

11<sup>th</sup> International Seminar on the Commercial  
Applications for Inherently Conductive Polymers  
Pittsburgh, October 6-7 2004

---

# **Solvent Processable Conducting Block Copolymers Based On Poly(3,4-ethylenedioxythiophene)**

**Silvia Luebben**, Shawn Sapp, Emily  
Chang, Raechelle D'Sa, Brian Elliott,  
Wallace Ellis

# Report Documentation Page

Form Approved  
OMB No. 0704-0188

Public reporting burden for the collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden, to Washington Headquarters Services, Directorate for Information Operations and Reports, 1215 Jefferson Davis Highway, Suite 1204, Arlington VA 22202-4302. Respondents should be aware that notwithstanding any other provision of law, no person shall be subject to a penalty for failing to comply with a collection of information if it does not display a currently valid OMB control number.

1. REPORT DATE <b>OCT 2004</b>		2. REPORT TYPE		3. DATES COVERED <b>00-00-2004 to 00-00-2004</b>	
4. TITLE AND SUBTITLE <b>Solvent Processable Conducting Block Copolymers Based on Poly(3,4-ethylenedioxythiophene)</b>				5a. CONTRACT NUMBER	
				5b. GRANT NUMBER	
				5c. PROGRAM ELEMENT NUMBER	
6. AUTHOR(S)				5d. PROJECT NUMBER	
				5e. TASK NUMBER	
				5f. WORK UNIT NUMBER	
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) <b>TDA Research Inc,12345 West 52nd Avenue,Wheat Ridge,CO,80033-1916</b>				8. PERFORMING ORGANIZATION REPORT NUMBER	
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)				10. SPONSOR/MONITOR'S ACRONYM(S)	
				11. SPONSOR/MONITOR'S REPORT NUMBER(S)	
12. DISTRIBUTION/AVAILABILITY STATEMENT <b>Approved for public release; distribution unlimited</b>					
13. SUPPLEMENTARY NOTES <b>The original document contains color images.</b>					
14. ABSTRACT					
15. SUBJECT TERMS					
16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT	18. NUMBER OF PAGES <b>26</b>	19a. NAME OF RESPONSIBLE PERSON
a. REPORT <b>unclassified</b>	b. ABSTRACT <b>unclassified</b>	c. THIS PAGE <b>unclassified</b>			

# Acknowledgements

---

- Shawn Sapp
- Emily Chang
- Carolina Wilson
- Raechelle D'Sa
- Brian Elliott
- Wallace Ellis



- NSF
- Air Force
- NIH
- TDA Research

# TDA Research

---

- Began operations in 1987
- 65 Full-time technical staff
- \$ 9.6 Million annual revenue
- 50,000 ft<sup>2</sup> Total facility
- Performs contract R&D
- 15 patents, 29 pending applications
- Commercializes technology by
  - Internal business units
  - Joint ventures
  - Licensing



# Outline

---

- **Problems with ICP commercialization**
- **Processing: current approaches**
- **TDA's approach**
- **PEDOT-PEG block copolymers**
- **Other conducting block copolymers**
- **Concluding remarks**

# ICPs in Numbers

---

- **Discovered in the late 70's**
- **Ten thousands of scientific papers published since discovery**
- **Some 40,000 patents filed since 1976**
- **Nobel Prize awarded in 2000**
- **Only a few commercial applications with limited markets**
- **North America ICP sales were \$140 million in 2003 and are projected to be \$610 million in 2008 (Conductive Polymers, BCC Report 2003)**

# ICP Problems

---

1. **Metallic conductivity is difficult to achieve**
2. **Dark in color**
3. **Poor long-term and thermal stability**
4. **Difficult processing**
  - ➔ Rigid rod chains
    - DON'T FLOW & DON'T MELT
  - ➔ Poly(ionic) chains with intercalated counterion
    - DON'T DISSOLVE

# TDA's Objectives

---

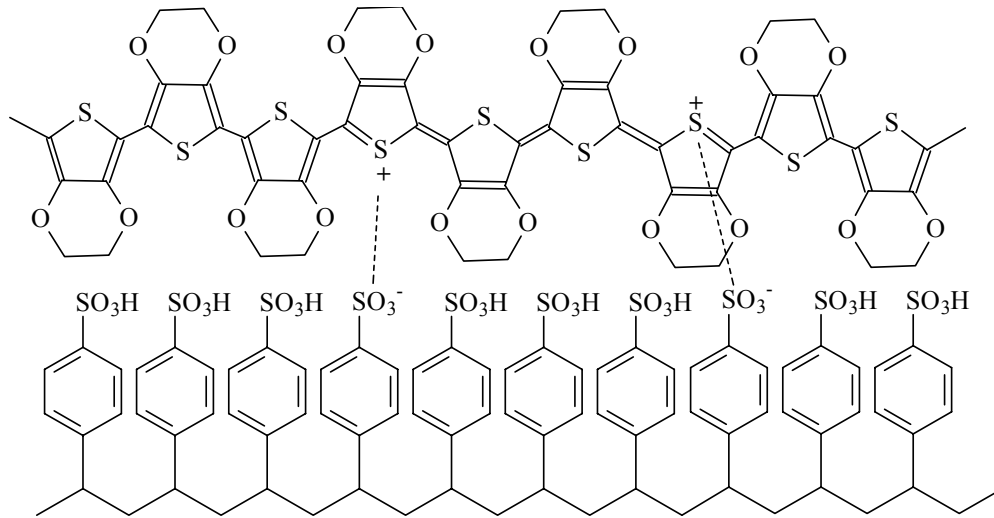
- **Develop new practical processing methods for existing ICPs**
- **Increase versatility and global use of ICPs**
- **Focus on PEDOT:**
  - Offer a range of solvents
  - Avoid a large excess of polyelectrolyte
  - Reduce hygroscopic and acidic properties
- **Also polypyrrole:**
  - Stimuli-responsive biodegradable biomaterial

# Current ICP Processing Methods

---

- From undoped state / post processing doping
- *In Situ* polymerization
- Fancy solvents, cosolvents, dopants
- Oligomer approach
- Dispersion techniques

