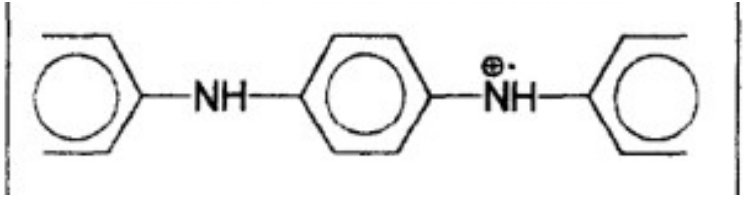
Study of interaction between polyaniline and β-cyclodextrin

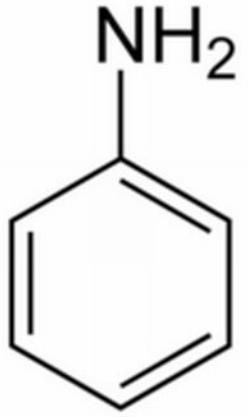
Kairon Márcio de Oliveira

Polyaniline

- Polyaniline (Pani) is a conductor polymer that can be obtained the reaction polymerization the monomers aniline.



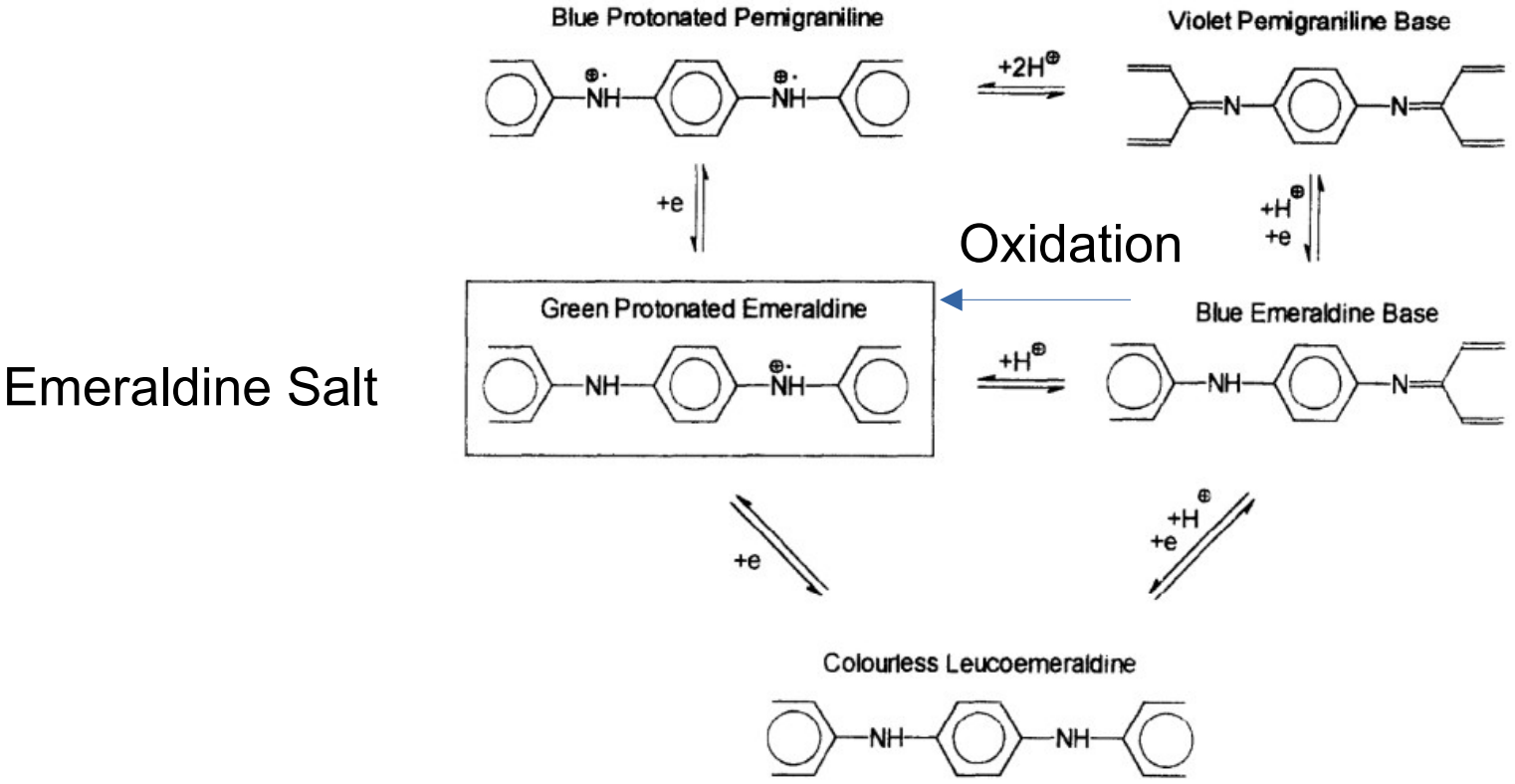
Pani



Aniline

Polyaniline

- We can obtained different kinds of Polyaniline using reduction and oxidation.



Polyaniline

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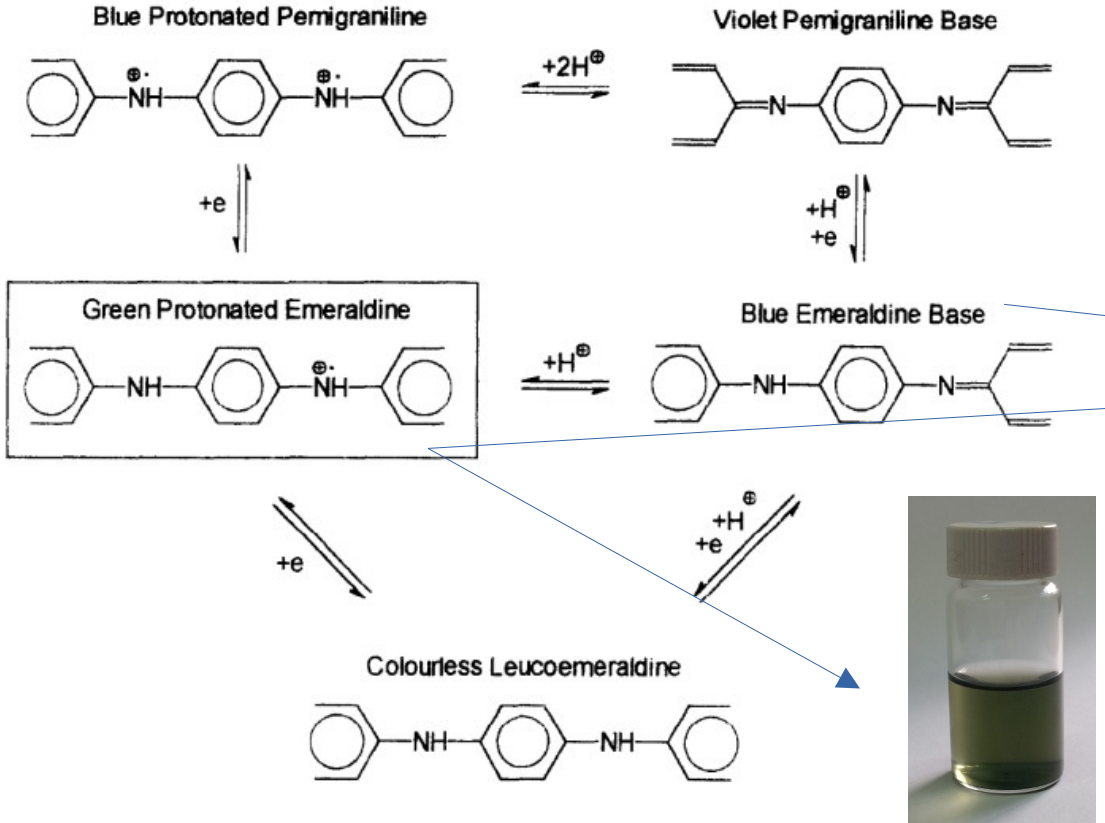
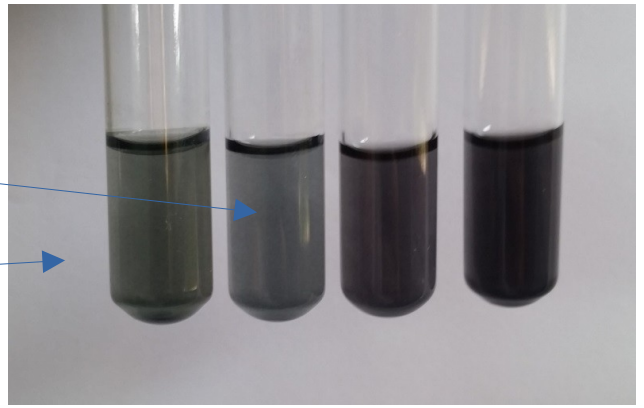
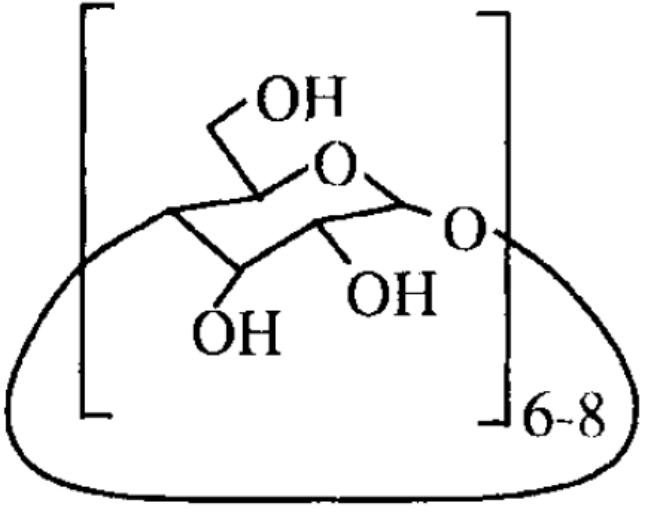


