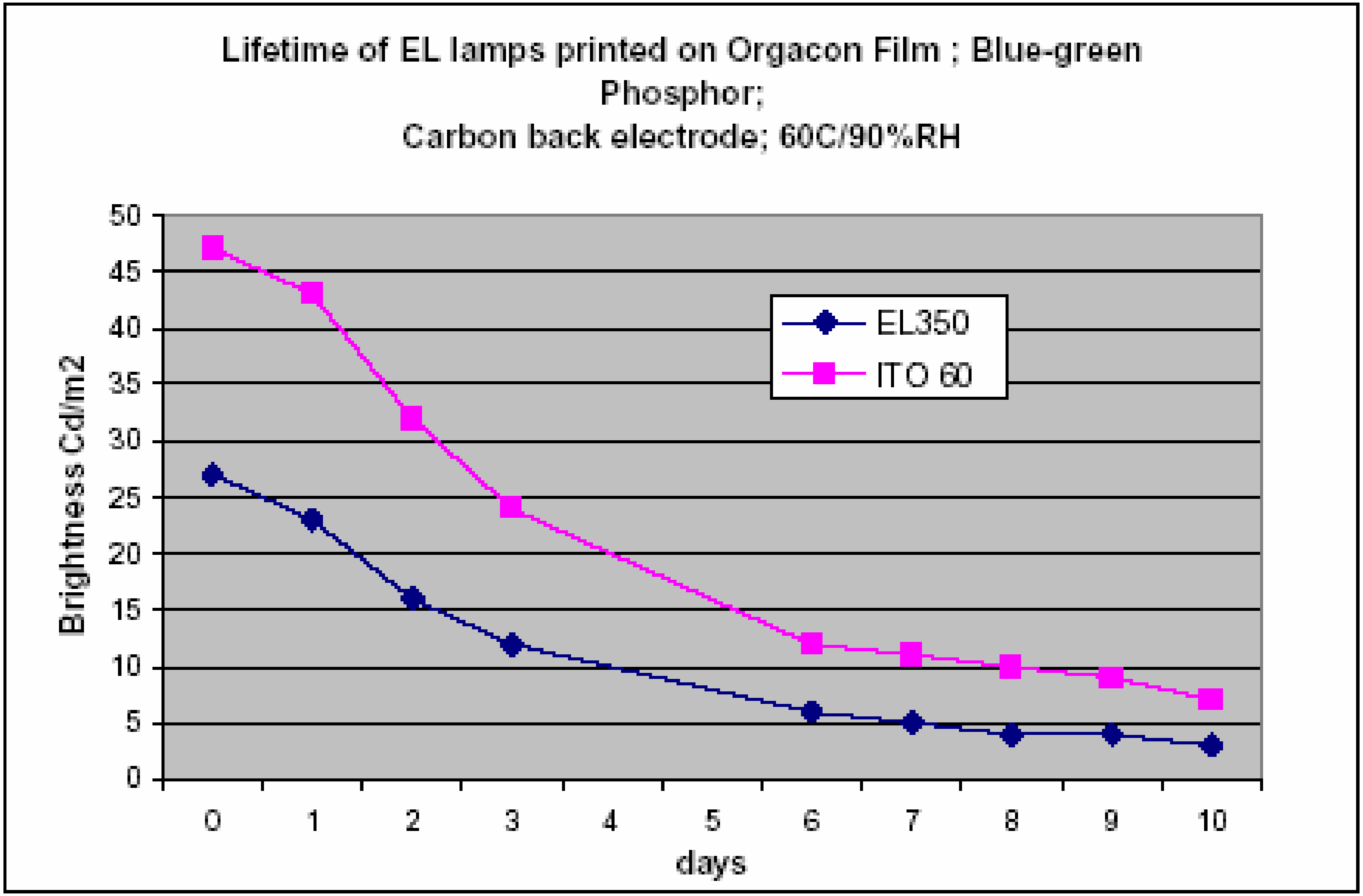
	AGFA's Orgacon™	金屬氧化物透明導電膜
導電機制	導電高分子(PEDOT)	金屬氧化物(ITO/IZO)
耐彎折能力	高	低(金屬氧化物易剝落)
作線路方式	將不須導通的區域 予以氧化deactivate	蝕刻法
線路作成後 表面形狀	平坦表面(相對)	凹凸排列
不導電區域電阻	10^9~$10^{14}\Omega$	$\rightarrow\infty$
蝕刻液	NaClO,$KMnO_{4(aq)}$	酸鹼液
目前最小有效線寬	20 μm	可小至1μm以下

工研院材料所資料

Optical Properties of Orgacon EL-350

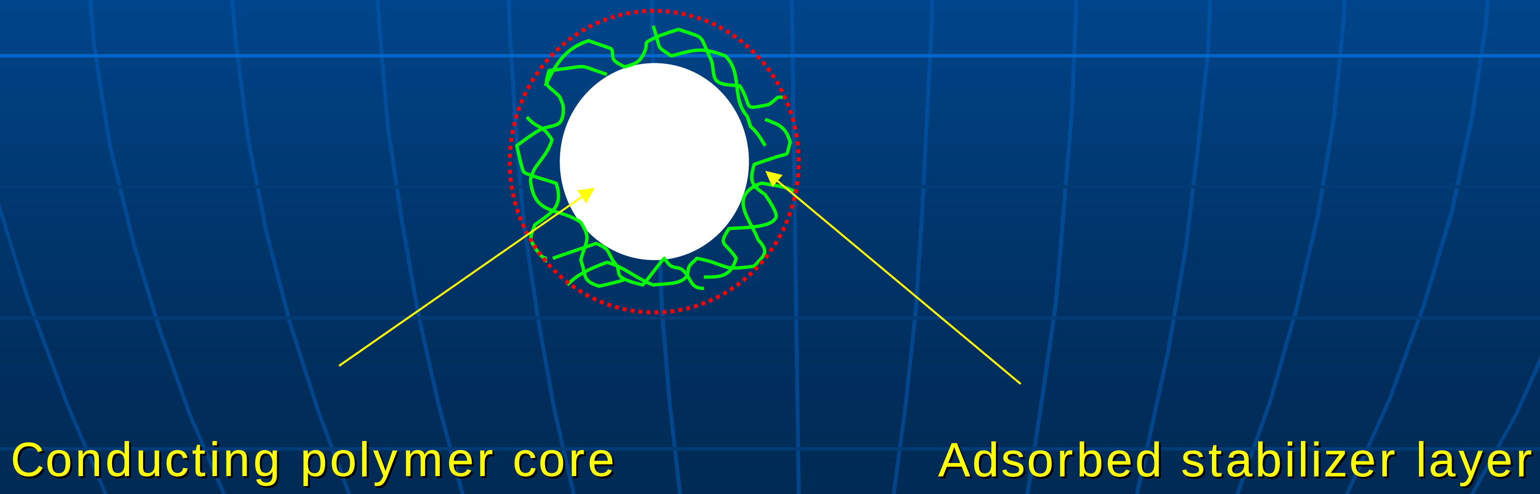


Spectral Transmission : Orgacon Versus ITO


Lifetime of EL lamps printed on Orgacon Film ; Blue-green Phosphor;
Carbon back electrode; 60C/90%RH
EL350
ITO 60
Brightness Cd/m2
days
0
5
10
15
20
25
30
35
40
45
50
0
1
2
3
4
5
6
7
8
9
10

Colloidal dispersions of conducting polymers

- **Steric stabilization** - this involves polymers added to the system adsorbing onto the particle surface and causing repulsion.
- This approach was used to produce stable dispersions, and improving the processability.



General Criteria for Effective Stabilizers

- Strongly anchored to the particle surface for preventing desorption or surface migration of the polymer during interparticle collision

- High surface coverage

- Sufficient anchored layer thickness to the minimum potential energy $G_{min} \sim 0$.

- The loops and tails of the anchored polymer should be associated with a good solvent environment in order to optimize the layer thickness.

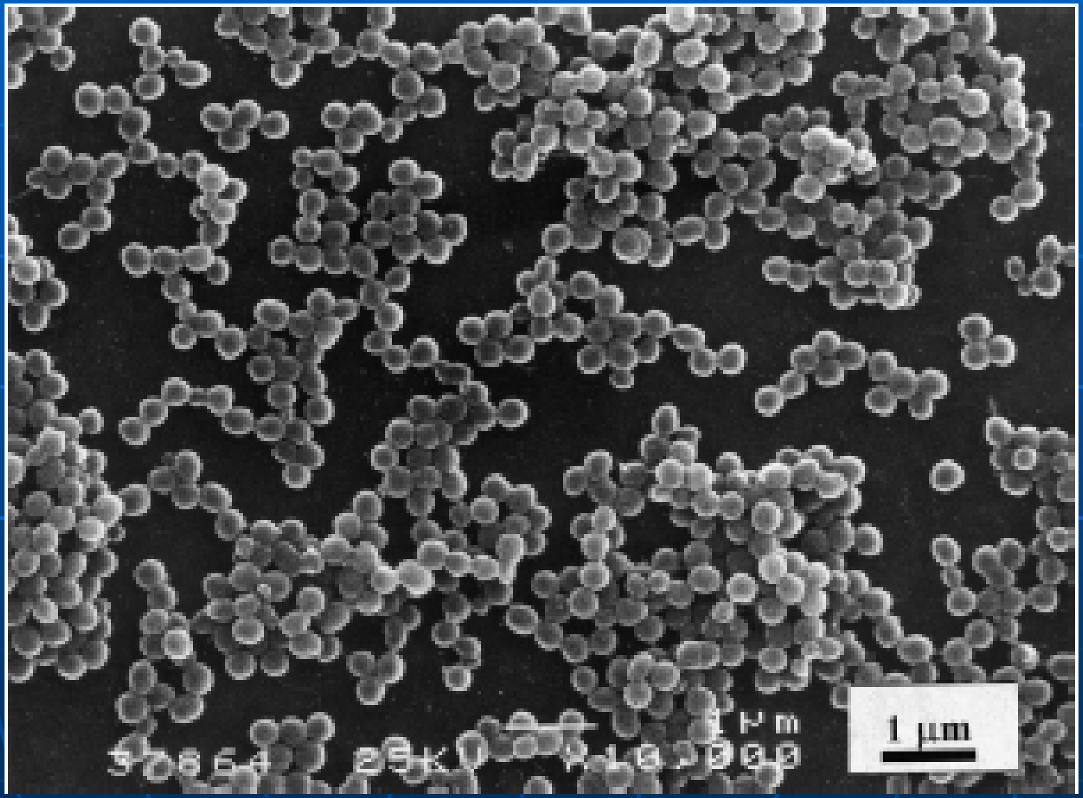
Stabilizers for Polyaniline Colloids

- Water soluble polymers
- Tailor-made polymers
- Particulate stabilizers
- Surfactants

Water soluble polymers

- Carboxymethylcellulose
- Ethy(hydroxyethyl)cellulose
- Hydroxypropylcellulose
- Methycellulose
- Polyacrylamide
- Poly(acrylic acid)
- Poly(ethylene oxide)
- Poly(methy vinyl ether)
- Poly(styrenesulfonic acid)
- Poly(vinyl alcohol)
- Poly(N-vinylpyrrolidone)
- Poly(vinyl alcohol-co-vinyl acetate)
- Protein

Polyaniline dispersion particles stabilized with hydroxypropylcellulose.

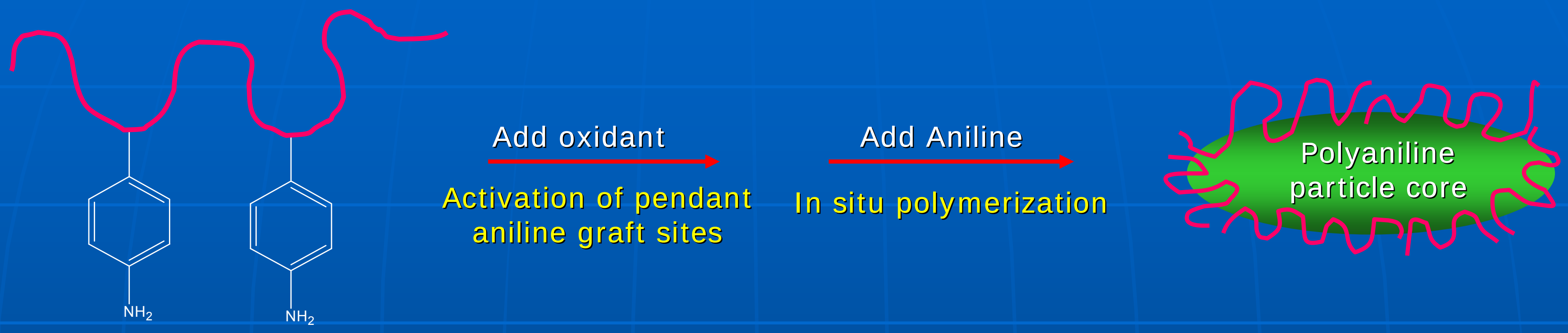


Polymer 40 (1999) 2487

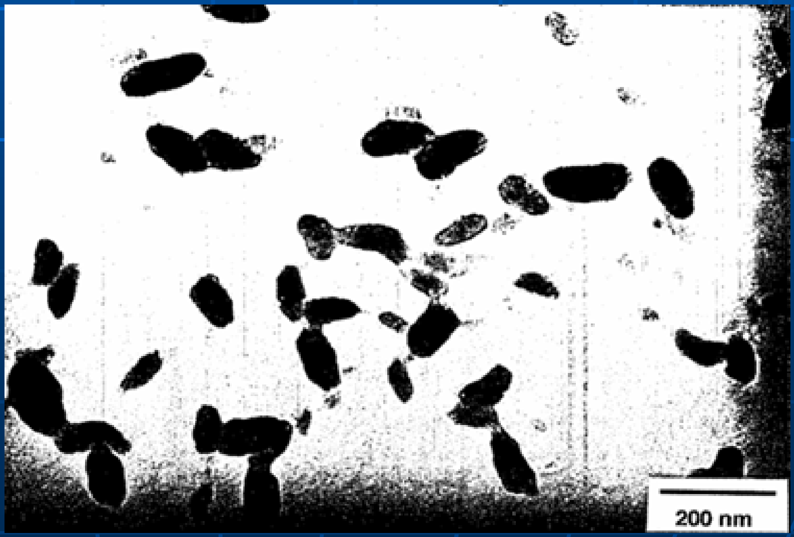
Tailor-made polymers

- Graft copolymers
- Block copolymers
- Reactive polymers

Polyaniline particles Prepared from Reactive Polymers



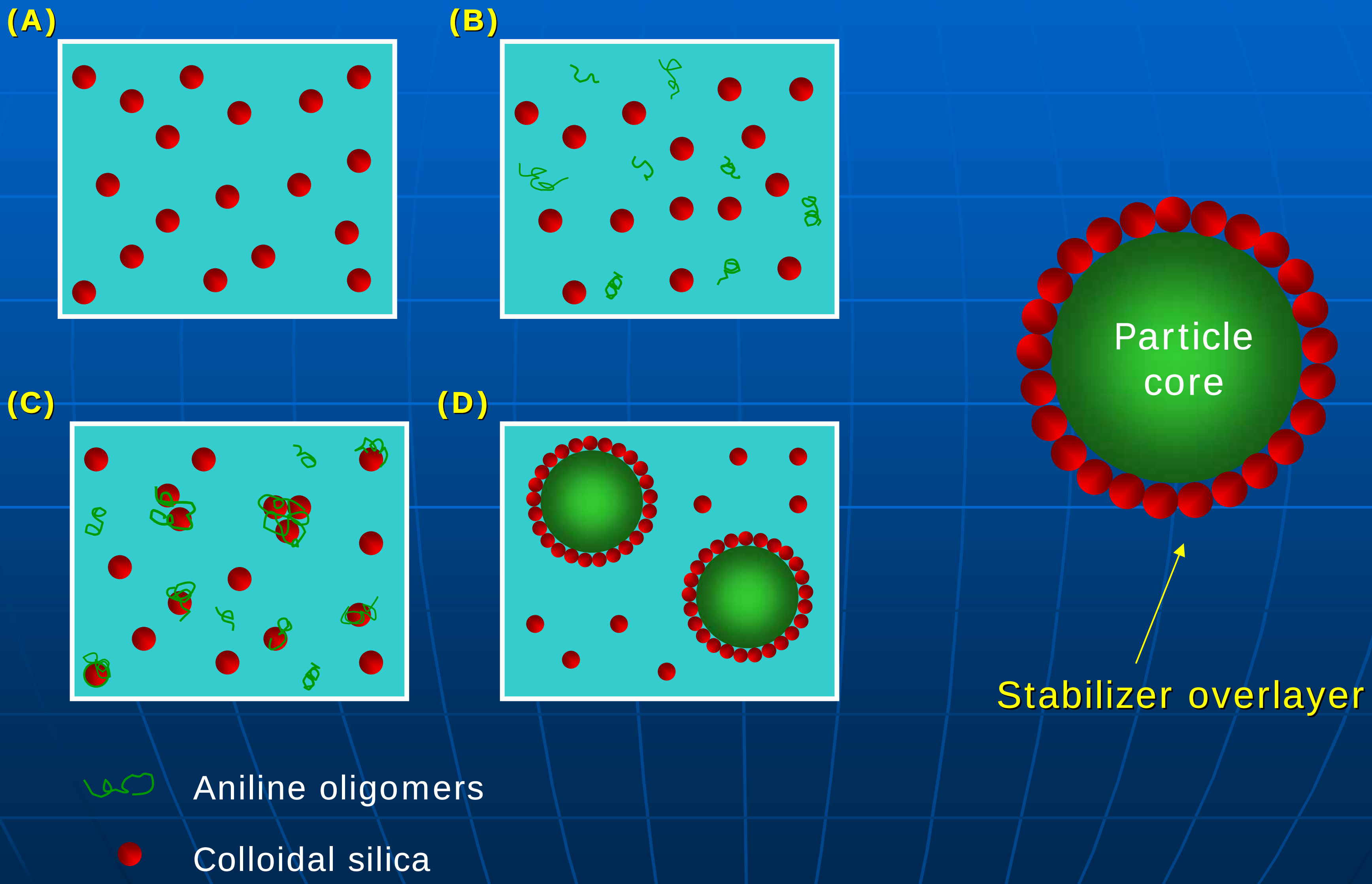
Polyelectrolyte stabilizer containing reactive pendant aniline groups



Polyaniline particles using reactive polyelectrolyte stabilizers.