# PEDOT/PSS Dispersion (Baytron<sup>®</sup> P)

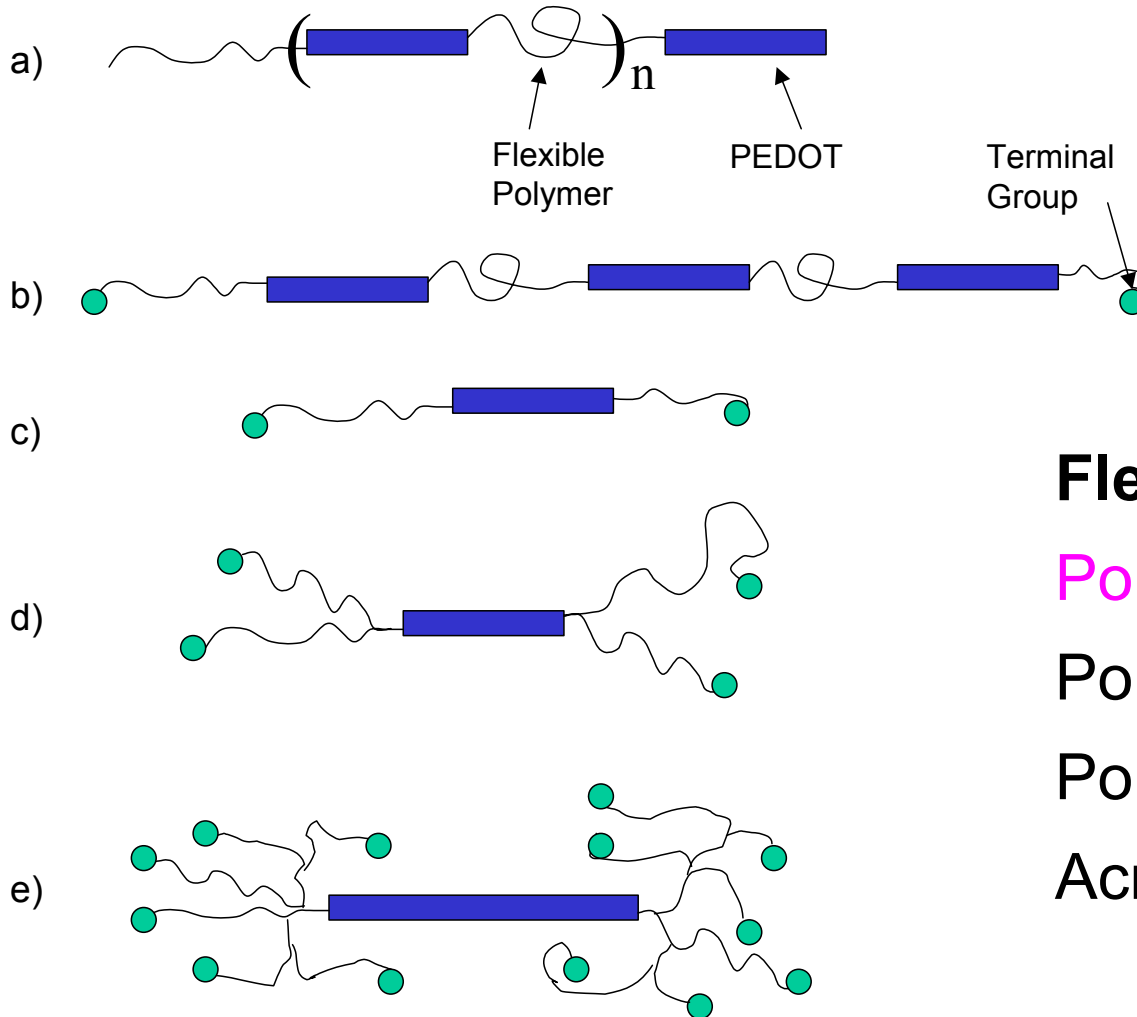


**Ionic-Stabilized  
Water-Based  
Dispersion**

- **Large excess of PSSH**
- **Hygroscopic, acidic, corrosive**
- **Poor wetting of organic substrates**
- **Difficult to blend with hydrophobic resins and polymers**

# TDA's Approach: Block Copolymers & Capped Oligomers

US Patent Application US2003/0088032 A1

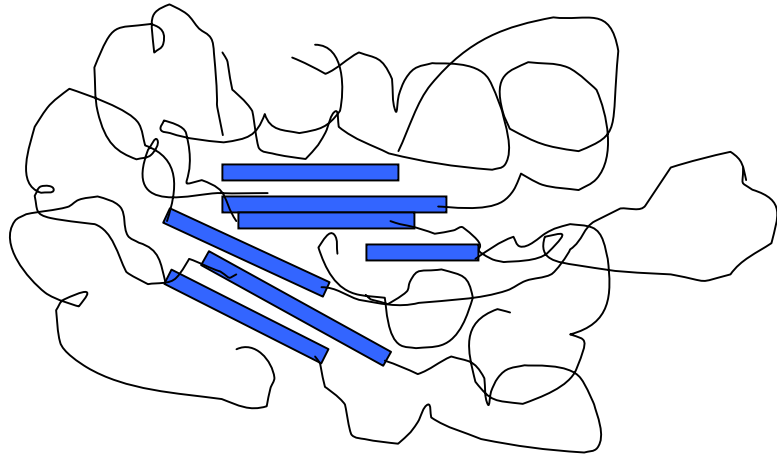


**Steric-Stabilized  
Solvent-Based  
Dispersions**

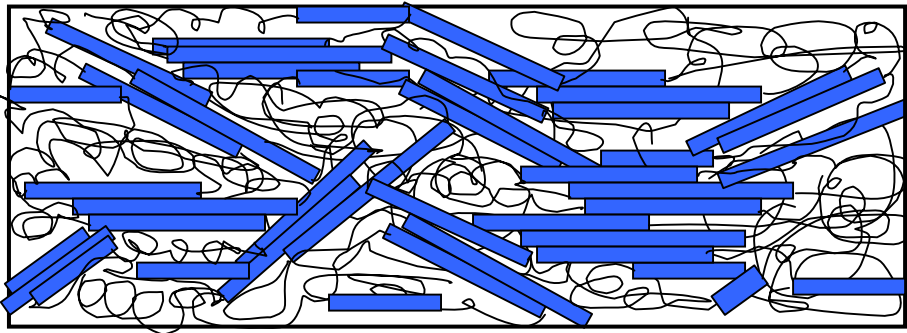
**Flexible segments:**  
Poly(ethylene glycol)  
Poly(propylene glycol)  
Poly(dimethylsiloxane)  
Acrylates

# Solution and Solid State Structures

---



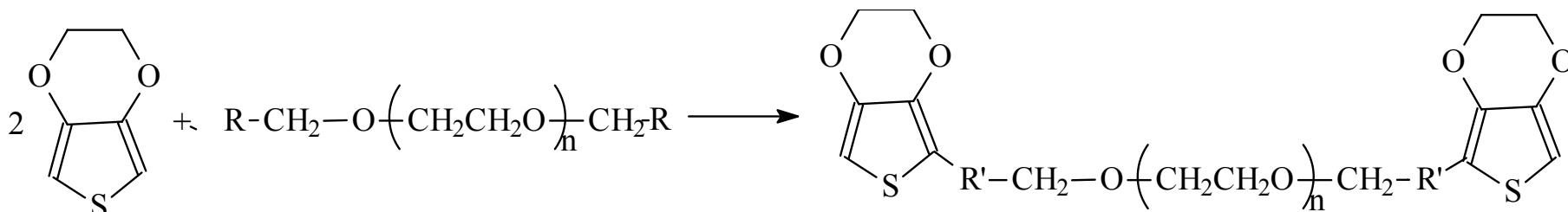
Steric-stabilized  
colloidal dispersion  
in solution