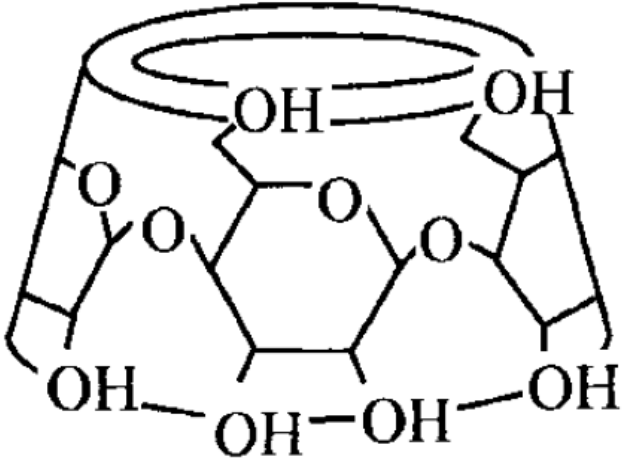
pH 7 pH 9 pH 11pH 13



Cyclodextrin

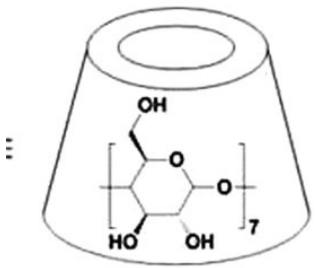
- Cyclodextrins are molecules that has truncated cone shape.
- Inside has a hydrophobic part and outside is hydrophilic.
- Cyclodextrins (CDs) are cyclic molecules which consist of six to eight glucose units: α-, *β*-, and *γ*-cyclodextrins with six, seven, and eight glucose units, respectively.

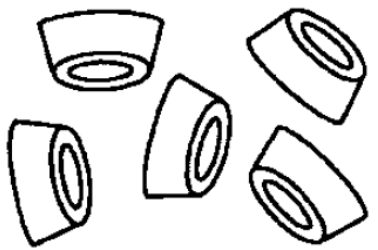




Cyclodextrin

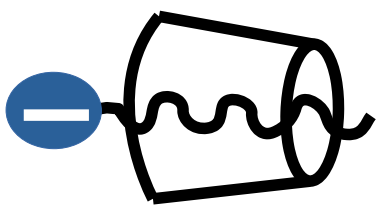
- Their cylindrical structures with cavities of about 0.7 nm deep and 0.5-0.8 nm inside diameter yield various unique properties.





β-cyclodextrins

- Because it is an amphiphilic molecule, cyclodextrins can make inclusion compound with other molecules.



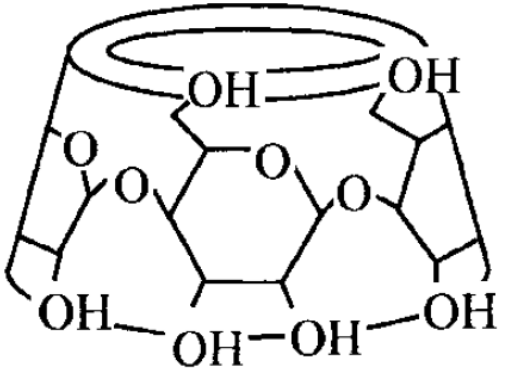
Trans all conformation

Inclusion compound

- The inclusion compound formation between CDs and a polymer chain is entropically unfavorable and encouraged at low temperature by noncovalent interaction such as hydrophobic one.

Trans all conformation

$$\Delta G = \Delta H - T.\Delta S$$



Objectives

- This articles have how the objectives study if have the formation inclusion compound between polyaniline and β-cyclodextrin and observe the effects when do oxidation in this polymer.

Langmuir **1999**, *15*, 910−913

Inclusion Complex Formation of Cyclodextrin and Polyaniline

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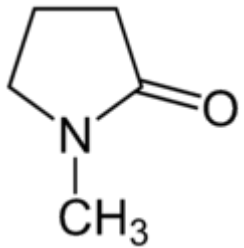
Received September 14, 1998. In Final Form: December 7, 1998

Synthesis

- One solution with β-cyclodextrin (βCD) diluted in N-methly-2-pyrrolidone.



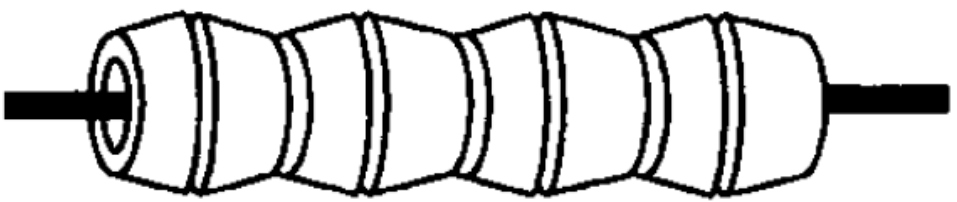
- Other solution make a polymerization the Pani in emeraldine base (without free charges).
- This solutions is mixture, 1:24, and cooled.

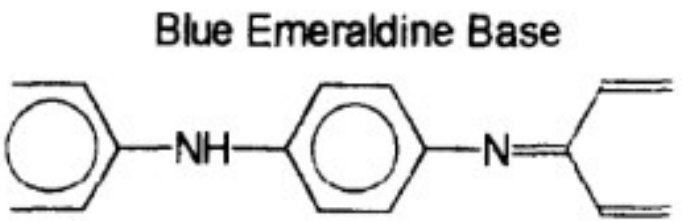
Yoshida, K. et al. Langmuir. 15, 910-913, 1999.

Synthesis

- Observed the blue precipitation, that can show have formation the compound inclusion.

- This not happen without N-methly-2-pyrrolidone.





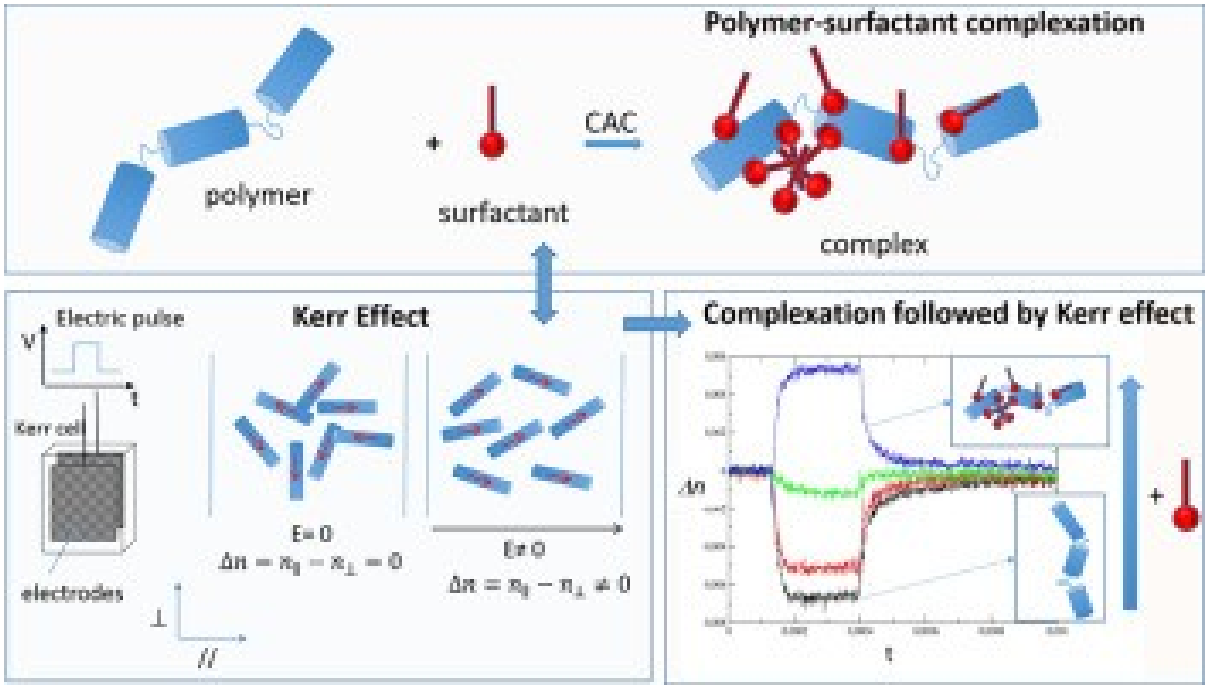
Yoshida, K. et al. Langmuir. 15, 910-913, 1999.

