LINZ LECTURES

Lecture 1. The Development of Organic Conductors: Metals, Superconductors and Semiconductors

Lecture 2A. Introduction and Synthesis of Important Conjugated Polymers

Lecture 2B. Solid State Polymerization

Lecture 3. Fullerene Chemistry

Lecture 3B. Molecular Engineering

Solid State Polymerization

Linz, June 10, 2008

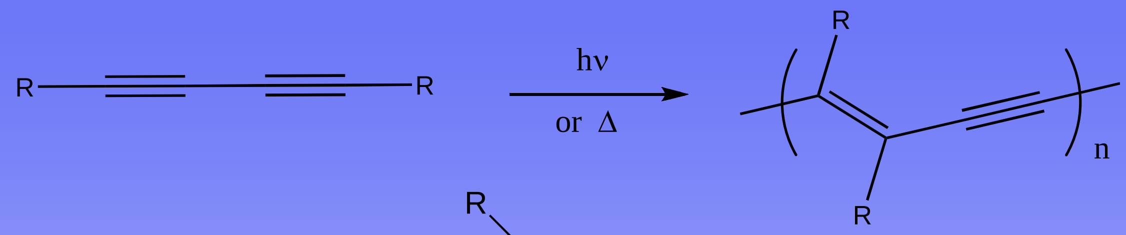
Polydiacetylenes

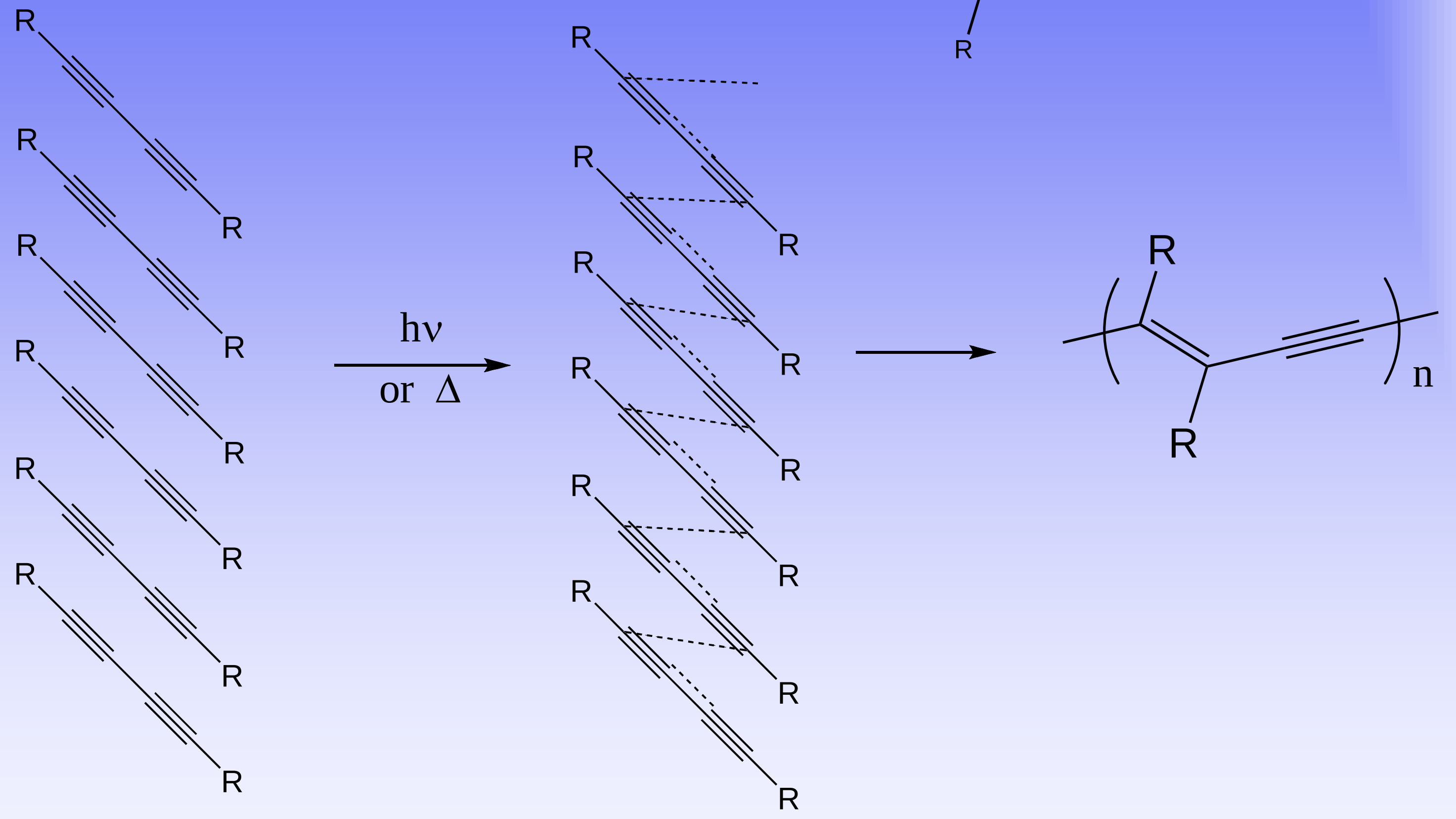
Polythiazyl

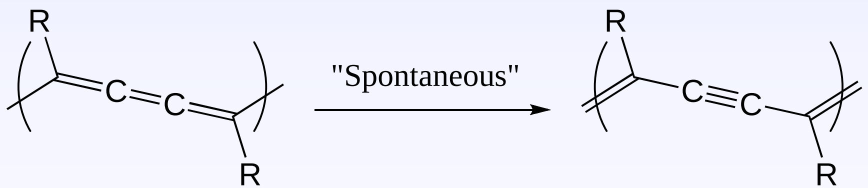
PEDOT Br_3

Solid State Polymerization

Polydiacetylenes







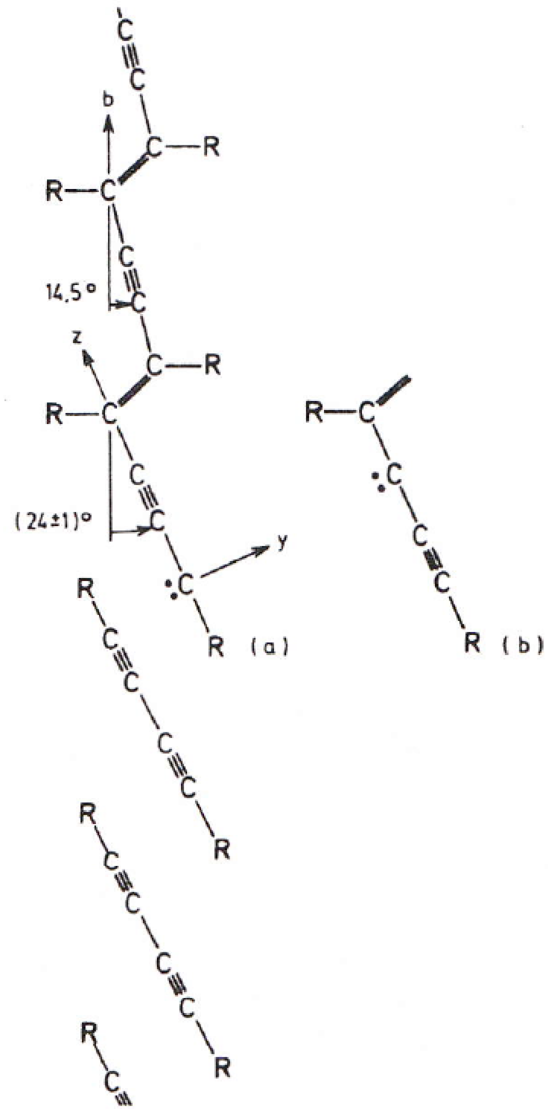


Fig. 2. Model of the active chain end species observed in PTS. y and z are the principal axes of the fine structure tensor (a) and (b) are mesomeric forms (13).

Wegner, G. in *Molecular Metals*, Hatfield, W. E. Ed. NATO Conference Series VI: Materials Science, Vol. 1, Plenum, 1979**.**

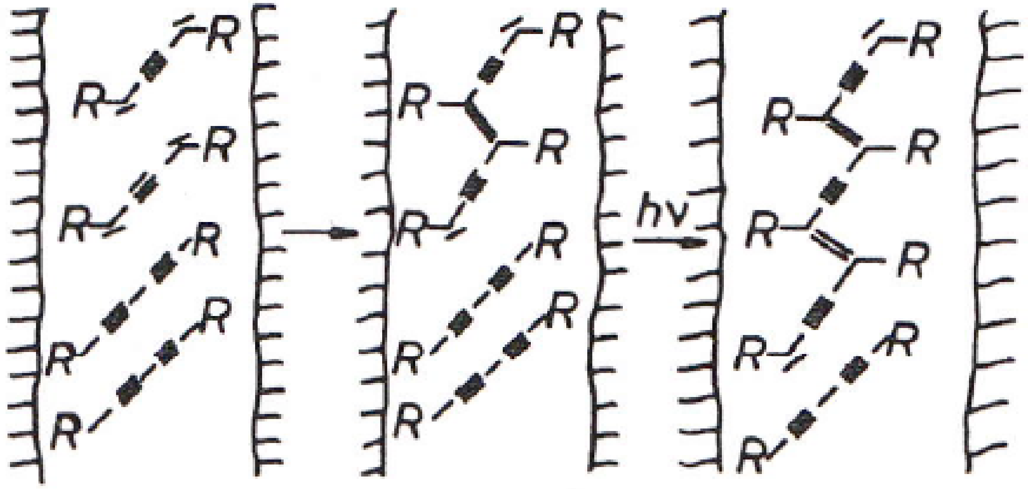


Fig. 3. Growth of the polymer chain by carbenes as active inter-mediates.

Schott, M *J. Phys. Chem. B* **2006,** *110,* 15864

Wegner, G. in *Molecular Metals*, Hatfield, W. E. Ed. NATO Conference Series VI: Materials Science, Vol. 1, Plenum, 1979.