Eur. Polym. J. 33 (1997) 245

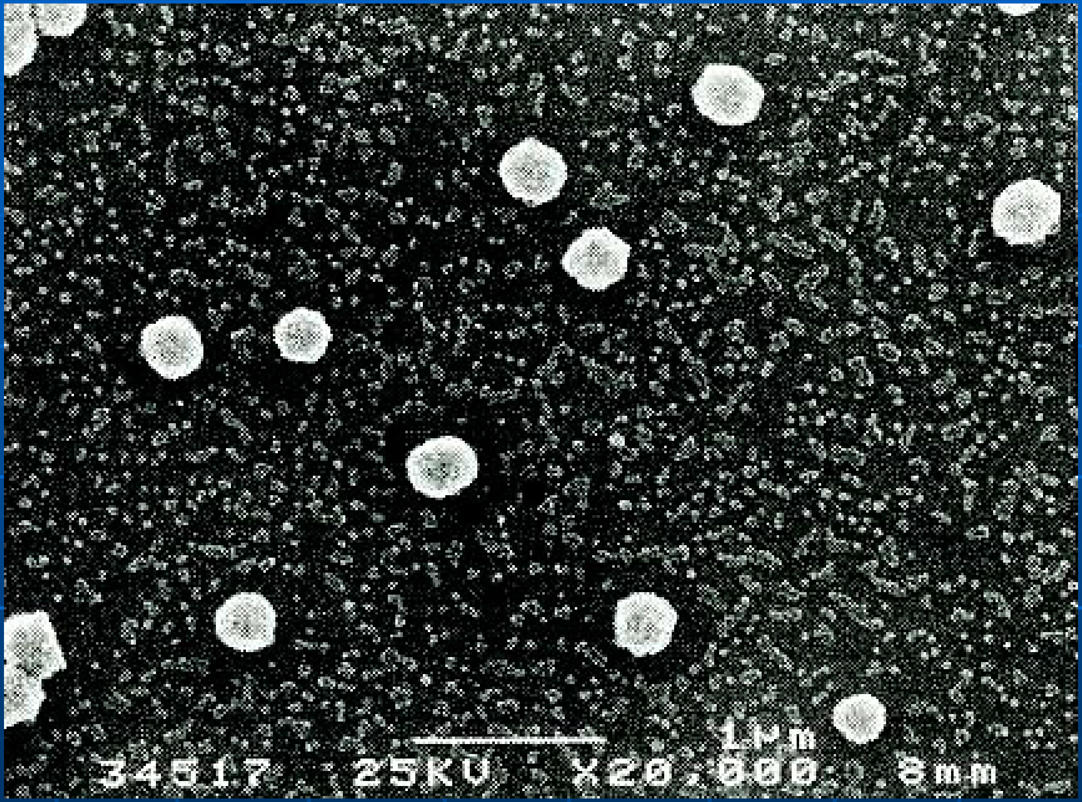
Inorganic Particulate Stabilizer



Particulate stabilizers

- Silica
- Manganese(IV) oxide
- Zirconium dioxide
- Titanium dioxide
- Polymer latexes

Polyaniline Particles Stabilized with Nanocolloidal Silica.



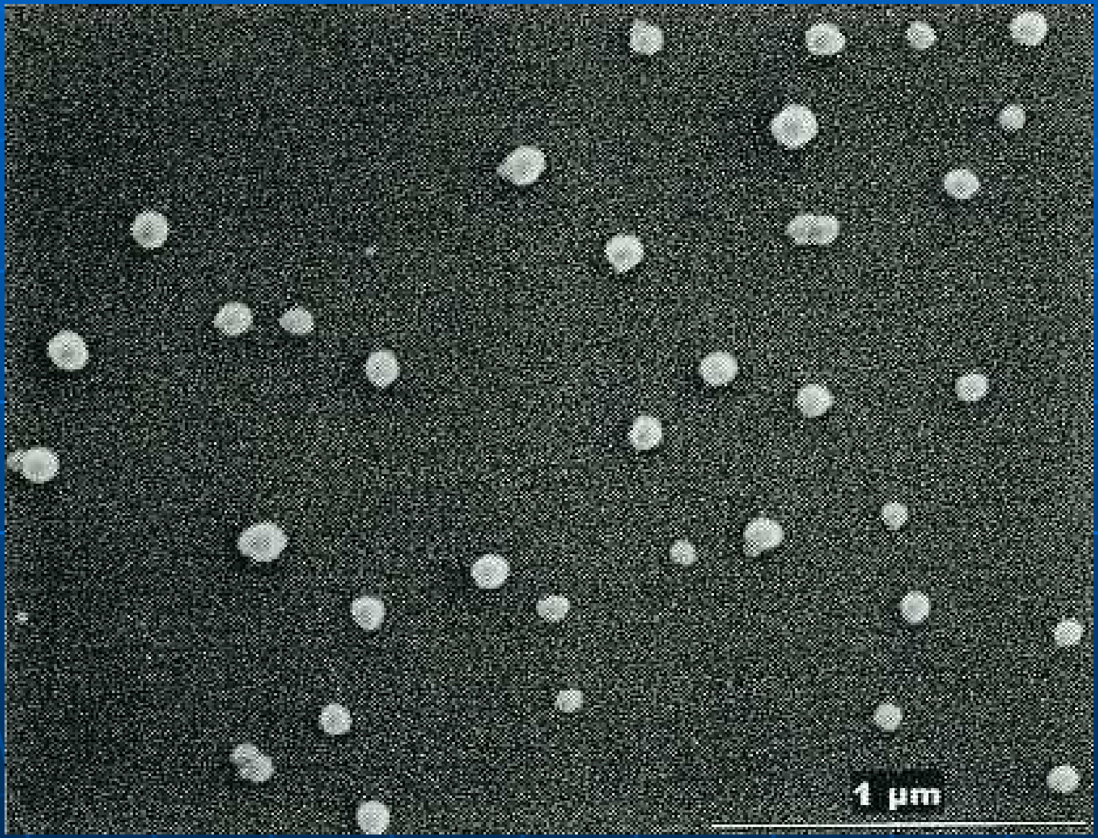
Free silica is visible on the background.

Macromolecules 29(1996) 6814

Surfactants

- Sodium dodecyl sulfate
- Dodecylbenzenesulfonic acid
- AOT

Colloidal polyaniline particles prepared in the presence of dodecylbenzenesulfonic acid

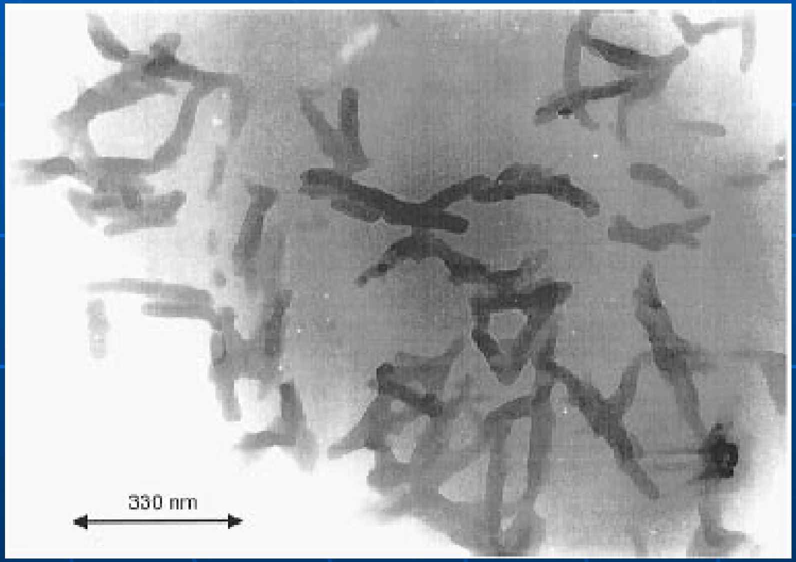


J. Polym. Mater. 18 (2001) 225

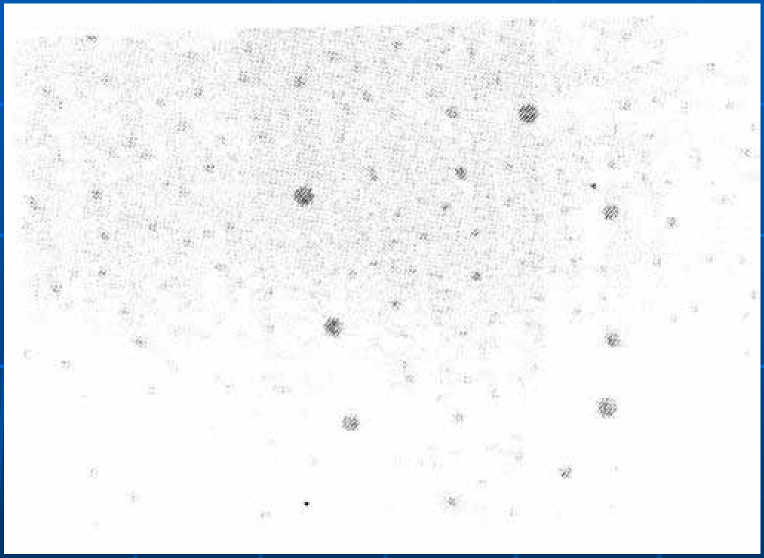
Particle Shape

The particle shape and morphology of polyaniline may be affected by several factors ---

- Stabilizer



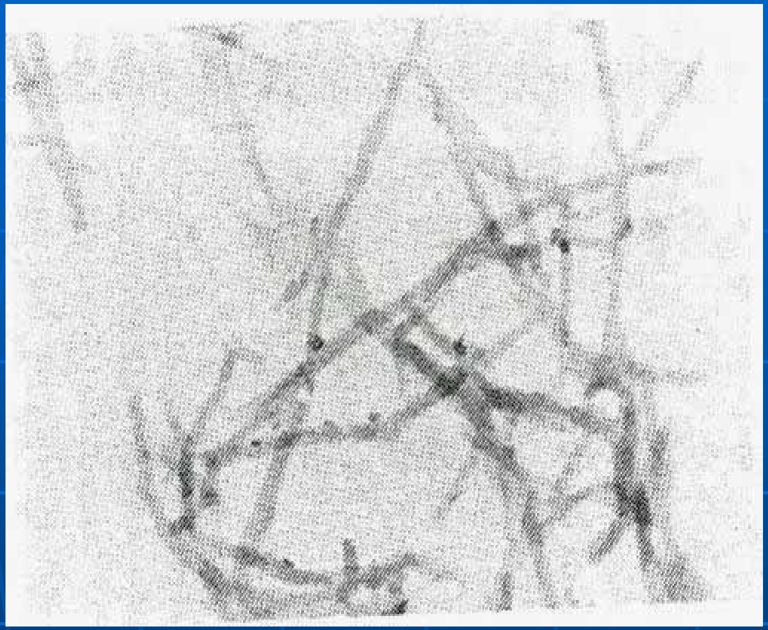
Needle-shape polyaniline particles (stabilizer: PVA)



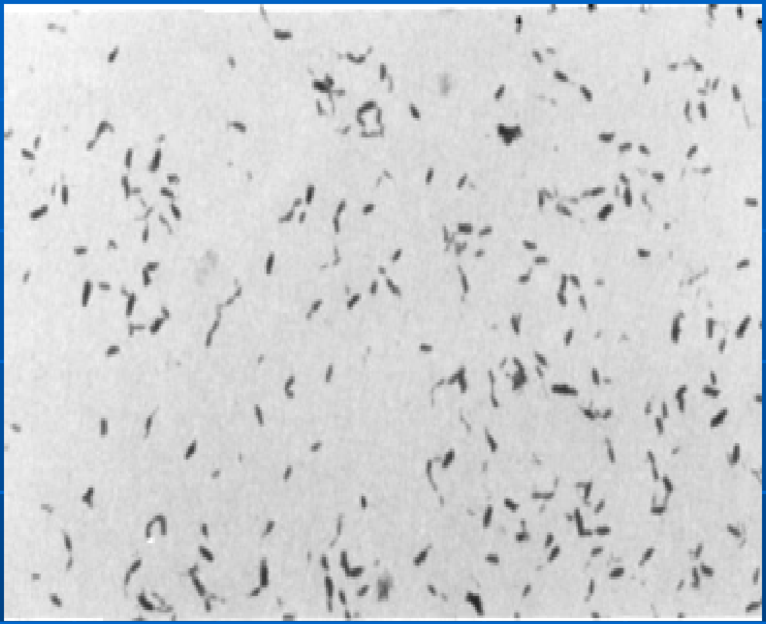
Spherical polyaniline particles (stabilizer: NaPSS)

Anal. Chem. 69 (1997) 1030

- Stabilizer



Needle-shape polyaniline particles using poly(ethylene oxide), M=300000, as stabilizer.

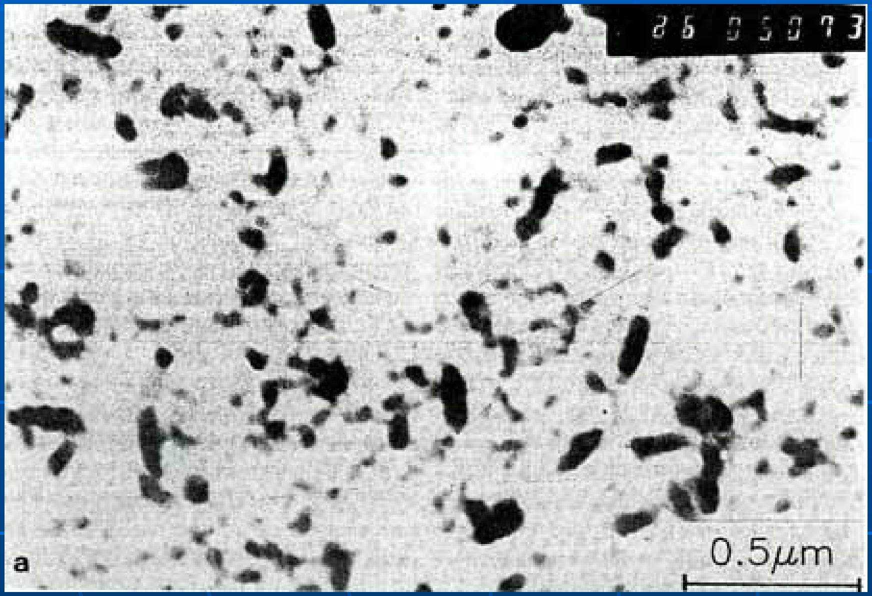


Rice-grain polyaniline particles using a graft copolymer stabilizer based on poly(ethylene oxide).