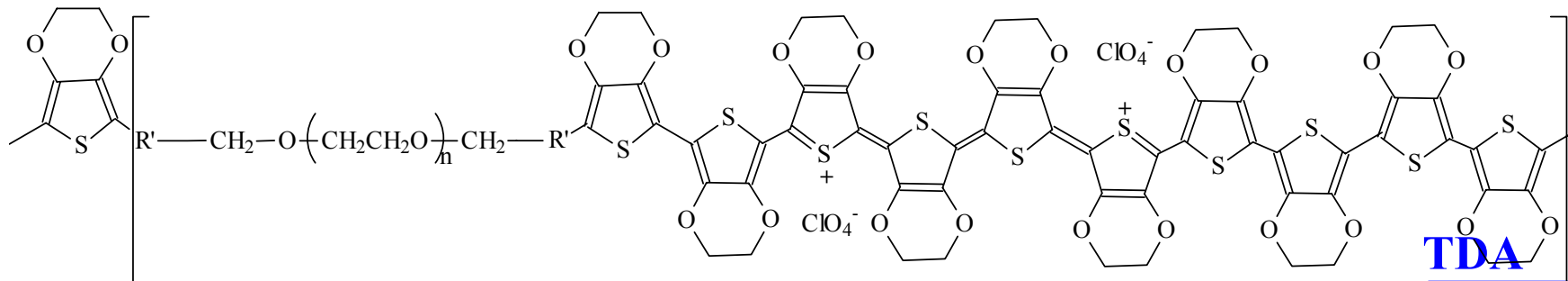
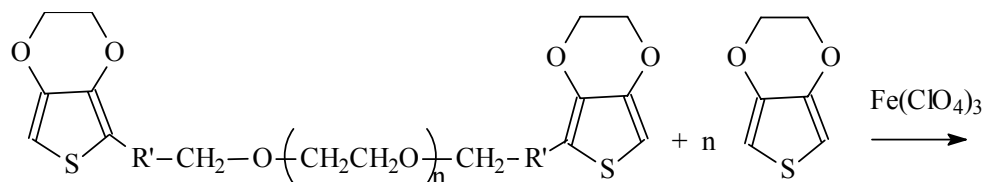
Phase-separated  
domains in solid state

# PEDOT-PEG Copolymers Synthesis

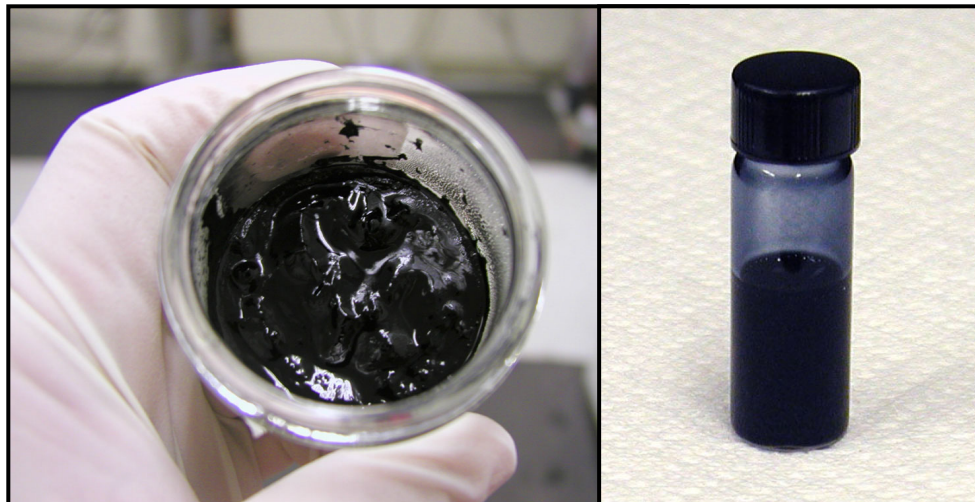
## 1) Synthesis of Polymerizable Macromonomers



## 2) Oxidative Polymerization



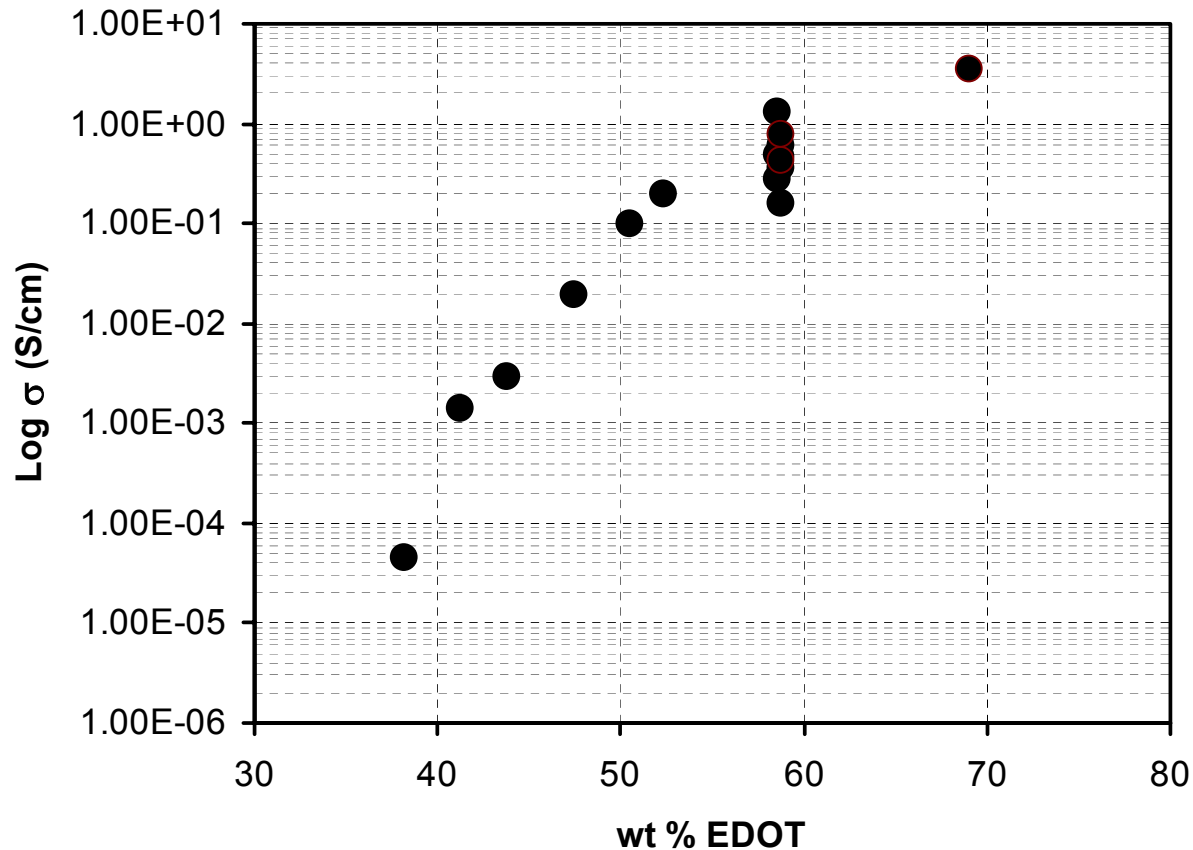
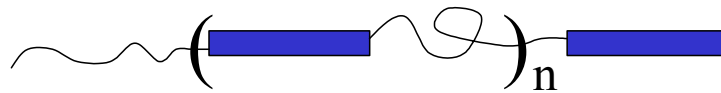
# Purification and Dispersion



