INTERNATIONAL ATOMIC ENERGY AGENCY
UNITED NATIONS EDUCATIONAL, SCIENTIFIC AND CULTURAL ORGANIZATION

INTERNATIONAL CENTRE FOR THEORETICAL PHYSICS
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"SCHOOL ON POLYMER PHYSICS"

27 April - 15 May 1987

"CONDUCTING POLYMERS"

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University of Massachusetts
Amherst, Ma.
U.S.A.

CONDUCTING POLYMERS

1. **INTRODUCTION**

   SURVEY OF ELECTRICAL CONDUCTION IN ORGANIC MATERIALS

   - CHARGE TRANSFER COMPLEXES
   - $(SN)_x$
   - $(CH)_x$, DOPING
   - OTHER CONJUGATED POLYMERS
   - PHTHALOCYANINE DERIVATIVES
   - "BECHGAARD" SALTS

2. **SYNTHESIS**

   $(CH)_x$ FILM SYNTHESIS, ZIEGLER-NATTA CATALYSTS

   OTHER $(CH)_x$ CATALYSTS

   EFFECT OF SOME VARIABLES

   "DURHAM/FEAST" $(CH)_x$ USING PRECURSORS

   REPRESENTATIVE OTHER SYNTHESES"

   - POLYPHENYLENE VINYLENE
     - WITTIG REACTION
     - PRECURSOR ROUTE

3. **DOPING**

   P- AND N-DOPANTS, UNIFORMITY

   COMPENSATION

   ANISOTROPY

   ELECTROCHEMICAL DOPING

4. **MORPHOLOGY**

   NASCENT $(CH)_x$ MORPHOLOGY

   CRYSTALLINITY

   OTHER MORPHOLOGIES

   STRUCTURE DETERMINATIONS

   OTHER POLYMERS

5. **PHYSICAL PROPERTIES**

   ELECTRICAL CONDUCTIVITY

   MAGNETIC SUSCEPTIBILITY

   TEMPERATURE DEPENDENCY

   BAND GAP

   ELECTRICAL ANISOTROPY

   ESR PROPERTIES

   CIS-TRANS ISOMERIZATION OF $(CH)_x$

   THERMOELECTRIC POWER

6. **CONDUCTION MECHANISIMS**

   BAND STRUCTURE THEORY: SOLITONS, POLARONS

   PERCOLATION MODELS

7. **APPLICATIONS**

   AS CONDUCTORS

   BATTERIES

   DEVICES

SELECTED BIBLIOGRAPHY

SYNTHETIC METALS (JOURNAL) FROM 1979, ELSEVIER

R. BAUGHMAN ET AL. CHEM. REV., 82, 209 (1982)

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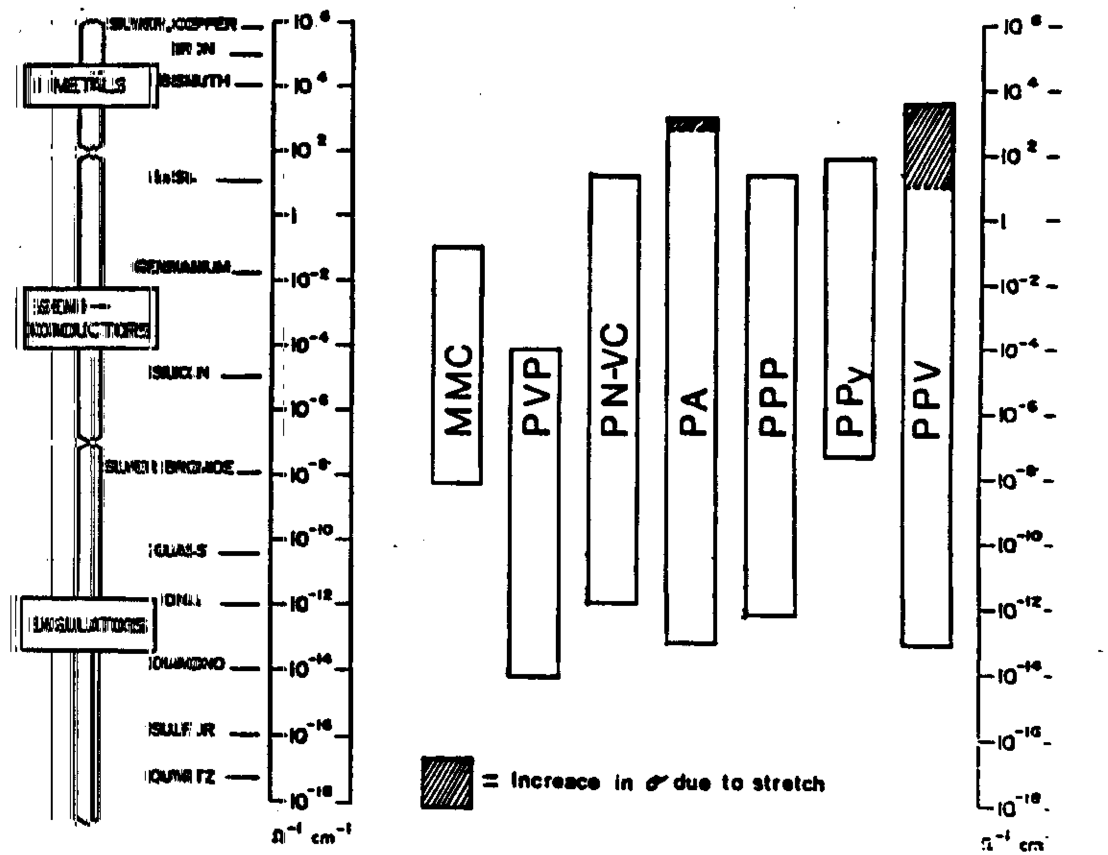
POLYACETYLENE, J. C. W. CHIEN, ACADEMIC PRESS, N.Y., 1984

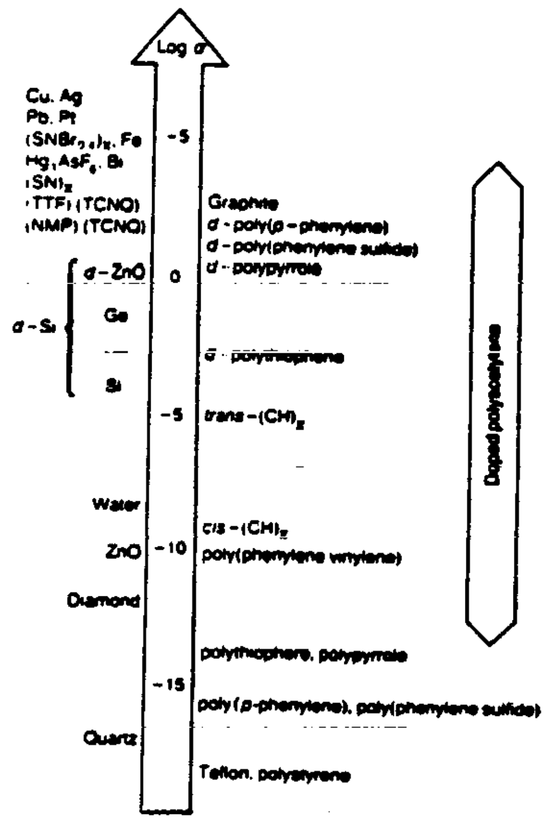
A. G. MACDIARMID, ANN. REV. PHYS. CHEM., 33, 443 (1982)

K. SEEGER, ANGEW. MAKROM. CHEMIE., 109, 227 (1982) (ON MORPHOLOGY)

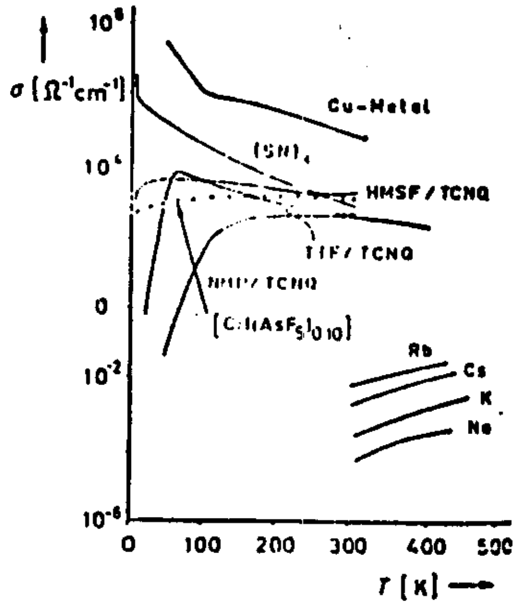
G. WEGNER, ANG. CHEM. INT. ED., 20, 361 (1981)

W. HAYES, CONTEMP. PHYS., 26, 421 (1985)

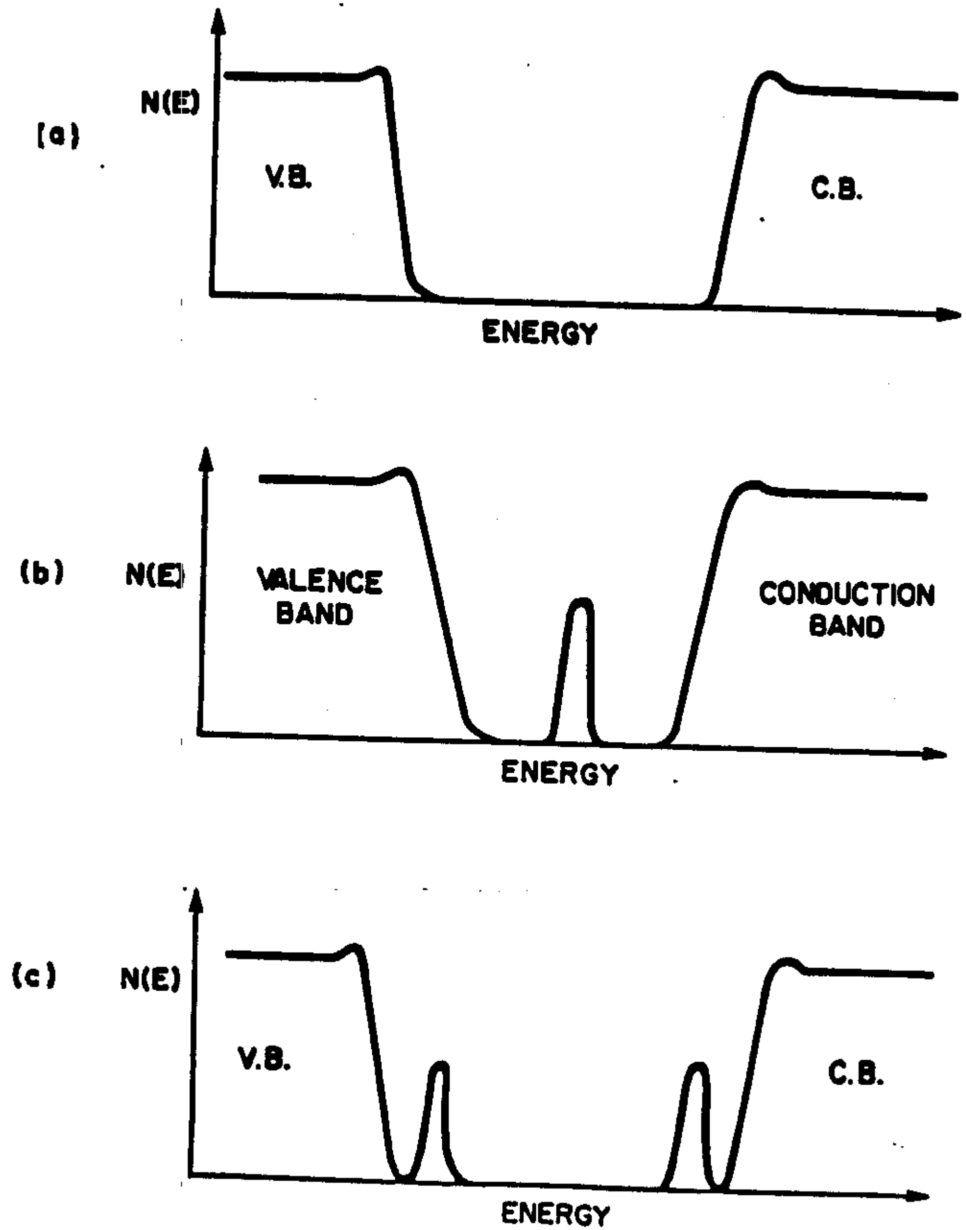




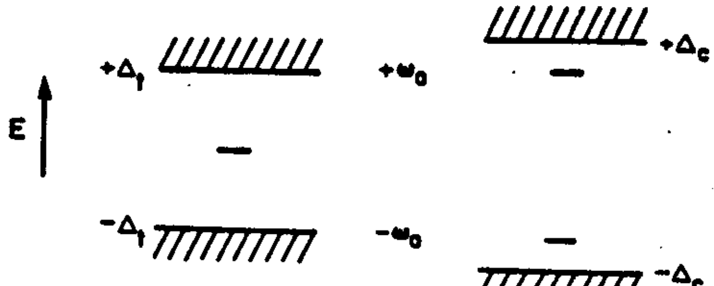
Comparison of electrical conductivities of metals, semiconductors, and insulators: *d* indicates doped material.