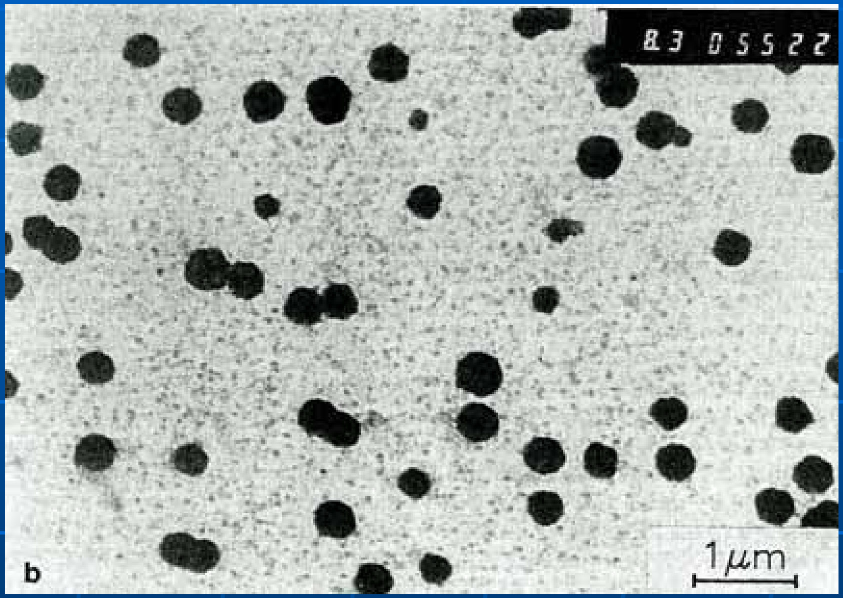
Chem. Commun. (1990) 683

● Oxidant

TEM Micrographs



Rice-grain shaped PANI colloids, using KIO_3 as oxidant

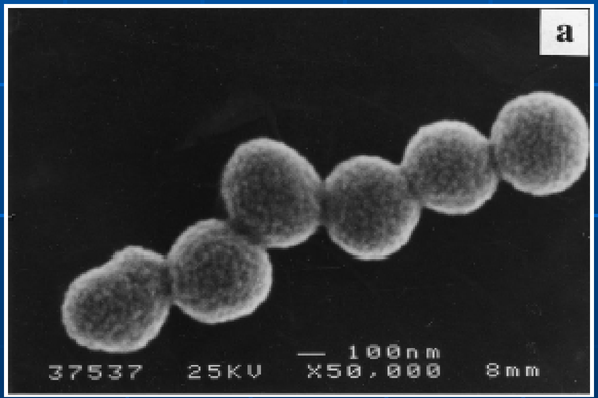


Spherical PANI colloids, using $(NH_4)_2S_2O_8$ as oxidant

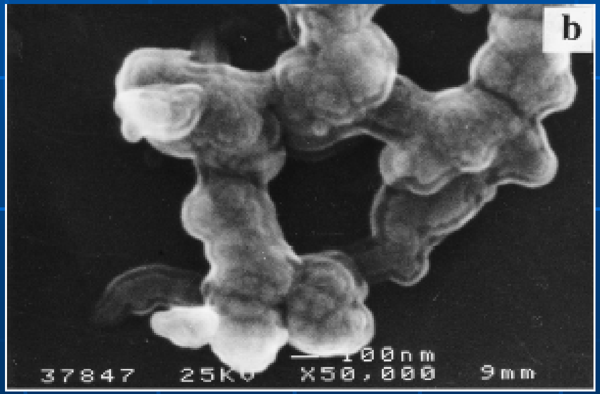
J. Colloid Interface Sci. 150 (1992) 134

● Temperature

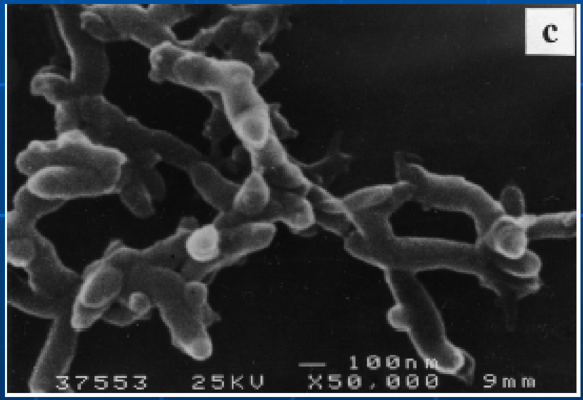
- The morphology of polyaniline particles may be different by changing the polymerization temperature of aniline.
- The micrograph shows the particles formed in dispersion polymerization of aniline hydrochloride at different temperatures.



0℃.



20℃.

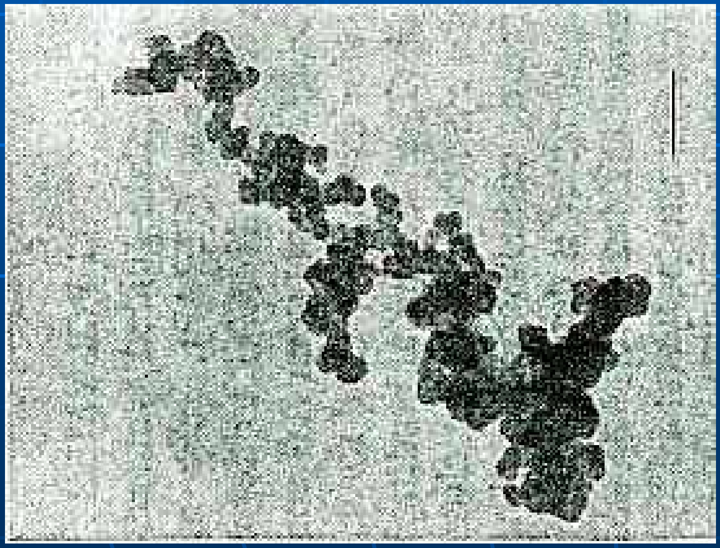


40℃.

Polymer 40 (1999) 2487

● Template

- Sun et al. found that the polymerization of aniline in a solution of poly(styrene sulfonic acid) yielded the globular structure while in the presence of poly(acrylic acid) it resulted in distinct coral-like morphology attributed to the template control in polymerization.



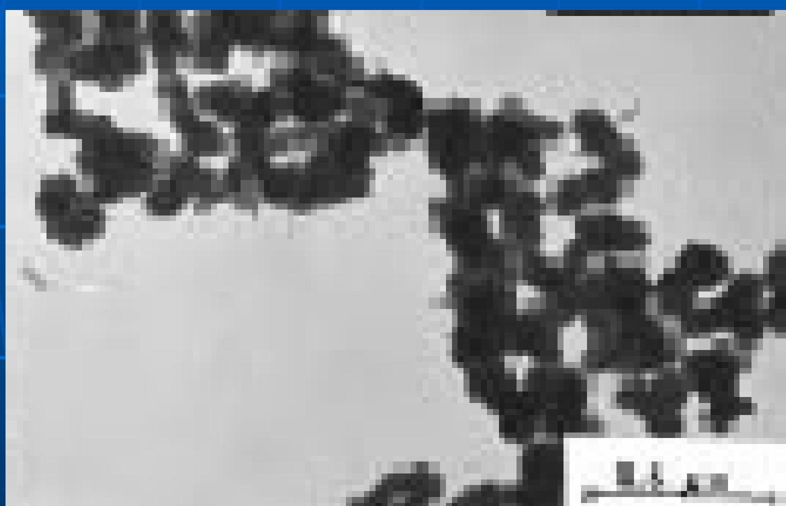
TEM of PSSA-PANI complex

SEM of PAA-PANI complex

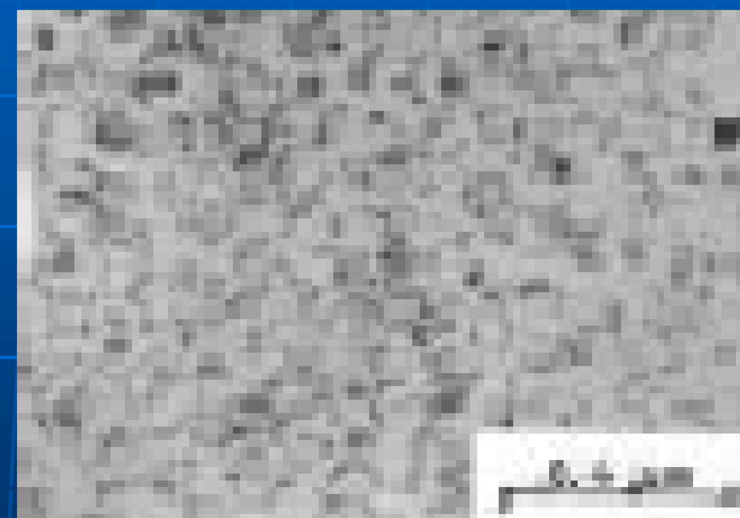
Polym. Prepr. 33 (1992) 379

● Solvent

- Chattopadhyay found that the morphology of PANI particles stabilized with cellulose ethers was controlled by the composition of ethanol/water mixture.



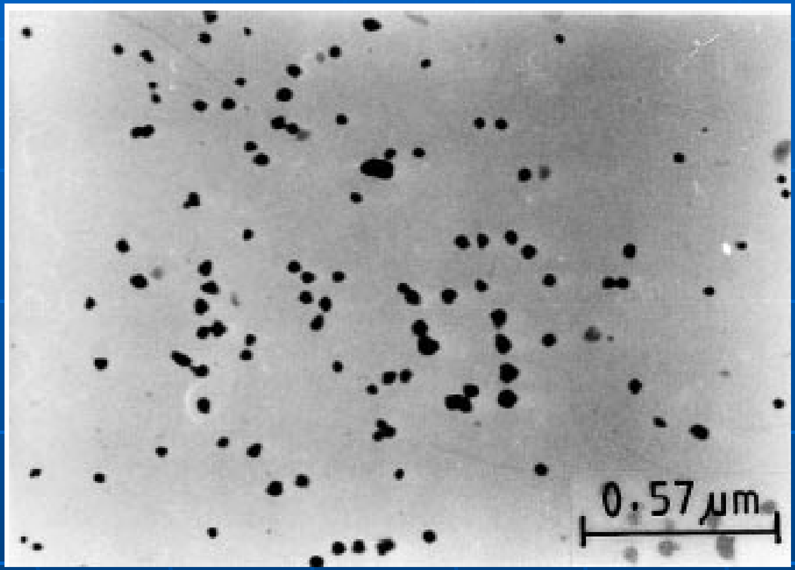
TEM of ethyl(hydroxyethyl)cellulose stabilized PANI dispersions prepared in water



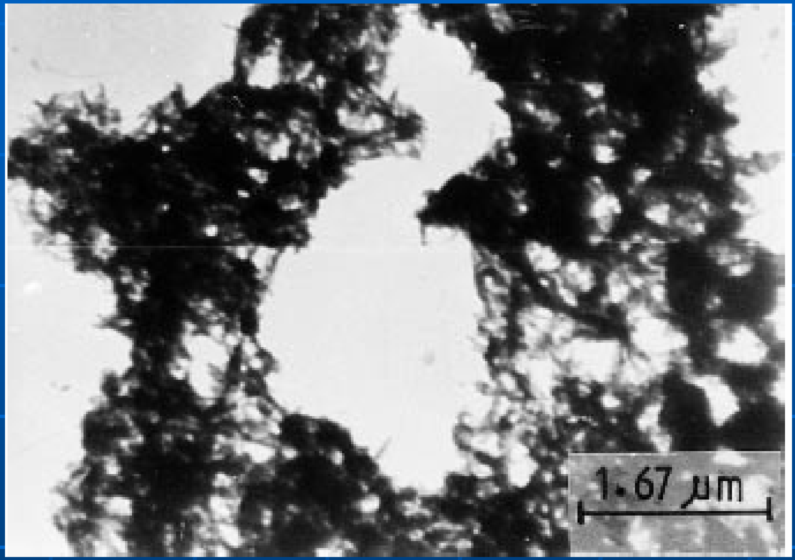
TEM of ethyl(hydroxyethyl)cellulose stabilized PANI dispersions prepared in 70% ethanol.

Langmuir 14 (1998) 1544

● Concentration of stabilizer and monomer



TEM of hydroxypropylcellulose (HPC) stabilized PANI particles prepared in 80% ethanol (HPC=1 g/cm^3 Aniline=0.5 g/cm^3)

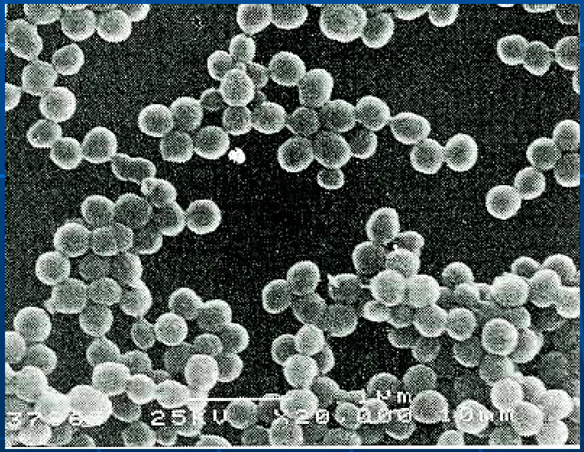


TEM of hydroxypropylcellulose (HPC) stabilized PANI particles prepared in 80% ethanol (HPC=0.5 g/cm^3 Aniline=0.75 g/cm^3)

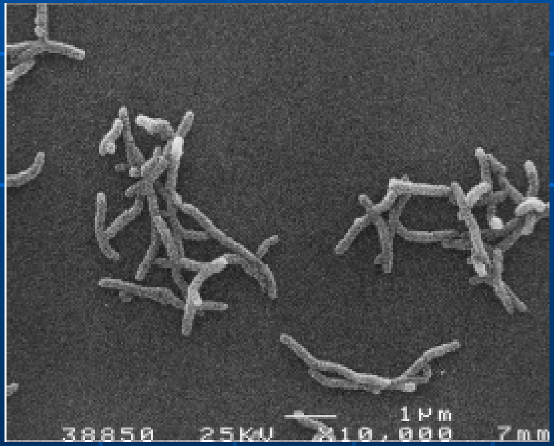
Polym. Int. 50 (2001) 538

Mediators

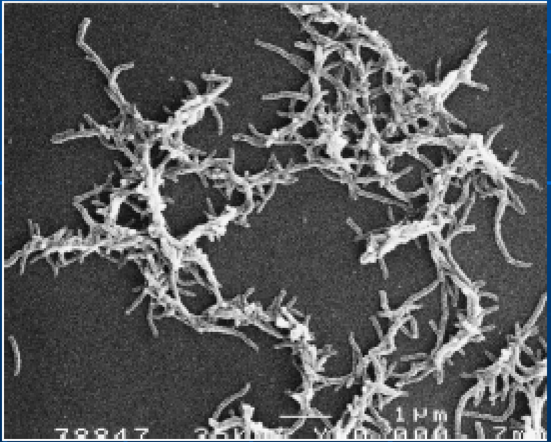
- The rate of aniline polymerization can be efficiently increased at fixed temperature by introducing small amounts of mediators during the polymerization of aniline, and the morphology of polyaniline particles may be different.
- The micrograph shows the particles formed in dispersion polymerization of aniline hydrochloride by addition of different concentration of mediators.



No mediators



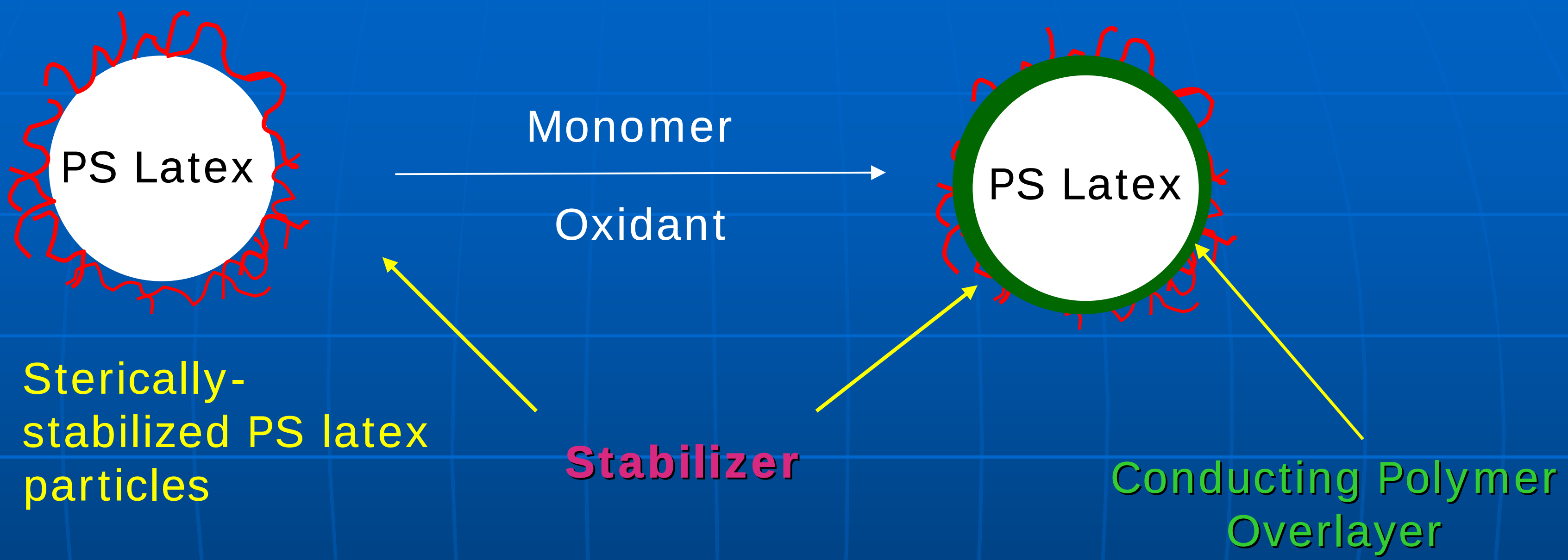
2×10^{-4} M p-phenylenediamine dihydrochloride



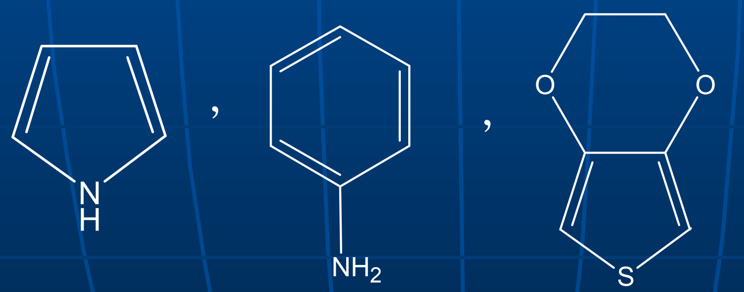
2×10^{-3} M p-phenylenediamine dihydrochloride

Polymer 40 (1999) 2487

Steric stabilized core-shell latex



Monomer:



Oxidant: $FeCl_3$, $(NH_4)_2S_2O_8$, $Fe(tosylate)_3$

●Core:

High Tg latexes: polystyrene、poly(methyl methacrylate) 、poly(styrene-co-styrene sulfonate)...