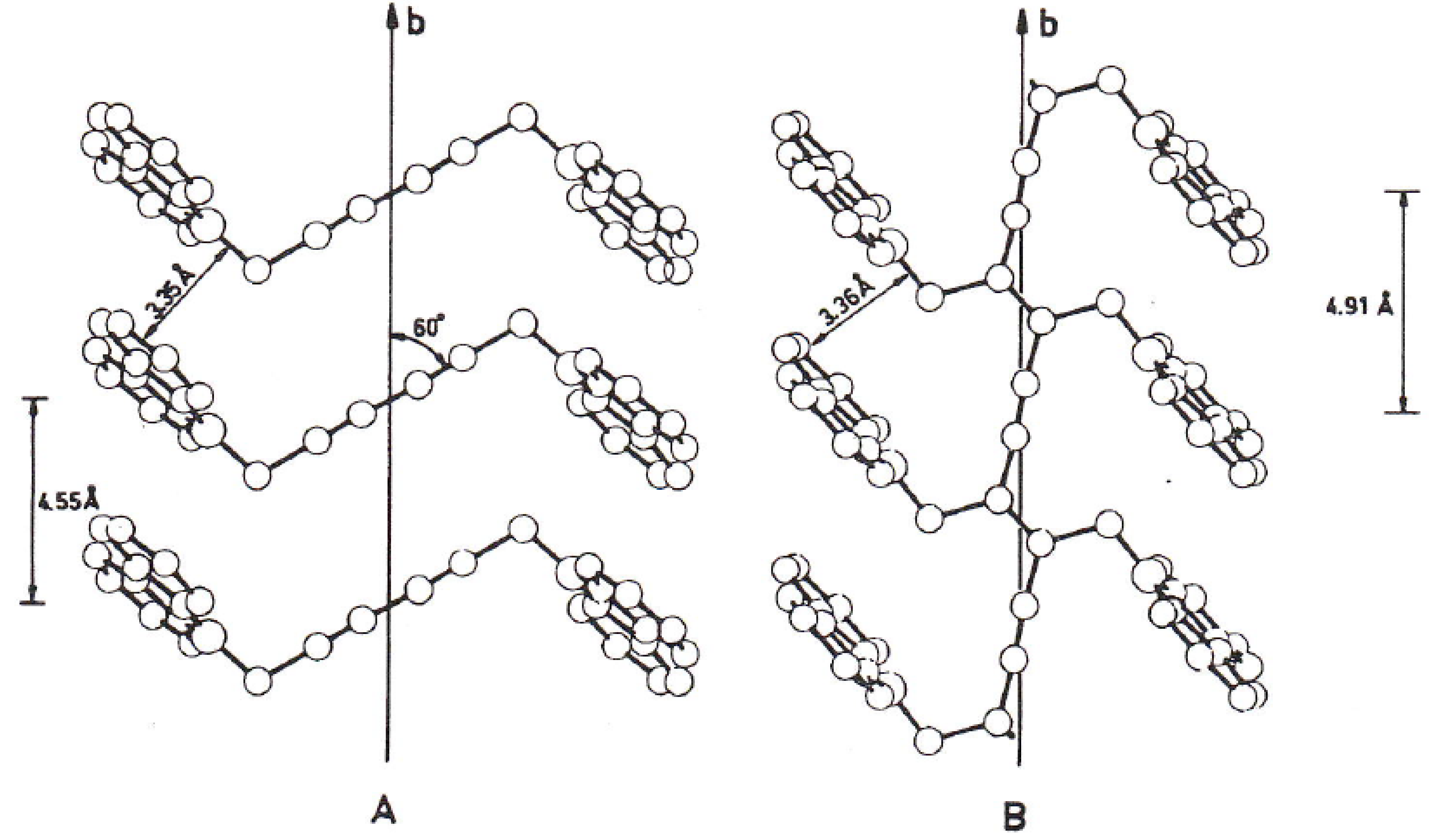


Fig. 6. Projection of the monomer and polymer structure of DCH onto the plane of the polymer backbone.

Wegner, G. in *Molecular Metals*, Hatfield, W. E. Ed. NATO Conference Series VI: Materials Science, Vol. 1, Plenum, 1979.

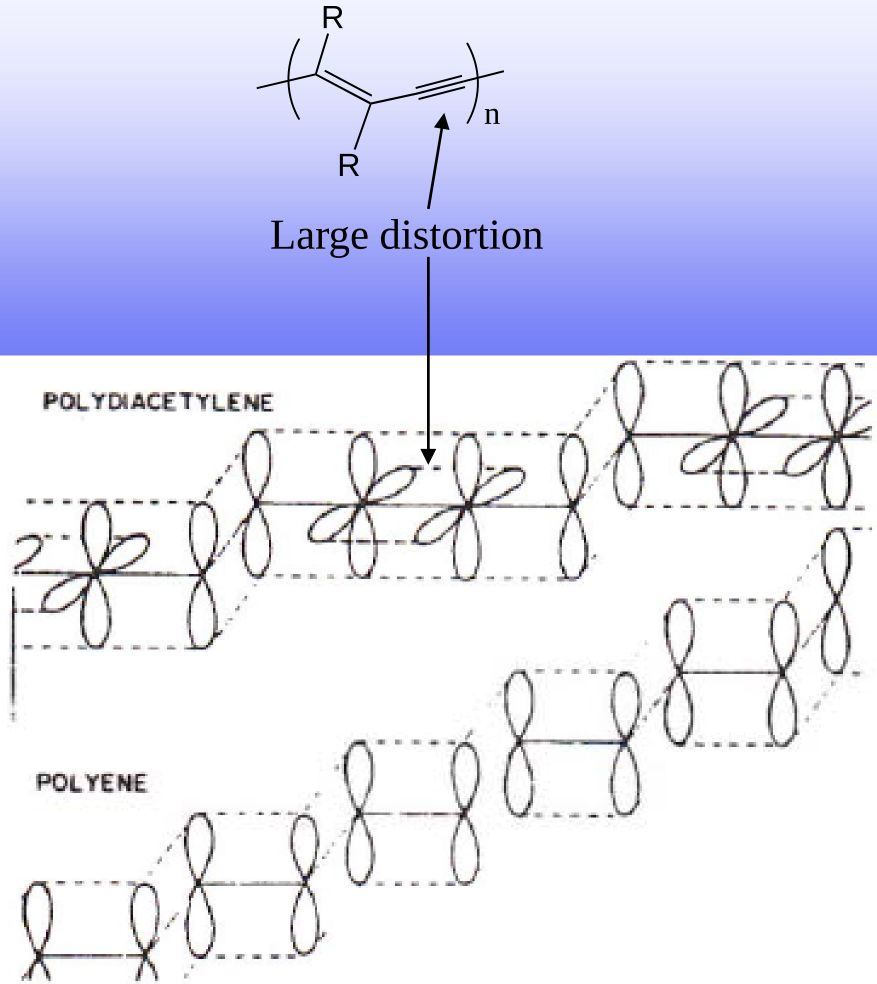


Fig. 4. Schematic description of the π-electron systems for the backbone of a polydiacetylene chain in comparison to a polyene chain.

Wegner, G. in *Molecular Metals*, Hatfield, W. E. Ed. NATO Conference Series VI: Materials Science, Vol. 1, Plenum, 1979.

Solid State Polymerization

Linz, June 10, 2008

Polydiacetylenes

Polythiazyl

PEDOT Br_3

Polythiazyl (SNx)

$S_2N_2 \longrightarrow SNx$

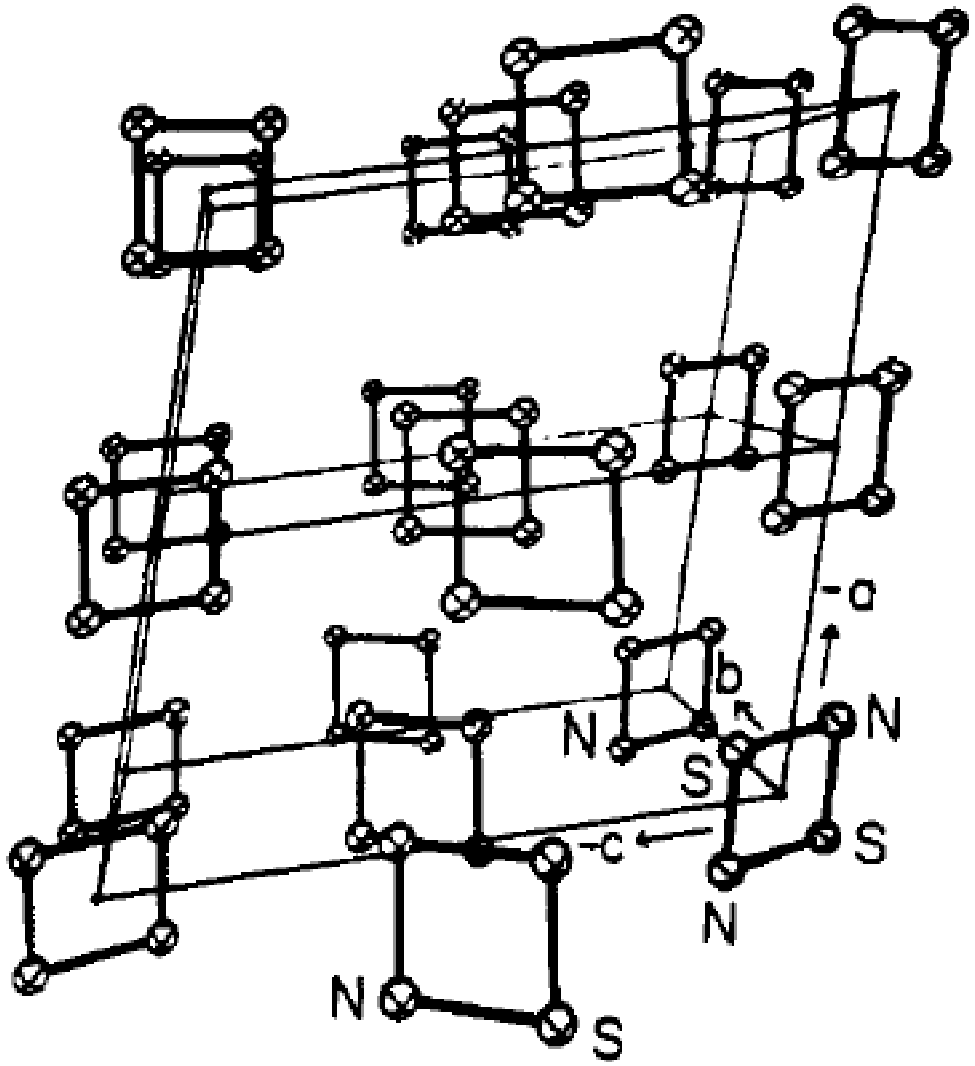


Figure 1. The crystal structure of S_2N_2.