Cu-Metal
HMSF / TCNQ
TTF / TCNQ
NMP / TCNQ
Rb
Cs
K
Na
0
100
200
300
400
T [K]

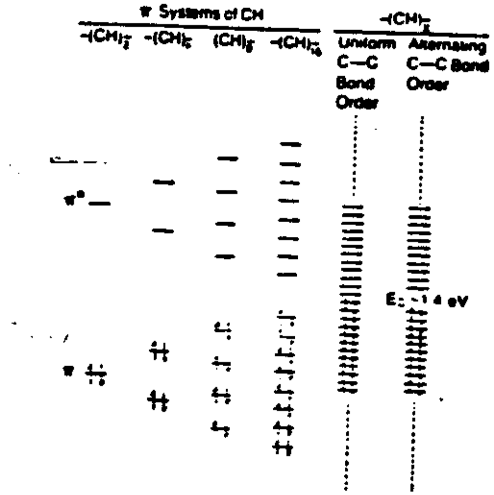


(a)
N(E)
V.B.
C.B.
ENERGY
(b)
N(E)
VALENCE BAND
CONDUCTION BAND
ENERGY
(c)
N(E)
V.B.
C.B.
ENERGY



(a)

(b)

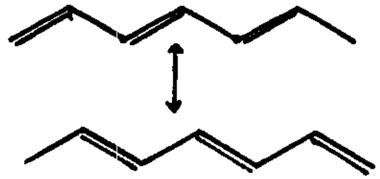


Diagrammatic representation of the energy levels of π MOs with increasing size of the molecule for $[CH]_x$.

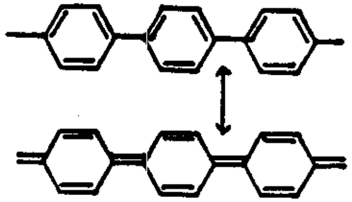
CONJUGATED POLYMERS

SYNTHESES & FORM

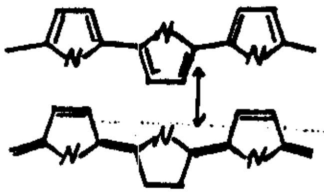
Poly (acetylene) — vapor/film



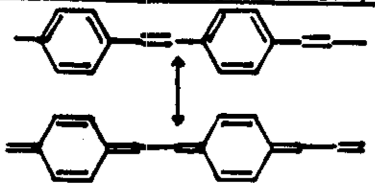
Poly (p-phenylene) — soln/powder

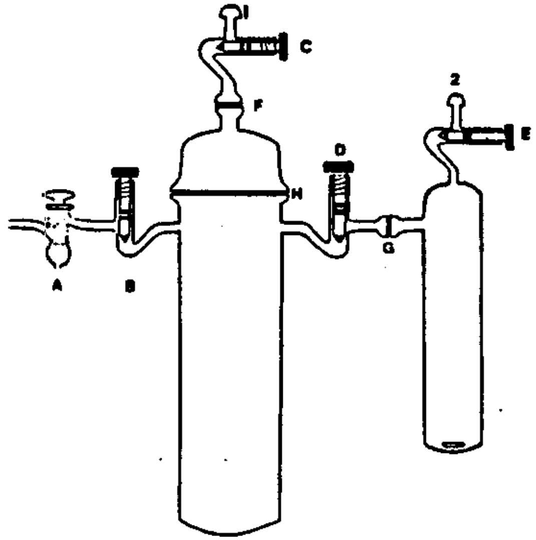


Poly (pyrrole) — e-chem/film

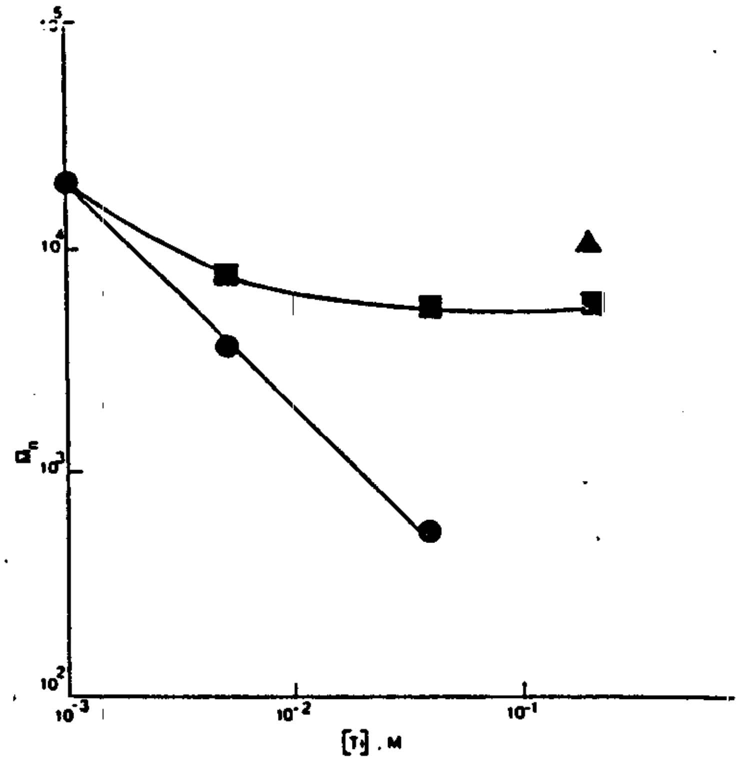


Poly (p-phenylene vinylene) — sol'n/powder, precursor/film

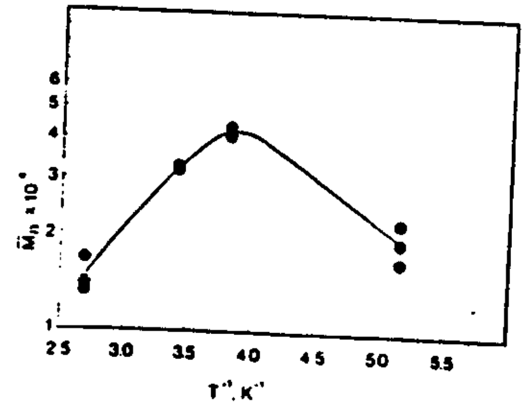




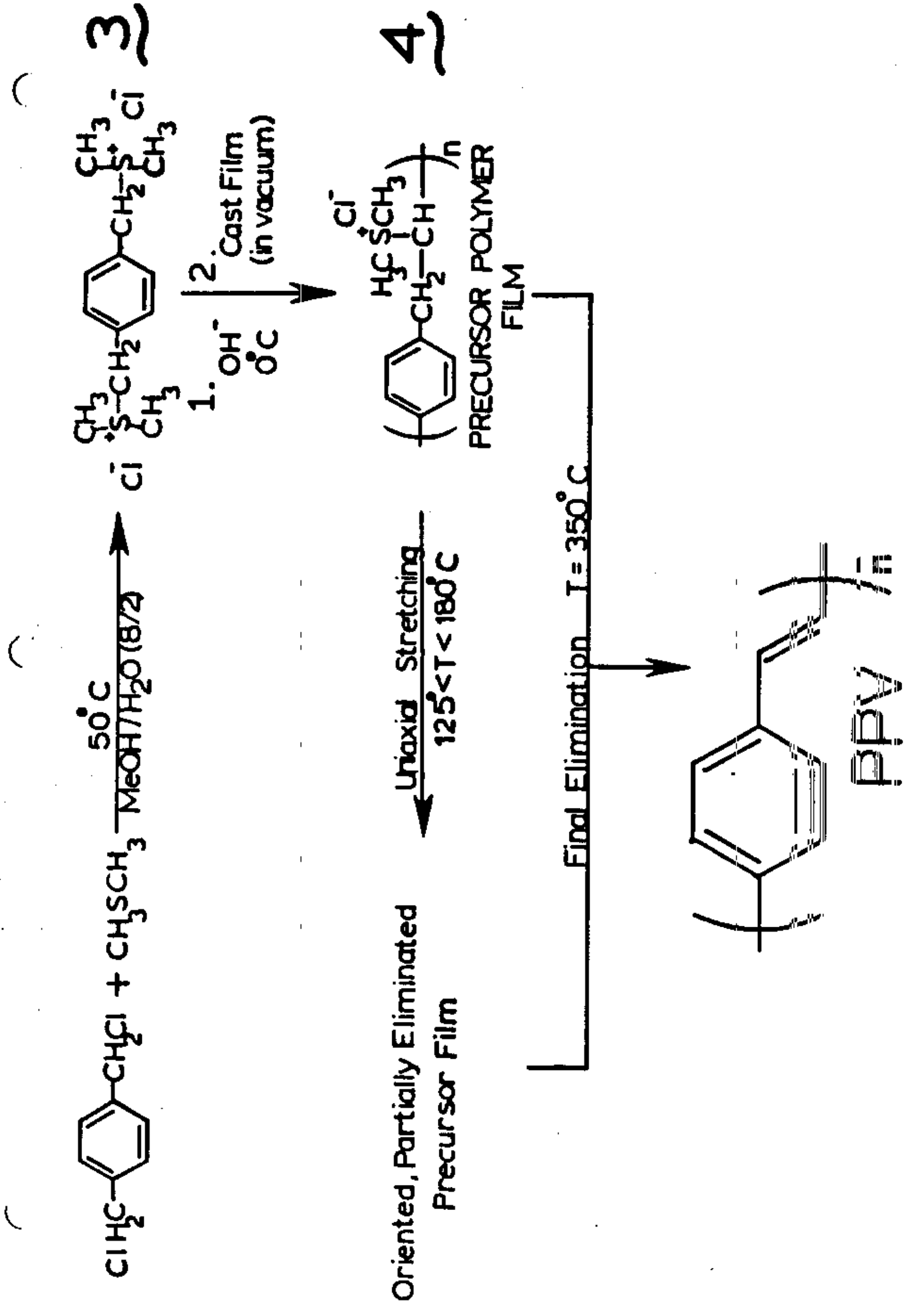
Apparatus for the synthesis of $(CH)_x$ films.



$\bar{D}_n$
10^4
10^3
10^2
10^{-3}
10^{-2}
10^{-1}
[T], M



$\bar{M}_n \times 10^{-4}$
1
2
3
4
5
6
2.5
3.0
3.5
4.0
4.5
5.0
5.5
T^{-1}, K^{-1}