Frequency-domain electric birefringence (FEB)

$$E = \mathrm{Re}[E_0 \exp(i\omega t)]$$

$$\check{K} \equiv \Delta n / E_0^2 = K_{dc} + \mathrm{Re}[K_{2\omega}^* \exp(i2\omega t)]$$

$$K_{2\omega}^* \ (= K_{2\omega}' - iK_{2\omega}'')$$



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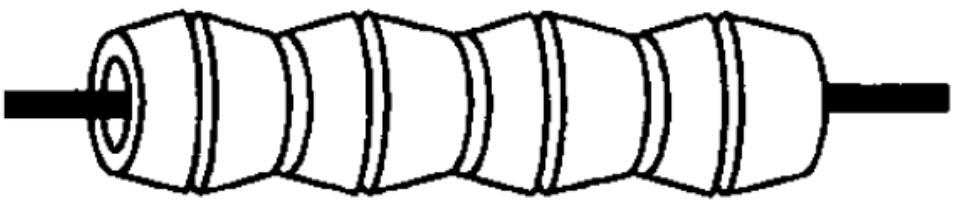

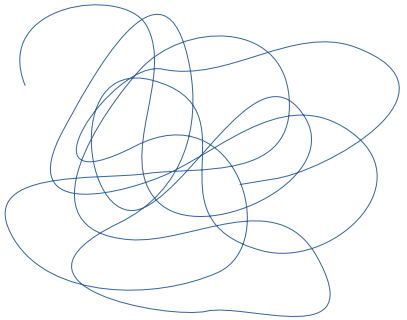

Optical and/or charge anisotropy

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Results

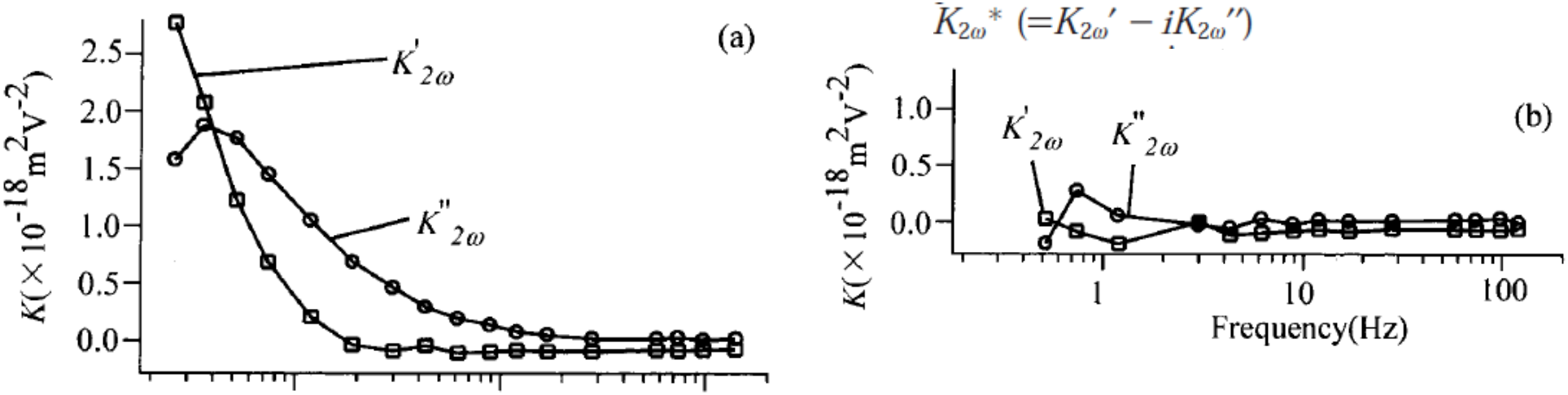

Figure 2. Typical experimental results of the FEB spectra in the mixture solution of β-CD and PAn in NMP (a) at 255 K and (b) at 300K.

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Results

From the rotational relaxation frequency ($f_r = 3/(4\pi\tau_r)$), at which $K_{2\omega}$" has a maximum

$$f_r = \frac{9k_B T}{2\pi^2 \eta_0 L_{eff}^3}(\ln(L_{eff}/d_r) + \gamma_r)$$

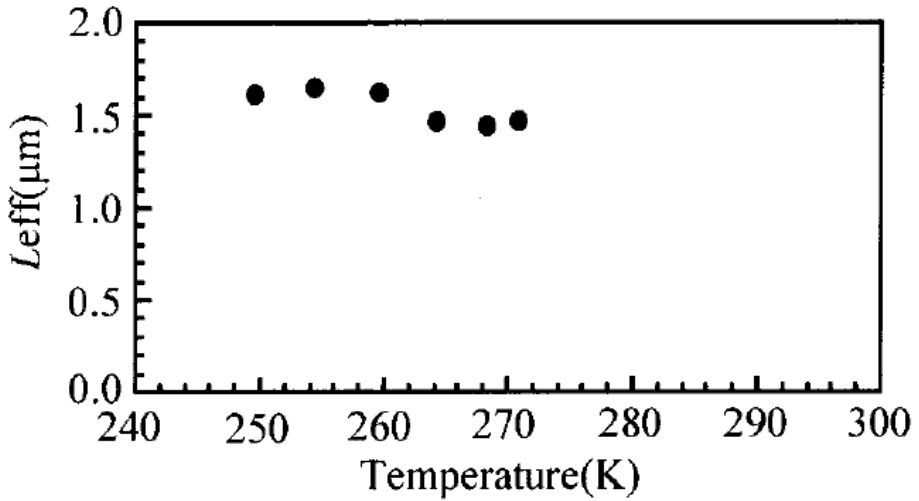
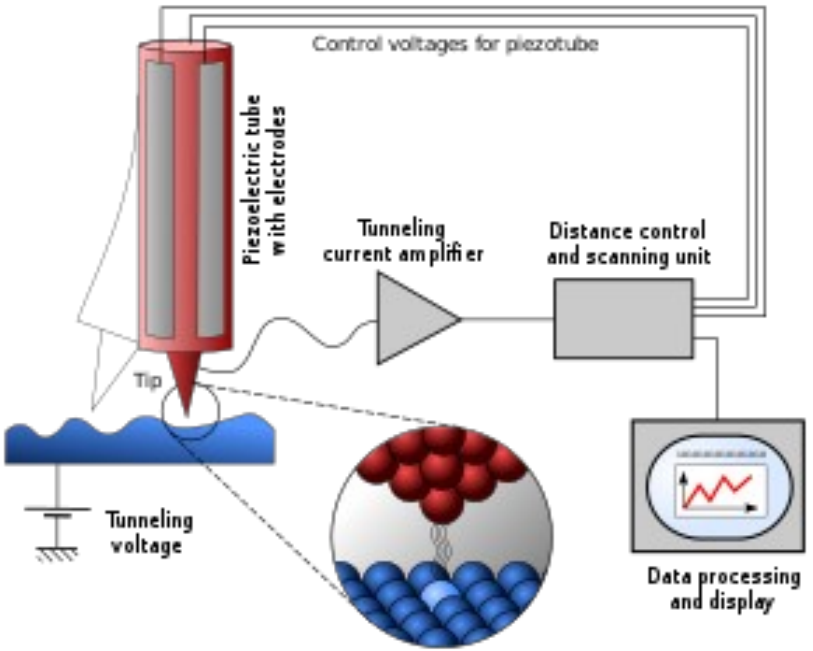


Figure 3. The temperature dependence of the effective length L_{eff} calculated from the rotational relaxation time τ_r with eq 1. At temperature above 275 K, the FEB signal was not detected.

Yoshida, K. et al. Langmuir. 15, 910-913, 1999.