M. J. Cohen, A. F. Garito, J. Heeger, A . G. MacDiarmid, C. M. Mikulski, M . *S.* Saran, J. Kleppinger *J. Am. Chem. Soc. 98*, ***1976*** 3844.

Street, G. B.; Gill, W. D. **The chemistry and physics of polythiazyl, (SN)x, and the polythiazyl halides.** NATO Conference Series VI: Materials Science (1979), Volume Date 1978, 1(Mol. Met.), 301-26.

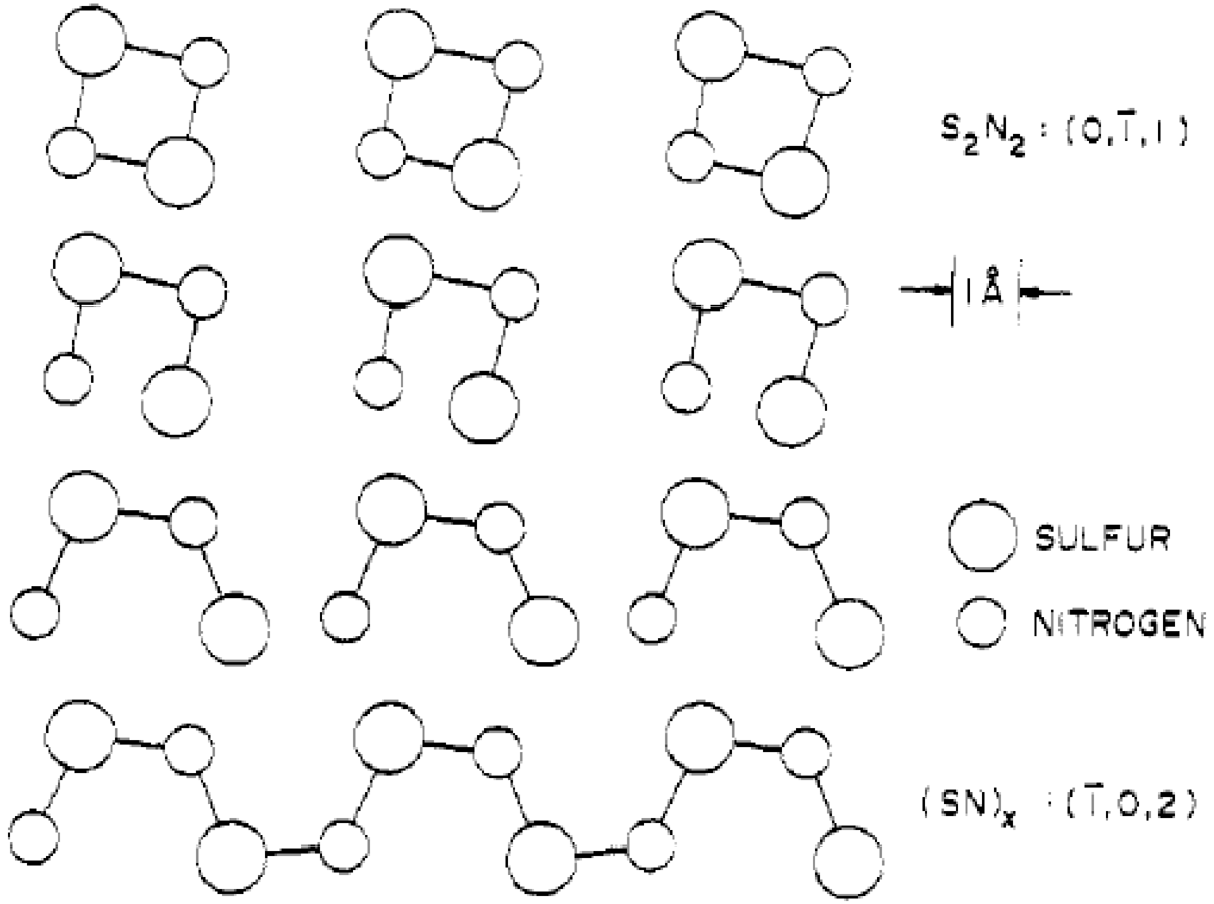


Figure 4. The polymerization of S_2N_2 to $(SN)_x$. The top view is a projection of the S_2N_2 structure onto the (0$\bar{1}$1) plane with the *a* axis horizontal. The bottom view is a projection of the $(SN)_x$ structure onto the ($\bar{1}$02) plane with the *b* axis horizontal. The middle views schematically show the polymerization process.

M. J. Cohen, A. F. Garito, J. Heeger, A . G. MacDiarmid, C. M. Mikulski, M . *S.* Saran, J. Kleppinger *J. Am. Chem. Soc. 98*, ***1976*** 3844.

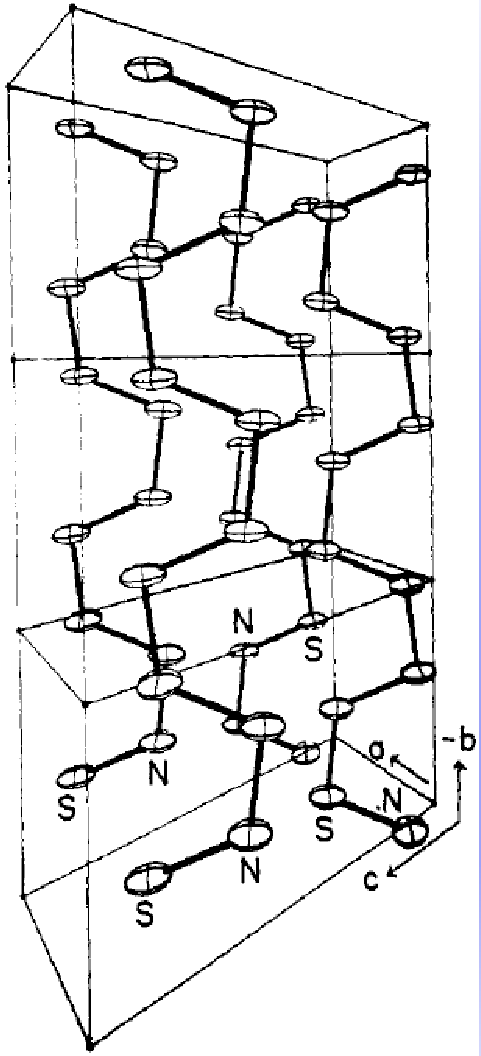
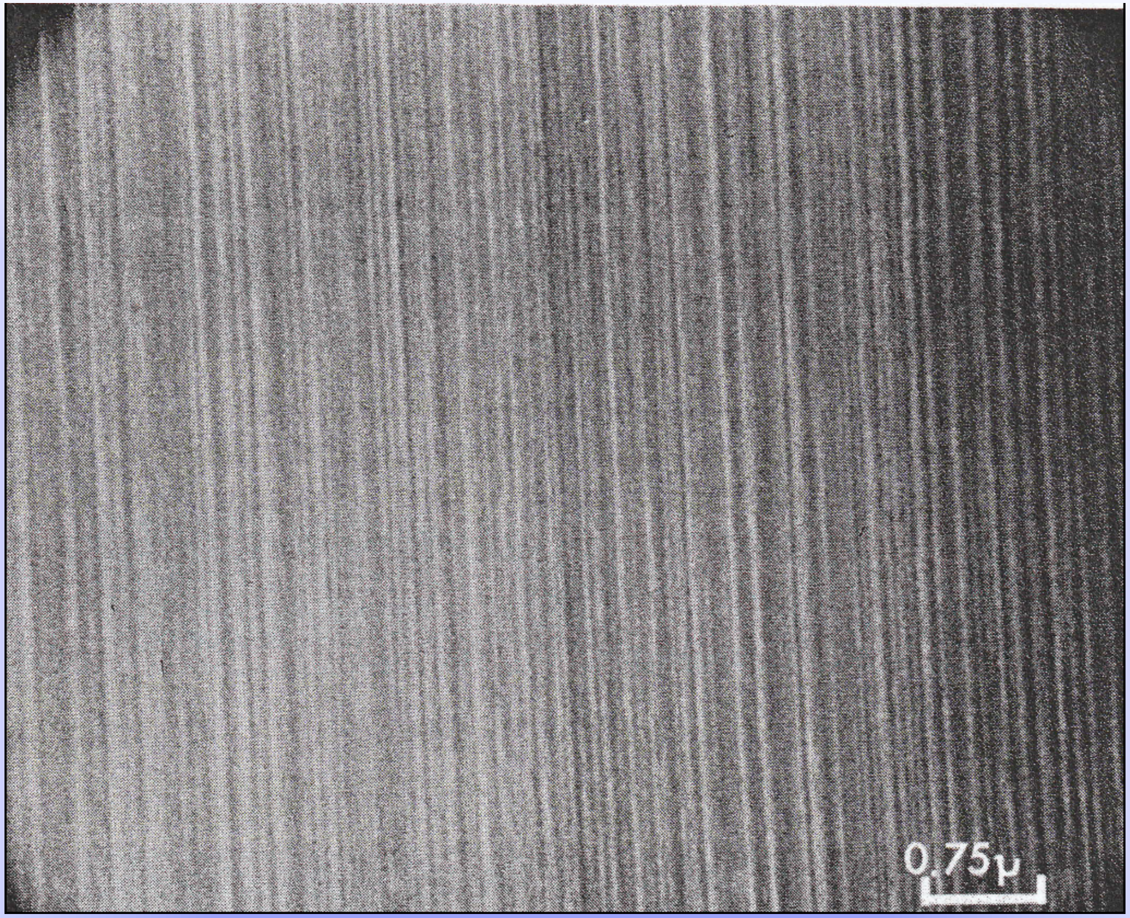