- These composite particles exhibit rigid, non-deformable properties, and can be readily synthesized with narrow size distributions over a wide size range (50nm~10 μm)

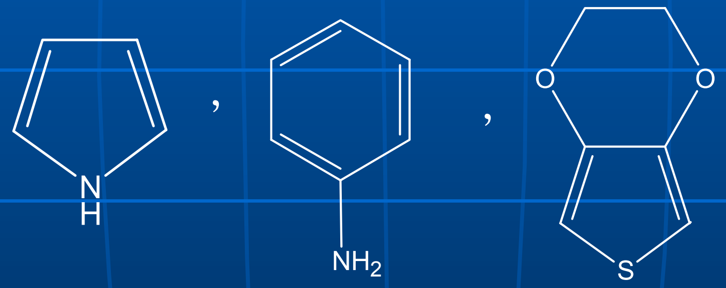
Low Tg latexes: polyurethane、poly(vinyl acetate) 、alkyd resin、poly(butyl methacrylate)...

- These composite particles exhibit remarkably good film formation properties.

●Stabilizers:

Poly(ethylene oxide)、 Poly(vinyl alcohol) 、
Poly(N-vinyl pyrrolidone) 、 PDMAEMA-PMMA、
poly(vinyl acetate) 、Methyl cellulose...

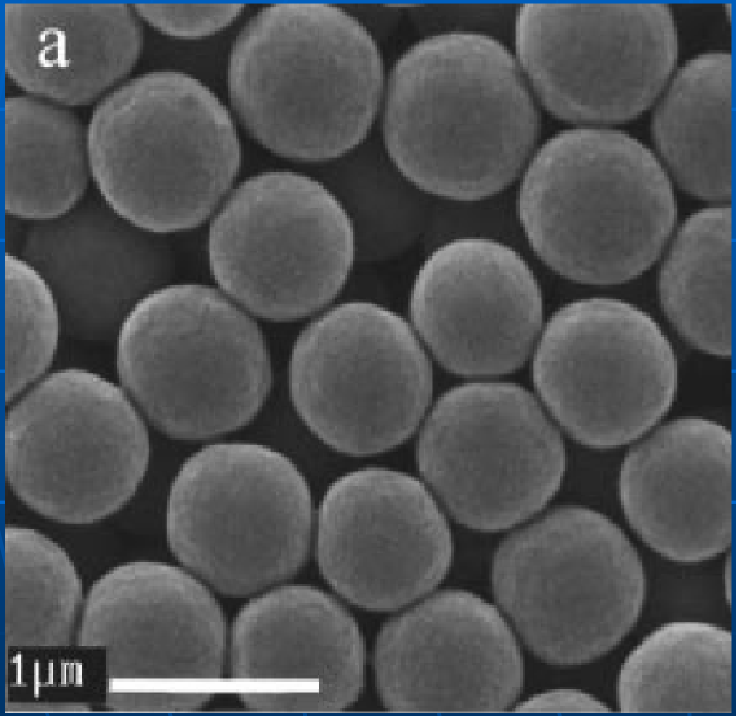
●Monomer:



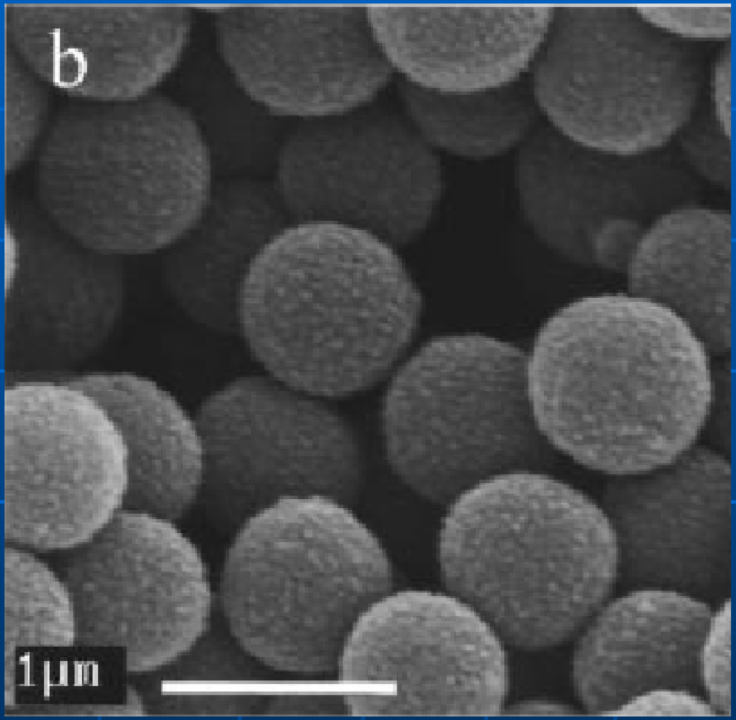
●Oxidant:

$FeCl_3$、 $(NH_4)_2S_2O_8$、Fe(tosylate)$_3$、H_2O_2

SEM micrographs of polyaniline-coated polystyrene latexes



Uncoated PS latexes

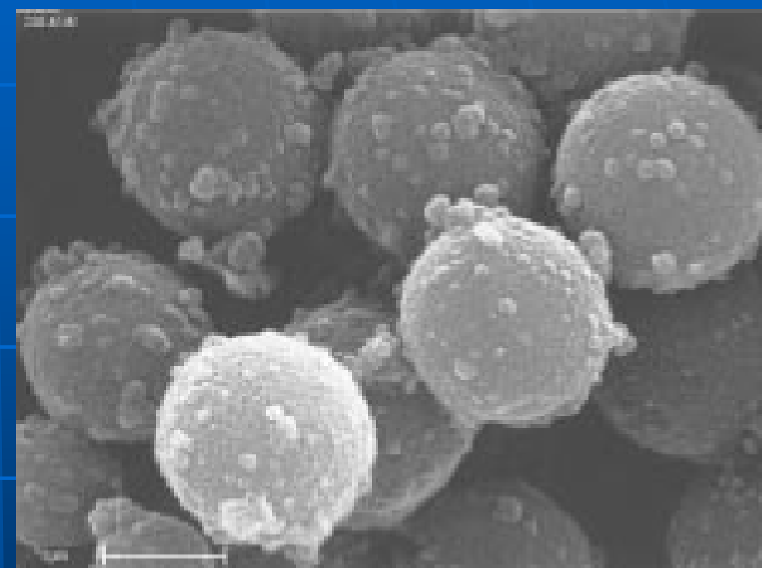


Polyaniline/PS=25.0%

JLangmuir 14 (1998) 2032

SEM micrographs of polypyrrole-coated polystyrene latexes

Polypyrrole/PS=6.1%



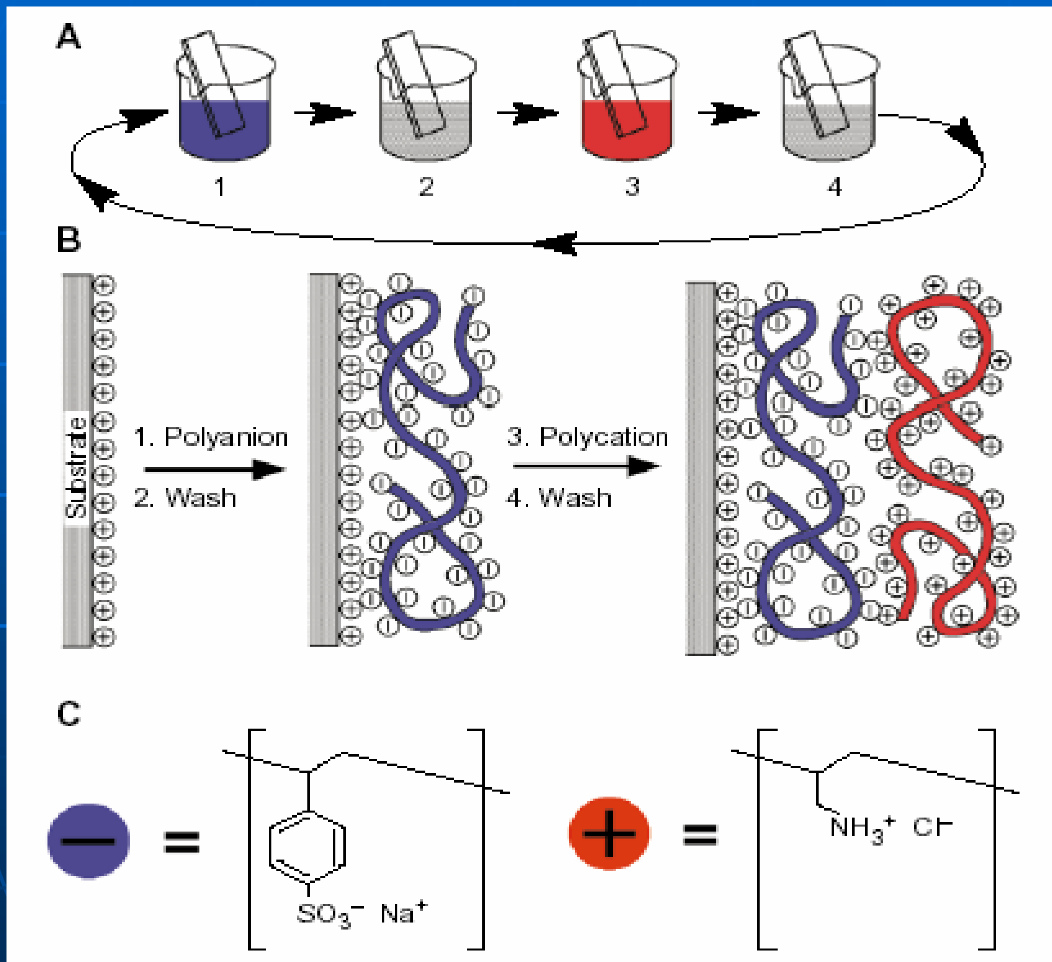
Polypyrrole/PS=25.1%

J. Mater. Chem 7 (1997) 1339

Self-assembled polymer layers

- Colloidal particles have been coated and stabilized by the direct adsorption of polymers from solution onto their surface.
- The polymers used are charged (i.e., polyelectrolytes) and their stabilizing influence arises from both electrostatic and steric effects.
- It is possible to coat colloids with uniform single- and multilayers of polyelectrolytes.

Layer-by-layer technique



— Polyanion

Poly(styrene sulfonate)

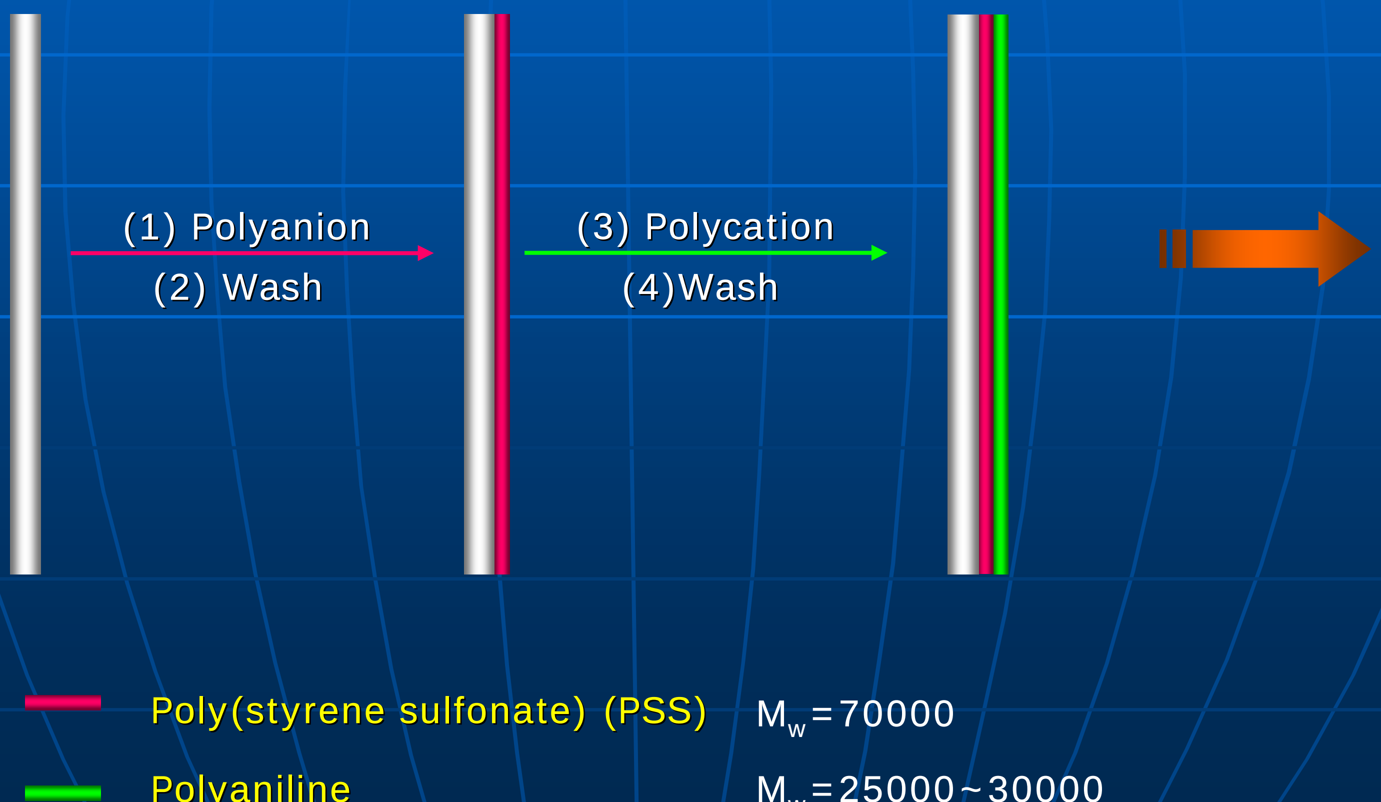
\+ Polycation

Poly(allylamine hydrochloride)

Schematic of layer-by-layer process.

Science 277 (1997) 1233

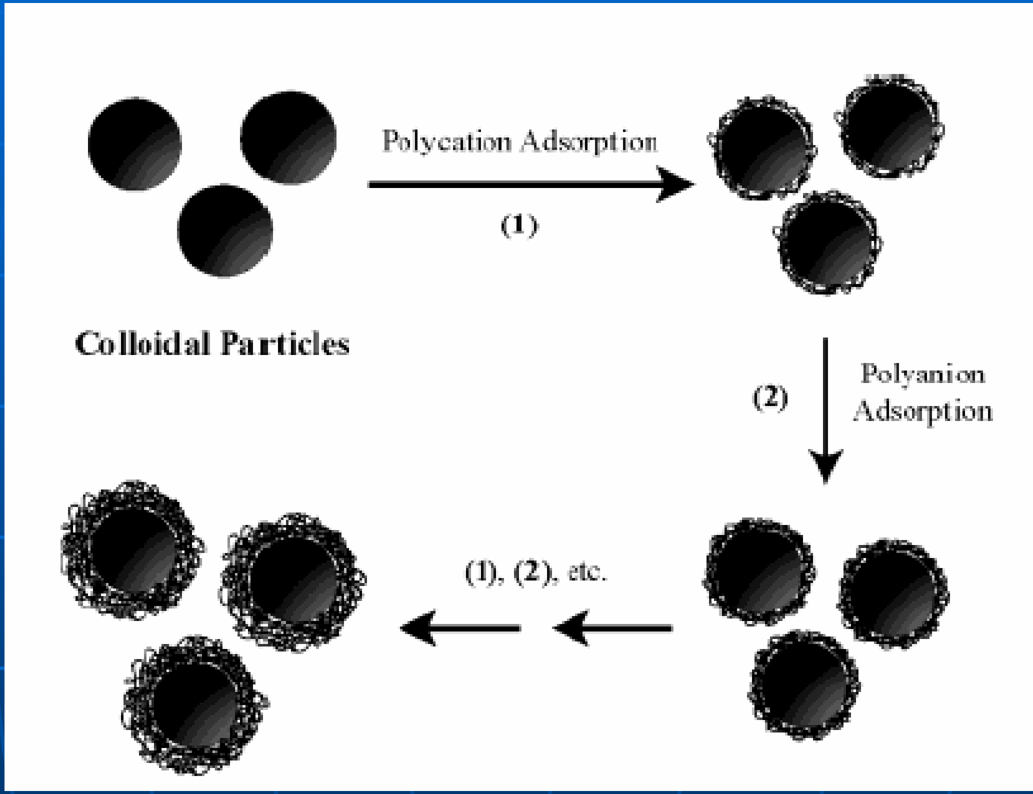
- Ram et al have reported the PSS/PANI layer-by-layer films deposited on glass substrates, and discussed their physical properties.
- It was shown that when the pH of the solution is lying between 5 to 6, it was not possible to control the film deposition because PANI is not sufficiently charged to the deposited on the polyanion PSS surface.
- When the pH value of the solution was controlled from 2.7 to 3.5, PANI was sufficiently charged and the uniform deposition took place.