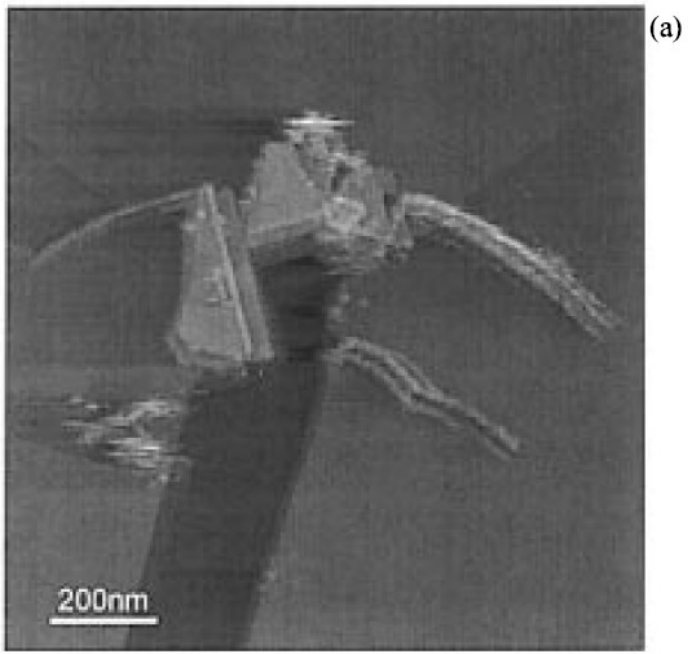
Scanning Tunneling microscopy (STM)

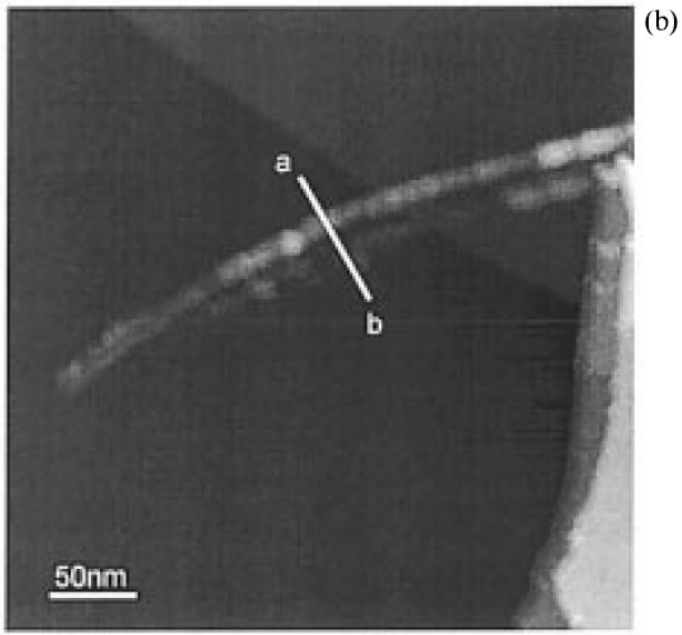


Yoshida, K. et al. Langmuir. 15, 910-913, 1999.

Results

- Some complexes were caught by roughness on the surface due to exfoliation of graphite layers as shown in Figure 4a.





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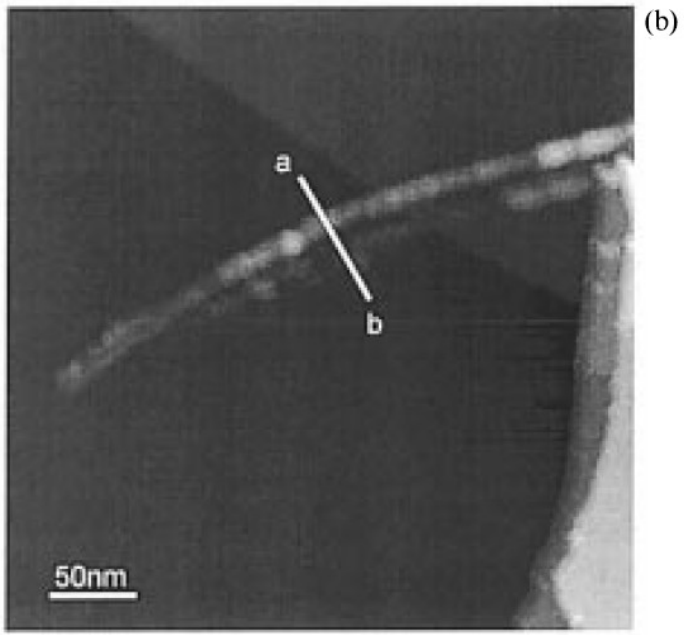
Results



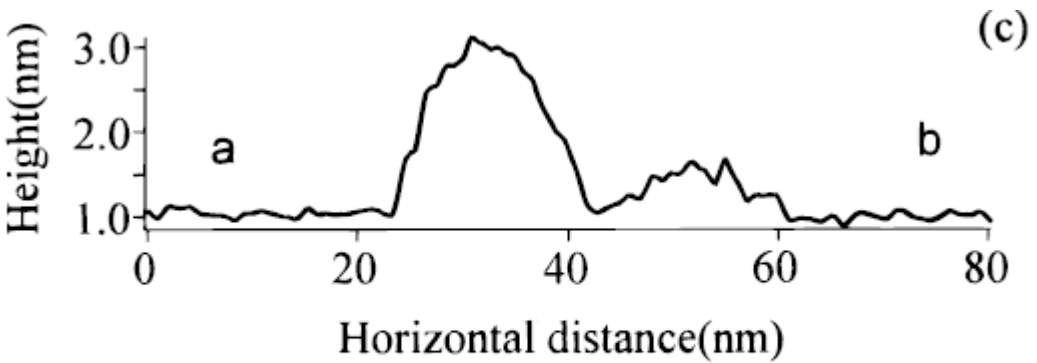


Figure 4. STM images where fields of view are (a) 1200 nm × 1200 nm and (b) 350 nm × 350 nm. (c) The height profile of the cross section.

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POLYMERS FOR ADVANCED TECHNOLOGIES
Polym. Adv. Technol. **11**, 837–839 (2000)

Insulation Effect of an Inclusion Complex Formed by Polyaniline and β-cyclodextrin in Solution

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[2]*Graduate School of Engineering, University of Tokyo, Hongo, Bunkyo-ku, Tokyo 113-8656, Japan*

Results

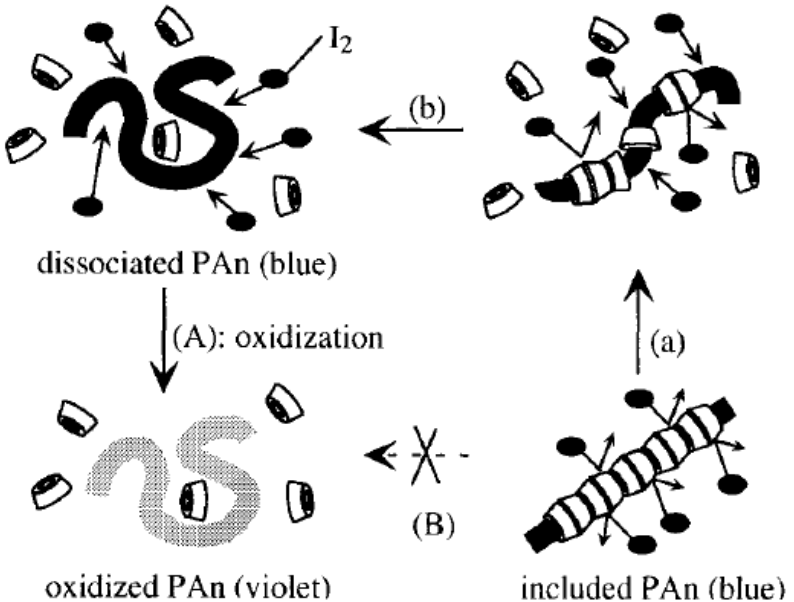
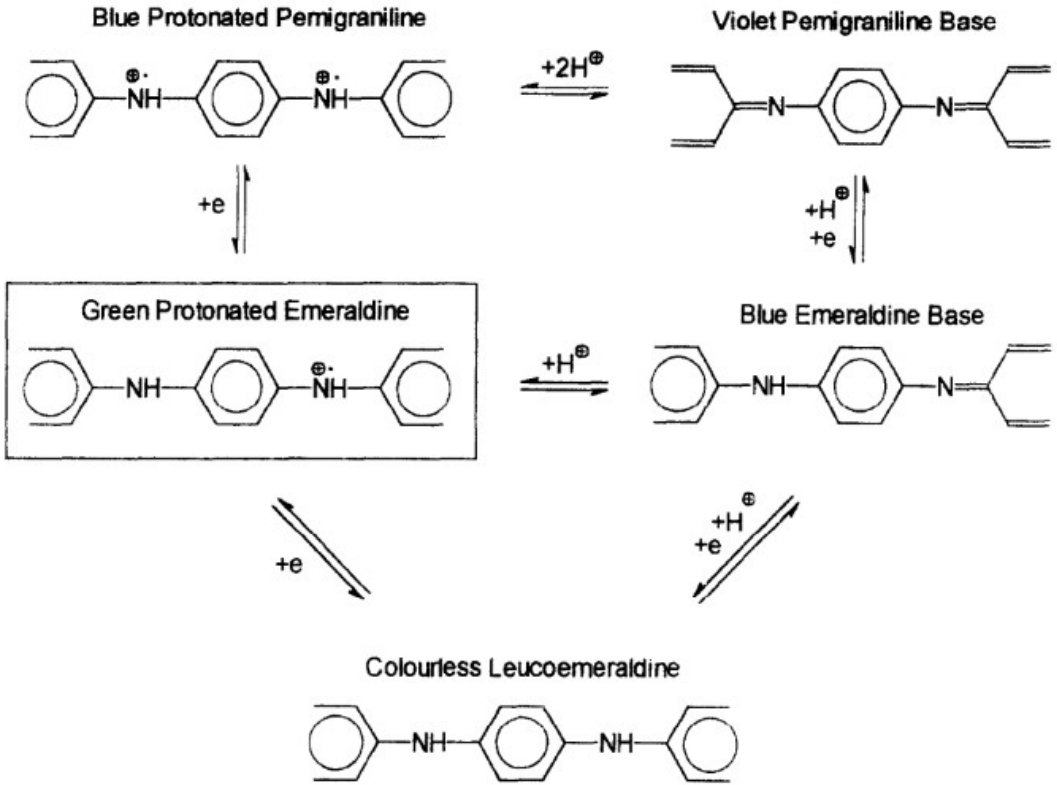


FIGURE 2. PAn in solution is oxidized by iodine but the insulated molecular wire is not oxidized without the dissociation process.