SCHEME 1: Synthesis and Processing of PPV

SHOW AND TELL

$\xrightarrow[\text{2 weeks}]{\text{R.T}}$

m/n ~ 1

FRESHLY CAST

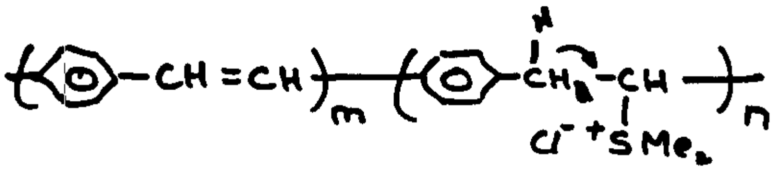
200°C/ 3 hours

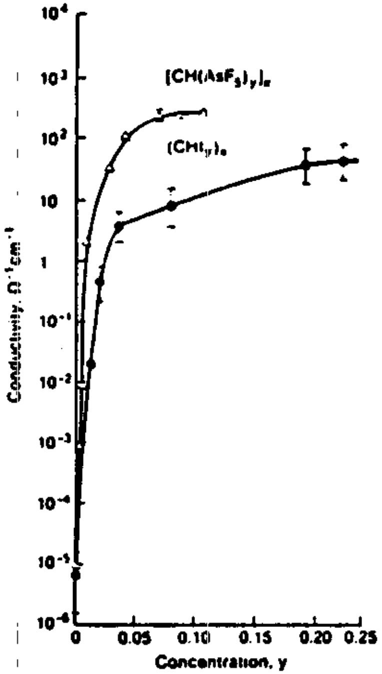
Metallic Opaque Film

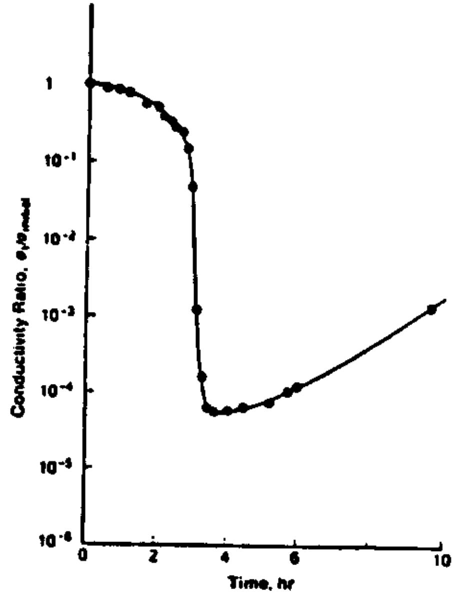
$\xleftarrow[\text{vapor}]{AsF_5-}$

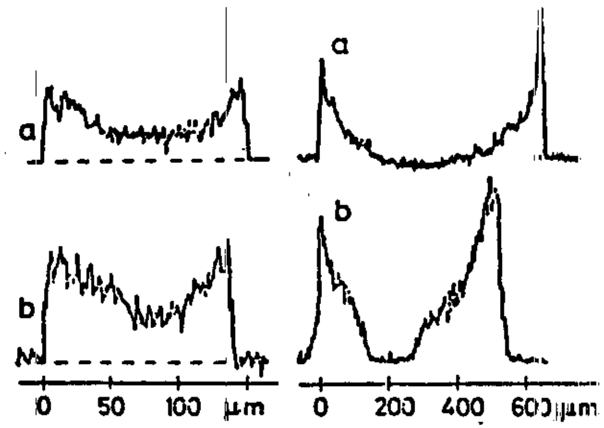
m/n ~ 10

σ ~ 10 S/cm

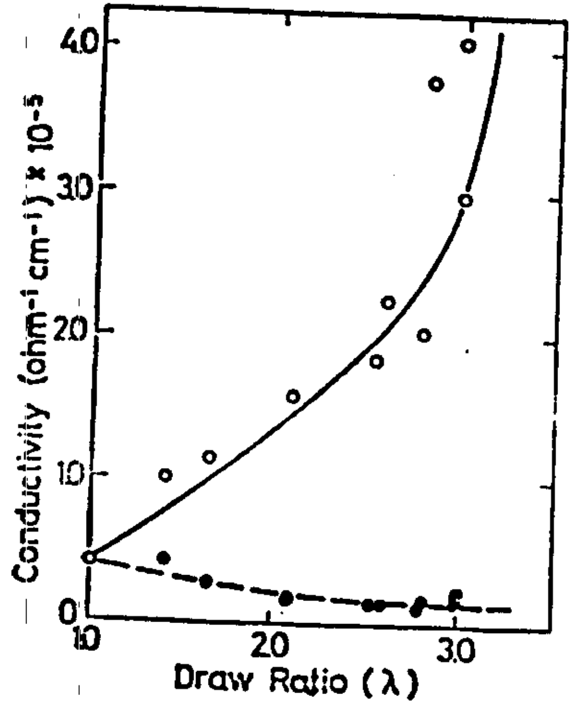



[CH(AsF5)y]x
(CHIy)x
Conductivity, Ω⁻¹cm⁻¹
Concentration, y


Conductivity Ratio
Time, hr

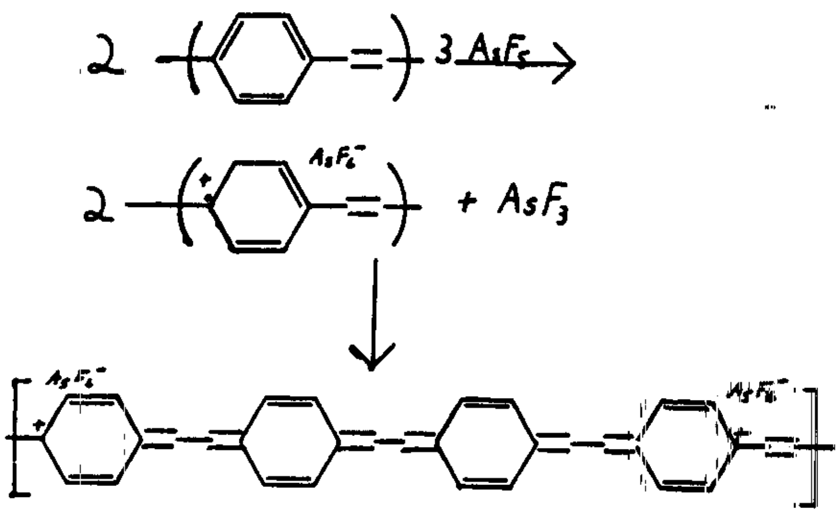


Iodine energy dispersive X-ray analysis profiles of doped polyacetylene of thickness 150 μm (left) and 600 μm (right)



Electrical conductivity of stretch-aligned trans-$(CH)_x$ films as a function of the draw ratio.

AsF_5 DOPING



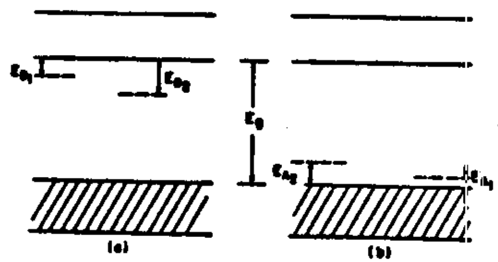
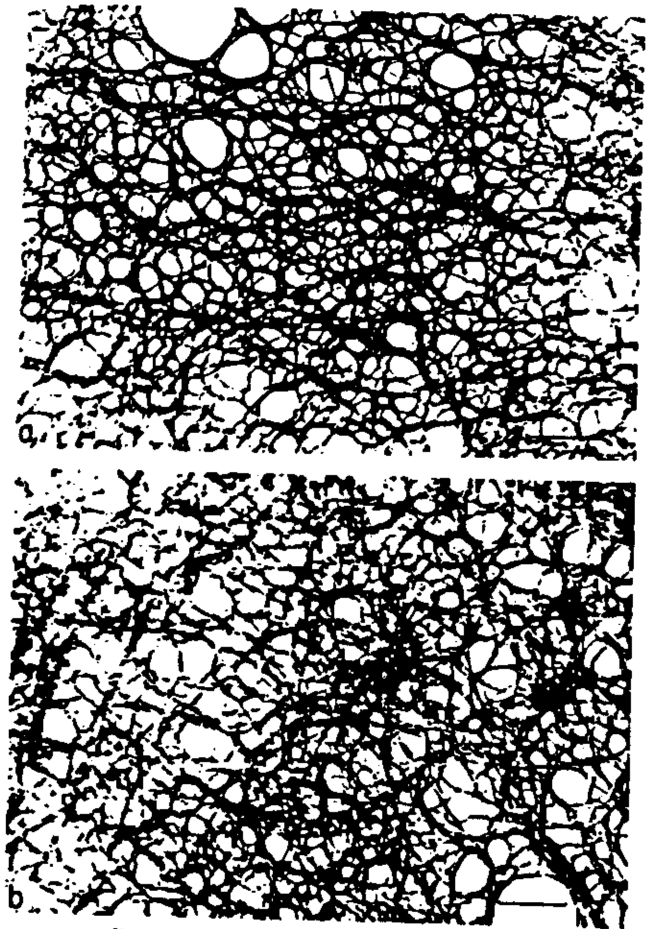
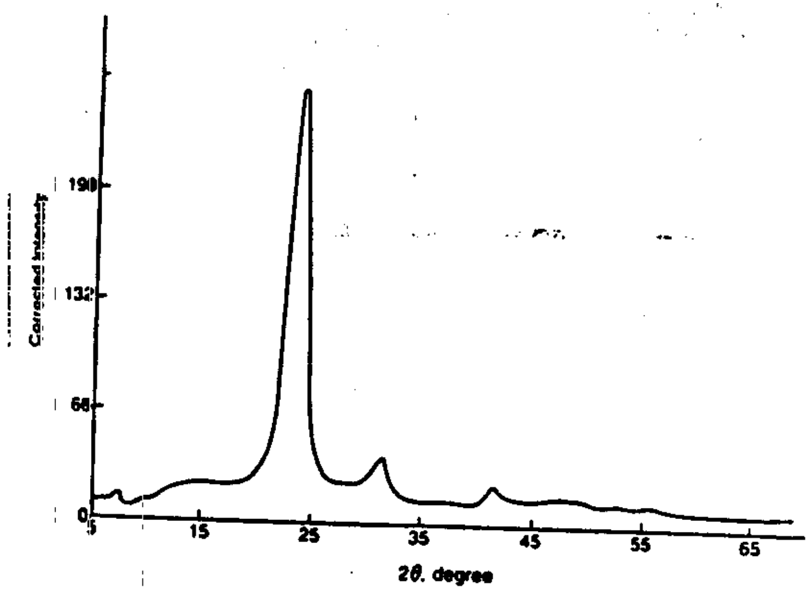


FIG. 8. (a) An energy band diagram for an n-type semiconductor containing two donor centers with different activation energies, E_{D_1} and E_{D_2}; (b) a p-type semiconductor with two different acceptor centers.

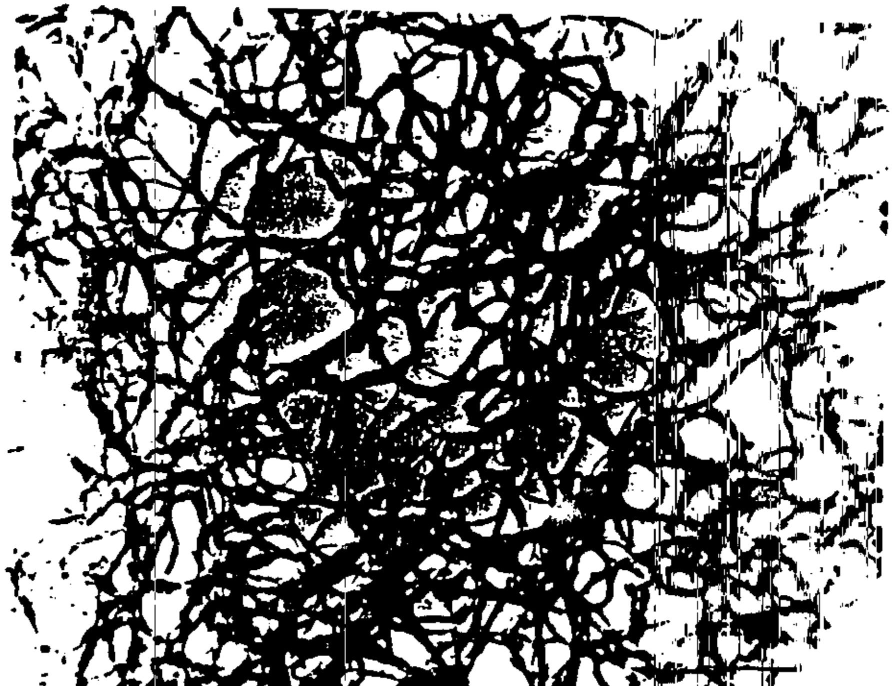


Electron micrograph of an ultrathin *trans*-polyacetylene film. (a) as prepared. (b) after exposure of 30 min to air at room temperature.

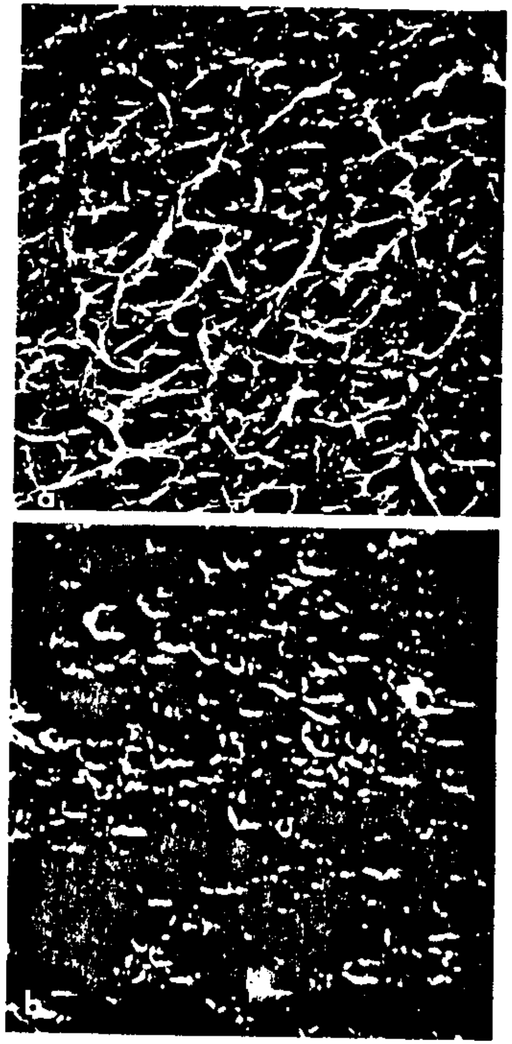
SEM micrographs of thin polyacetylene films polymerized directly onto a gold grid at 760 torr of acetylene for ~ 1 min., dried and sputter coated with 3 nm of gold: (a) ×900, scale bar = 10 μm; (b) ×9000, scale bar = 1 μm; (c) ×60,000, scale bar = 0.1 μm.



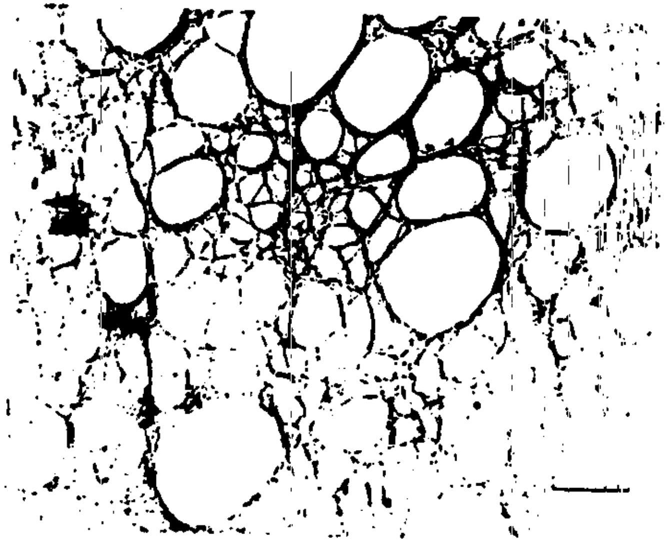
Wide-angle X-ray diffraction patterns for *cis*-polyacetylene film.