$M_w = 70000$

$M_w = 25000 \sim 30000$

Layer-by-layer colloid templating strategy

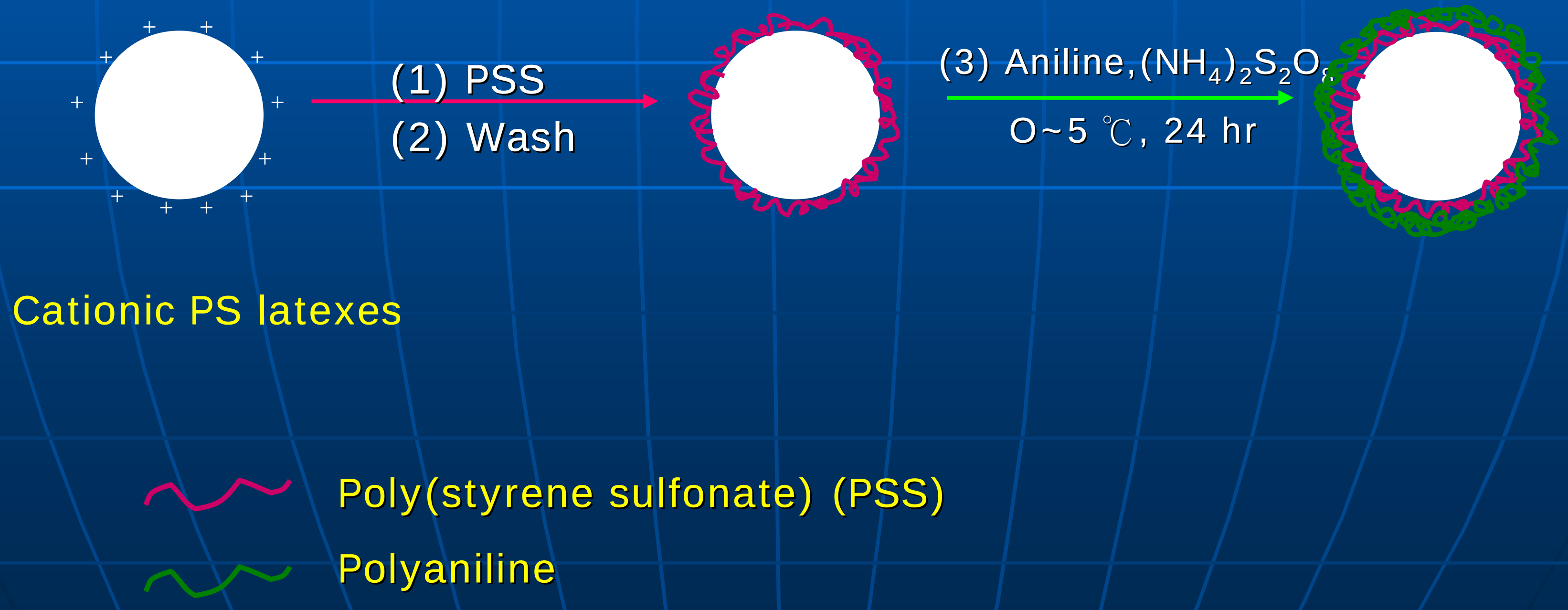


Schematic illustration of the LbL process for forming polyelectrolyte multilayers on particles. The scheme is shown for negatively charged particles.

Adv. Mater. **2001**, 13, 11

Lay-by Layer colloid templating strategy

- We can adopt the layer by layer colloid templating strategy to synthesis the PANI coated PS core shell latexes.



Advantages of the layer-by-layer technique

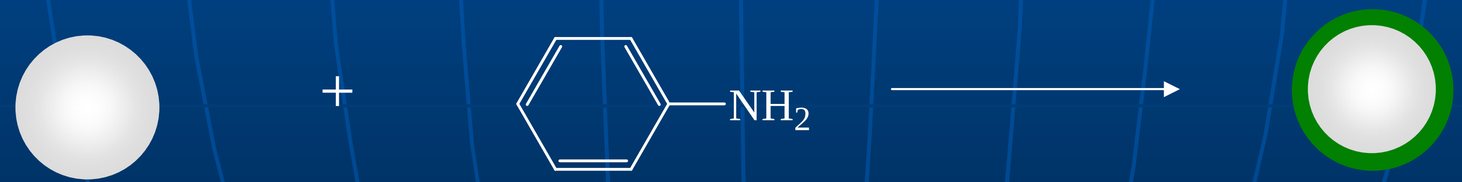
- The thickness of the polymer coating can be fine turned by altering the number of layers deposited and the solution conditions from which the polymers are adsorbed.
- Multicomposite polymer films can be assembled through choice of a large variety of polymers.
- Colloids of different sizes, shapes and composition can be employed as templates since polyelectrolytes self-assemble onto numerous surface.

Synthesis of Polyaniline-Coated Polystyrene Latexes

- **Core: polystyrene**

  By emulsifier-free emulsion polymerization method.

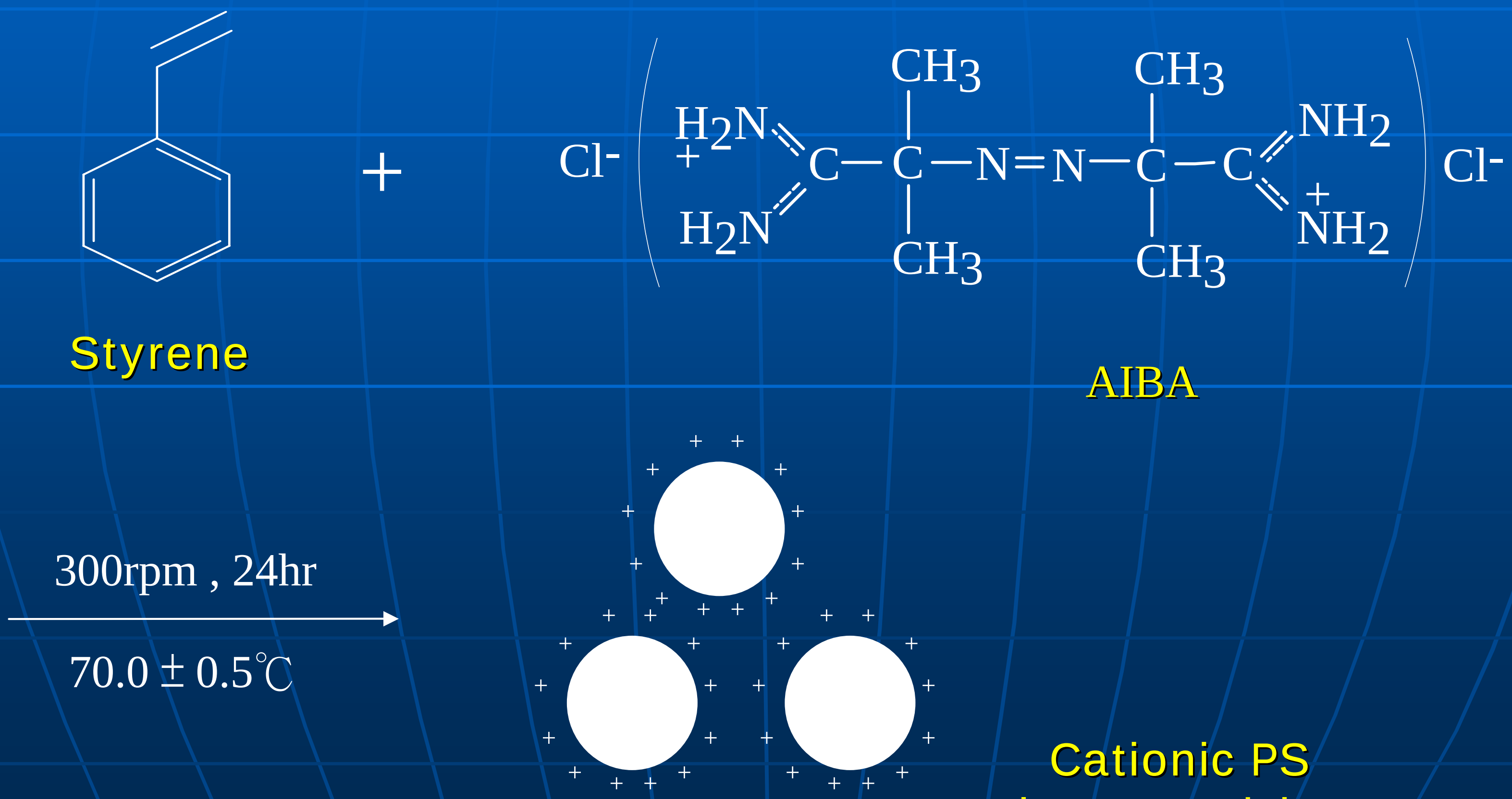
- **Shell : polyaniline**



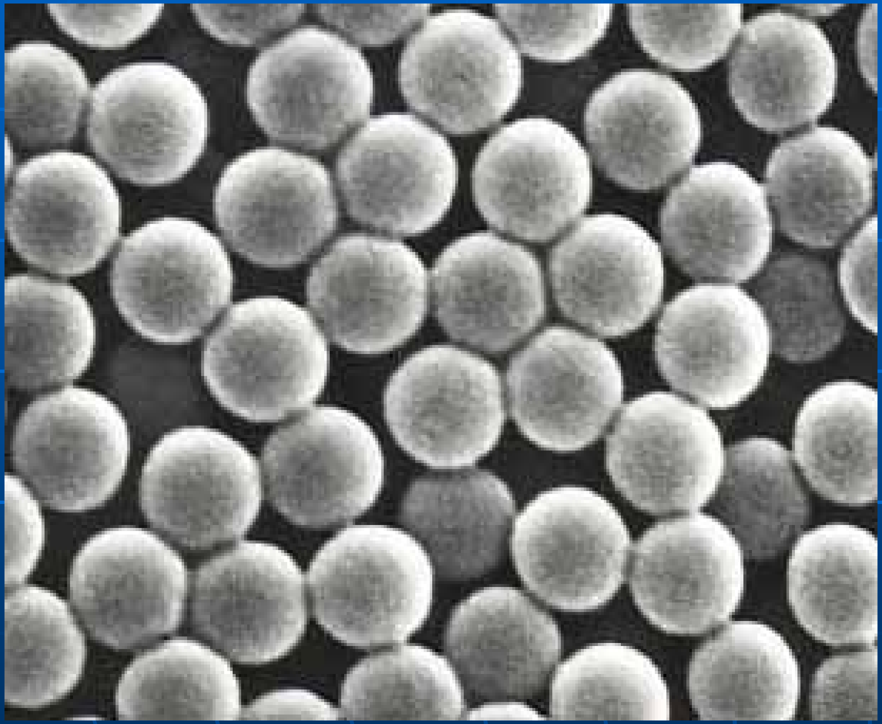
Core (PS) Shell (PANI) Core-shell latex

Synthesis of cationic polystyrene latex

Initiator : azobis(isobutylamidine hydrochloride)



SEM micrograph of cationic polystyrene latex

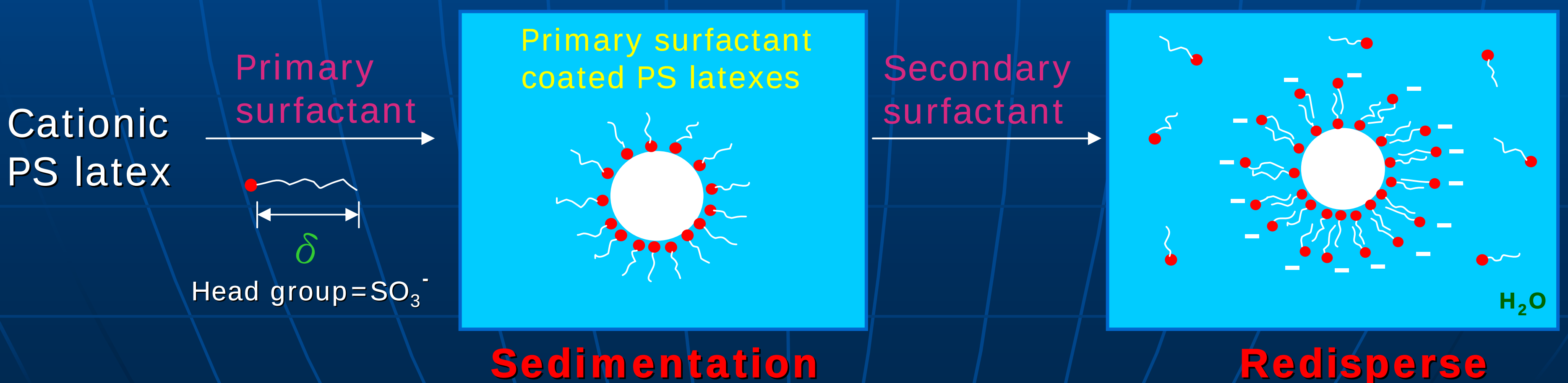


Near-monodisperse spherical particles morphology observed for the uncoated PS latex.

Preparation of PS/PANI Core-Shell Latexes

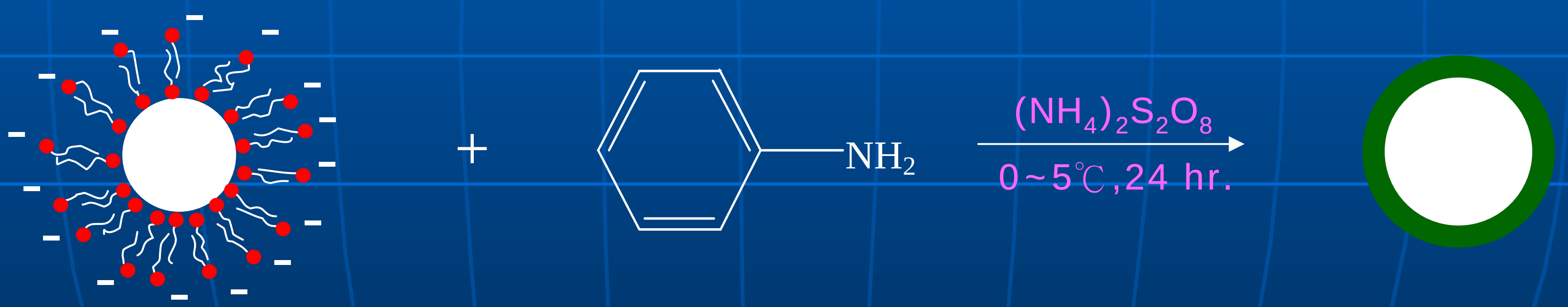
Step1: Adsorption of anionic surfactants

Schematic representation for the bilayer surfactant stabilized PS latexes



Preparation of PS/PANI Core-Shell Latexes

Step 2: In situ polymerization of aniline

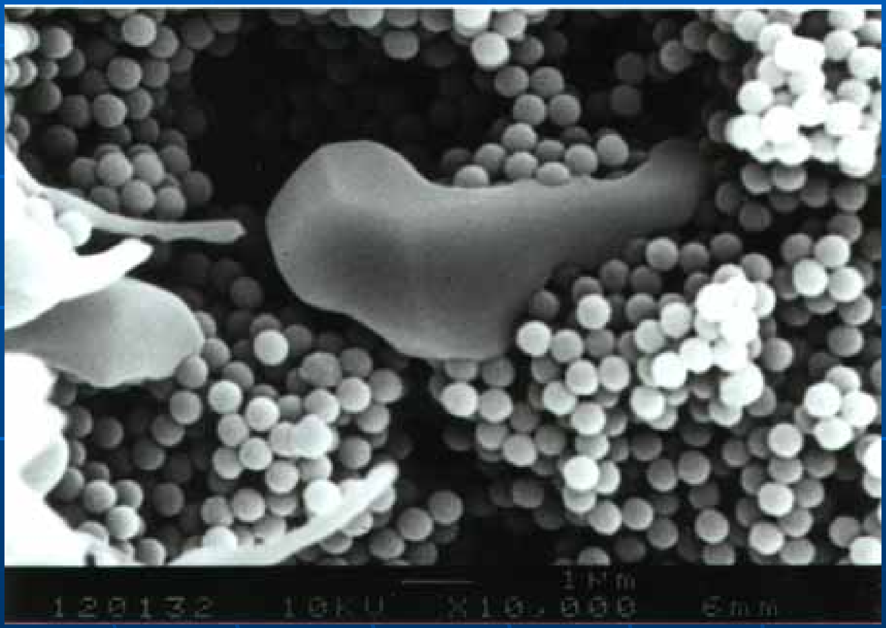


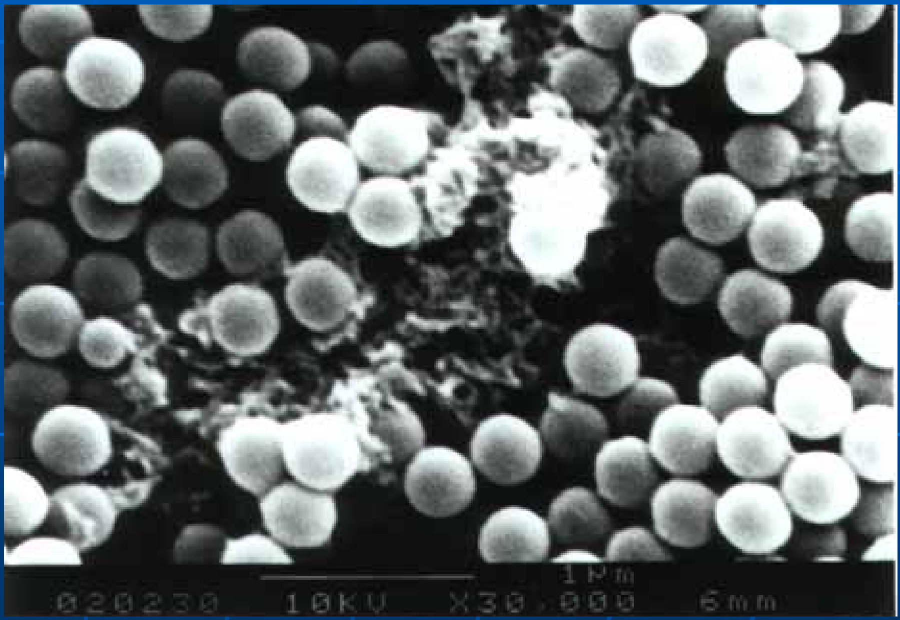
Bilayer surfactant stabilized PS latex particles