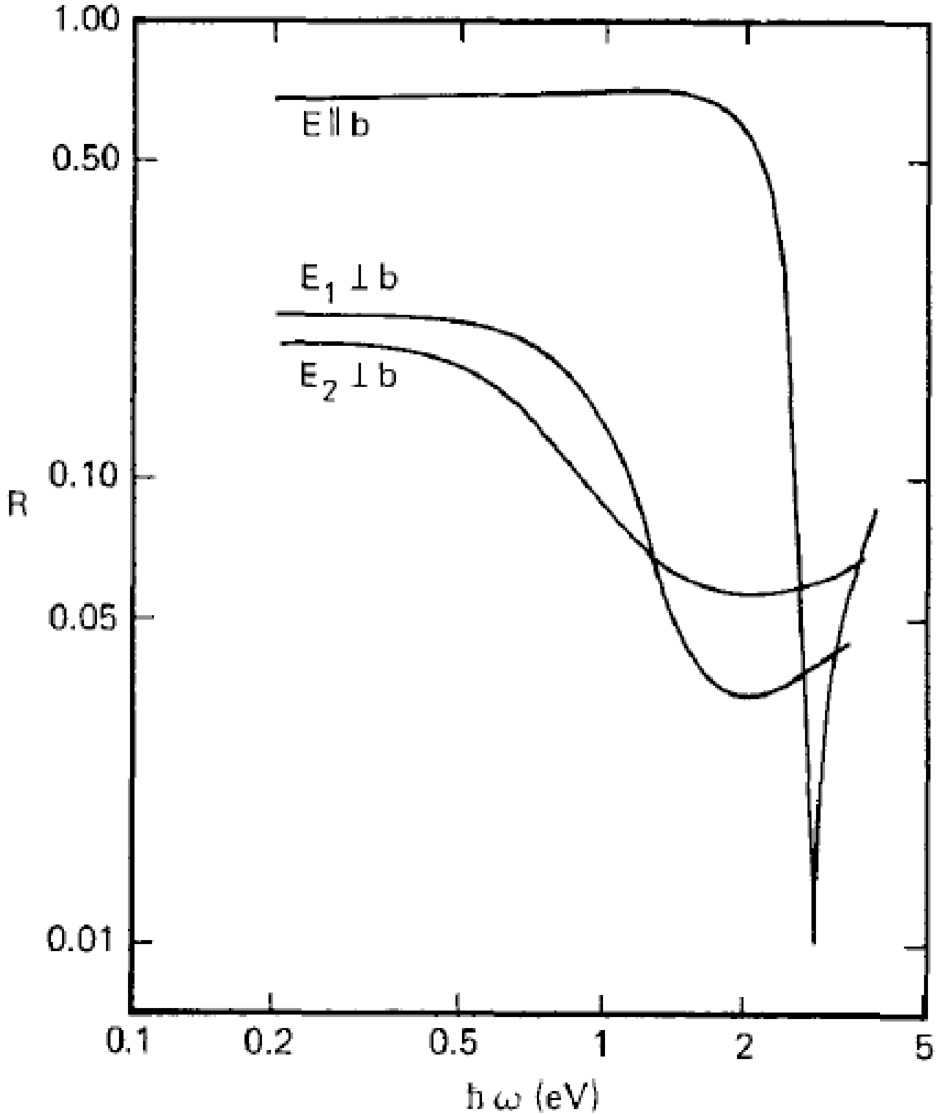
Figure 2. The crystal structure of $(SN)_x$.

M. J. Cohen, A. F. Garito, J. Heeger, A . G. MacDiarmid, C. M. Mikulski, M . *S.* Saran, J. Kleppinger *J. Am. Chem. Soc. 98*, ***1976*** 3844*.*



Electron micrograph of a smooth area of an SN_x Crystal

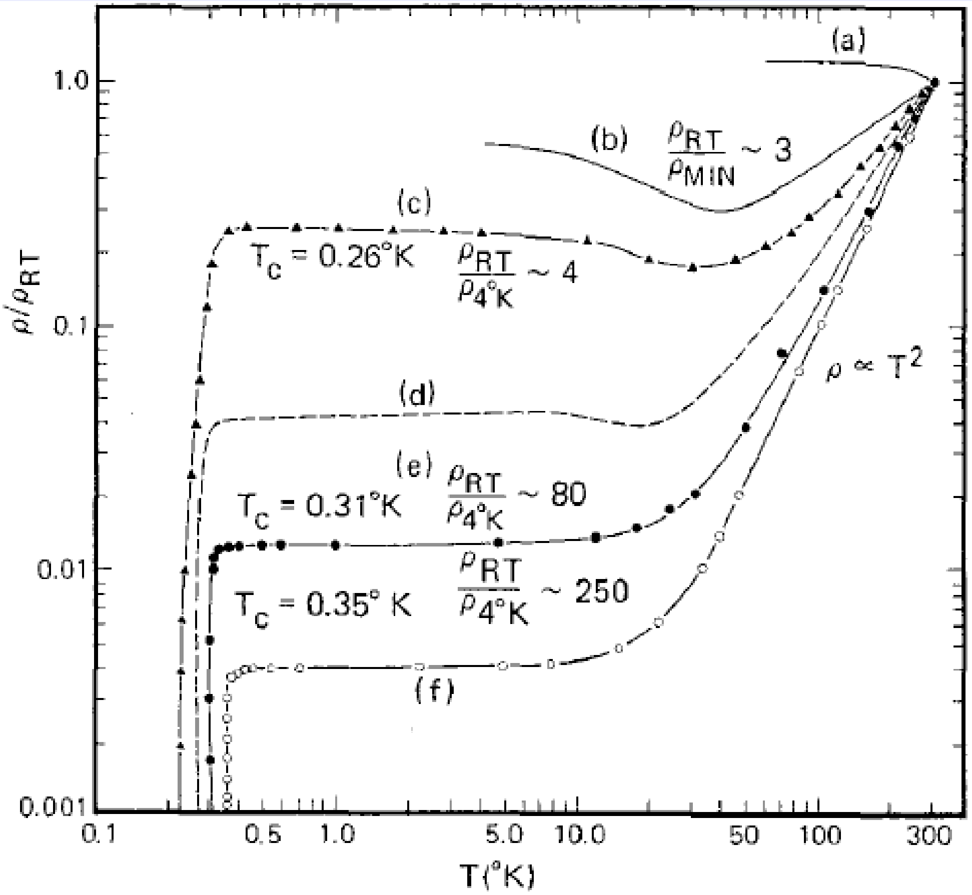
Geene R.L.; Street G.B.,*Proceedings of the NATO-ASI on Chemistry and Physics of One-Dimensional Metals, Bolzano, Italy, August* 1976. (Edited by KELLER H.). Plenum Press, New York (1977)



Polarized reflectance (R) of $(SN)_x$ crystals at room temperature [43].

Geene R.L.; Street G.B.,*Proceedings of the NATO-ASI on Chemist,y and Physics of One-Dimensional Metals, Boizano, Italy, August* 1976. (Edited by KELLER Hi.). Plenum Press, New York (1977)

First and Only Superconducting Polymer



Temperature dependence of the dc resistivity of $(SN)_x$ crystals along the polymer chains (b-axis). Different curves are discussed in text.

Geene R.L.; Street G.B.,*Proceedings of the NATO-ASI on Chemist,y and Physics of One-Dimensional Metals, Boizano, Italy, August* 1976. (Edited by KELLER Hi.). Plenum Press, New York (1977)

Solid State Polymerization

Linz, June 10, 2008

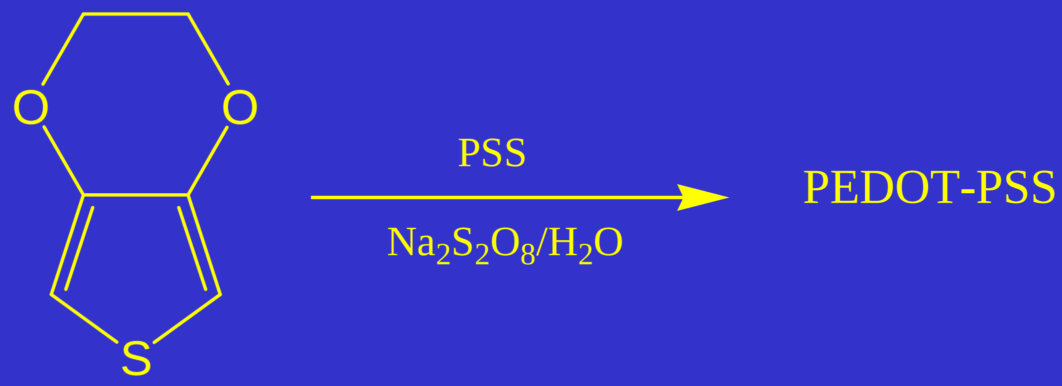
Polydiacetylenes

Polythiazyl

PEDOT Br_3

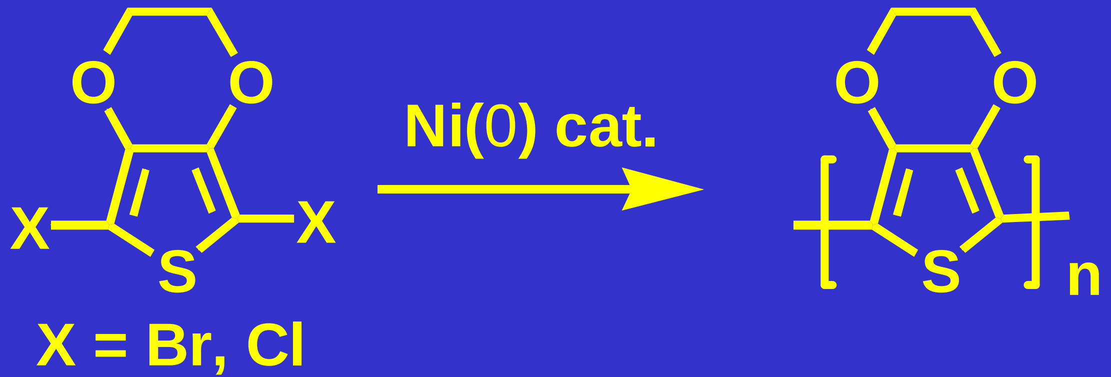
Traditional Synthetic Methods of PEDOT

EDOT **PEDOT**



Meng, H.; Perepichka, D.F.; Wudl, F. *Angew. Chem. Int. Ed.*, **2003**, 42(6), 658-661