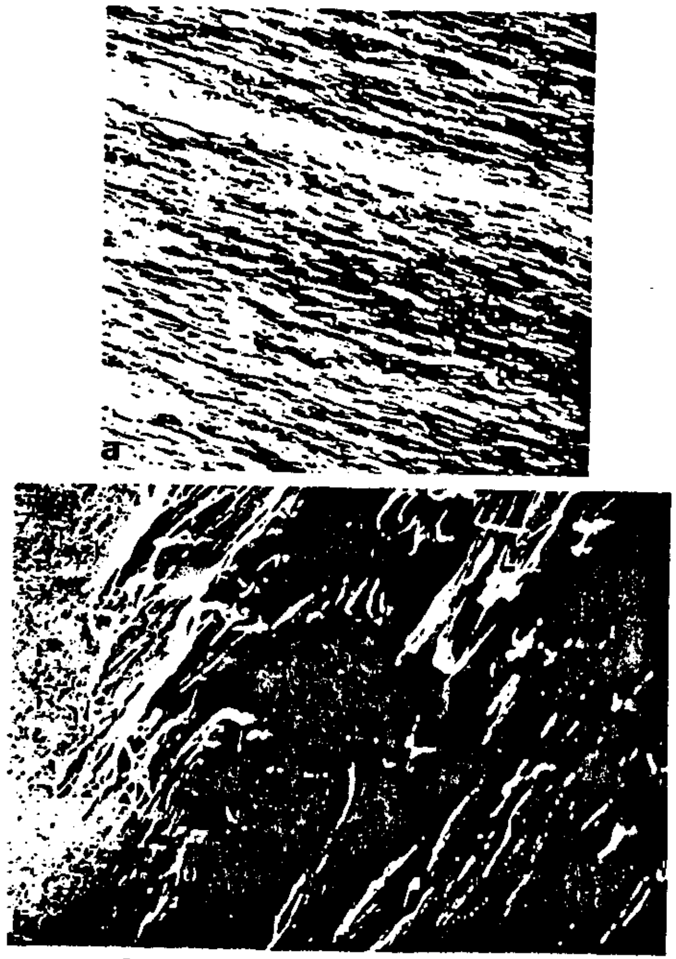
Electron micrograph of nascent polyacetylene polymerized directly onto the EM grid with the Ziegler catalyst. Marker = 500 nm.



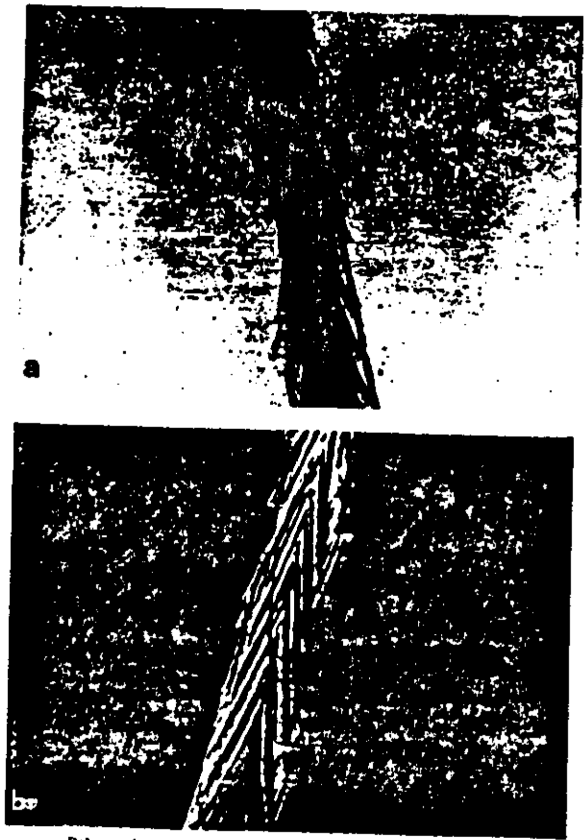
Scanning electron micrographs of free-standing polyacetylene film: (*a*) dull face away from the reactor surface; (*b*) shiny face toward the reactor surface. Magnification 50,000×.



Electron micrograph of nascent *cis*-polyacetylene. Marker is 500 nm.

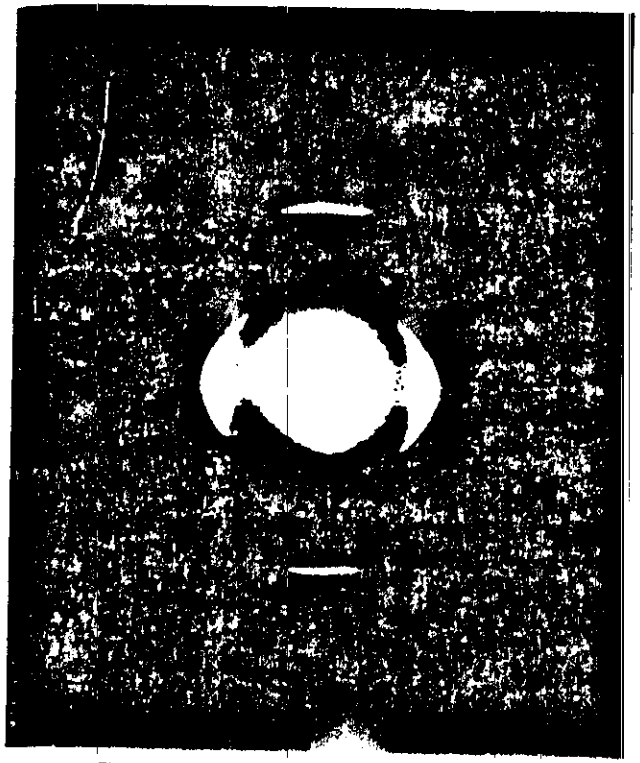


Coextruded polyacetylene film: (a) smooth surface, magnification 5000×; (b) fractured area, magnification 8000×.

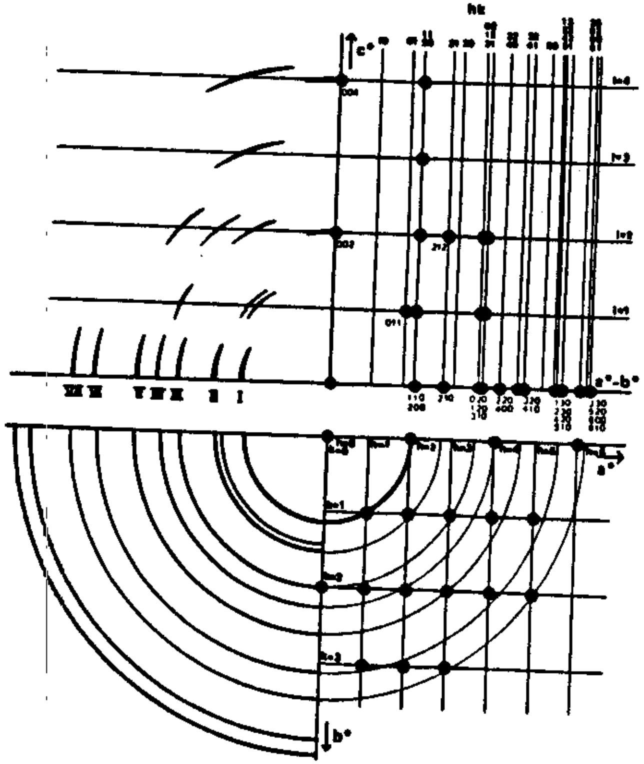


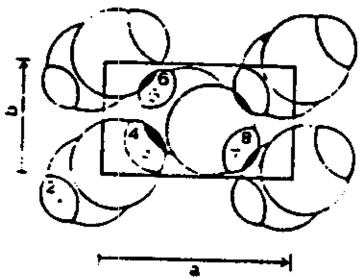
Polyacetylene "whisker": (a) polarizer perpendicular to the long direction, (b) polarizer and analyzer crossed.

Polymerization of acetylene under a hydrodynamic flow field: (a) polymers grown from ends of a magnetic stirring bar, 1.35 × magnification; (b) pieces broken off from the stirrer.

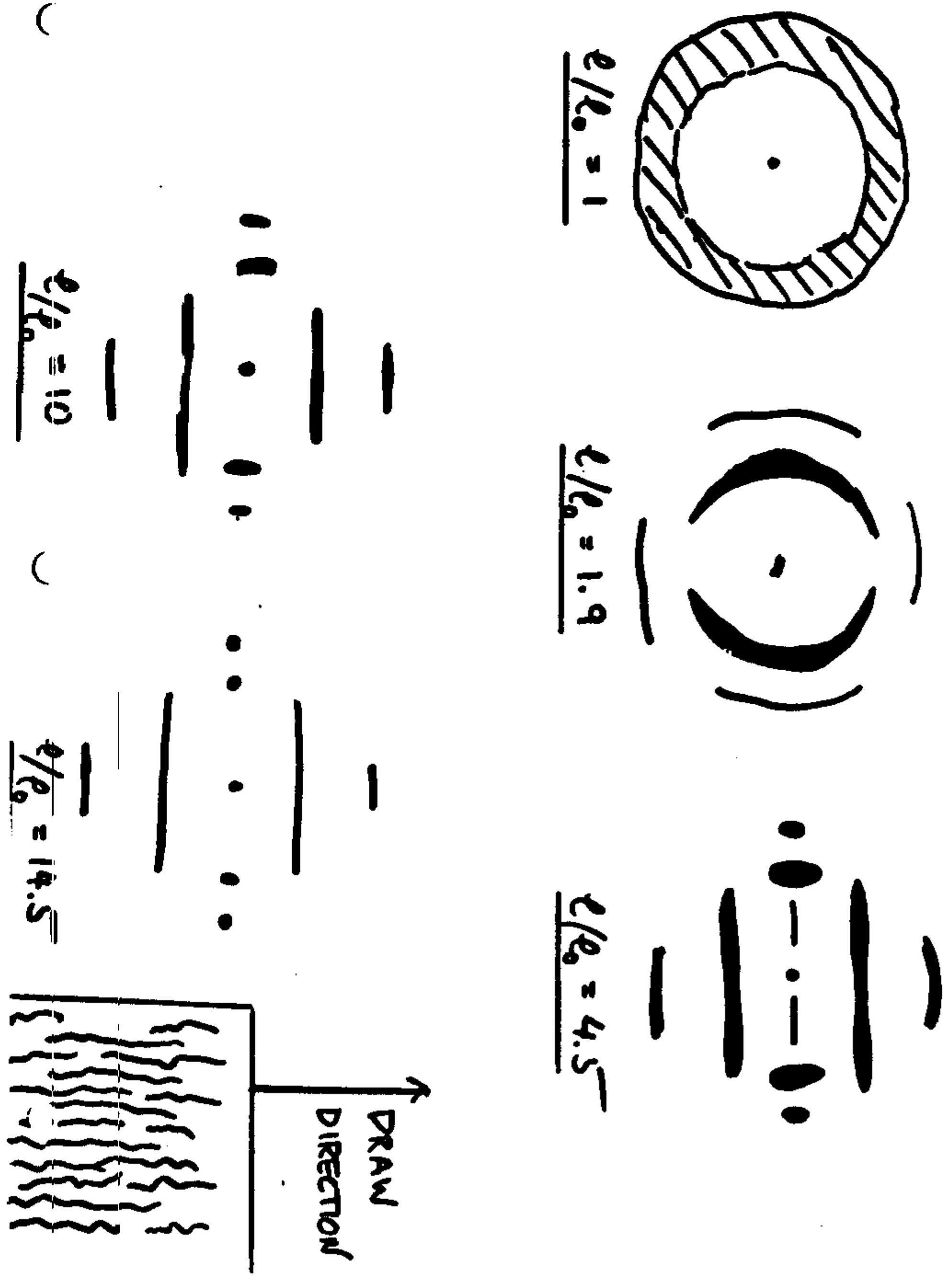


Electron diffraction patterns of aligned fibrils of nascent *cis*-polyacetylene.





Molecular conformation of *cis*-polyacetylene.