Shimomura, T. et al. Polymers For Advanced Technologies. 11, 837-839, 2000.

Results

- The solution of Pani-βCD at 255 K for a day, then added the diluted iodine solution and heated them to 273 K. As a result, the Pani solution changed color from blue to violet in a couple of days while the mixture solution still remained blue.
- Pani in the inclusion complex is almost completely covered by βCD molecules and insulated from the chemical oxidation by iodine.
- The author make this solution in 300K added the diluted iodine solution and after cooled them to 273K. The solution change the color.

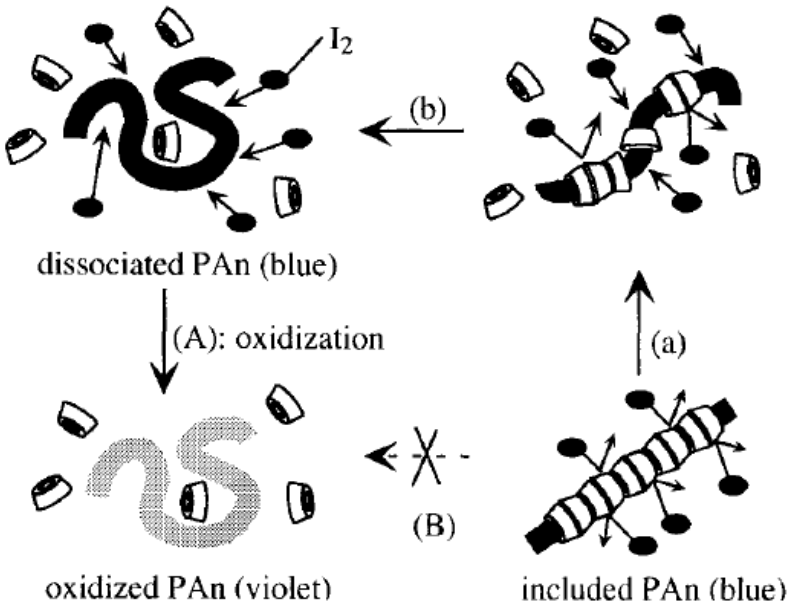


FIGURE 2. PAn in solution is oxidized by iodine but the insulated molecular wire is not oxidized without the dissociation process.

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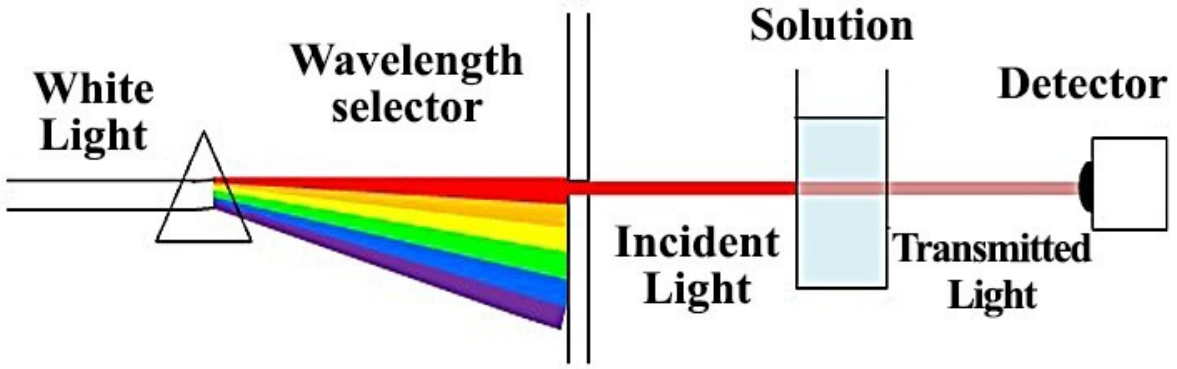
Technique used

- Measured the optical absorption spectra of the sample solution with a spectrophotometer (Hitachi U-110).



The difference between the incident and transmitted light indicates the absorbance

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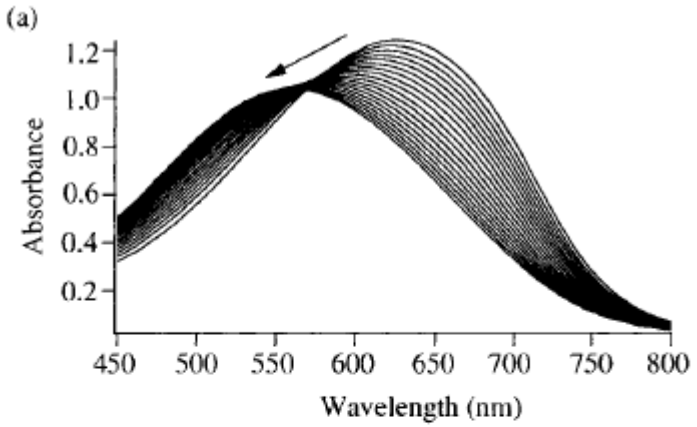
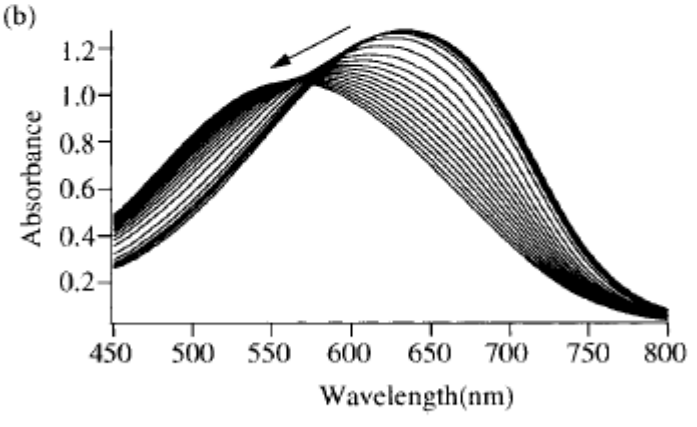
Results





- It is seen a gradual blue shift of the spectra the mixture solution for 4 or 5 hr after the temperature increase and then shows the spectral shift. This indicates that the inclusion complex is maintained for a while even at 288 K.

FIGURE 3. The time dependence of the optical absorption spectra of (a) the PAn solution and (b) the mixture solution of PAn and β-CD every hour after the temperature increase from 255 to 288 K. The spectral shift reflects the chemical oxidation of PAn by iodine. In (b), the spectra have little change for 4 or 5 hr after the temperature increase.

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POLYMERS FOR ADVANCED TECHNOLOGIES
Polym. Adv. Technol. **14**, 428–432 (2003)
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Preparation of Inclusion Complex Between Polyaniline and β-Cyclodextrin in Aqueous Solution

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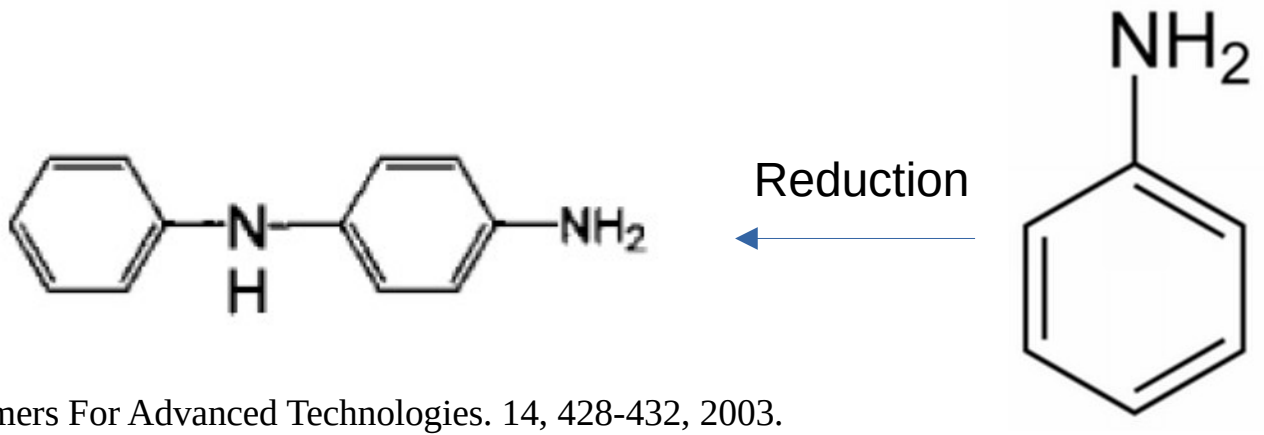
[2]*Department of Polymer Science and Engineering, Yamagata University, 4-3-16 Jonan, Yonezawa, Yamagata 992-8510, Japan*