Sample Description	Chlorine Content (ppm)	Iron Content (ppm)
raw product	6310	3410
first rinse	2900	700
second rinse	2200	100
third rinse	2310	19

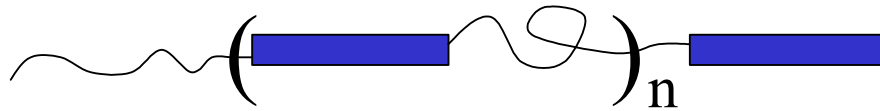
Doping level  $\cong$  24% based on # of EDOT units

# Linear Copolymers: Conductivity Versus PEDOT/PEG Ratio



# Linear Copolymers: Conductivity Versus Dopant

---



- **Perchlorate doped copolymer:**

$$\sigma = 10^{-1}-10^0 \text{ S/cm}$$

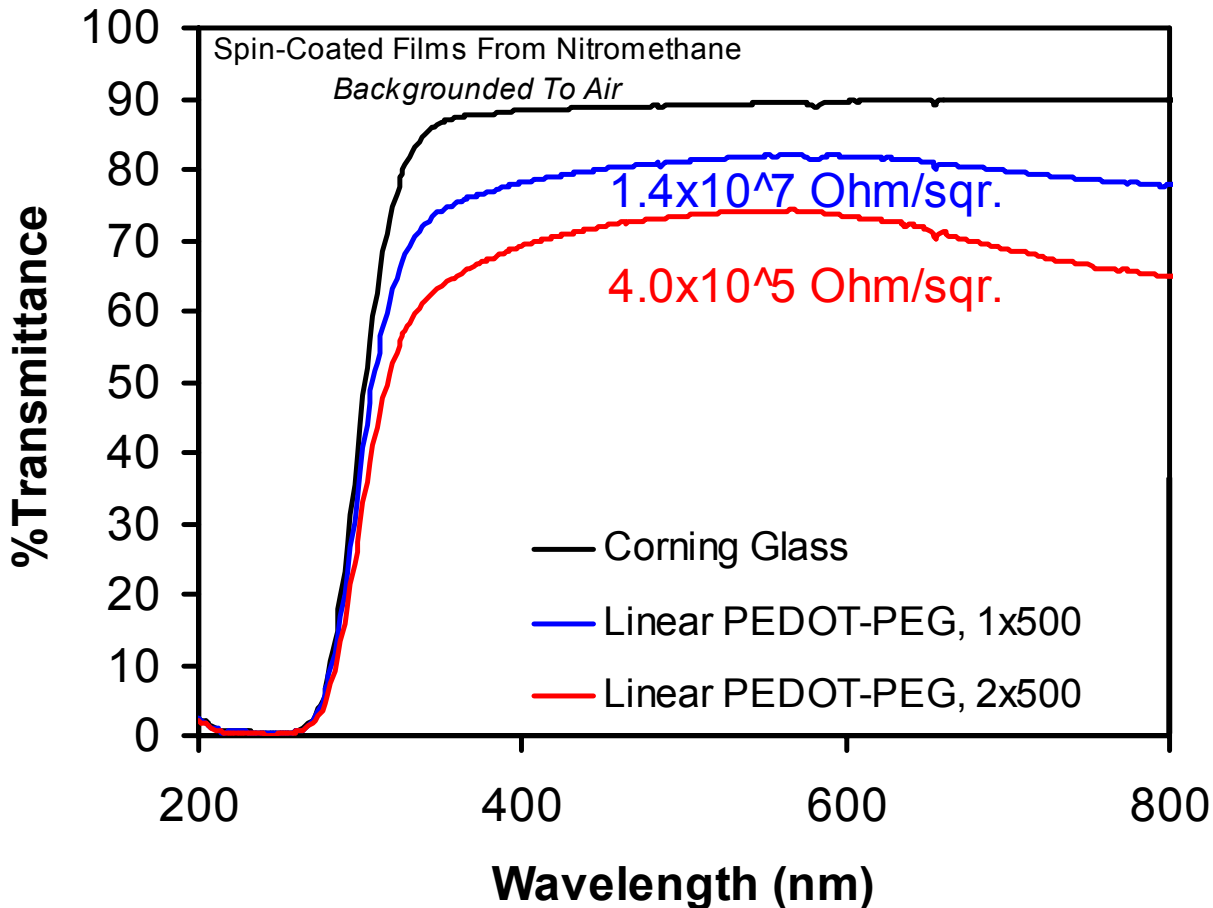
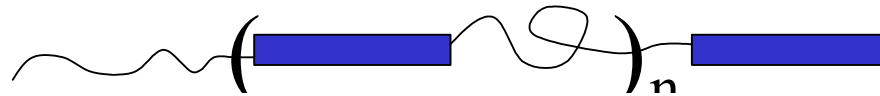
- **Triflate doped copolymer:**

$$\sigma = 10^{-2} \text{ S/cm}$$

- ***Para*Toluensulfonate doped copolymer:**

$$\sigma = 10^{-4}-10^{-3} \text{ S/cm}$$

# Linear Copolymers: Optical Clarity

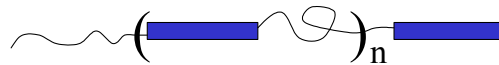


$1.4 \times 10^7$  Ohm/sqr.