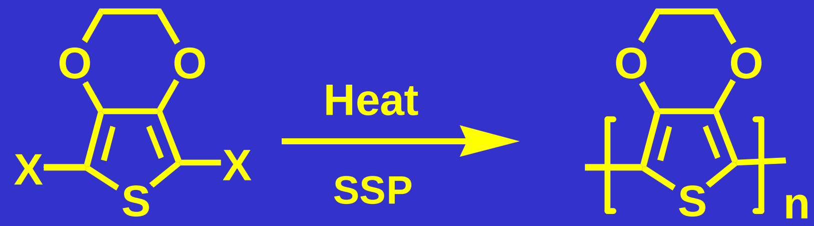
Traditional Synthetic Methods of PEDOT



PEDOT via Solid-state Polymerization

Å

A Facile Solid-state Synthesis of PEDOT

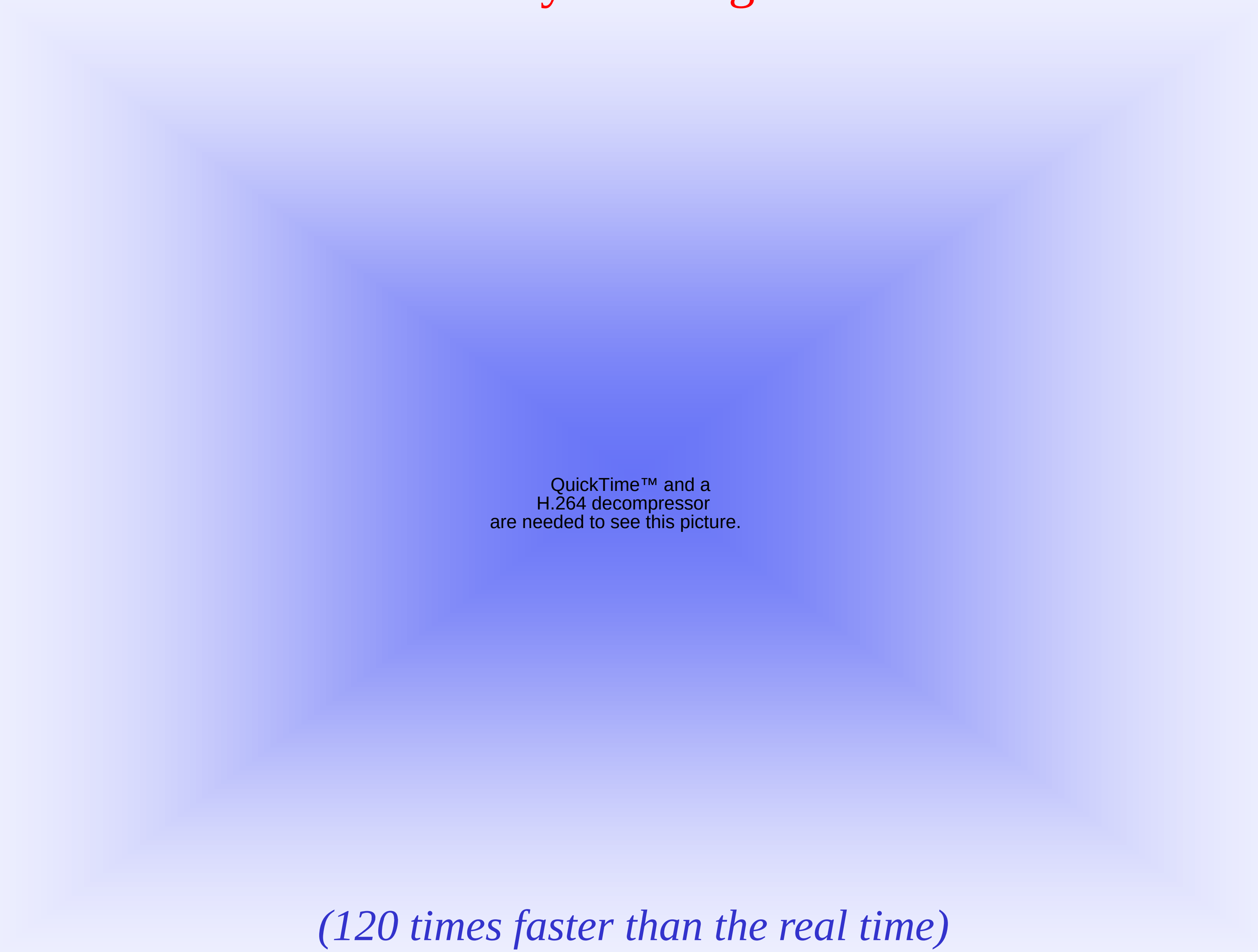


X = Br, I

60 °C, 8 h.

Meng, H.; Perepichka, D.F.; Wudl, F. *Angew. Chem. Int. Ed.*, **2003**, *42*, 658.

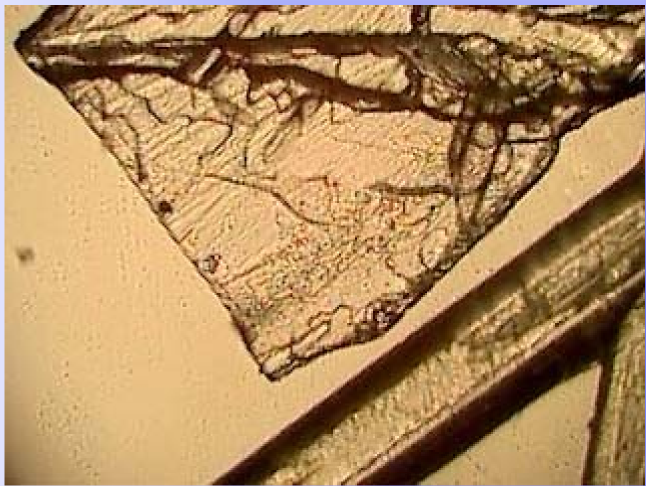
Non Polymerizing Melt



(120 times faster than the real time)

Ramp to 100 ^{o}C, **heat** 100-150 ^{o}C at 10 deg/min, **hold** 150 ^{o}C, total time *100 min*

Microscopy of Solid State Polymerization



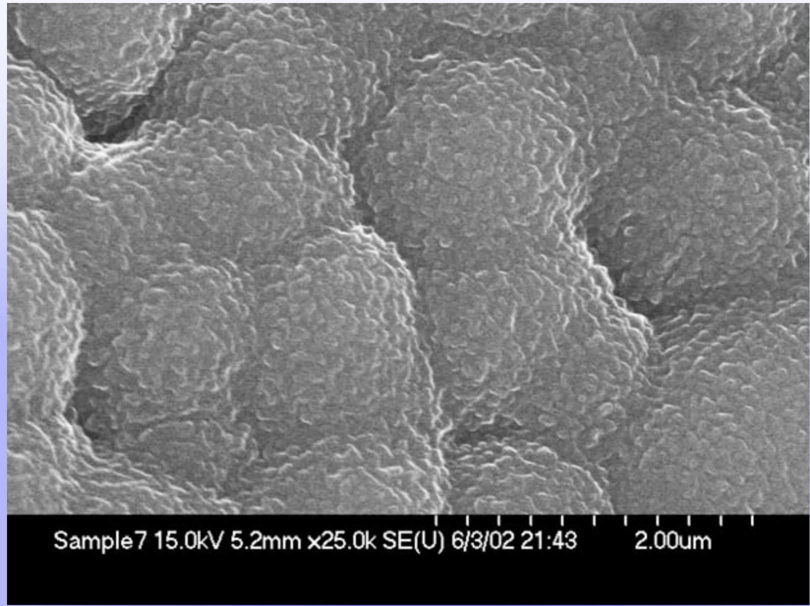
QuickTime™ and a
H.264 decompressor
are needed to see this picture.

(480 times faster than the real time)

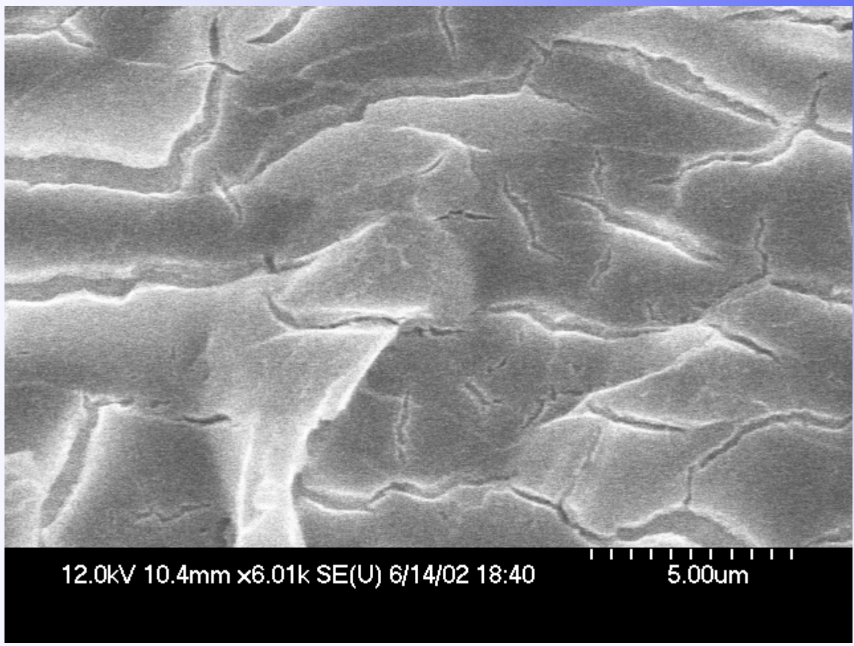
(240 times faster than the real time)