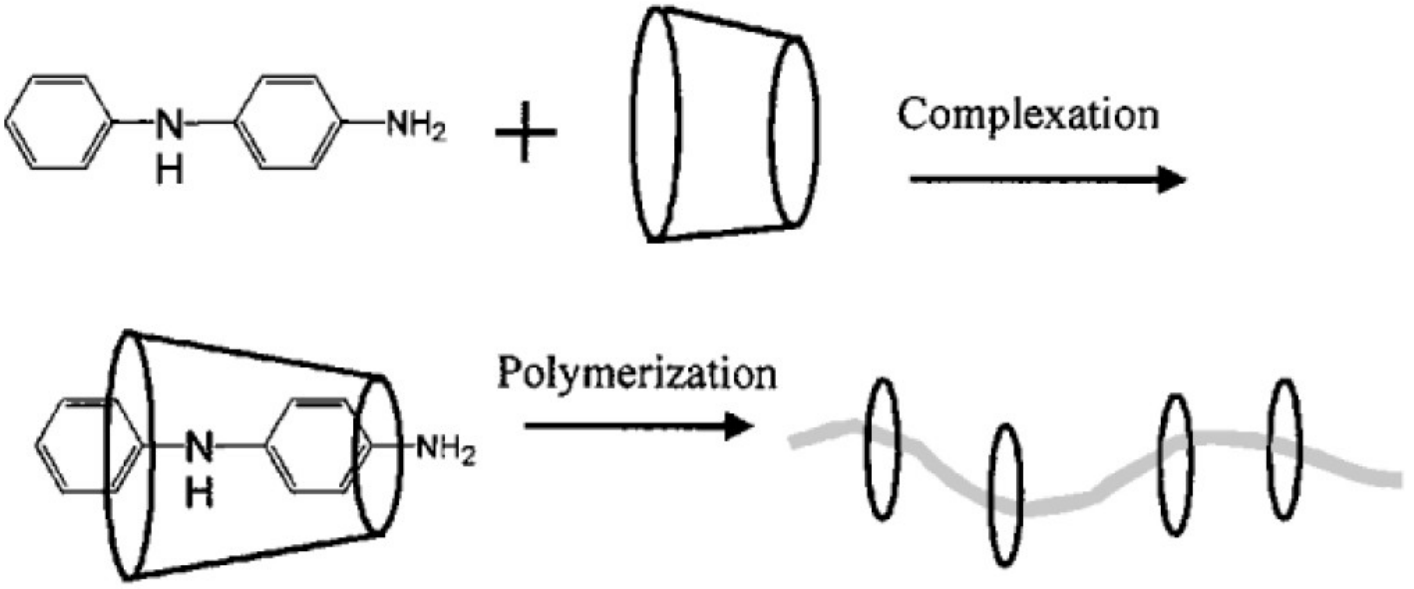
Synthesis

- In this article the author make two different production the compound inclusion: Polymerization in situ and mixture Pani (emeraldine base) in solution with βCD.
- In polymerization he used N-phenyl-1,4-phenylenediamine (PPD) and dilute this in ethanol solution and added βCD.
- Using acetone to remove unencapsulated PPD and produced the powder.



Yuan, G. et al. Polymers For Advanced Technologies. 14, 428-432, 2003.

Synthesis



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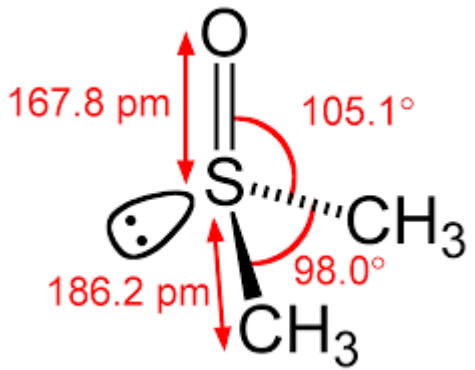
Synthesis

- For the mixture, the author added Pani (EB –> blue) in a solvent dimethylsulfoxide (DMSO) and after was slowly added to βCD aqueous solution.
- After dispersed gave a blue suspension.



Is more polar than water

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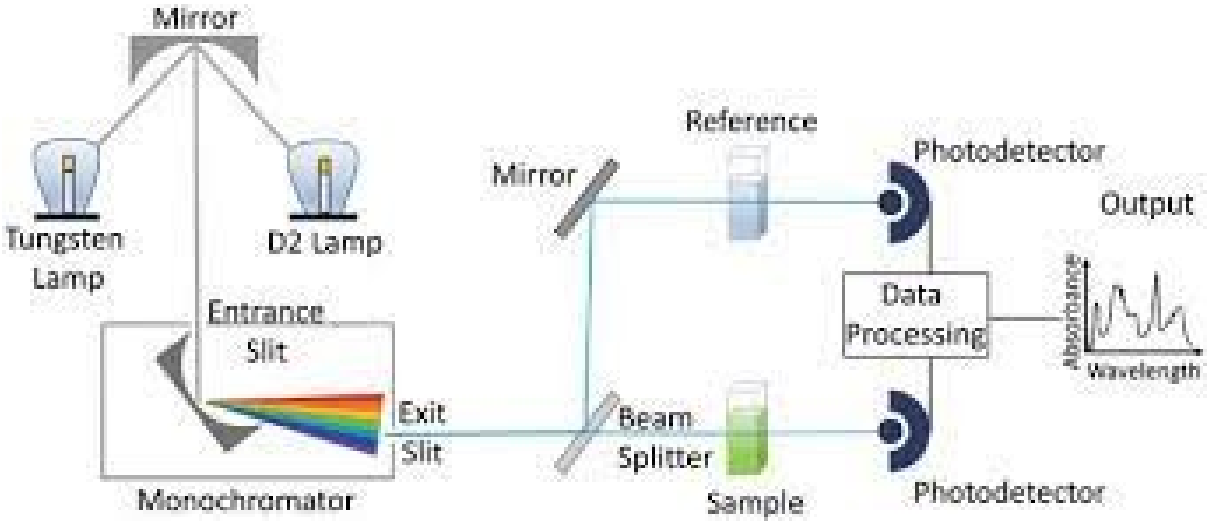
UV-vis spectroscopy



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Results

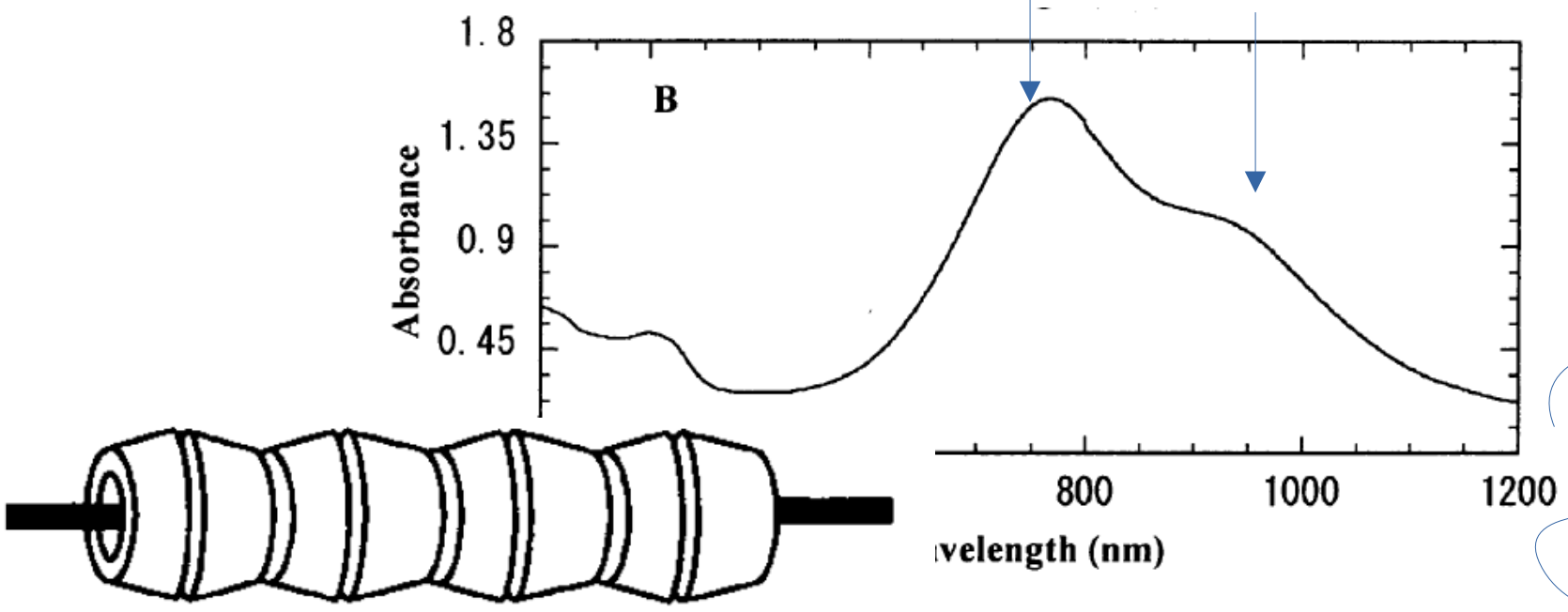

FIGURE 4. The CD and corresponding UV-vis spectra of as-synthesized PANI-βCyD in aqueous solution by *in situ* polymerization of PPD-βCyD.