Aniline

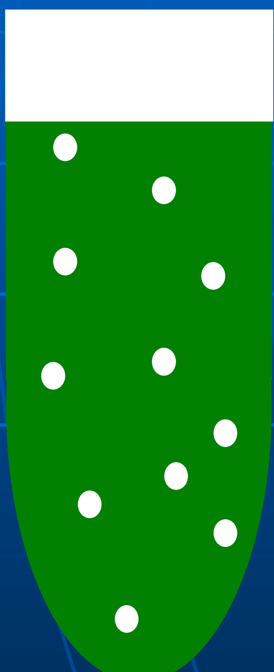
Polyaniline-coated polystyrene “core-shell”particles

SEM micrograph of PS/PANI latexes
(Without SDS)





Isolation of the PS/PANI composite particles



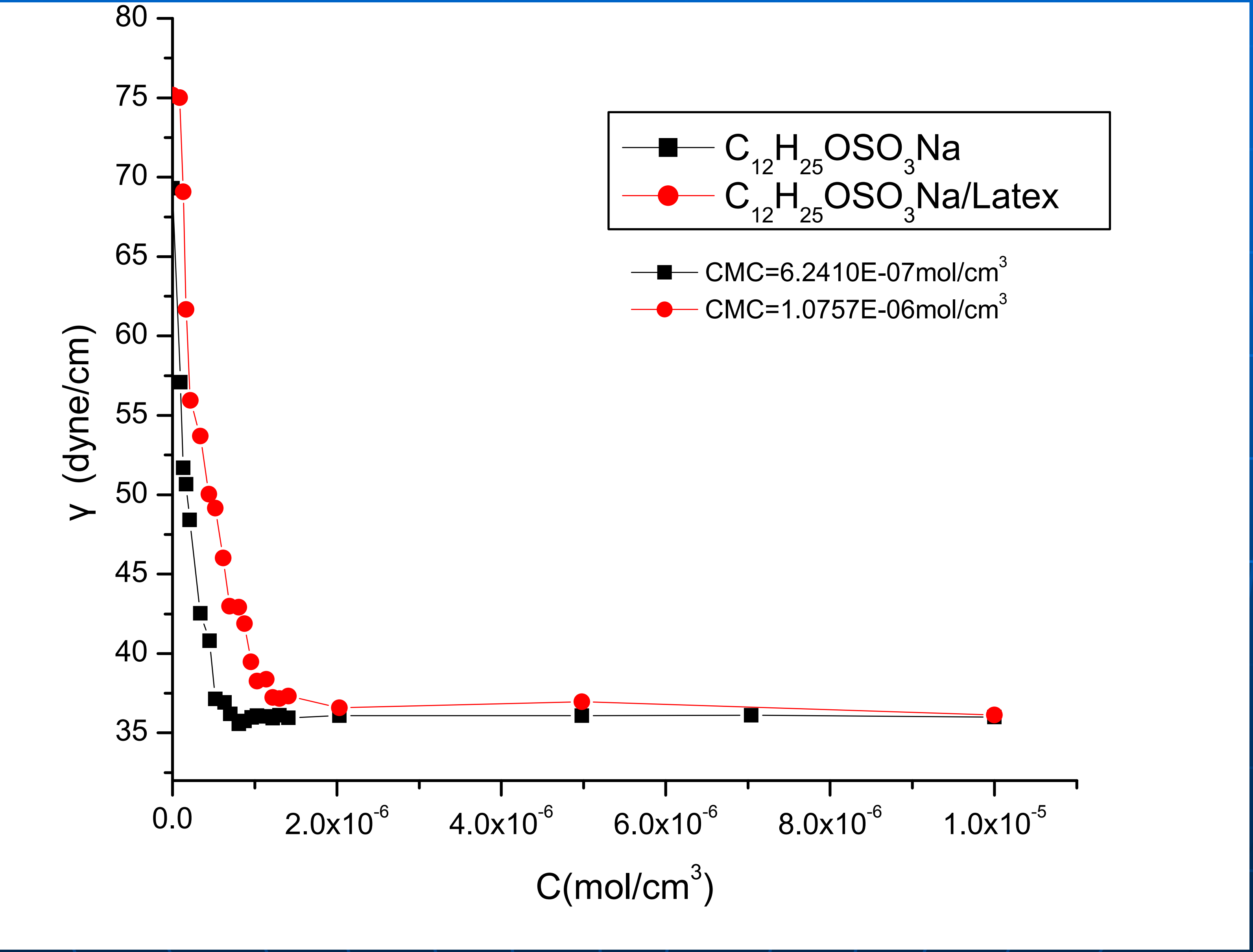
Centrifuge

10 minutes

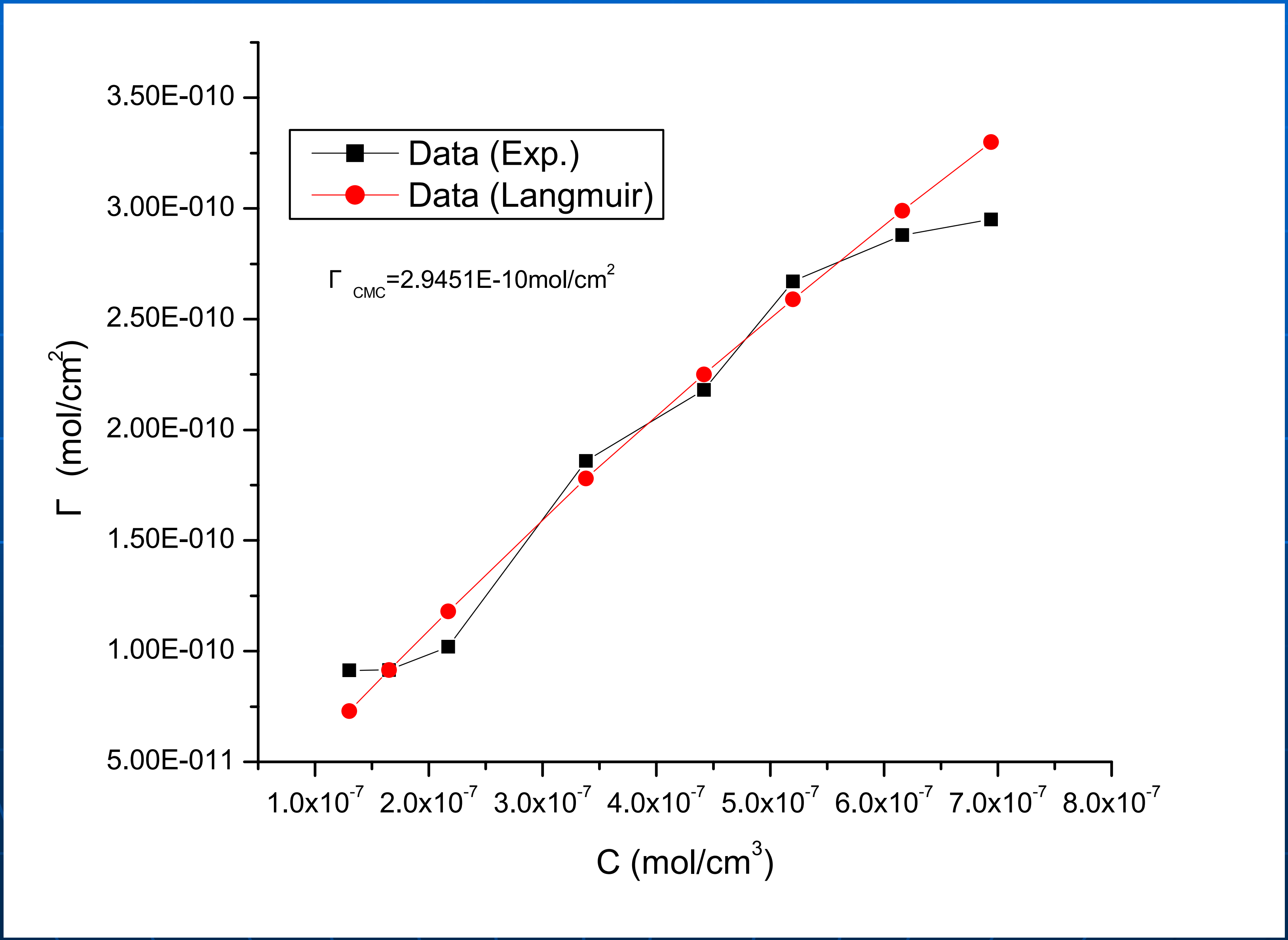
Green supernatant containing polyaniline.

Sedimented mixture of light green and white cationic PS particles

Surface tension of $C_{12}H_{25}OSO_3Na$

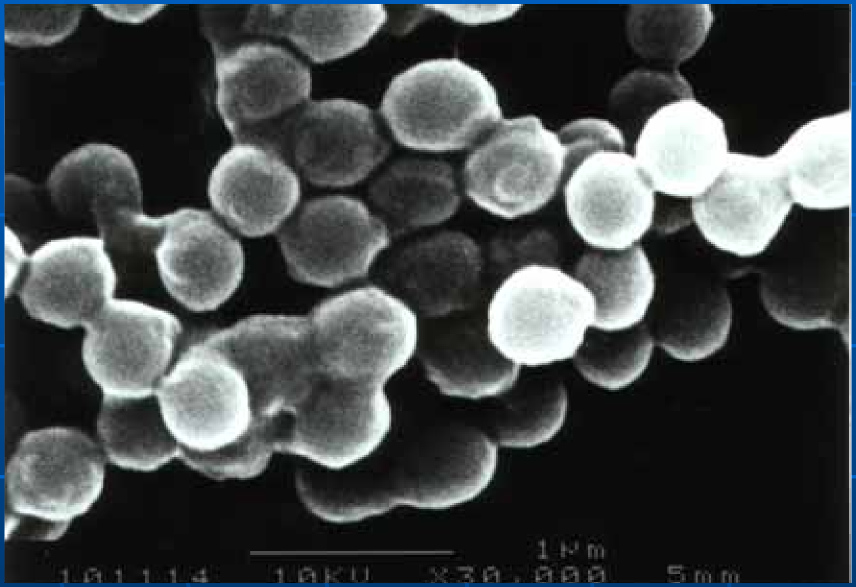


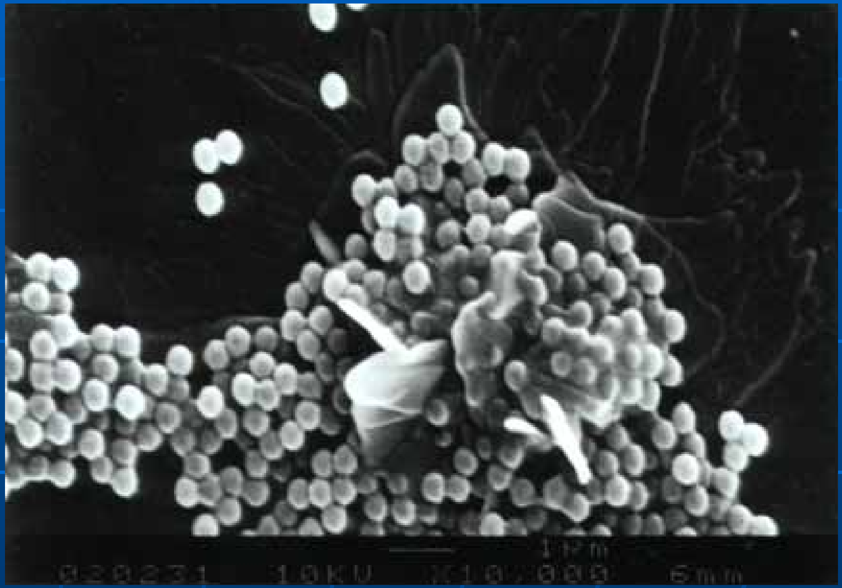
Adsorption isotherm of $C_{12}H_{25}OSO_3Na$ on PS spheres



SEM micrograph of PS/PANI core-shell latexes

(C_{SDS} < CMC)



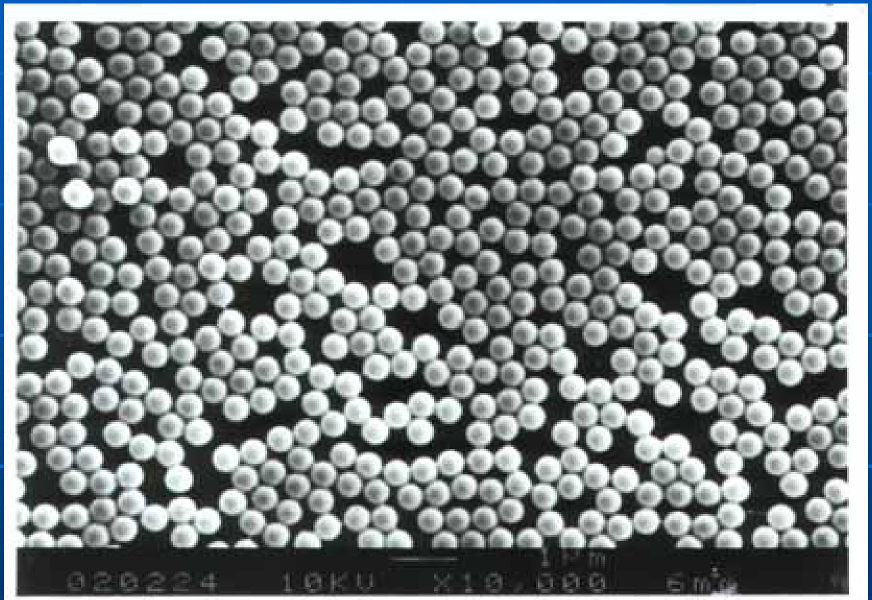


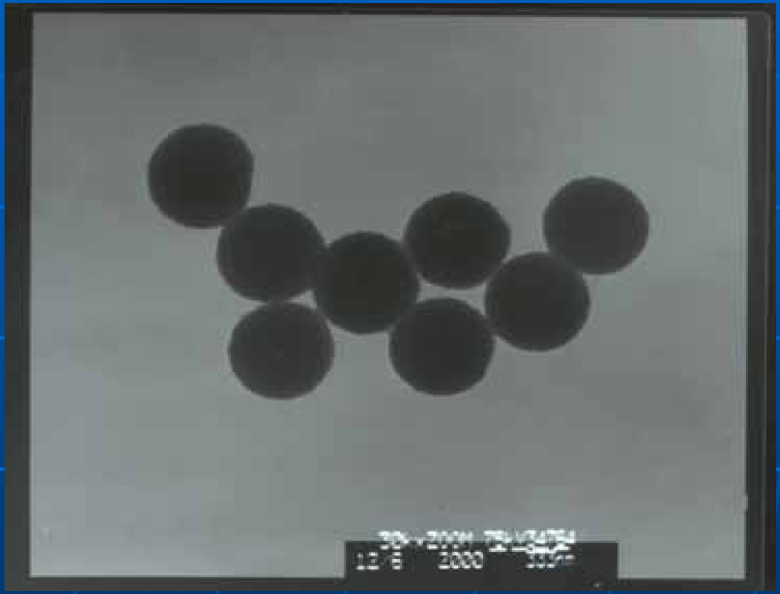
Photograph of PS/PANI core-shell latexes

Sedimented green core-shell particles

SEM micrograph of PS/PANI core-shell latexes

(C_{SDS} > CMC)





Centrifuge of the PS/PANI core-shell latexes

Centrifuge

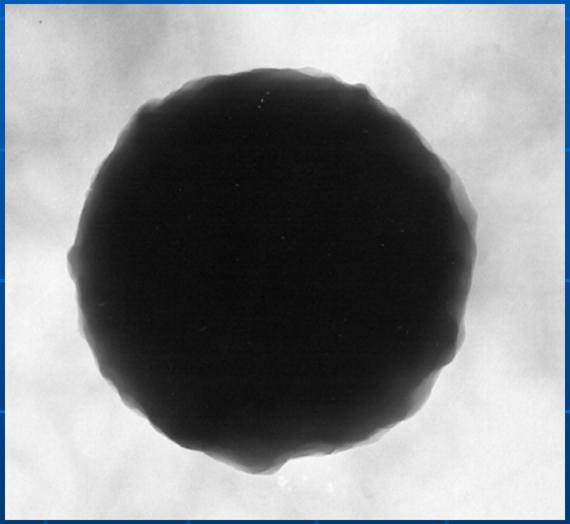
10 minutes

Green supernatant containing PANI.

Sedimented green core-shell particles

Micrographs of PS/PANI composite latex.