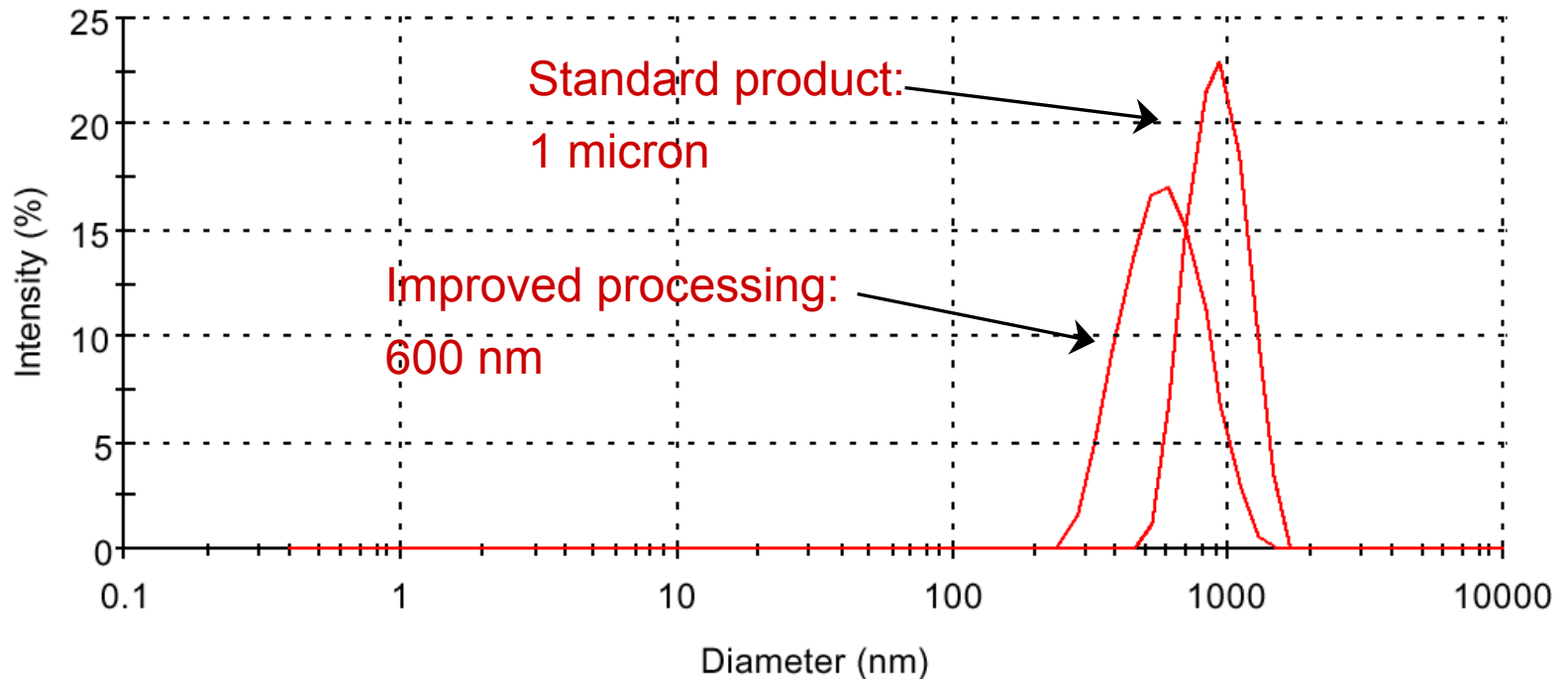
$4.0 \times 10^5$  Ohm/sqr.

Bulk Conductivity  
0.4 S/cm

# Linear Copolymers: Particle Size

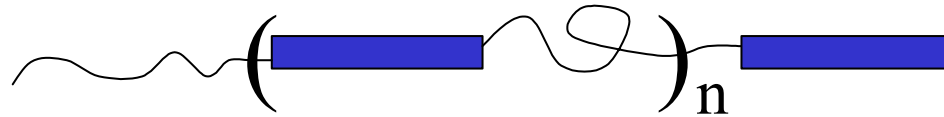


Size Distribution by Intensity



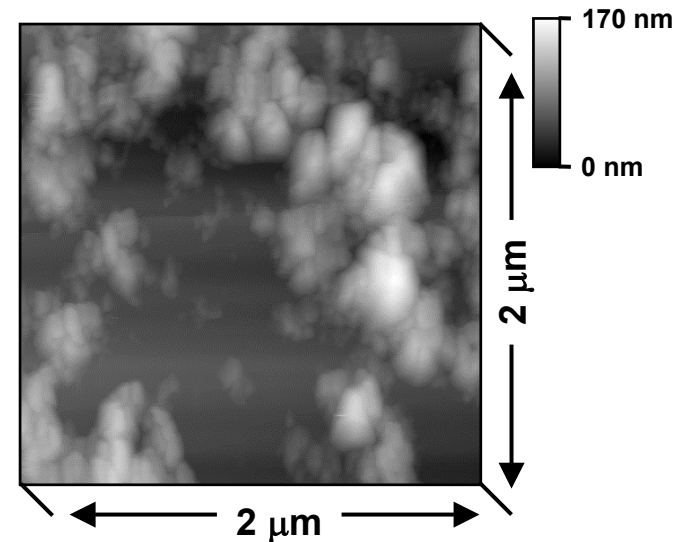
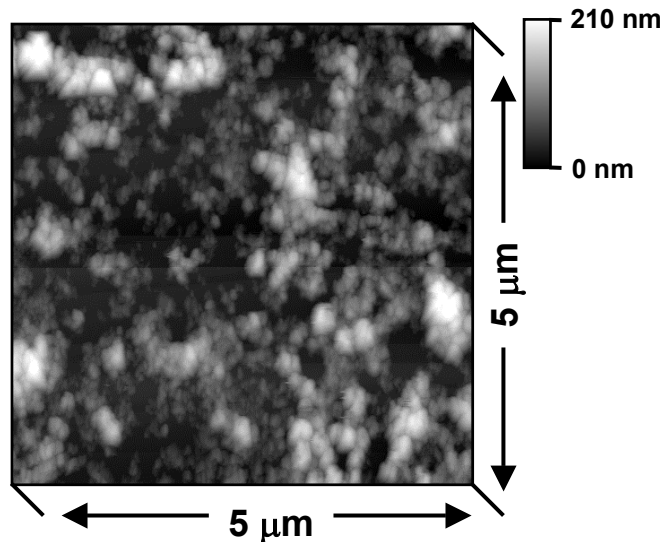
Light Scattering of Solvated Colloidal Particles