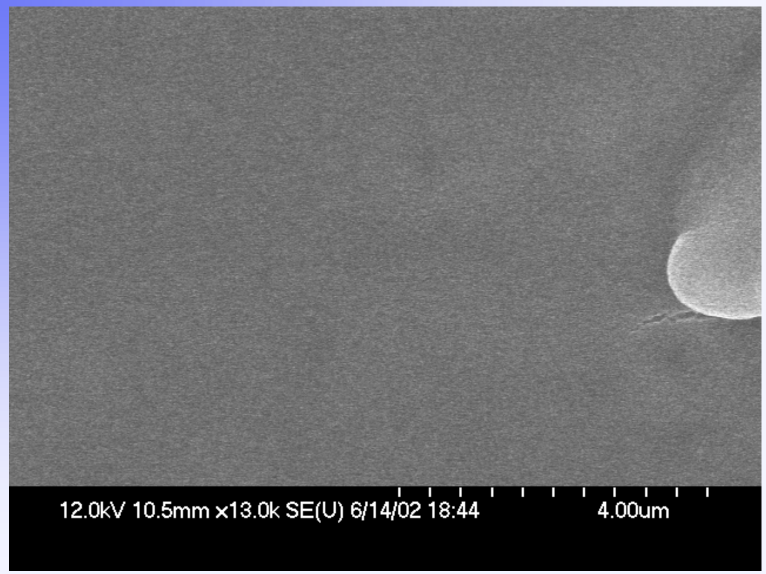
Hold at 87 ^{o}C, *1 h*

Hold at 92 ^{o}C, *1 h*



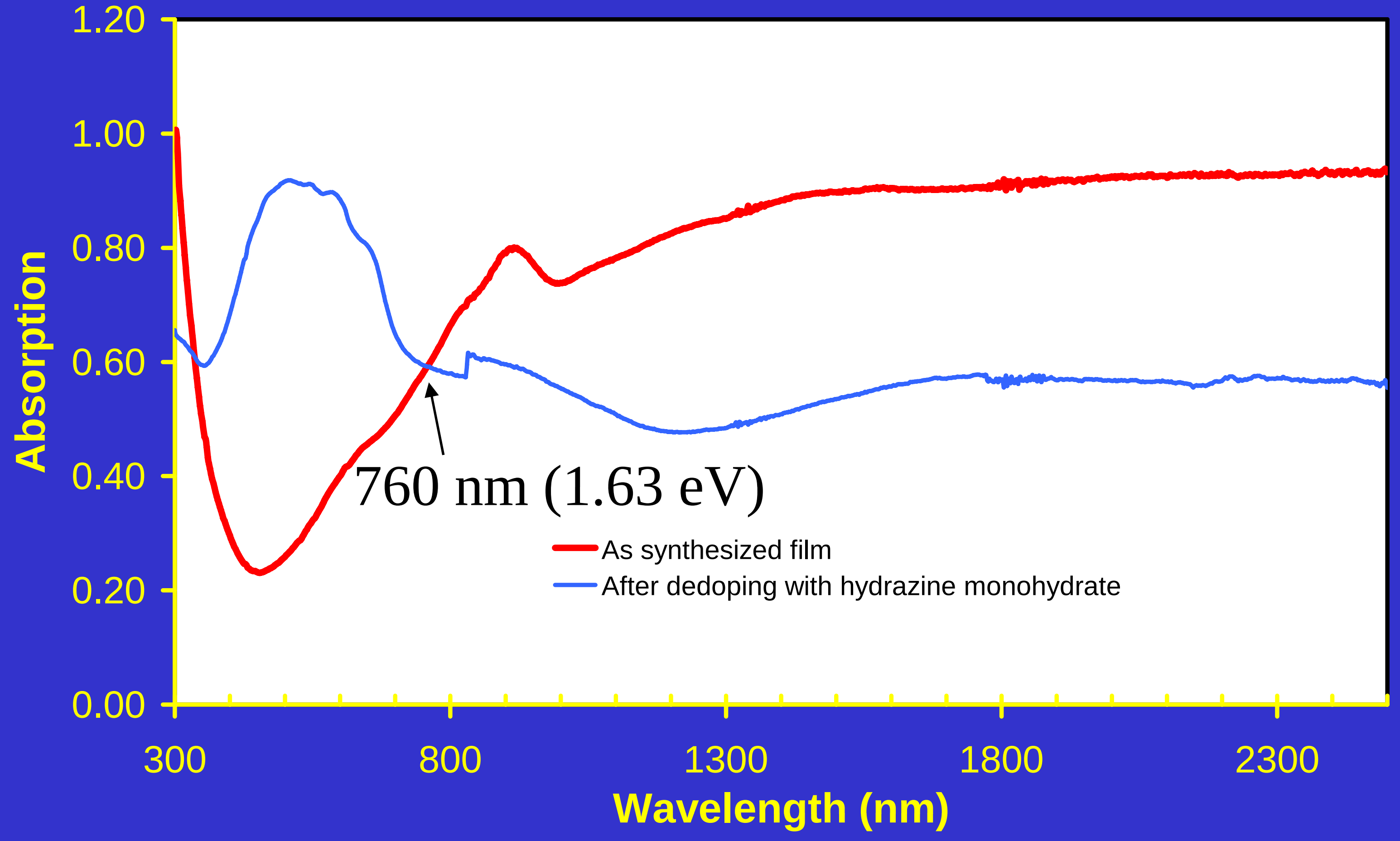
Two year sample





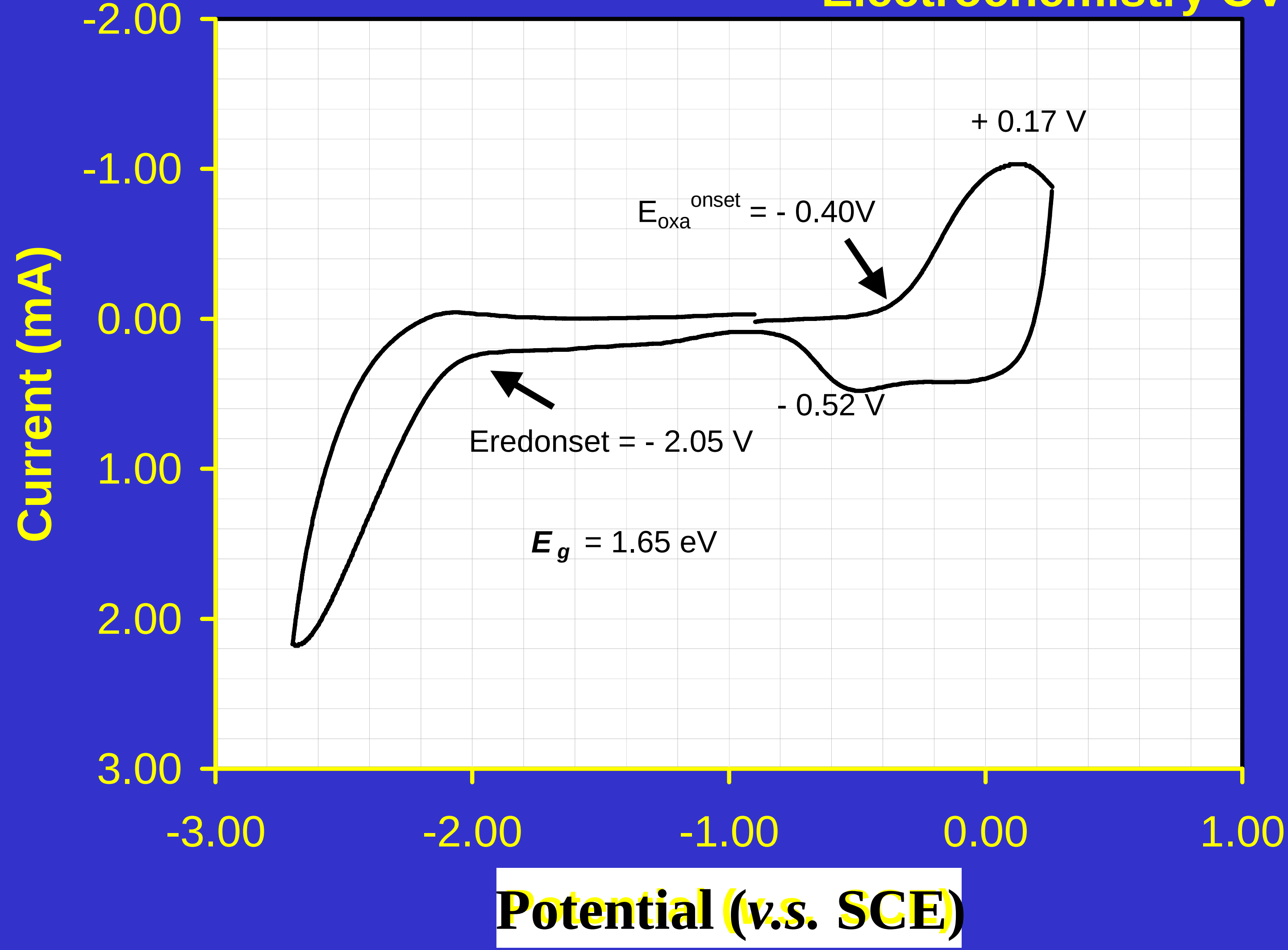
A Facile Solid-state Synthesis of PEDOT

---UV-vis-NIR



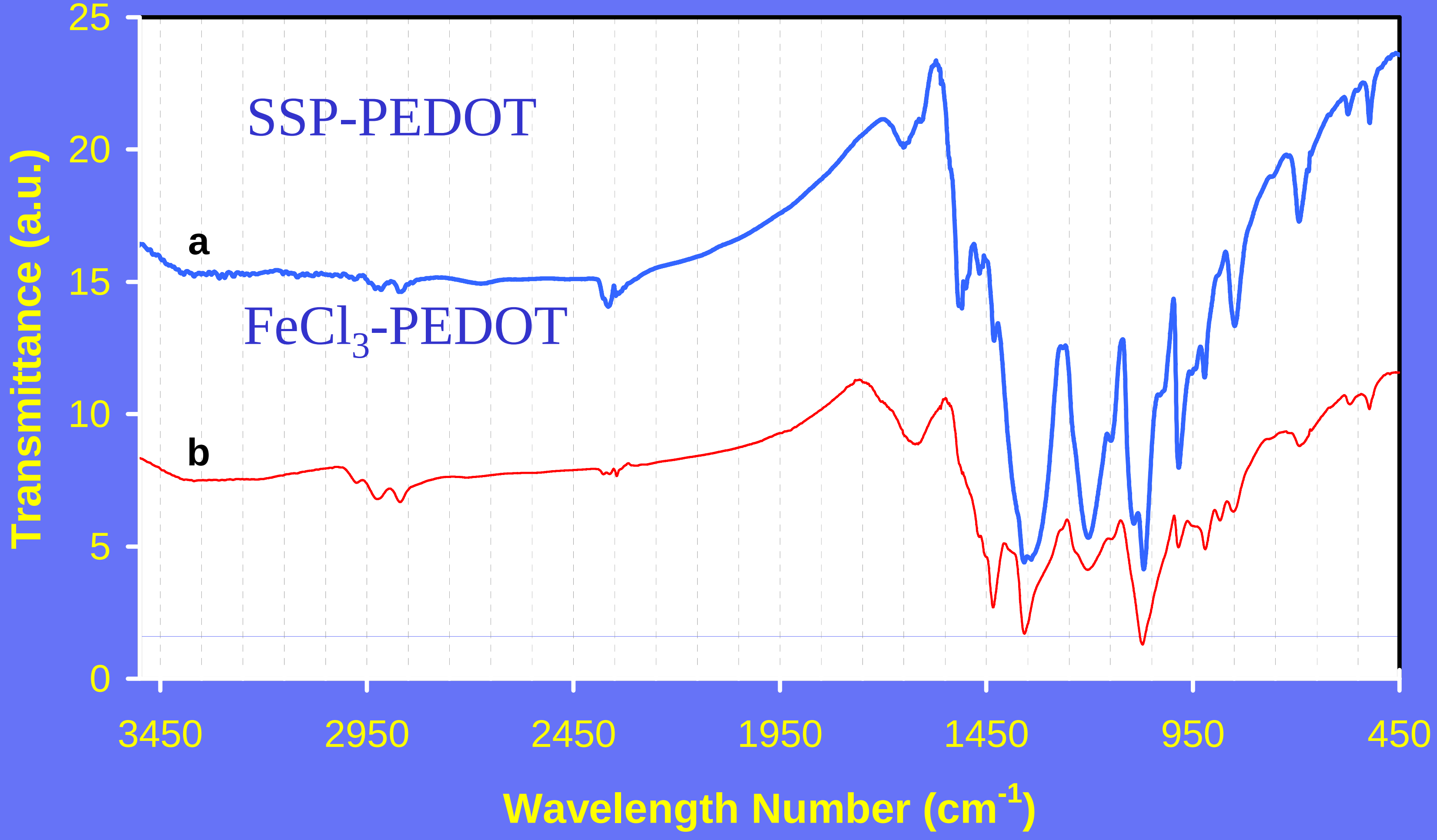
A Facile Solid-state Synthesis of PEDOT

---Electrochemistry CV



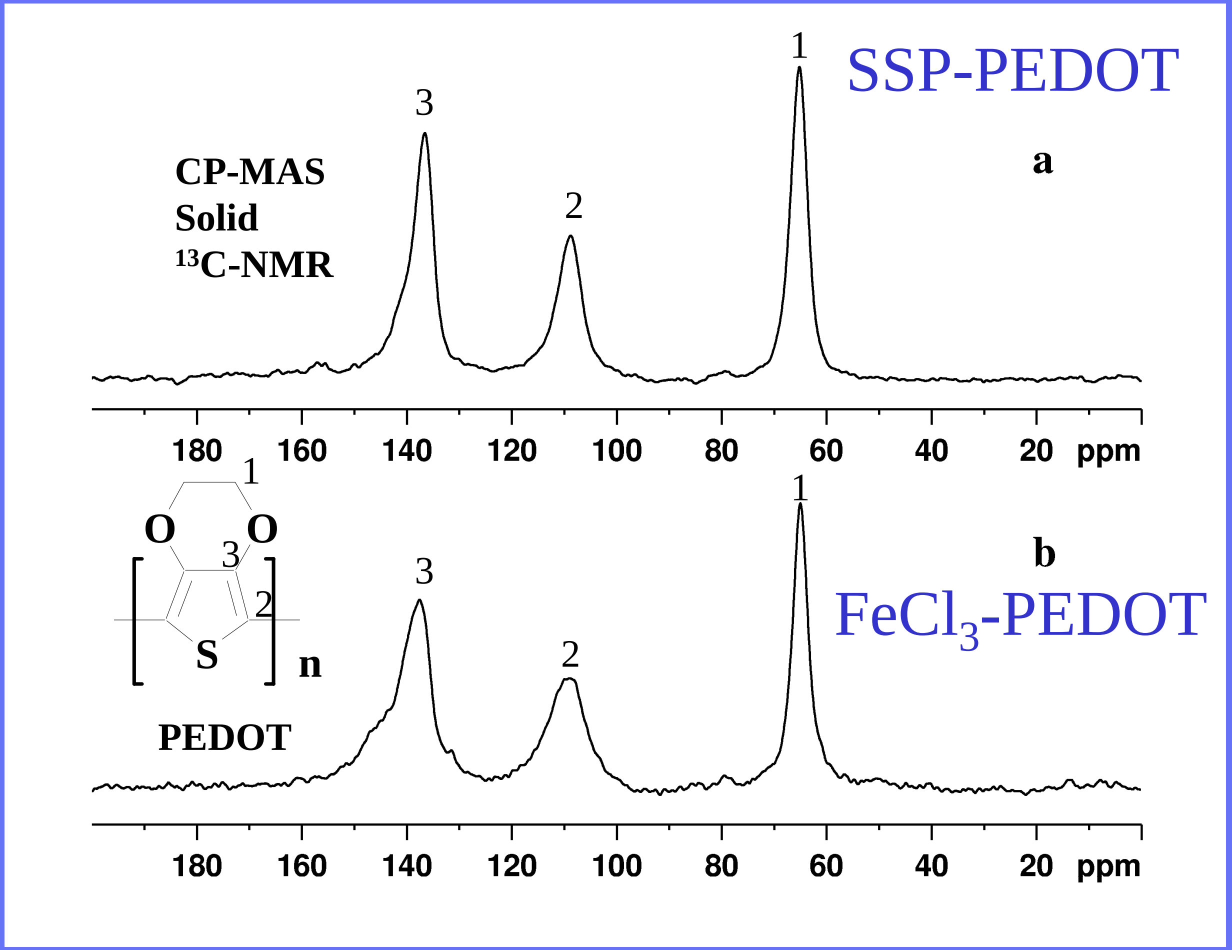
A Facile Solid-state Synthesis of PEDOT

---FTIR



A Facile Solid-state Synthesis of PEDOT

---^{13}C NMR



A Facile Solid-state Synthesis of PEDOT

---Conductivity

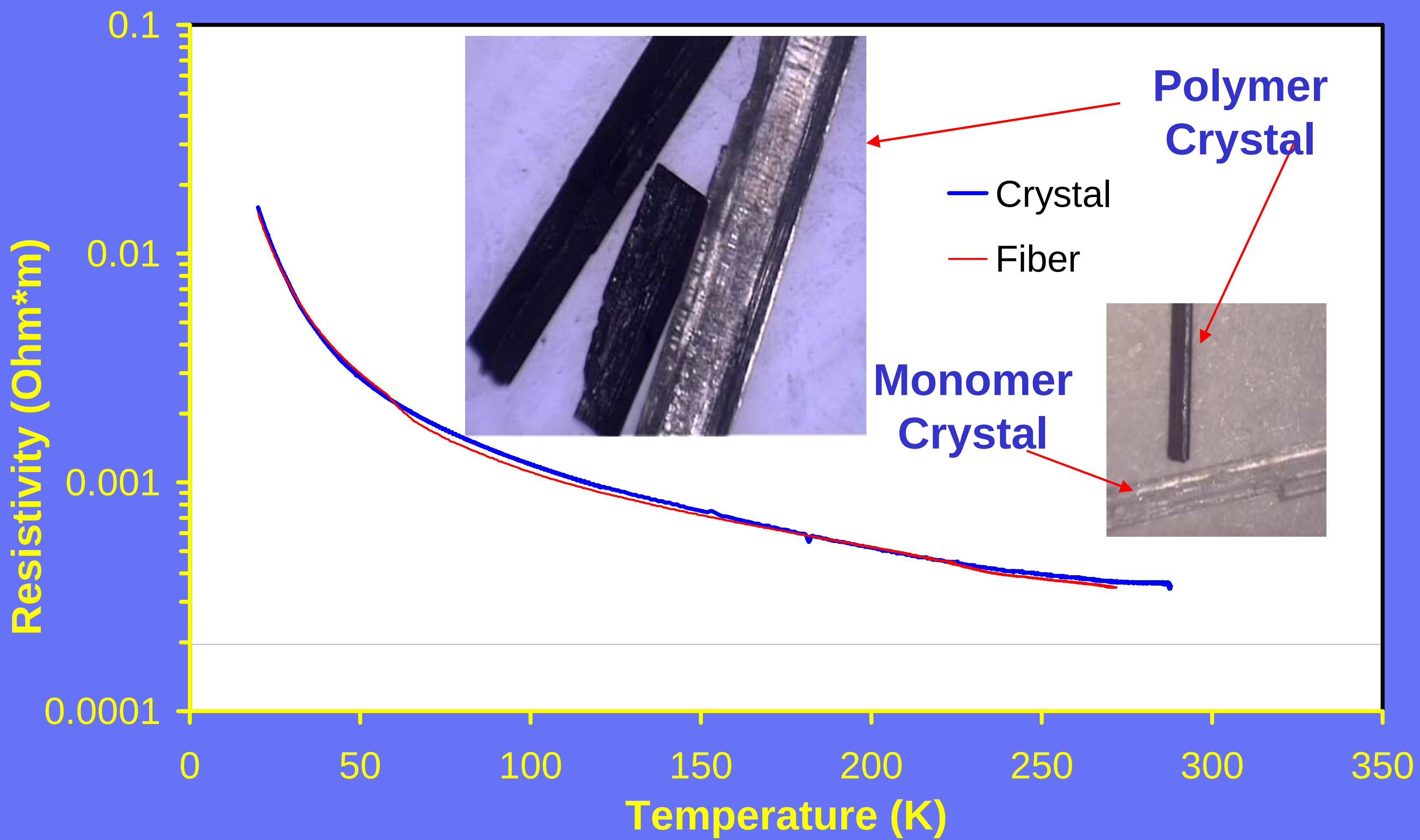
	Conductivity of solid-state polymerized **PEDOT**				$FeCl_3$ polymerized **PEDOT**
Sample [a)]	A	B	C	D	0-5 ^oC
Reaction time	2 years [b)]	24 h	4 h	24 h	24 h
Crystals / fibers	80 S/cm	33 S/cm	20 S/cm	NA	NA
Pellets as synthesized	30 S/cm	18 S/cm	16 S/cm	0.1 S/cm	NA
Pellets after I_2 doping	53 S/cm	30 S/cm	27 S/cm	5.8 S/cm	7.6 S/cm
Thin films	NA	23 S/cm	NA	NA	NA
Thin films after I_2 doping	NA	48 S/cm	NA	NA	NA

a) Conversion temperature A = *ca*. 20 ^oC, B = 60 ^oC, C = 80 ^oC, D = 120 ^oC

b) The monomer was stored in a closed jar for 2 years at room temperature (*ca*. 20 ^oC)