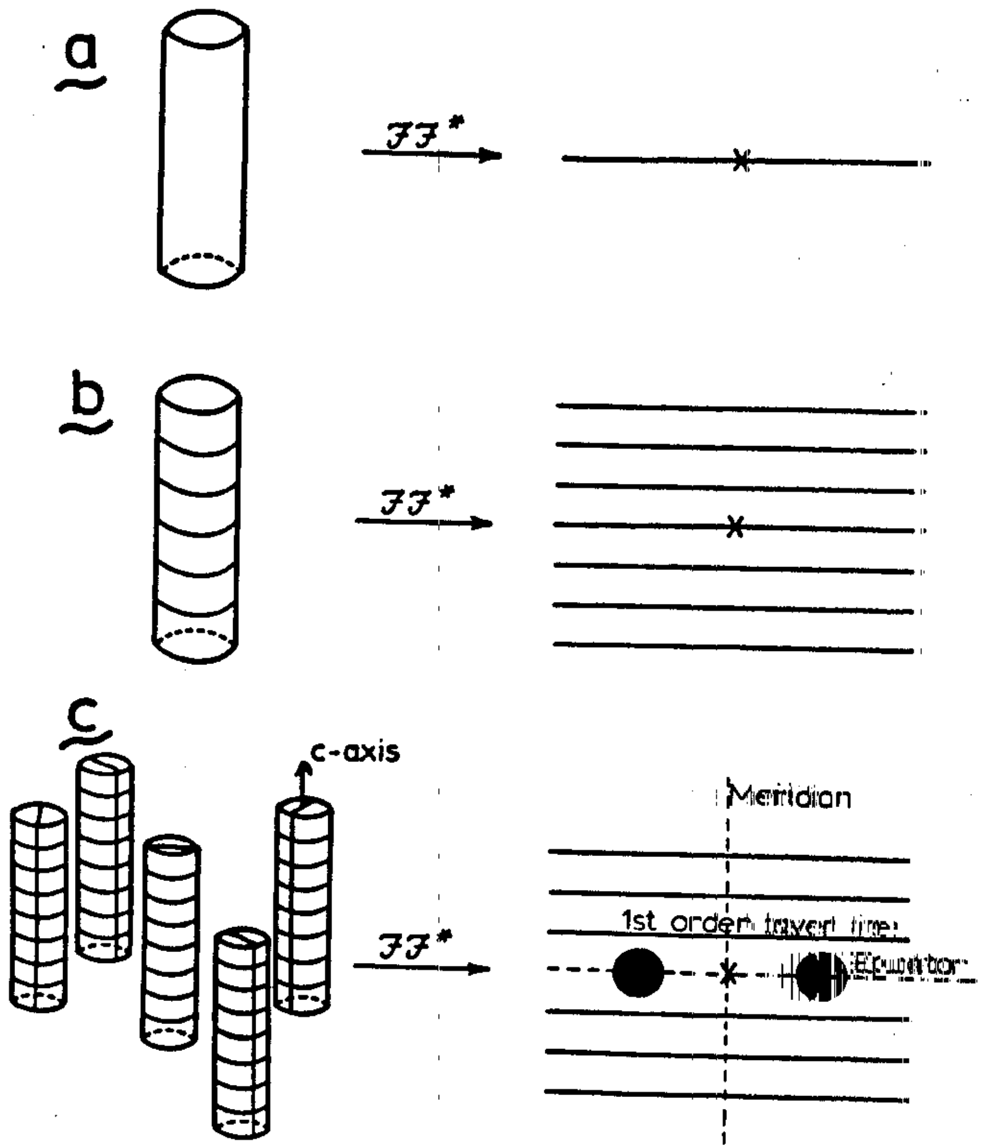


Figure 2

SUMMARY OF STRUCTURES

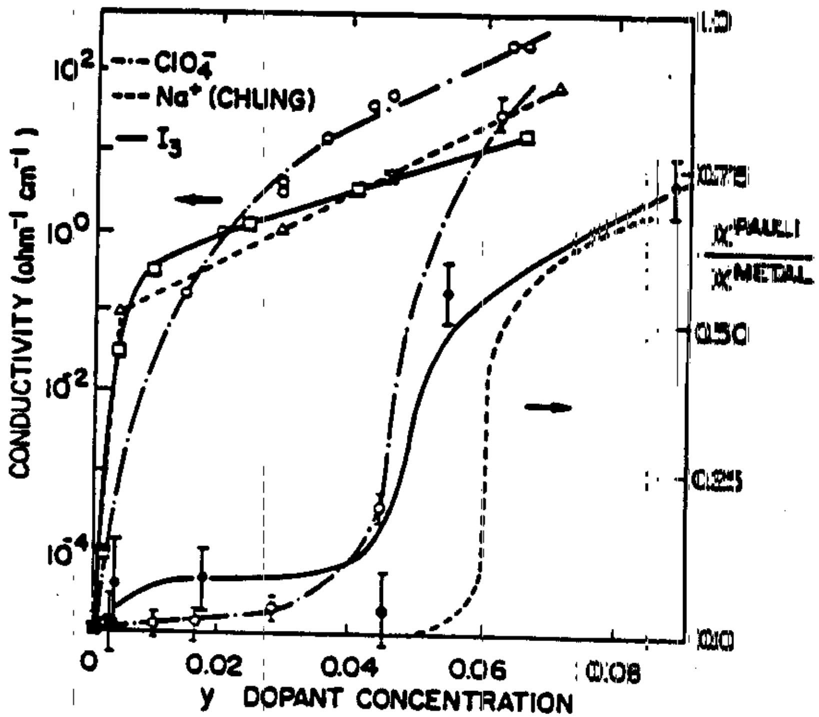
using Me_2S as "plasticizer"

Fibers; Oriented Films

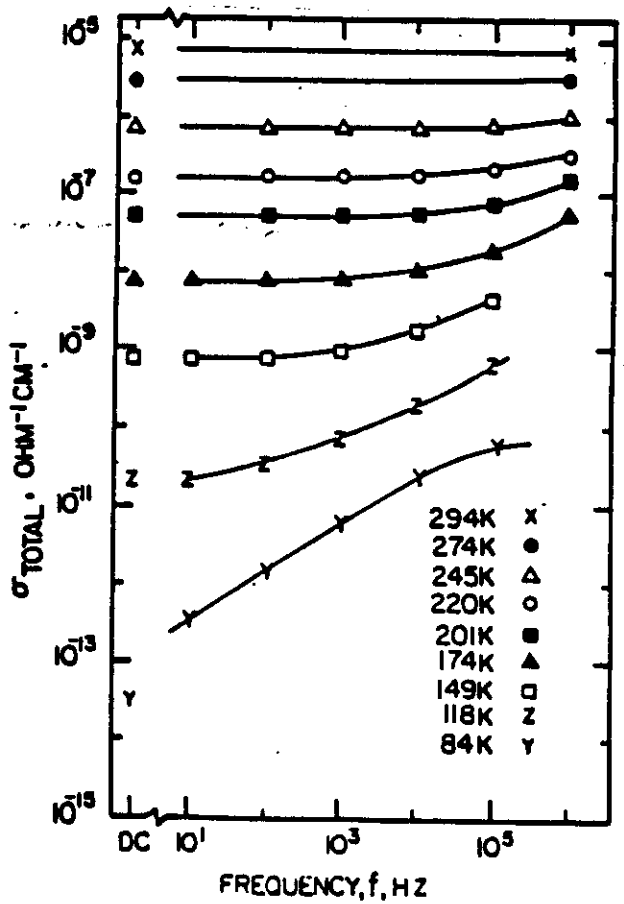
- Drawn at 150–200°C ; air or argon
- Fibrillation at $\ell/\ell_0 > 10$
- Alternative : solid state coextrusion
- Or : drawn from gel

Foams

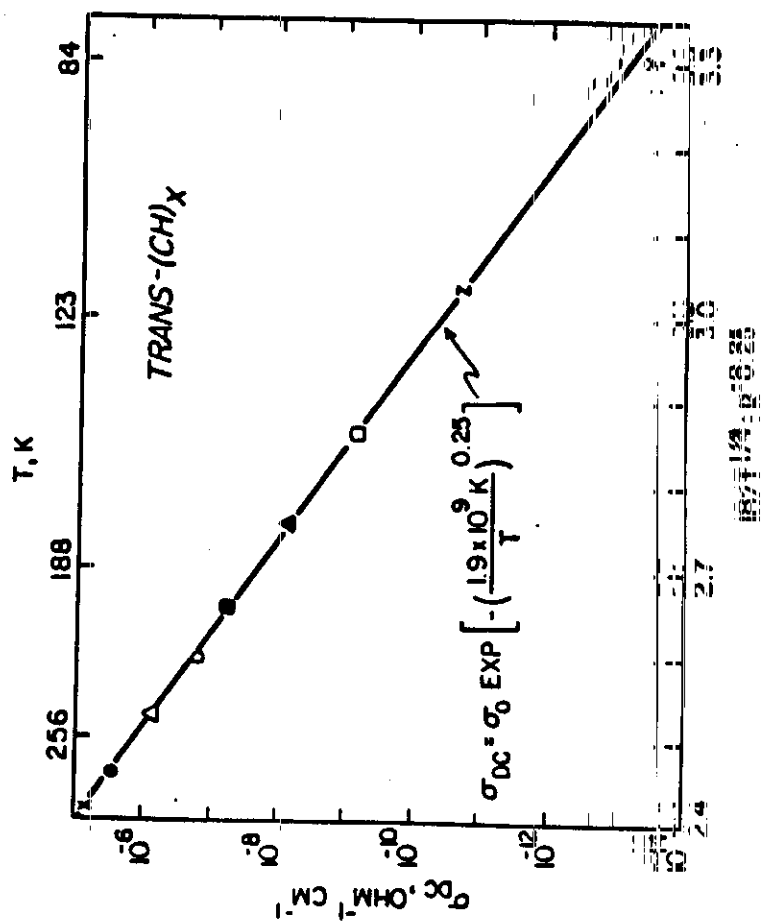
- 600% volume increase ie $\rho \sim 0.2$
- Flexible ; open-celled.

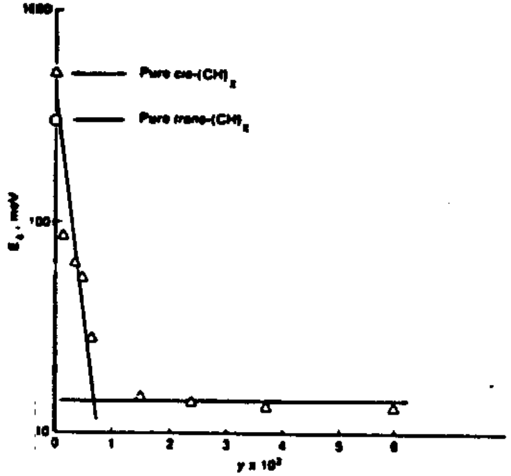


ClO$_4^-$
Na$^+$ (CHUNG)
I$_3$
CONDUCTIVITY (ohm^{-1} cm^{-1})
χ^{PAULI} / χ^{METAL}
y DOPANT CONCENTRATION

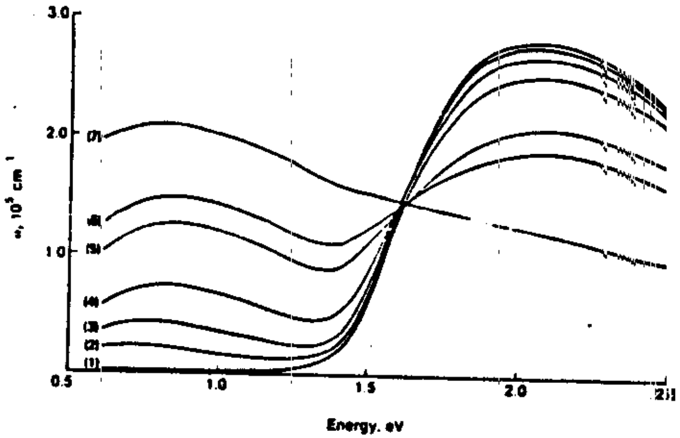


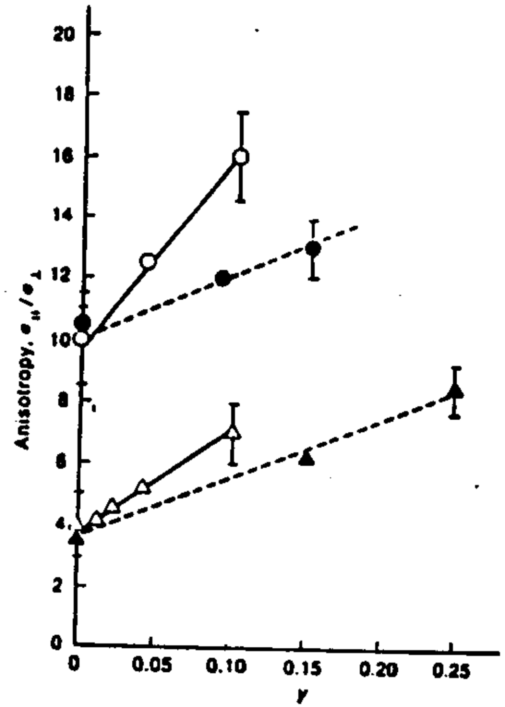
σ_{TOTAL}, OHM^{-1}CM^{-1}
FREQUENCY, f, HZ
294K X
274K ●
245K △
220K ○
201K ■
174K ▲
149K □
118K Z
84K Y

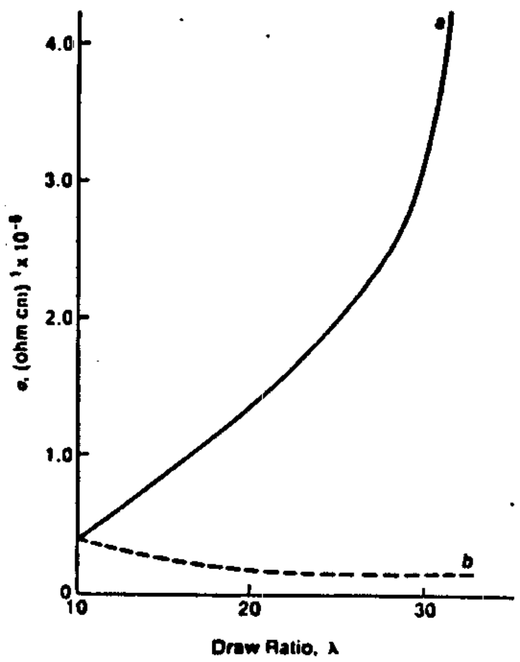




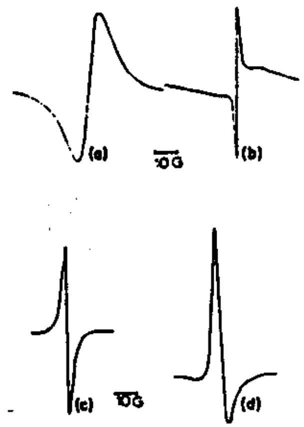
Activation energy for conductivity of *trans*-[CH(SbF$_3$)$_y$]$_x$ as a function of *y*.