# Linear Copolymers: Surface Roughness



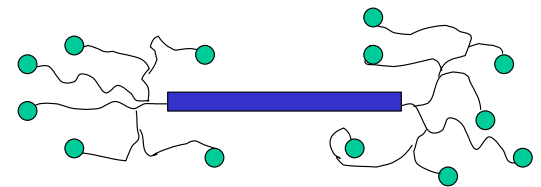
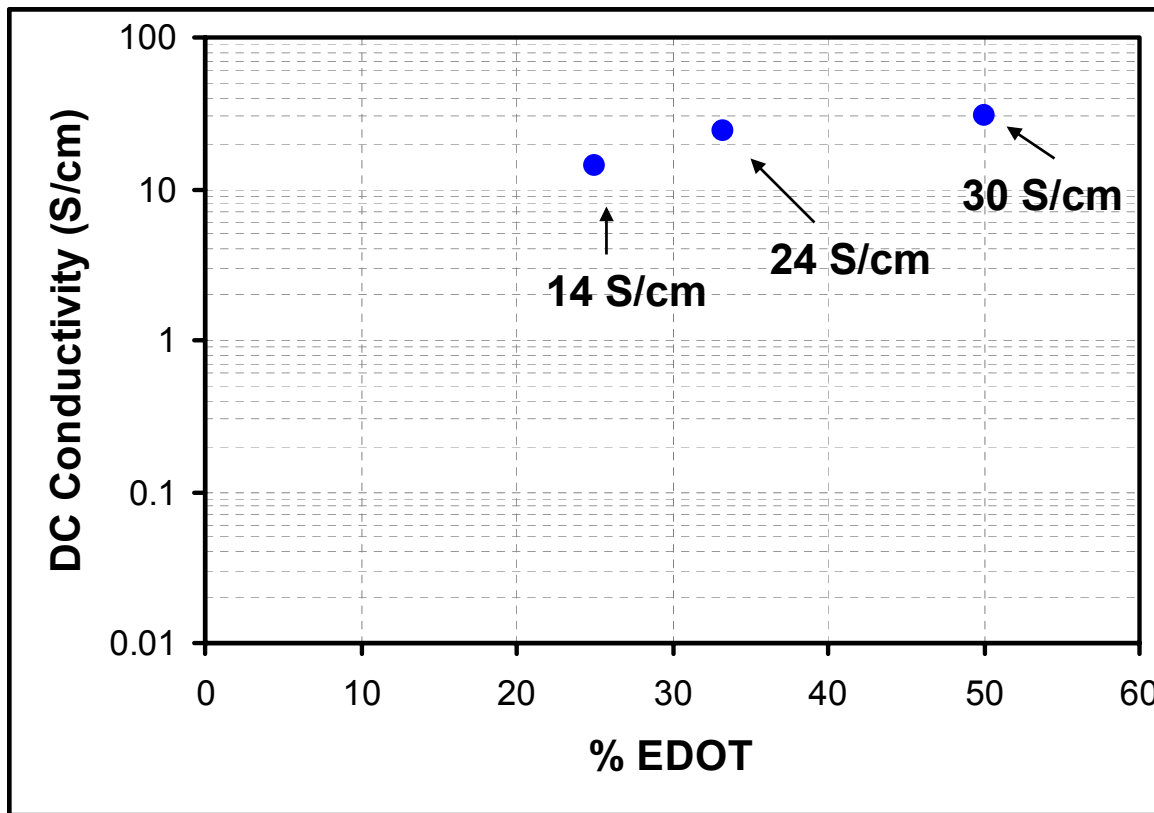
RMS Roughness = 42.9 nm  
Avg. Roughness = 31.8 nm

RMS Roughness = 36.5 nm  
Avg. Roughness = 30.0 nm

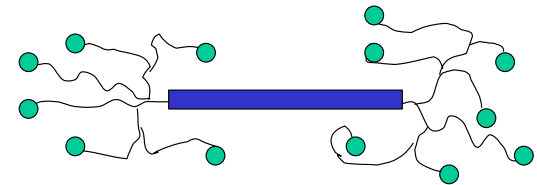
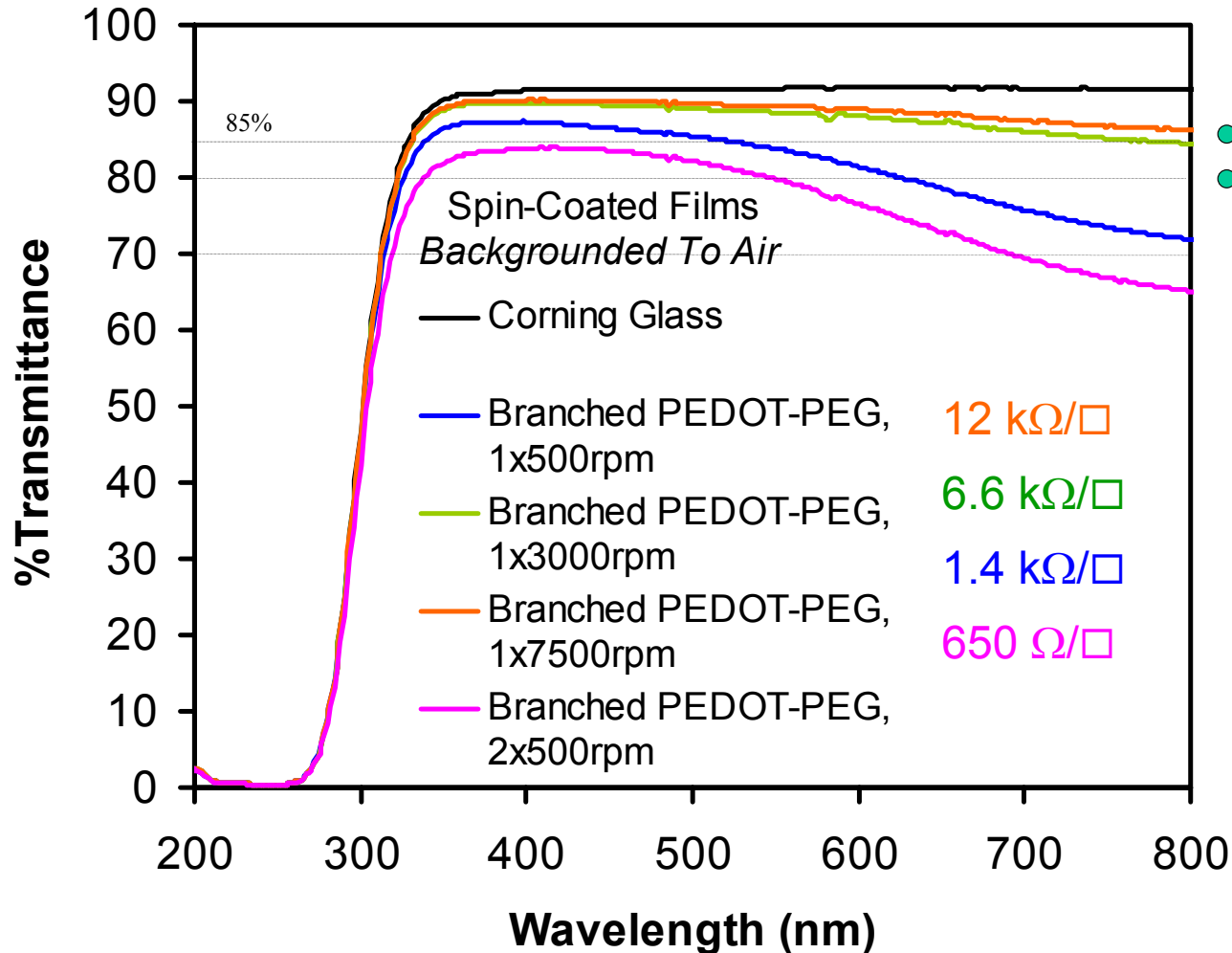