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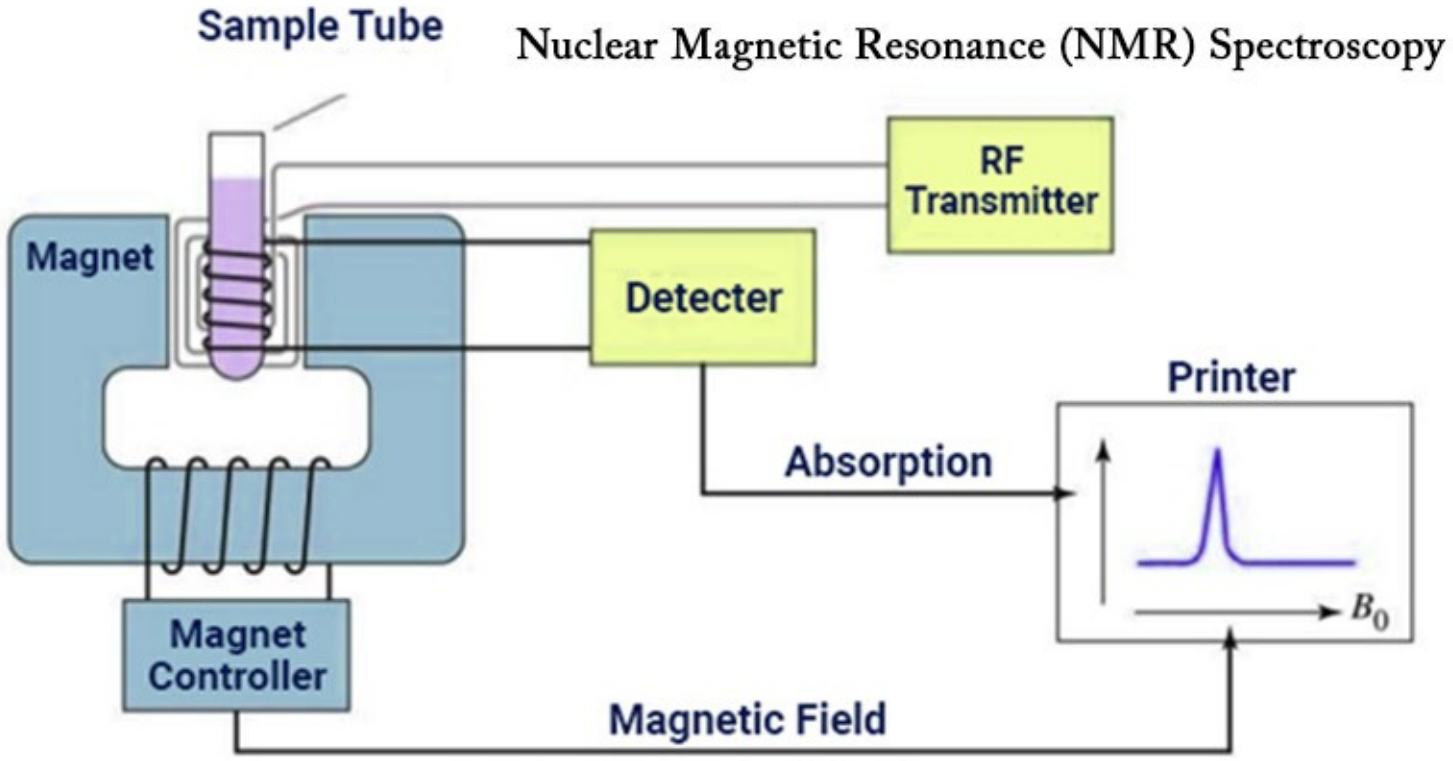
Nuclear Magnetic Resonance Spectroscopy (H-NMR)



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Results

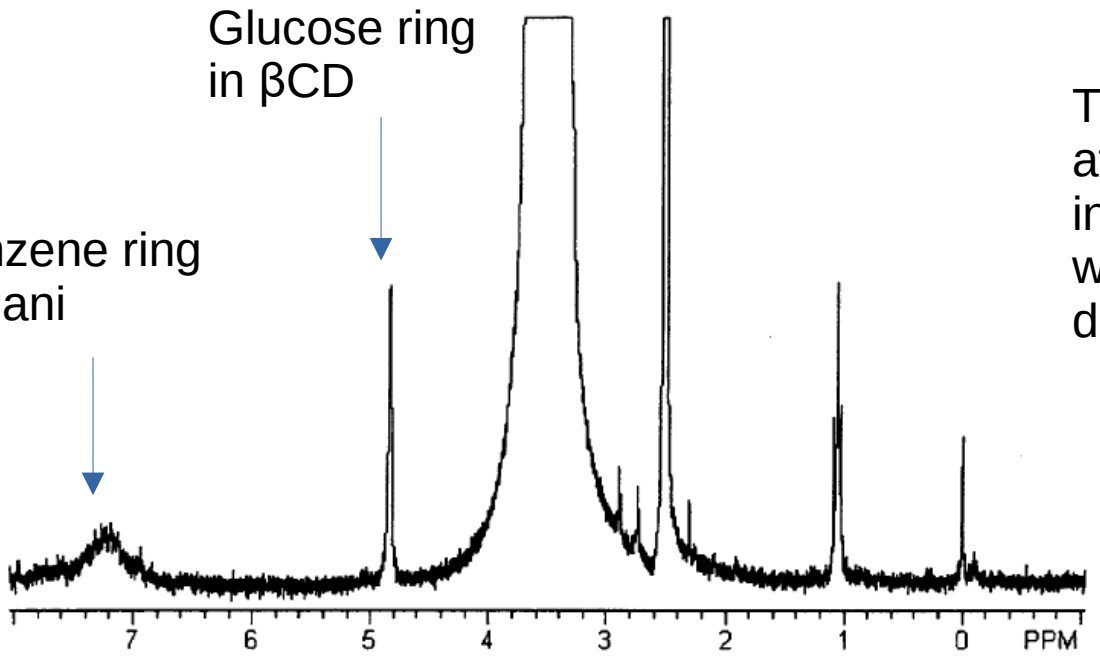

FIGURE 5. ^{1}H-NMR spectrum of PANI-βCyD (in DMSO-d_6) prepared by *in situ* polymerization.

This measured is after washing the inclusion compound with acetone and dried.

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Results

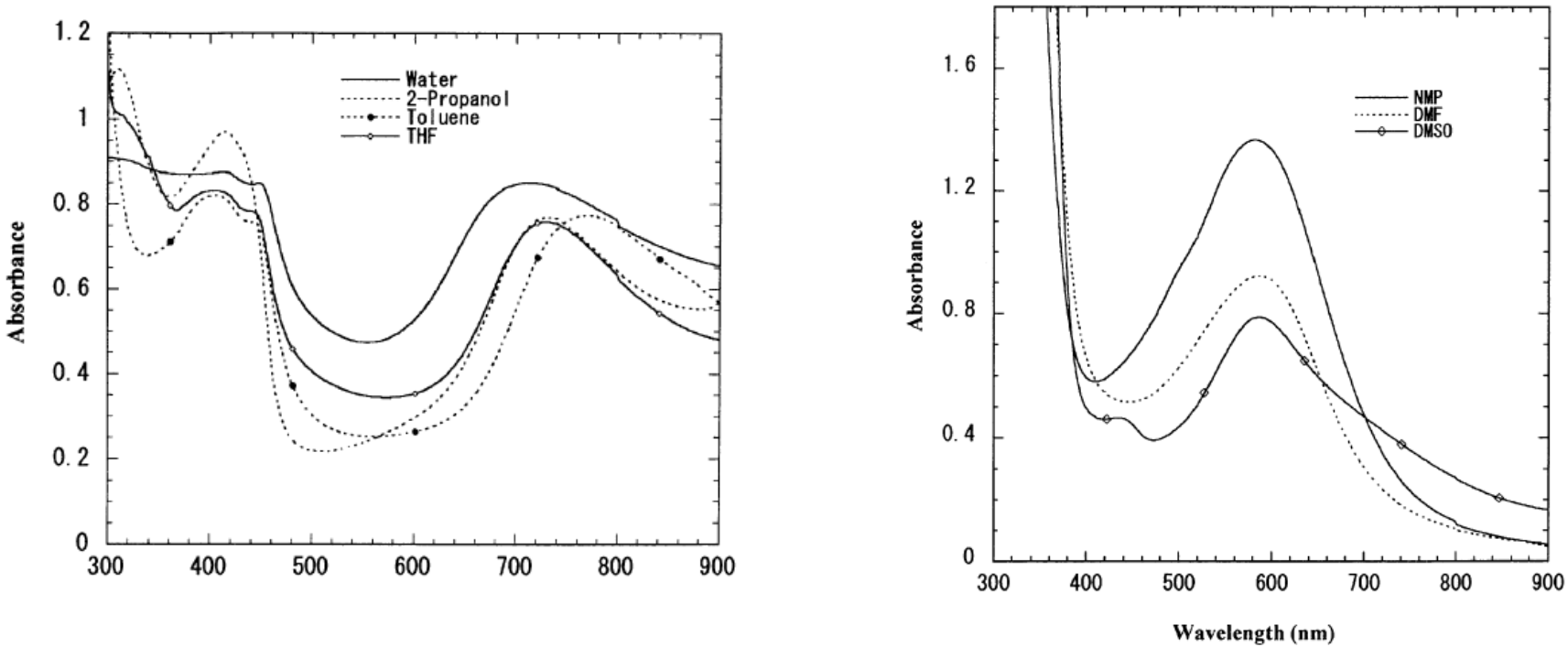

FIGURE 6. The UV-vis spectra of PANI-βCyD in various solvents.