3.0
2.0
1.0
0.5
1.0
1.5
2.0
(7)
(6)
(5)
(4)
(3)
(2)
(1)
Energy, eV

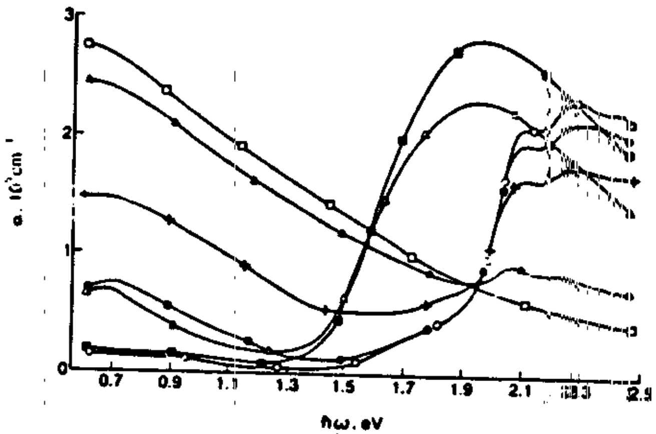

20
18
16
14
12
10
8
6
4
2
0
0.05
0.10
0.15
0.20
0.25
y



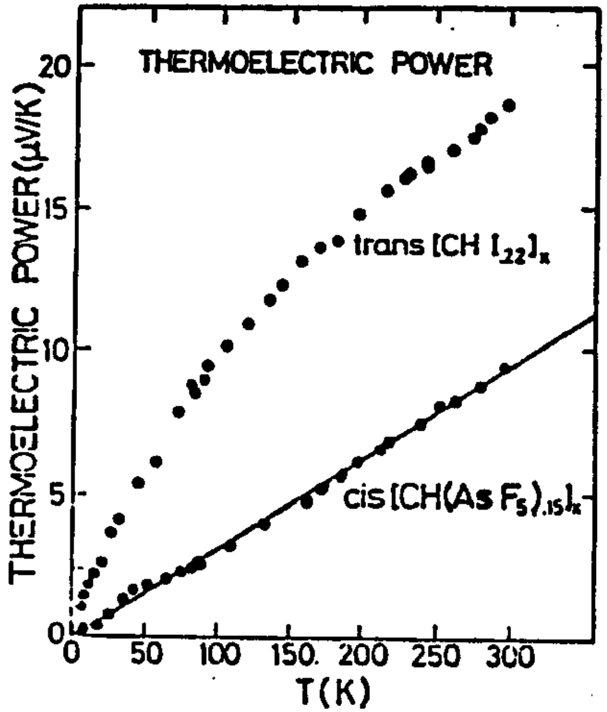
4.0
3.0
2.0
1.0
0
10
20
30
a
b
Draw Ratio, λ



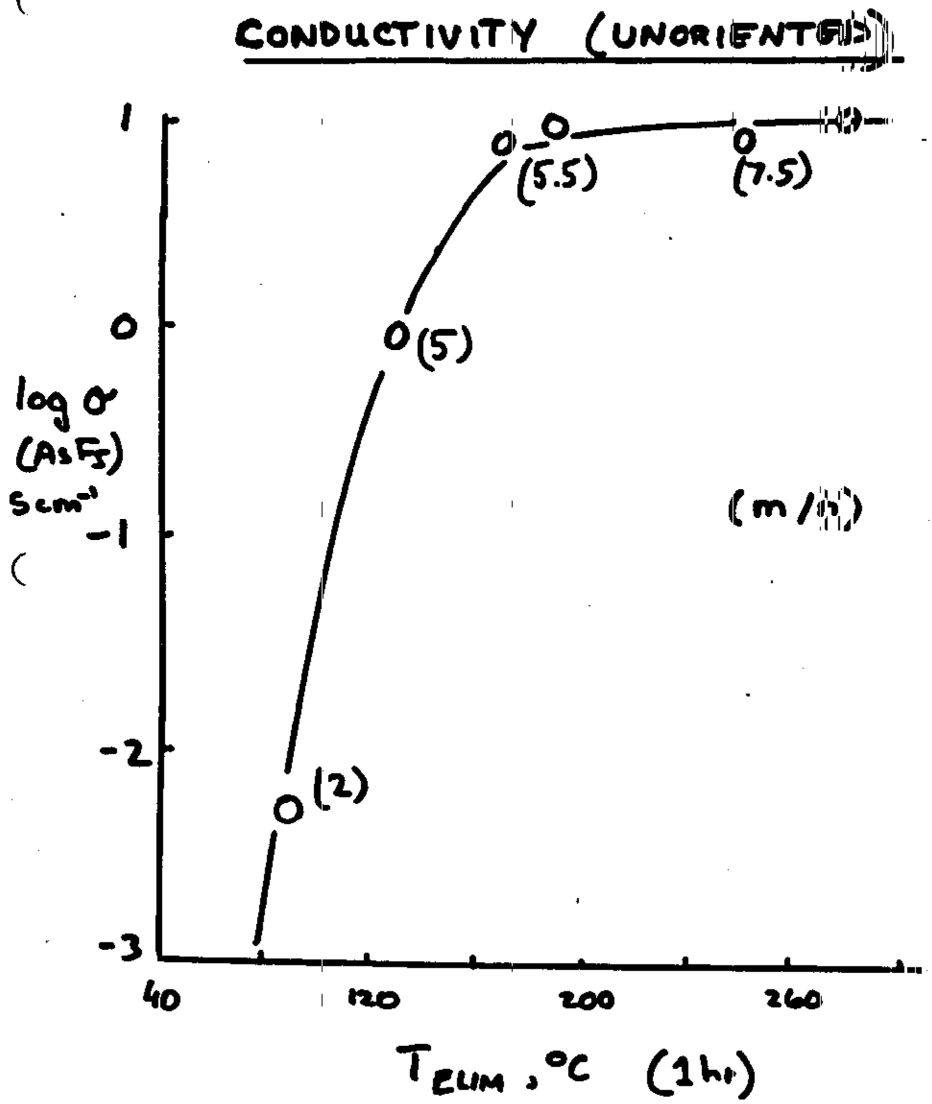
(a)
10G
(b)
(c)
10G
(d)

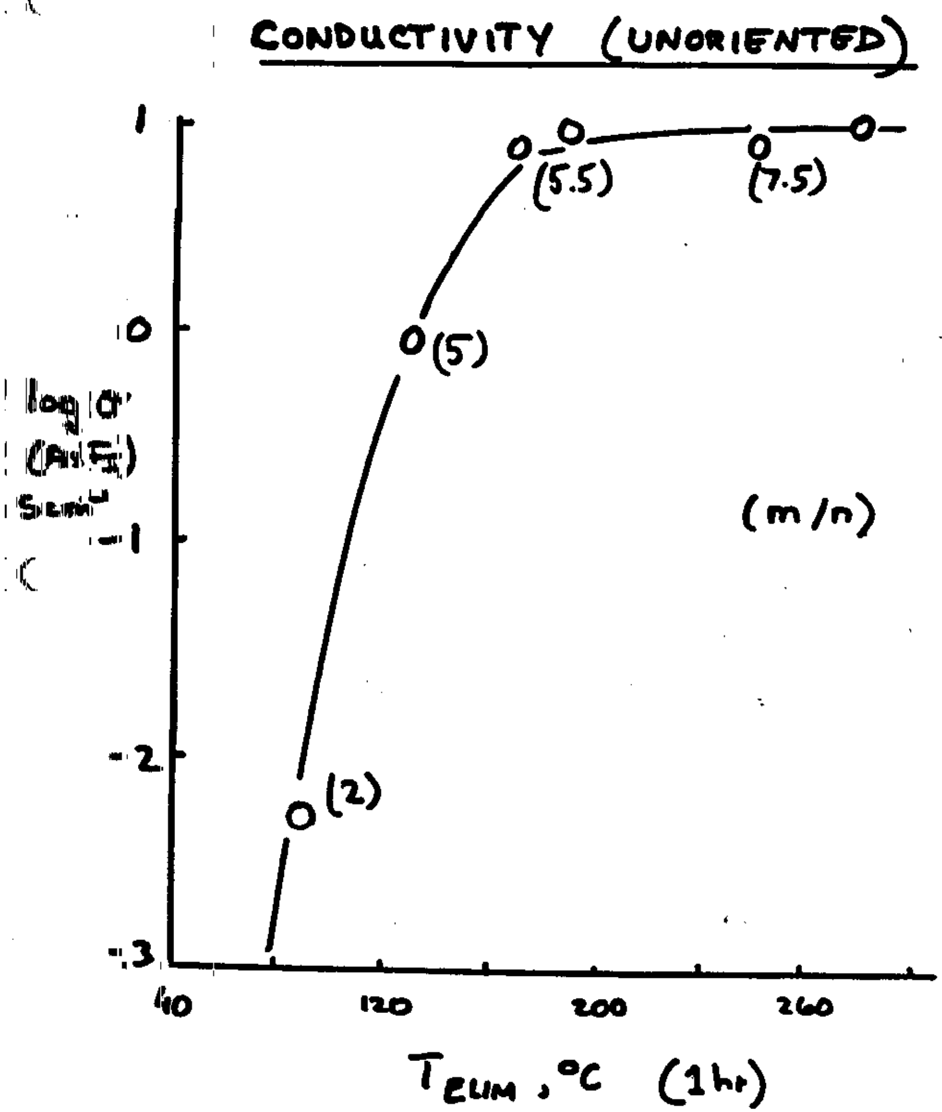


ħω, eV

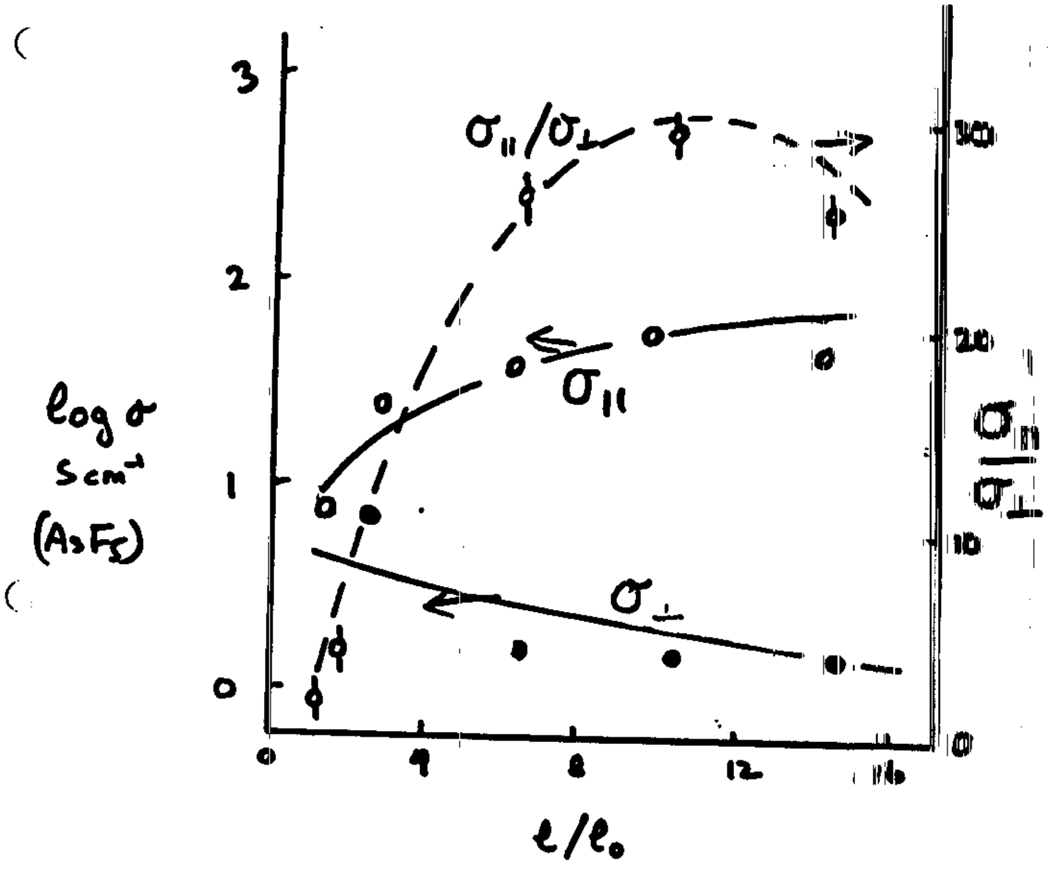


THERMOELECTRIC POWER
THERMOELECTRIC POWER (μV/K)
trans [CH I.22]x
cis [CH(As F5).15]x
T(K)