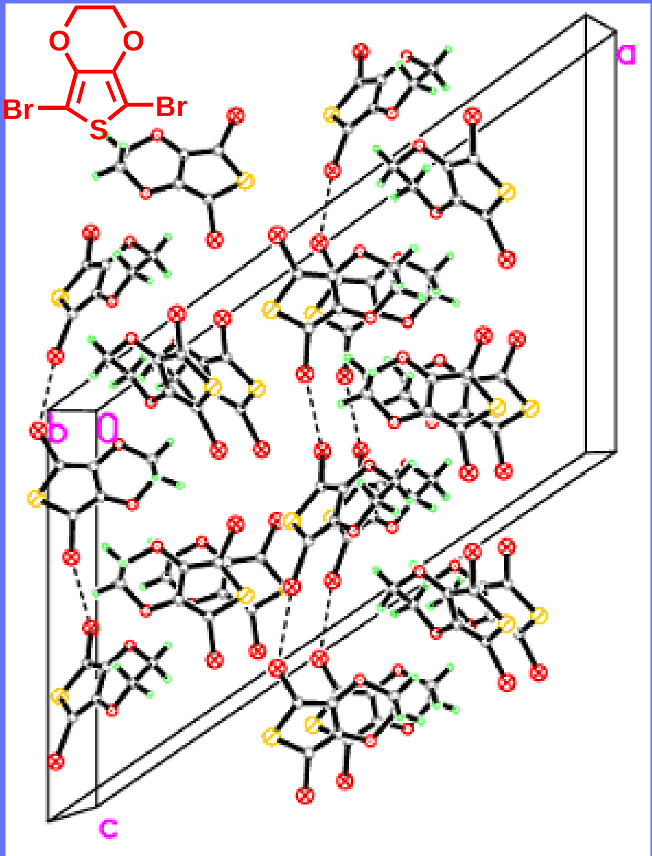
A Facile Solid-state Synthesis of PEDOT

---Conductivity vs. Tempeature



A Facile Solid-state Synthesis of PEDOT

---Monomer Crystal Packing



The closest neighboring Br - Br distance (3.45 Å) is shorter than the sum of the Van der Waals radii (3.6 --- 4.0 Å)

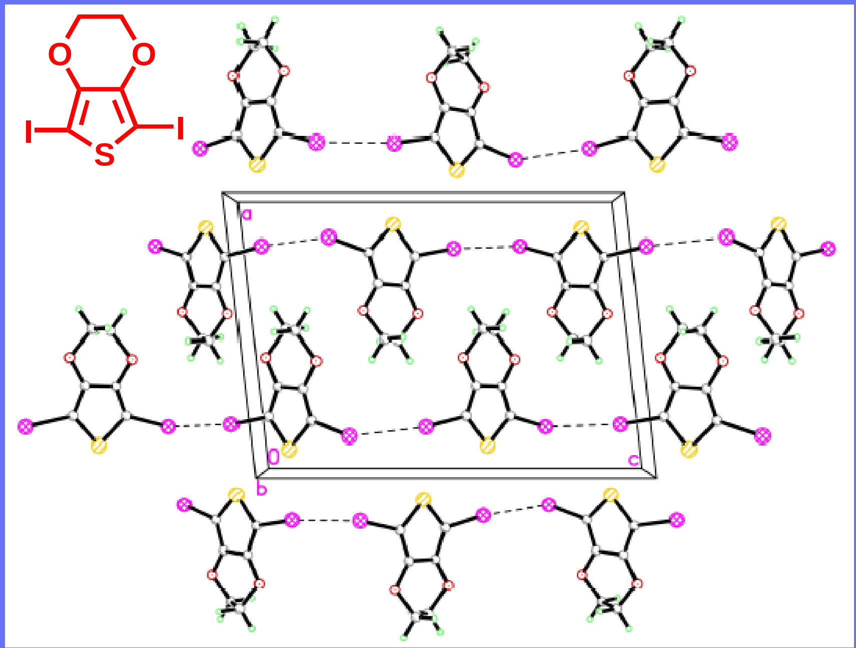
a = 25.27 Å, b = 5.01 Å, c = 15.67 Å

$\alpha = 90°$, $\beta = 123.96°$, $\gamma = 90°$

Monoclinic

A Facile Solid-state Synthesis of PEDOT

---Monomer Crystal Packing



The closest neighboring I - I distance (3.73 Å) is shorter than the sum of Van der Waals radii (4.10 Å)

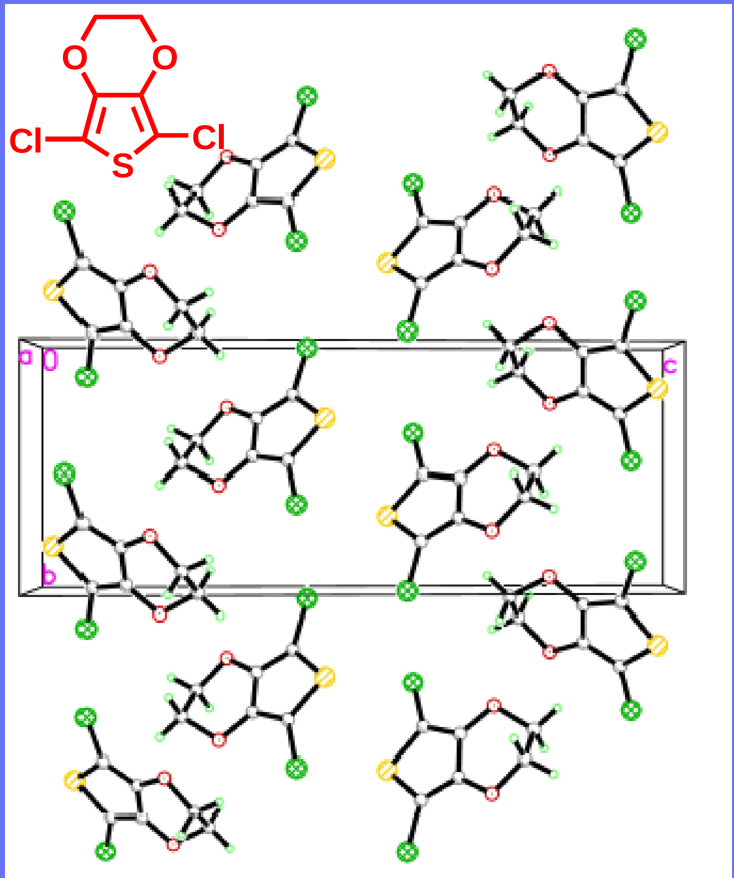
a = 11.43 Å, b = 4.90 Å, c = 15.93 Å

α= 90 °, β = 96.40 °, γ = 90 °

Monoclinic

A Facile Solid-state Synthesis of PEDOT

---Monomer Crystal Packing



a = 5.11 Å, b = 7.80 Å, c = 20.31 Å

α= 90 º, β = 93.75 º, γ = 90 º

Monoclinic

The closest neighboring Cl - Cl distance (3.58 Å) is longer than the sum of Van der Waals radii (3.40 Å)

A Facile Solid-state Synthesis of PEDOT

---Conducting Thin Film Preparation

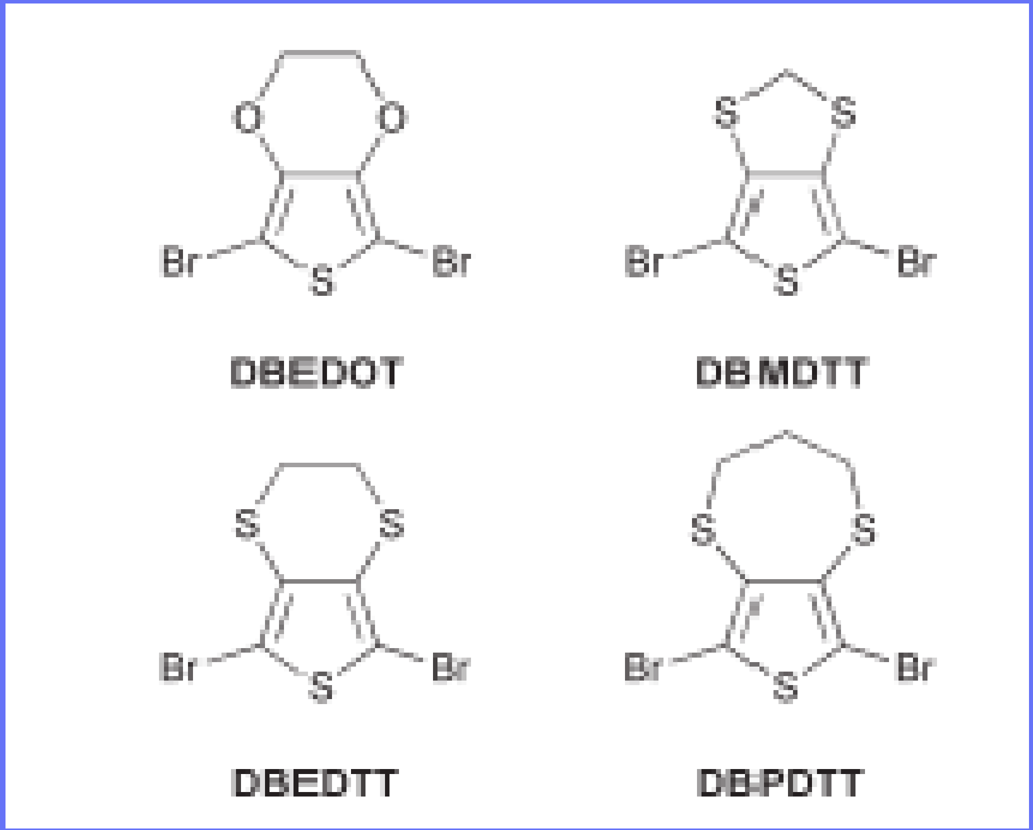
The average surface resistance:

Glass substrate: 2.1×10^3 Ω/ (Film thickness: 2700 Å)

Plastic substrate: 3.6×10^3 Ω/ (Film thickness: 1300 Å)

Surface conductivity: > 200 S/cm.

Other Thiophene Derivatives



Spencer, H.J.; Berridge, R.; Crouch, D.J.; Wright, S.P.; Giles, M.; McCullough, I. Coles, S.J.; Hursthouse, M.B.; Skabara, P.J. *J. Materials Chem.* **2003**, *13*, 2075.

Conclusion

- PEDOT synthesized by solid-state polymerization (SSP)
- Polymerization appears to involve radical intermediates
- Monomer crystal packing favors the solid-state reaction cf DIEDOT and DBEDOT *vs* DClEDOT
- The reaction is first-order with E_a ca 27 kcal/mole
- The solid-sate polymerization can be applied to the fabrication of conducting thin films on insulating substrates
- The solid-sate polymerization appears to be generally applicable to electron rich dibromothiophenes

The End

Thanks!

Monomer Synthesis