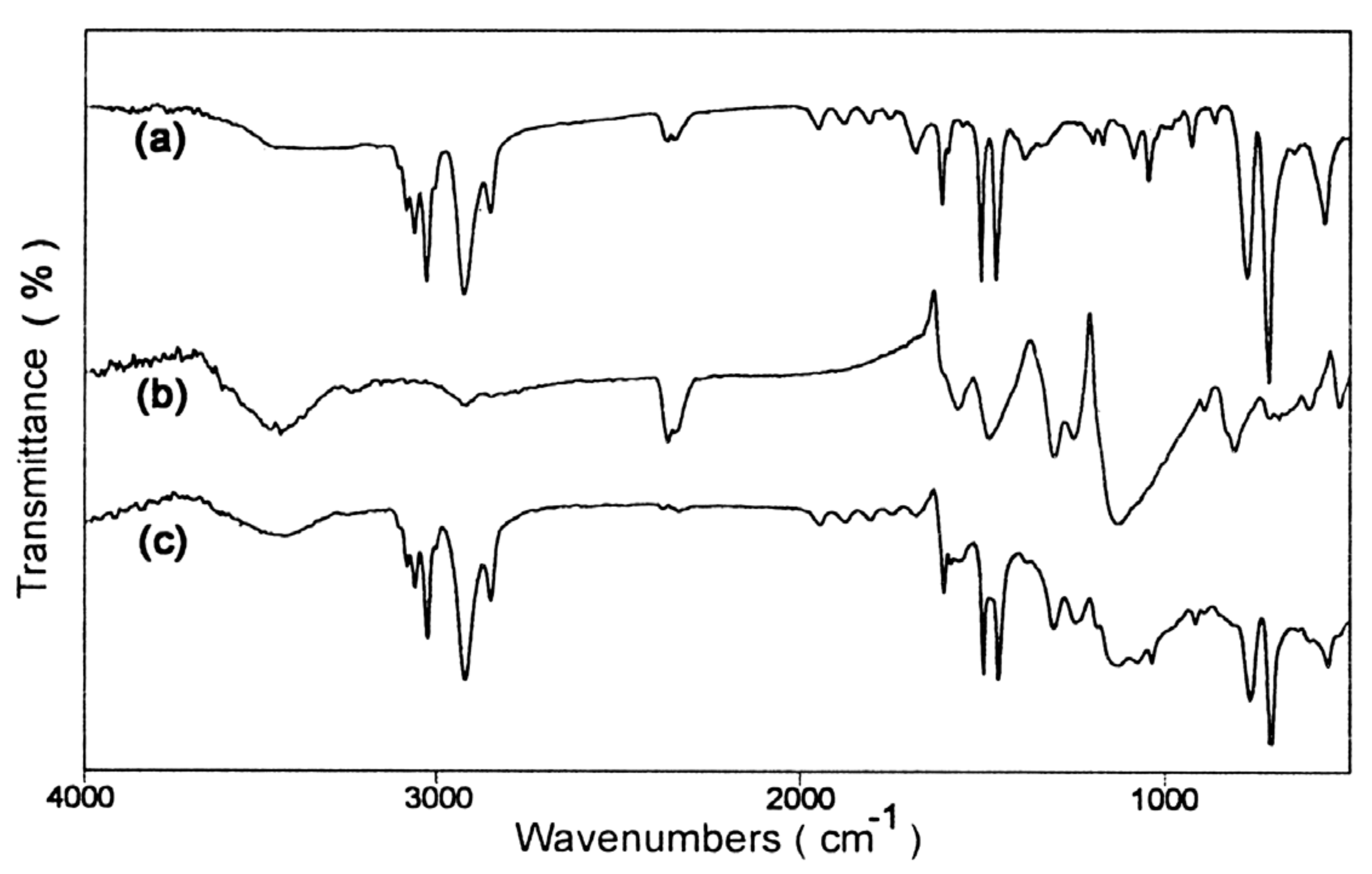
SEM



TEM

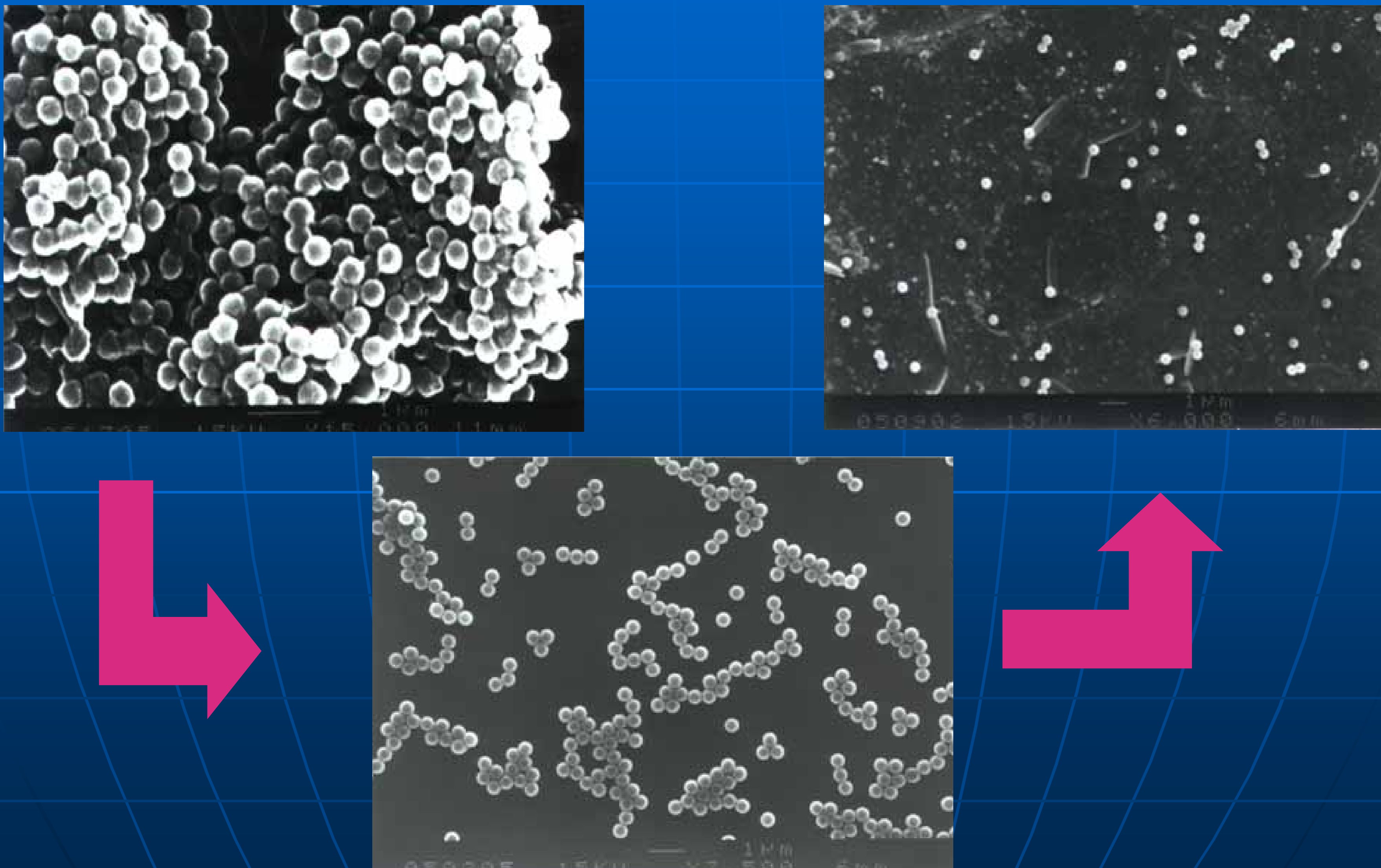
PANI/PS=1%

FT-IR Spectroscopy of (a) Polystyrene; (b) Polyaniline and (c) PS/PANI Composite Latex Containing 3wt% of PANI



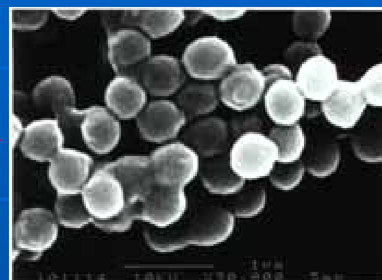
Morphology of the core-shell latexes

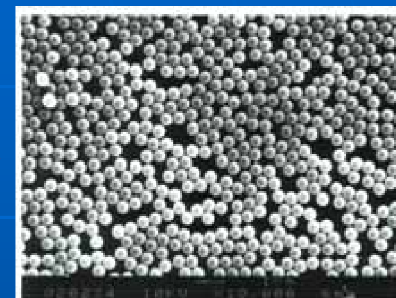
(With anionic surfactant $C_{14}H_{29}OSO_3Na$)



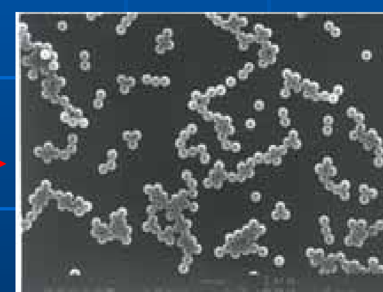
The effect of hydrophobic chain length of anionic surfactants

❖$C_{12}H_{25}OSO_3Na$

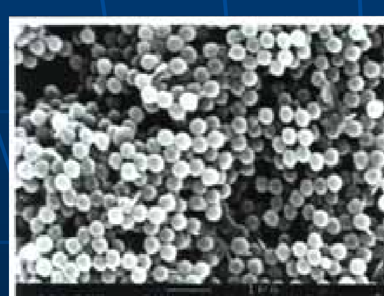




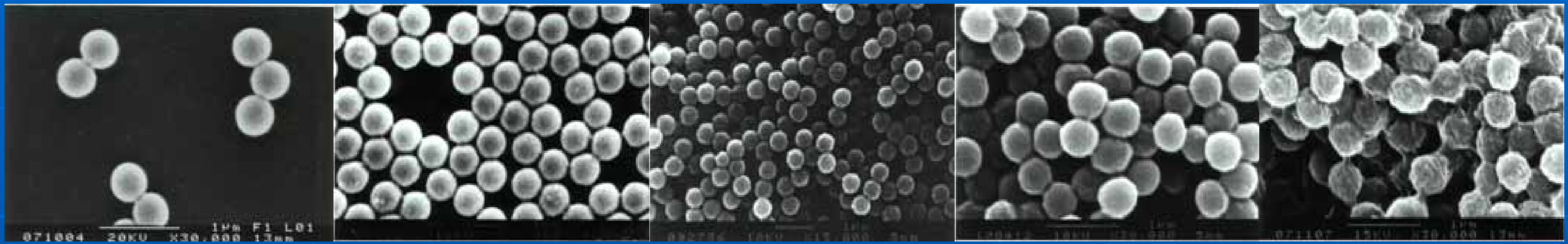
❖$C_{14}H_{29}OSO_3Na$



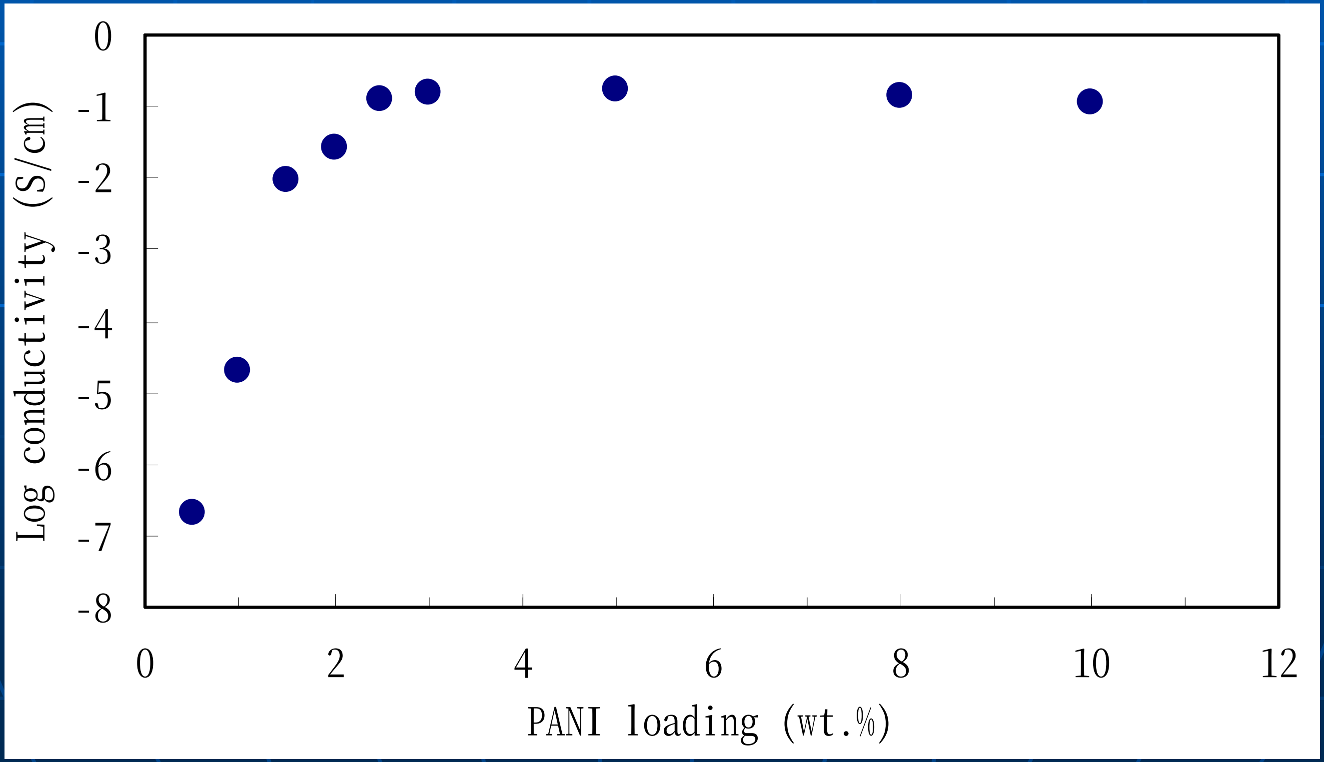
❖$C_8H_{17}OSO_3Na$



The effect of polyaniline loading on polystyrene spheres



1% PANI 5% PANI 10% PANI 15% PANI 20% PANI



Conducting Organic-Inorganic Hybrides

- Coating polypyrrole on Hematite(α-Fe_2O_3), silica-modified hematite, CeO_2, CuO etc..

- The use of electrochemical or soluble initiators can be eliminated by utilizing catalytically active cores to effect polymerization of monomer.
- These inorganic cores were coated with polypyrrole by exposing the cores to the polymerization medium of pyrrole in an ethanol/water mixture and heating to 100℃.
- The polypyrrole coated α-Fe_2O_3 and CeO_2 particles were found to be electrically conductive, and the thickness of the polymer coating can be controlled.

Polyaniline-coated silica gel

(A) Silica gel coated with polyaniline camphor-sulfonate

Aniline

Camphor-10-sulfonic acid (CSA)

+ Silica gel (Template) 7 μm

$\xrightarrow[20℃, 1hr.]{(NH_4)_2S_2O_8}$

PANI coated silica gel microspheres
+
Macroscopic PANI precipitate

(B) Dispersion approach

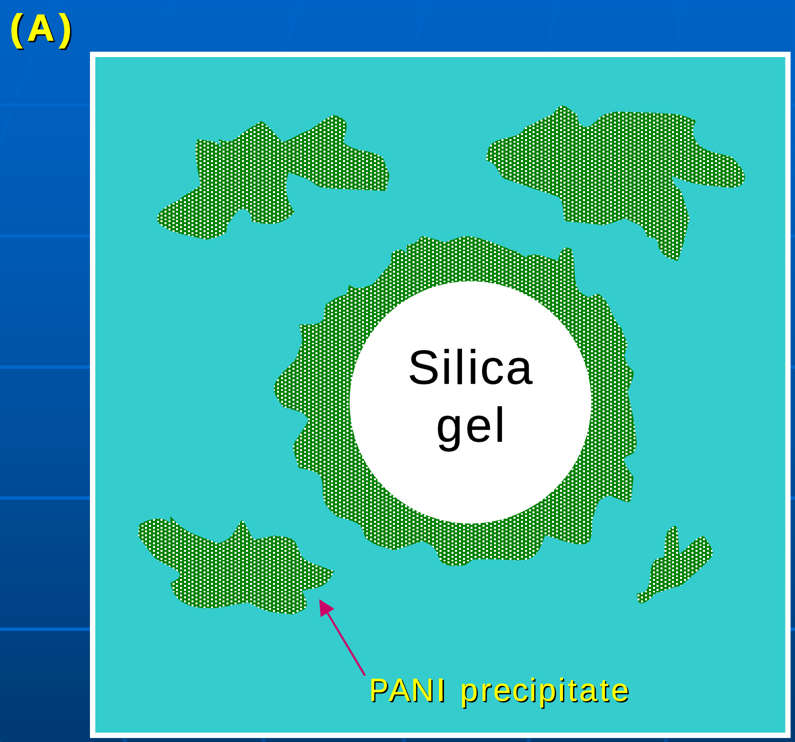
Introducing nano-colloidal silica (35 nm) as a colloidal stabilizer