CONDUCTIVITY (UNORIENTED)
log σ (AsF5) Scm⁻¹
1
0
-1
-2
-3
40
120
200
260
(2)
(5)
(5.5)
(7.5)
(m/n)
T ELIM , °C (1hr)


CONDUCTIVITY (UNORIENTED)
log σ (AsF5) Scm⁻¹
1
0
-1
-2
-3
40
120
200
260
(2)
(5)
(5.5)
(7.5)
(m/n)
T ELIM , °C (1hr)

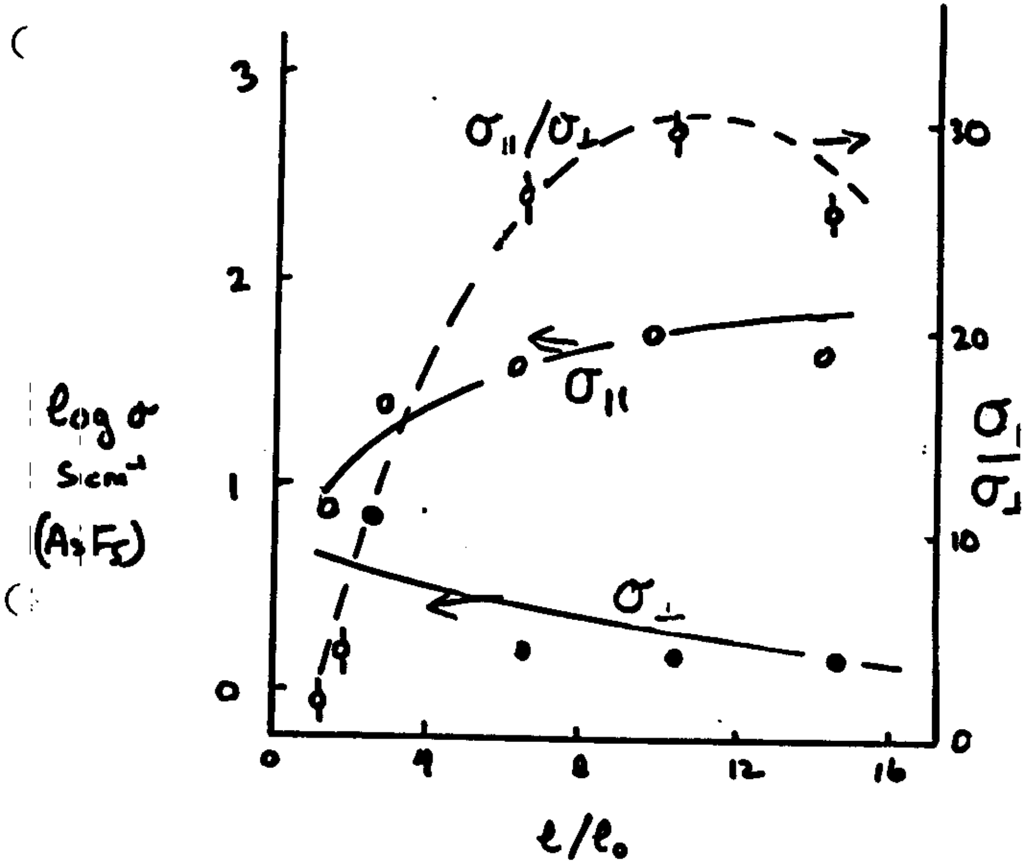
CONDUCTIVITY AND ORIENTATION



- Somewhat higher with H_2SO_4 (results not complete)

- σ (AsF_5: $\ell/\ell_0 \sim 10$) $> 10^3$ (Murase etc Poster P1-51

CONDUCTIVITY AND ORIENTATION



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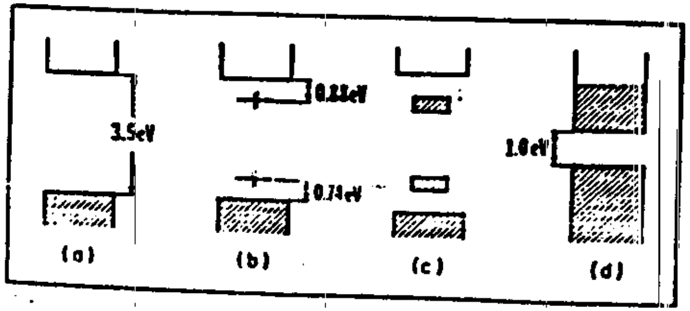
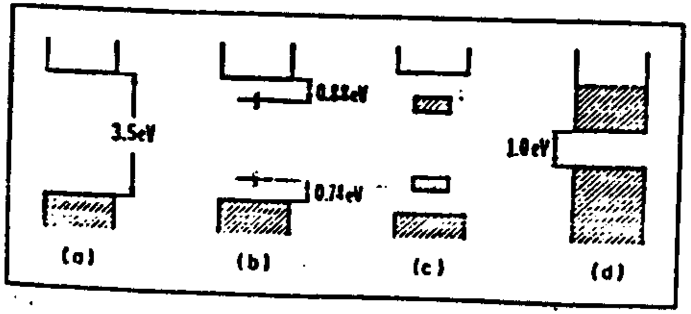
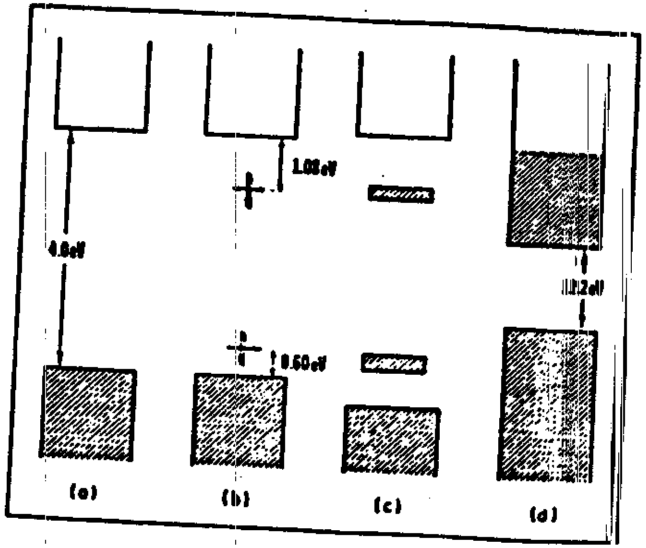


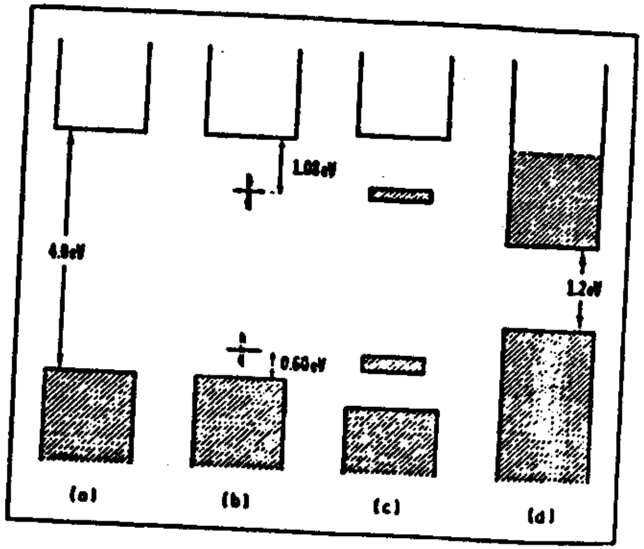
3.5eV
0.88eV
0.74eV
1.0eV
(a)
(b)
(c)
(d)



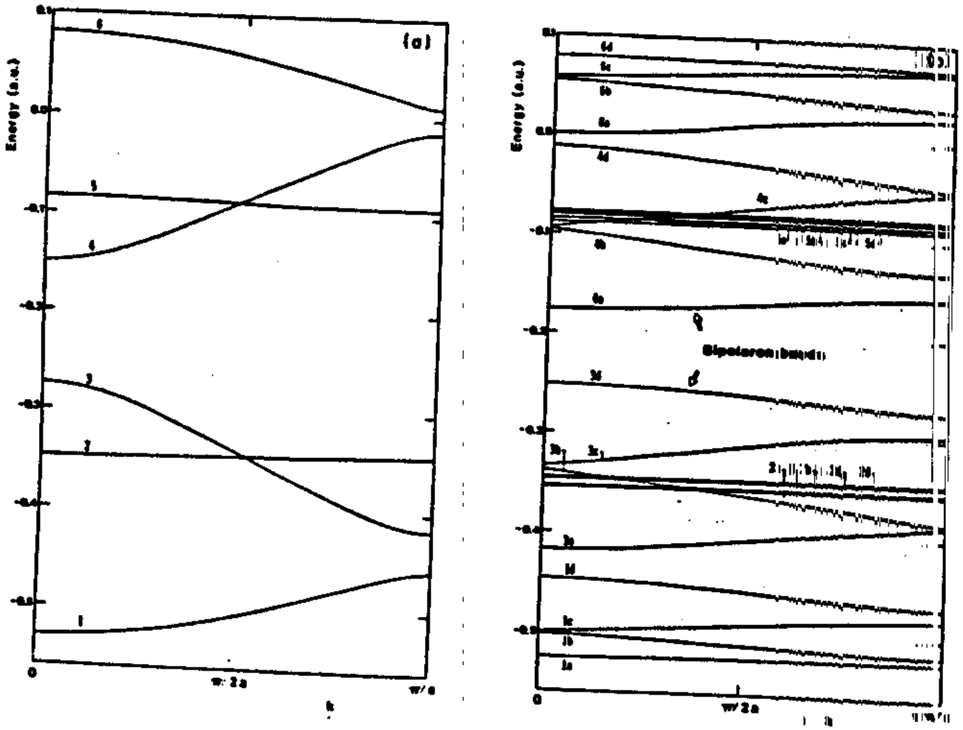
3.5eV
0.88eV
0.74eV
1.0eV
(a)
(b)
(c)
(d)

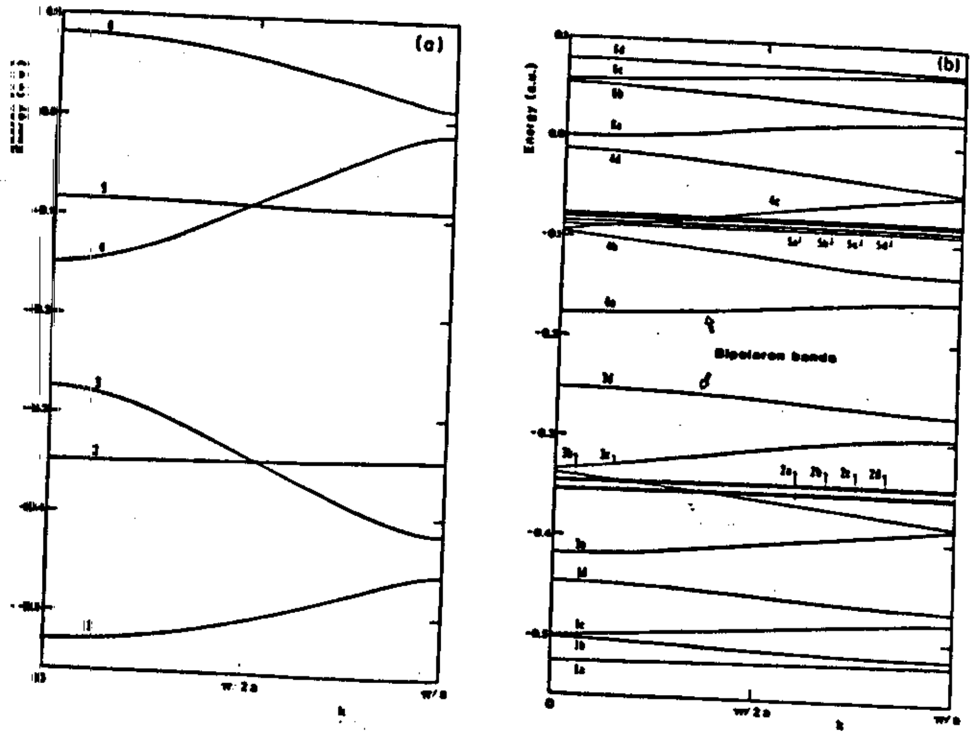


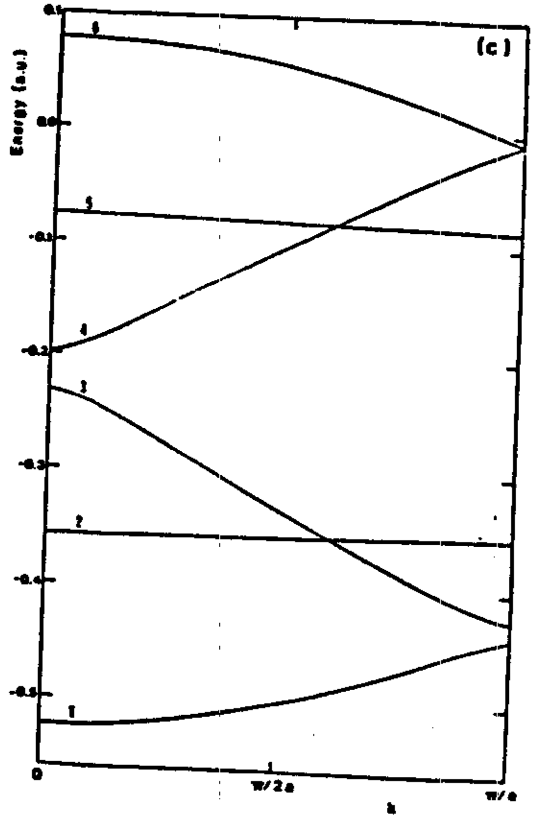
4.8eV
1.08eV
0.60eV
1.2eV
(a)
(b)
(c)
(d)