Contact Mode AFM: dry film on float glass

# Hyperbranched Copolymers: Conductivity Versus Composition



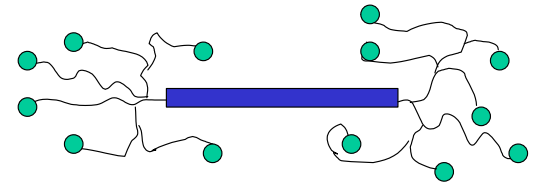
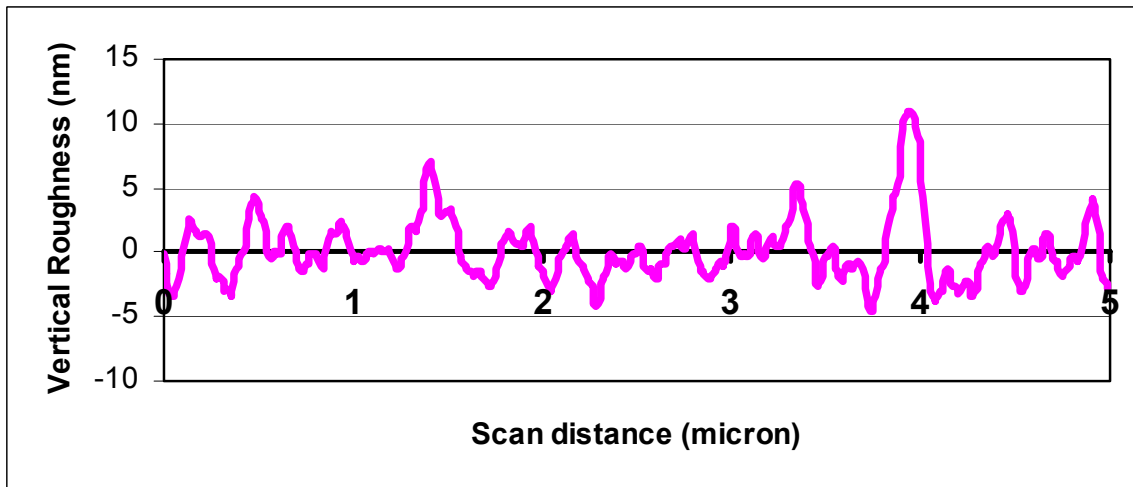
# Hyperbranched Copolymers: Optical Clarity