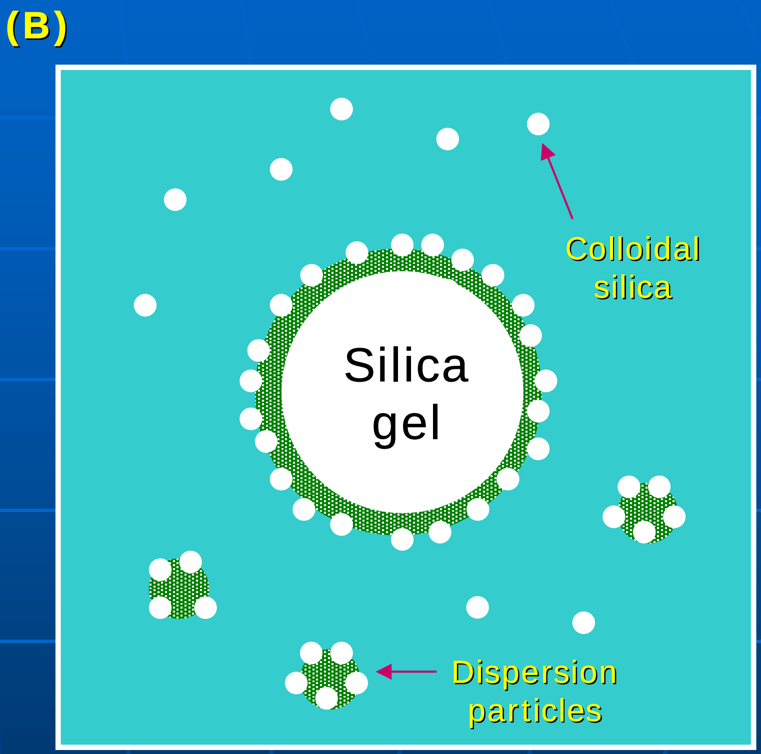
Aniline CSA + Silica gel (Template) 7 μm + 40 wt.% colloidal silica (Stabilizer) 35nm

$\xrightarrow[20℃, 1hr.]{(NH_4)_2S_2O_8}$

PANI coated silica gel microspheres
+
PANI dispersion particles (300~500nm)

Polyaniline-coated silica gel

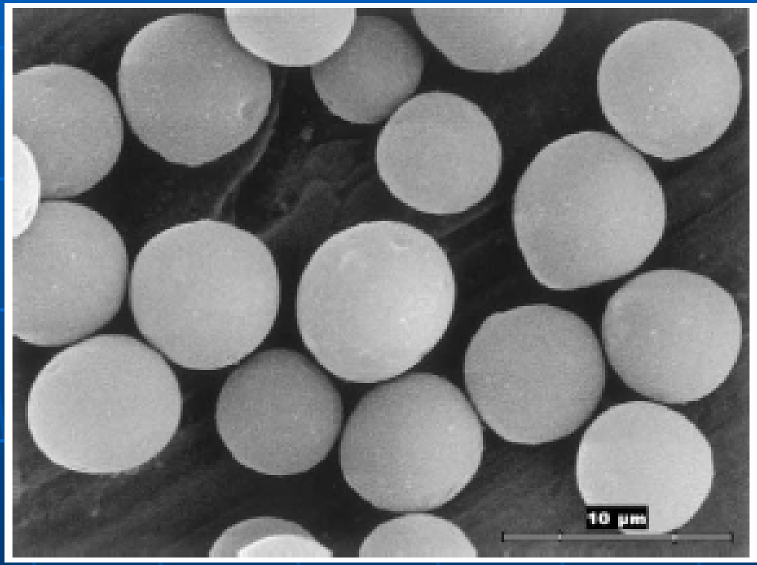




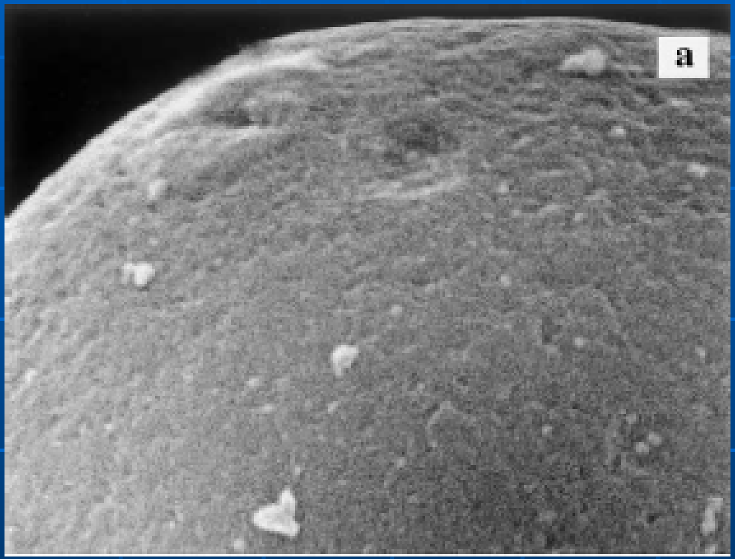
Template silica gel microspheres become coated with an overlayer of PANI during the polymerization of aniline. PANI precipitate is produced simultaneously.

The formation of precipitate is prevented by the presence of a steric stabilizer, small silica particles.

SEM micrographs of silica gel microspheres.



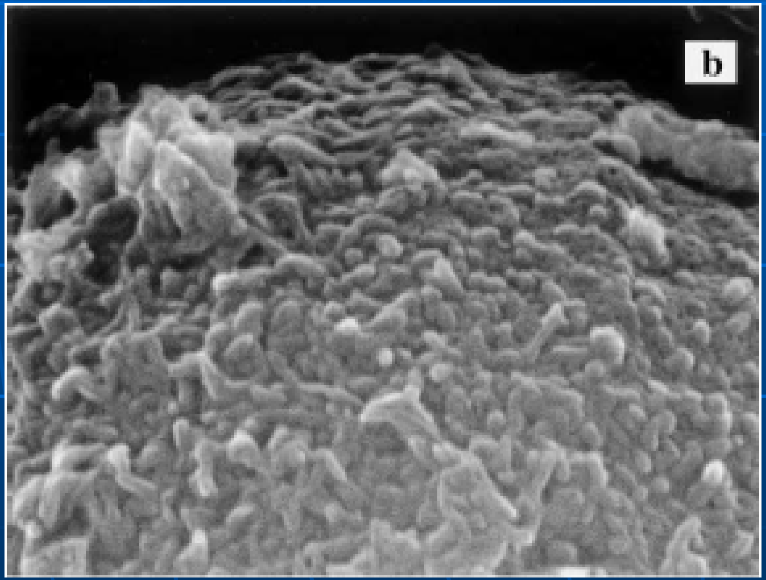
Template 7 μm silica gel microspheres.



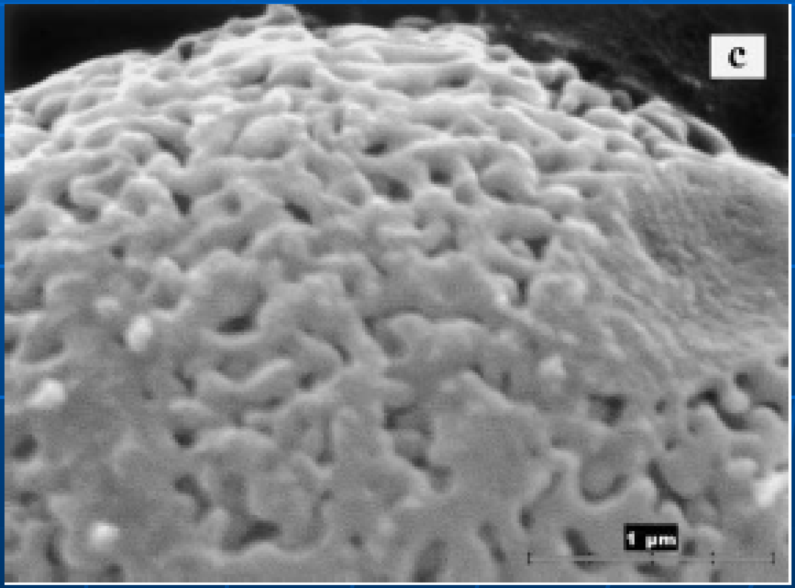
The surface of bare silica gel.

European Polymer Journal 38 (2002) 631

Micrographs of polyaniline-coated silica gel



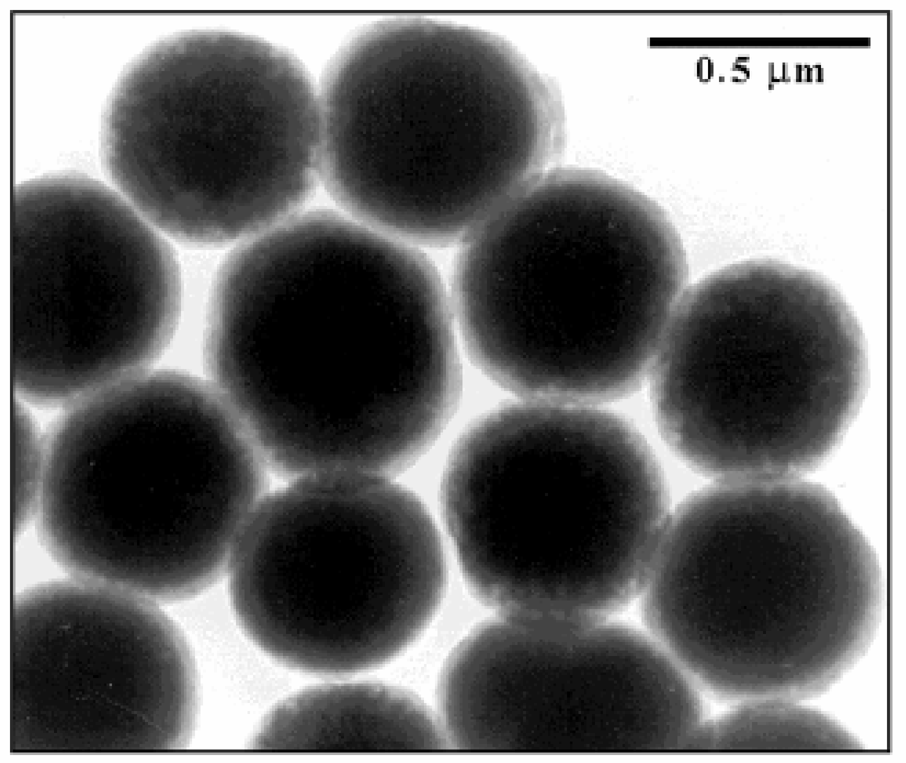
PANI coated silica particle



PANI coated silica particle in the presence of nano-colloidal silica

European Polymer Journal 38 (2002) 631

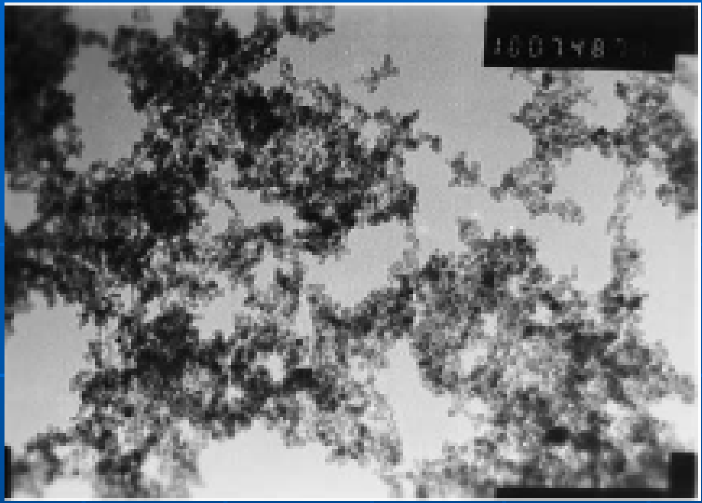
TEM micrograph of SiO_2 coated with polypyrrole



TEM of SiO_2 particles coated with polypyrrole

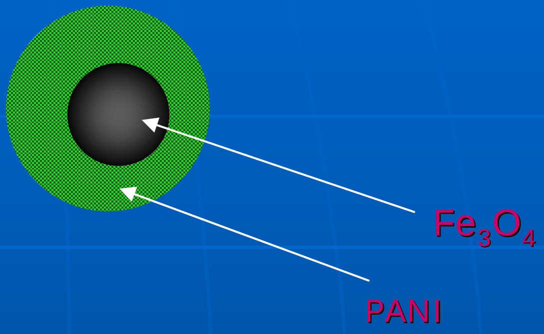
C. L. Huang, E. Matijevic, *J. Mater. Res.* **1995**, 10, 1327

Magnetic and conducting Fe_3O_4-cross-linked Polyaniline particles with core-shell structure



TEM micrograph of Fe_3O_4 particles

TEM micrograph of PANI/Fe_3O_4 composite particles

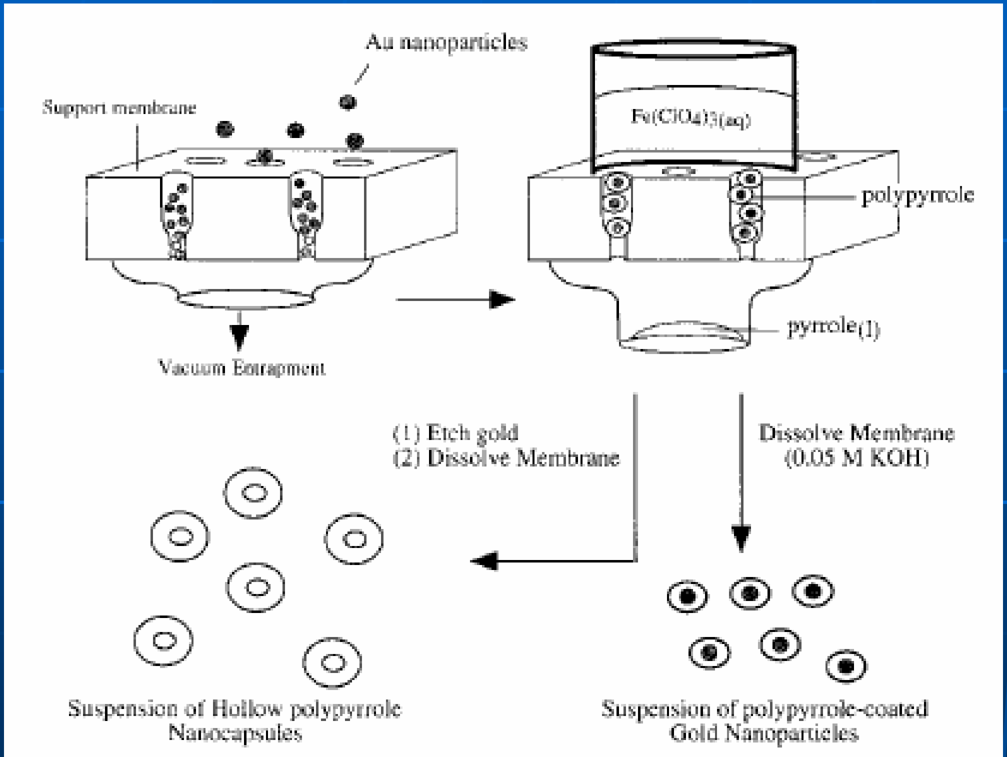


- The PANI coated Fe_3O_4 core shell particles showed ferromagnetic and electric properties.
- The saturated magnetization increased with an increase of Fe content.
- The conductivity depends on the Fe content and the doping degree.

Polymer 43 (2002) 2179

Template Approaches

➢ Trapping the particles in the pores of membranes and polymerization of a conducting polymer inside the pores.



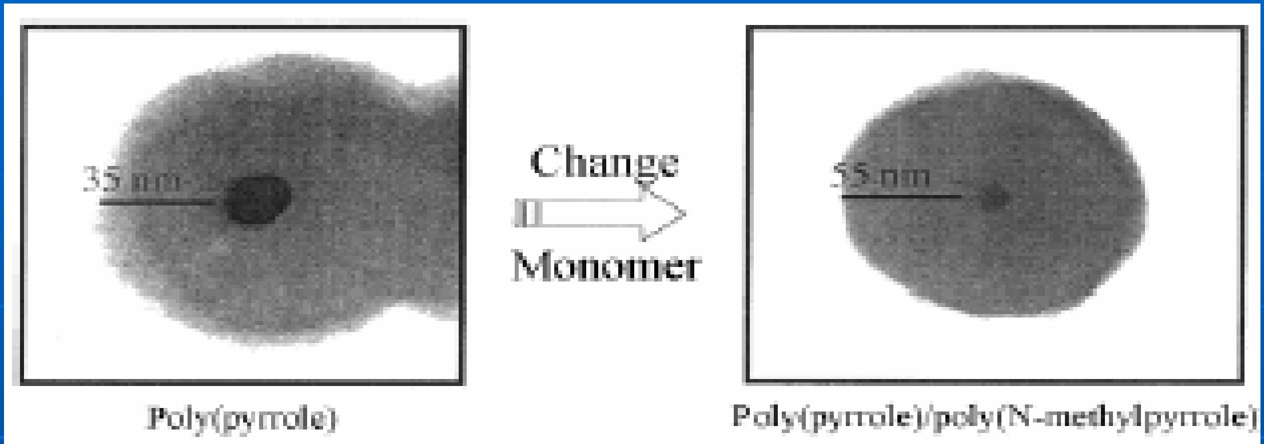
Schematic diagram of the membrane-based method for synthesizing gold-core/polymer-shell nanoparticles.

Procedure:

1. Gold nanoparticles being filtered into a porous membrane with a pore size of 200 nm.
2. Initiator $Fe(ClO_4)_3$ was then poured into the top of the membrane and several drops of the monomer (pyrrole) were placed underneath the membrane.
3. Upon diffusion of the monomer vapor into the membrane, it contacted the initiator to form polymer, with deposition occurring on the surface of the gold particles.

J. Am. Chem. Soc. **1999**, 121, 8518

TEMs of core-shell gold-polymer nanoparticles prepared by the membrane-based strategy



In both micrographs the gold nanoparticle is seen in the center as a dark core.

- Multilayer composites were also produced by simply replacing the first monomer with a second and allowing polymerization to proceed.
- The thickness is dependent on the polymerization time and can be varied from 5 to 100 nm.
- This method shows promise for the coating of various template particles with a range of polymers.

J. Am. Chem. Soc. **1999**, 121, 8518