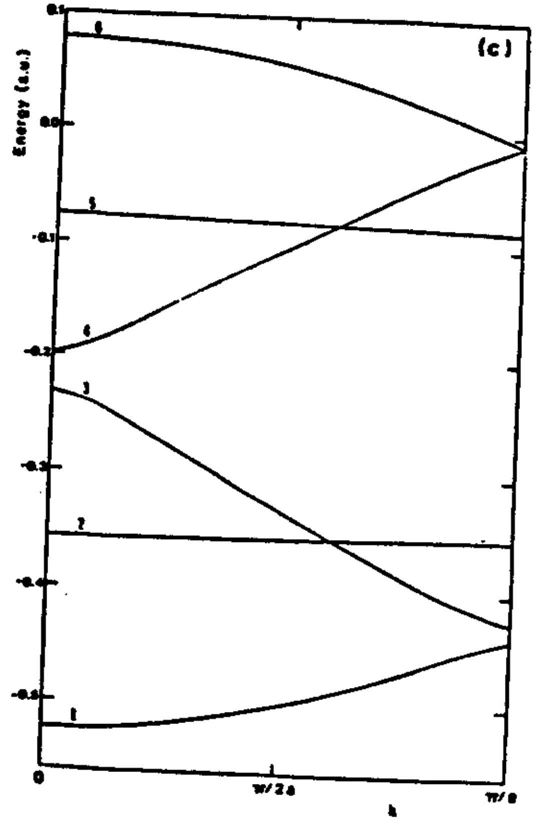


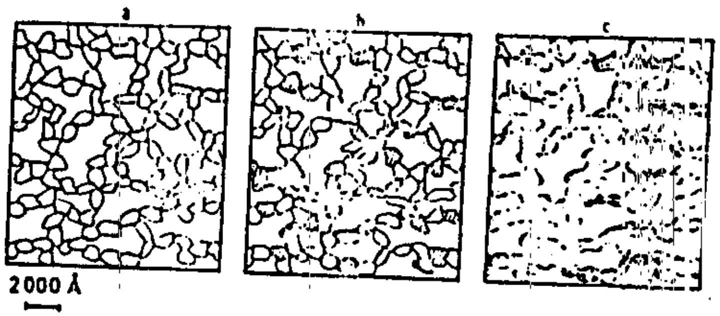
4.8eV
1.08eV
0.60eV
1.2eV
(a)
(b)
(c)
(d)

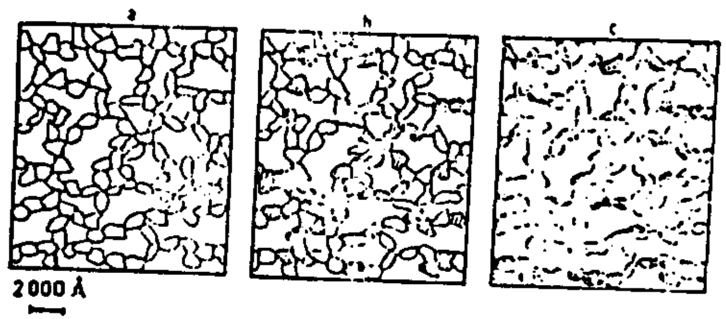

(a)
Energy (a.u.)
(b)
Bipolaron bands
π/2a
k
π/a

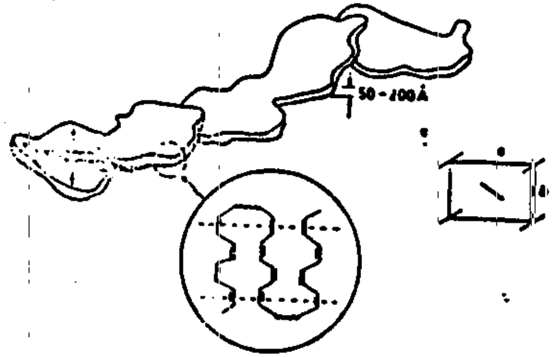

(a)
(b)
Energy (a.u.)
Bipolaron bands
π/2a
k
π/a

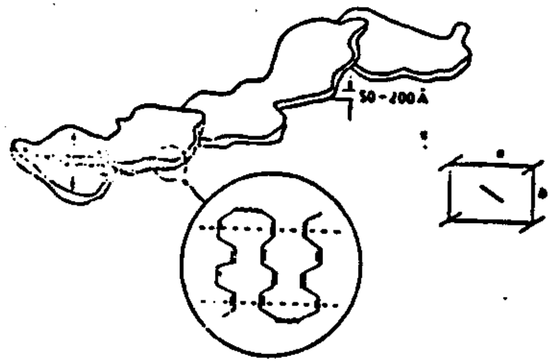

(c)
Energy (a.u.)
0.1
0.0
-0.1
-0.2
-0.3
-0.4
-0.5
1
2
3
4
5
6
0
π/2a
π/a
k

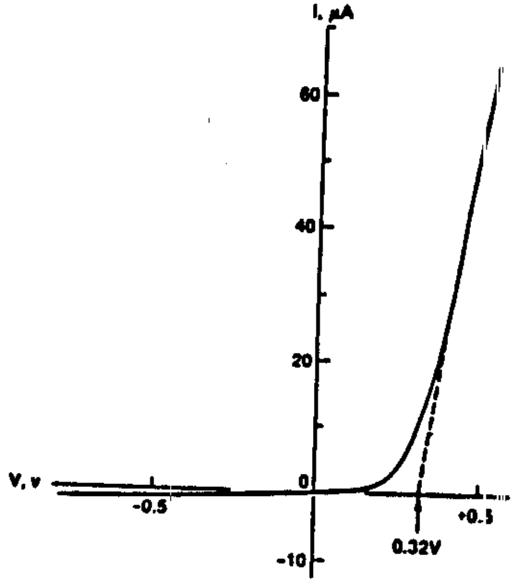

(c)
Energy (a.u.)
0.1
0.0
-0.1
-0.2
-0.3
-0.4
-0.5
1
2
3
4
5
6
0
π/2a
π/a
k


a
c
2000 Å

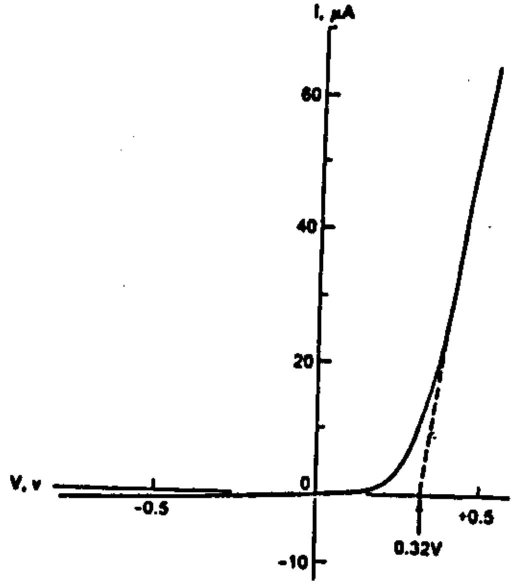

a
c
2000 Å


50-100Å

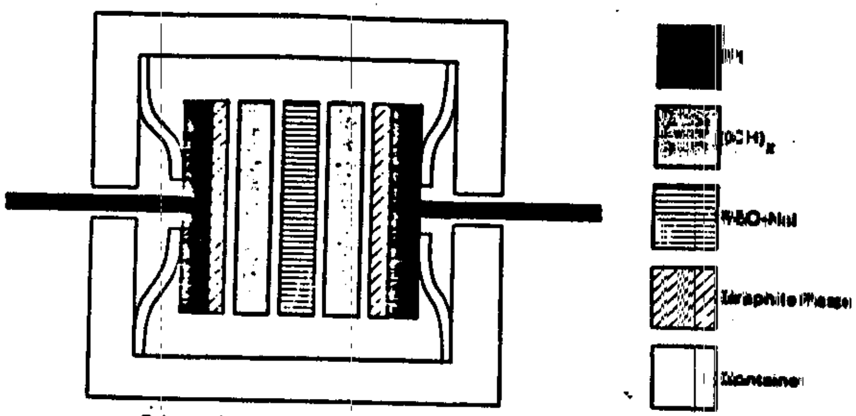

50-100Å



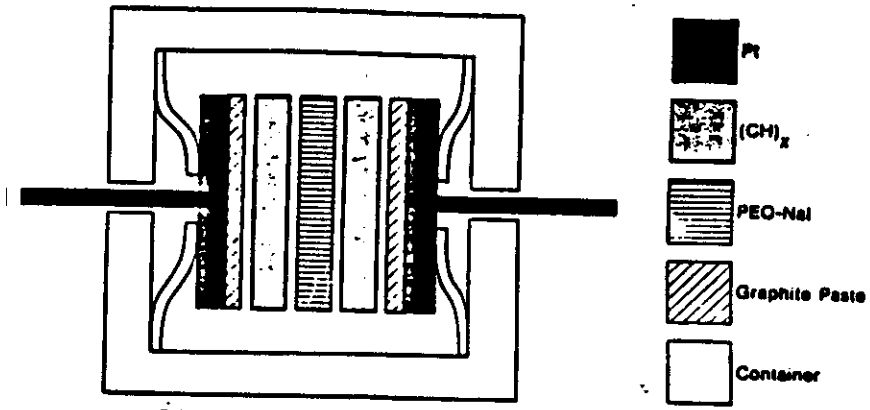
I–V characteristic of a lightly doped $[CH(AsF_5)_y]_x$:In.



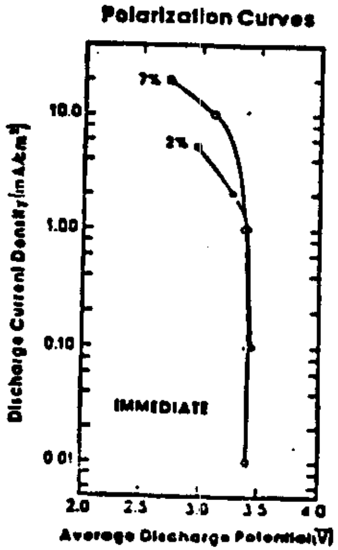
I–V characteristic of a lightly doped $[CH(AsF_5)_y]_x$:In.

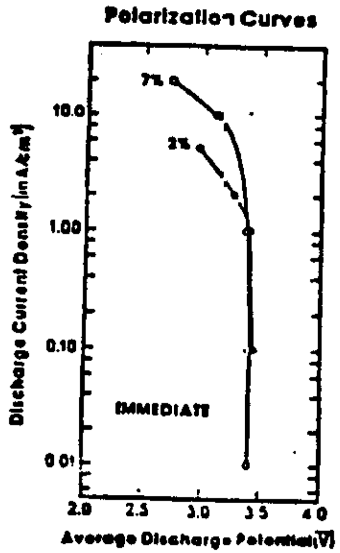


Schematic structure of an all-polymeric solid-state battery.



Schematic structure of an all-polymeric solid-state battery.


Polarization Curves
Discharge Current Density (mA/cm²)
Average Discharge Potential (V)
7%
2%
IMMEDIATE
10.0
1.00
0.10
0.01
2.0
2.5
3.0
3.5
4.0


Polarization Curves
Discharge Current Density (mA/cm²)
Average Discharge Potential (V)
7%
2%
IMMEDIATE
10.0
1.00
0.10
0.01
2.0
2.5
3.0
3.5
4.0