Bulk Conductivity  
14 S/cm

# Hyperbranched Copolymers: Surface Roughness

Contact Mode AFM: dry film on float glass



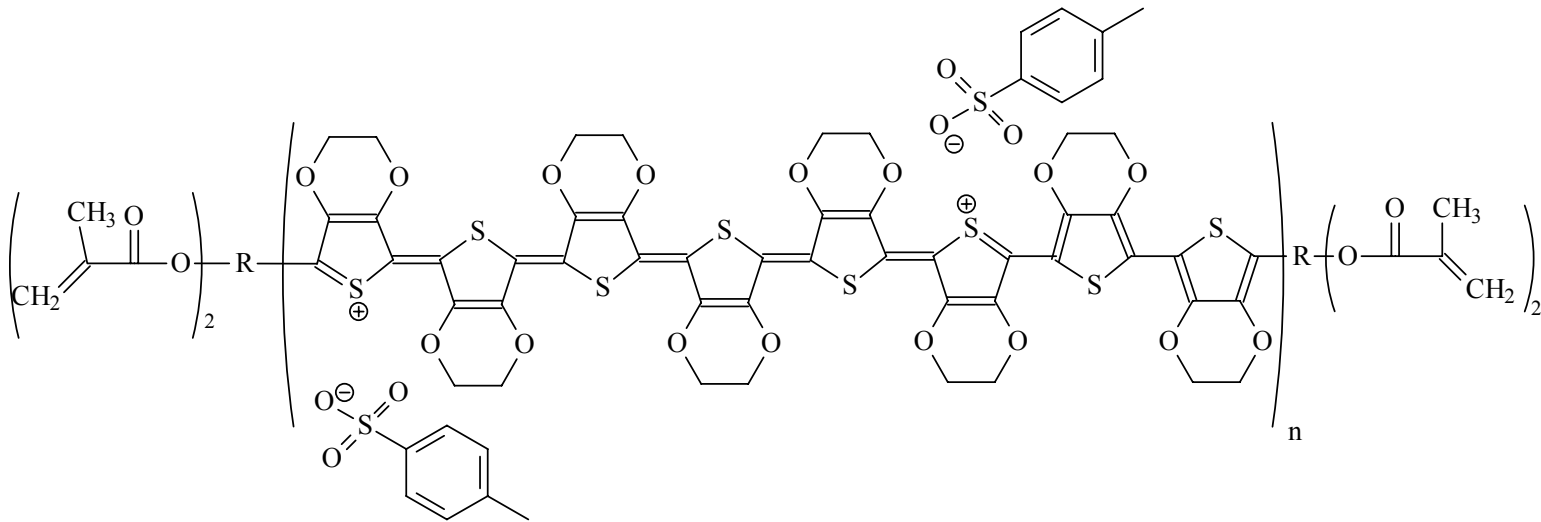
**RMS Roughness = 3.9 nm**

Film cast at 3000 RPM

No annealing needed

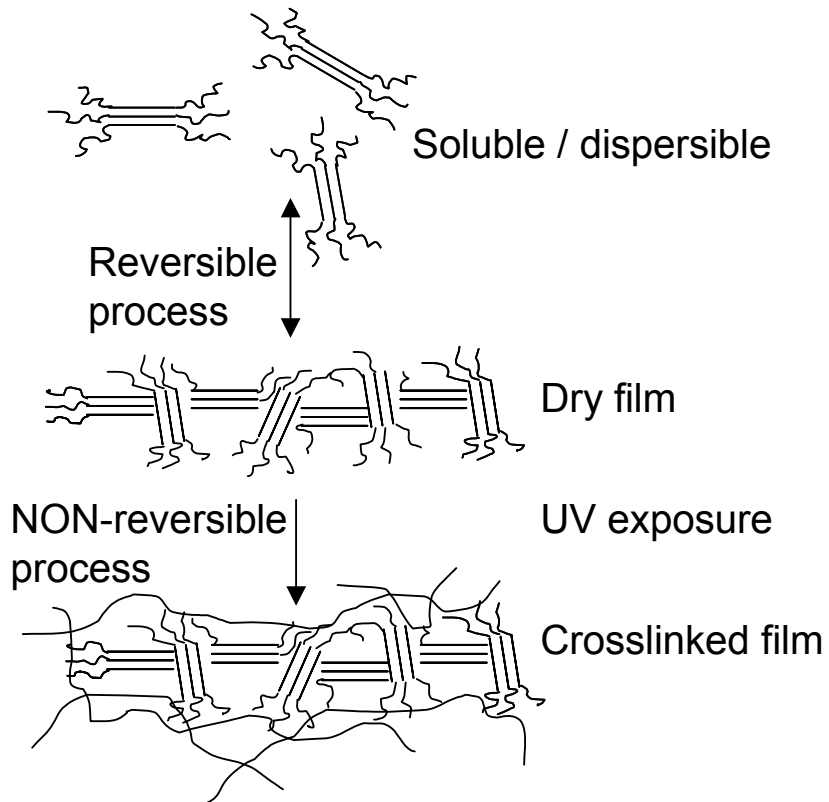
Surface Resistivity = 6,600  $\Omega$ /sq.

# Methacrylated Capped Oligomers



- **Post-curing cross-linking for:**
  - Photo-lithographic patterning
  - Improved scratch resistance
  - Post-inkjet print curing
- **Added functionality for reaction with specific functional compounds**
- **Bulk conductivity = 10<sup>-2</sup>-10<sup>0</sup> S/cm (PTSA doped)**

# Photoprinting of Methacrylated Oligomers



**Areas that are exposed to the light become “fixed” and the rest of the film can be rinsed away**



Ink (above), mask (middle) and printed image (bottom)



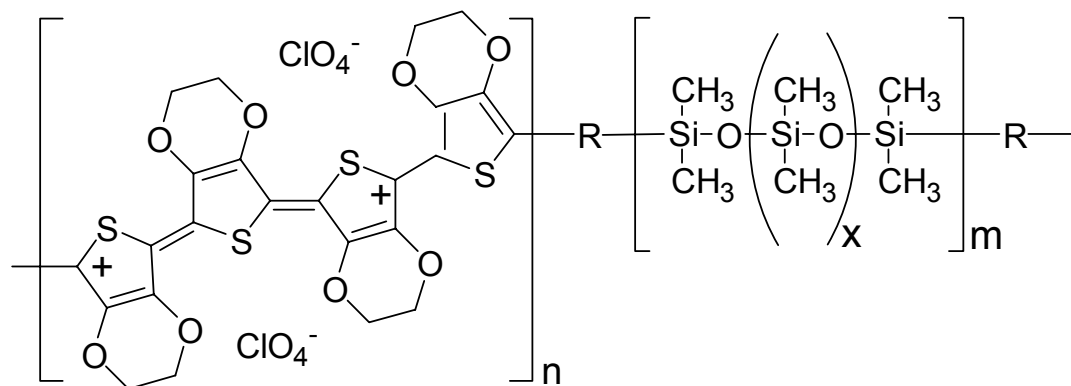
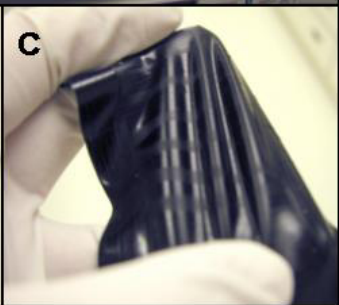
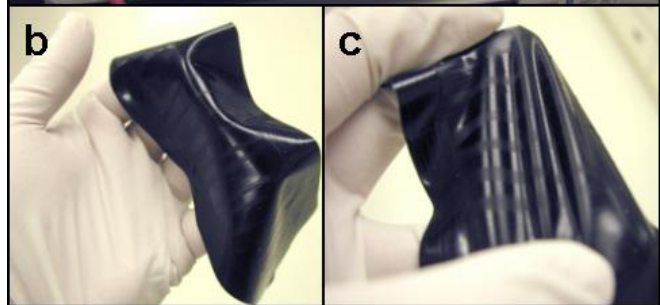
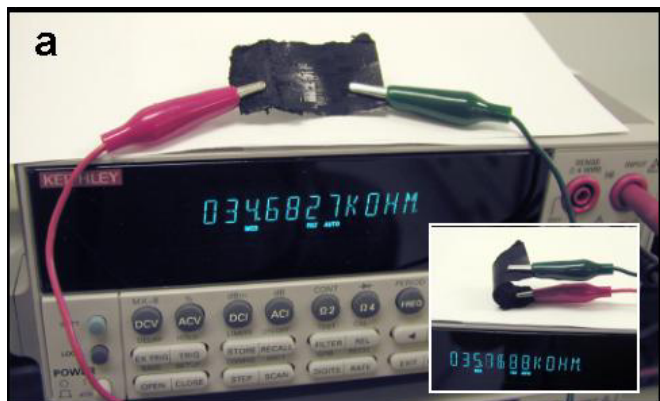
The printable conducting ink contains a mixture of our conducting polymer and other polymerizable monomers.

# Commercial Products

1. **Aedotron™ C polymer:**  
Linear PEDOT-PEG/CIO<sub>4</sub> in nitromethane (64980-5)
2. **Aedotron™ C polymer:**  
Linear PEDOT-PEG/CIO<sub>4</sub> in propylene carbonate (64978-3)
3. **Aedotron™ P polymer:**  
Linear PEDOT-PEG/PTSA in nitromethane (64979-1)
4. **Oligotron™ material:** PEDOT-tetramethacrylate/PTSA in propylene carbonate (64981-3)
5. **Oligotron™ material:** PEDOT-tetramethacrylate/PTSA in nitromethane (64982-1)



# PDMS-PEDOT Copolymers



Conductivity =  $10^{-2}$ - $10^0$  S/cm

Elongation = 80-190%

Tensile Strength = 60-100 psi

Glass Transition =  $-50$  °C

# Advantages of TDA's Materials

---

- Processable from non-acidic organic dispersions
  - ○ No ITO etching      ○ Not hygroscopic
- Wet glass and organic substrates
- Conductivity from  $10^{-4}$  to 10 S/cm
  - ○ PEDOT/PEG ratio      ○ Dopant
- Colloidal dispersion independent from dopant
- Hyperbranched oligomers have improved conductivity/transparency and lower surface roughness
- Methacrylated materials can be cross-linked
- PDMS-PEDOT materials show high conductivity and elongation