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Results

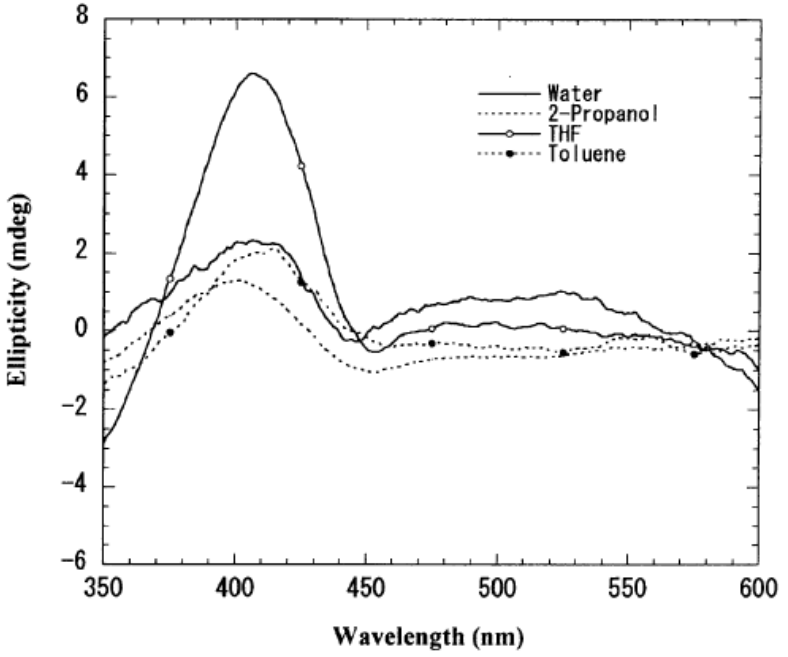

FIGURE 7. The CD spectra of PANI-βCyD re-dissolved in some solvents corresponding to that in Fig. 6.

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Results

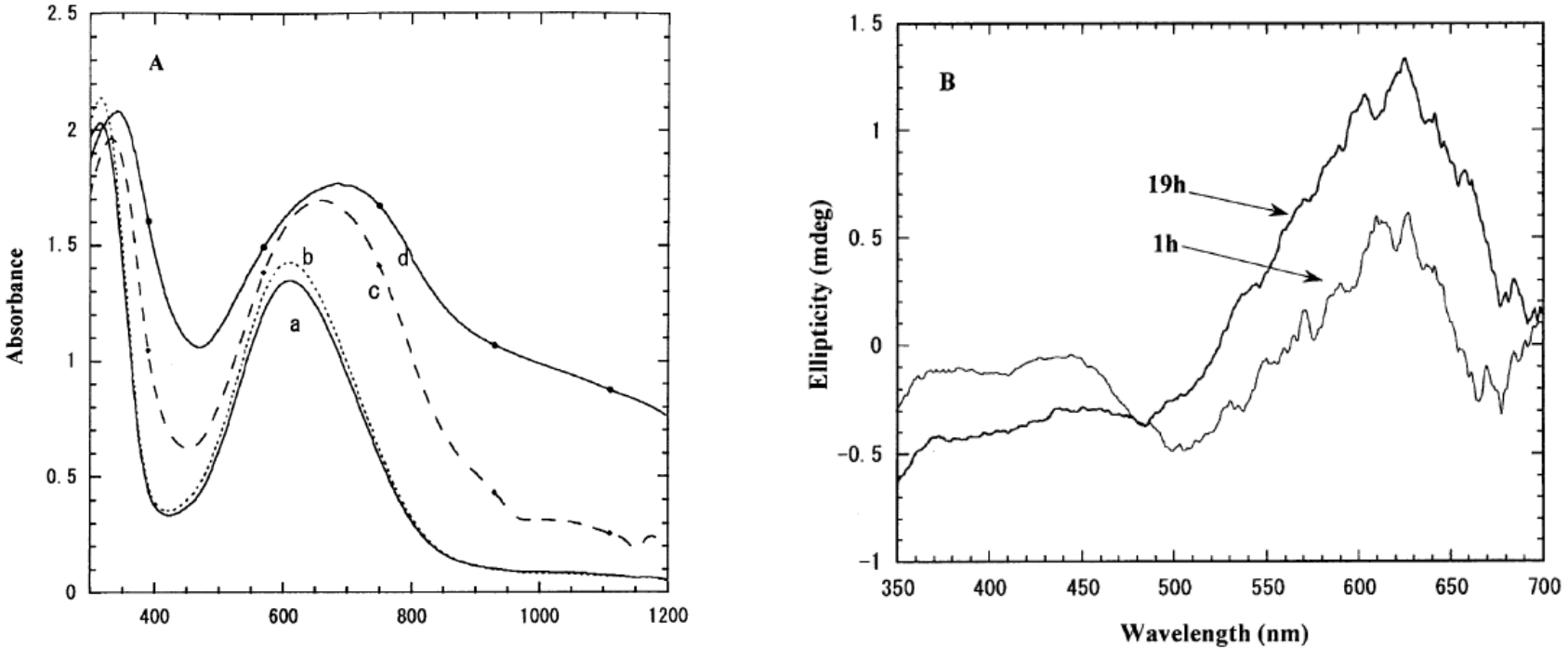

FIGURE 8. The spectra change in the formation of EB-βCyD complex: (A) UV-vis spectra (a) 30 mins, (b) 1 hr, (c) 19 hr, (d) redispersed in water after precipitated; (B) CD spectra at 1 and 19 hr.

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Results

C=C strecthing aromatic ring

C-N strecthing Pani

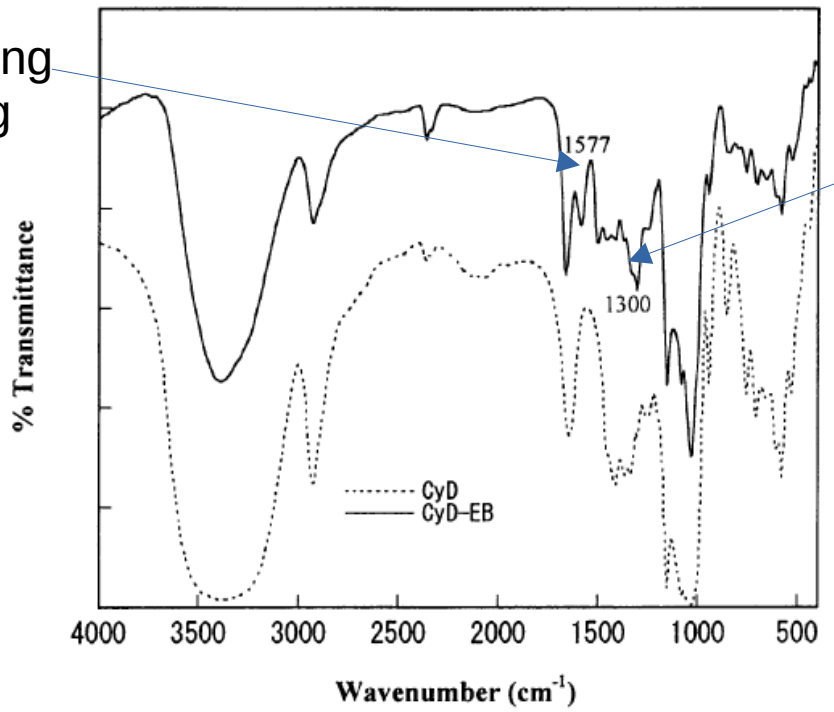

FIGURE 9. FT-IR spectra of βCyD and EB-βCyD inclusion complex.

Yuan, G. et al. Polymers For Advanced Technologies. 14, 428-432, 2003.

Conclusions

- Polyaniline and β-cyclodextrin inclusion compound can be make in polymerization polymer with cyclodextrin or mixture the two, but in this case is necessary using a solvent.
- The βCD protect the encapsulated Pani the oxidation for ionide solution.
- The characteristic for Pani is not altered when is encapsulated.
- The Pani change the shape.

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Thank you