Polymers: Energy, electronics, photonics

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Polymers as Functional Materials:

Competition with well-established (and, often, better-performing) conventional materials?

Basic ‘virtue’ must be processibility

Large-area electronics – ‘flexible’ or ‘unbreakable’

Low ‘system cost’ through low process temperatures (low-cost solar cells?)

Polymers have made considerable progress – and are now viable in some areas of technology.

What are the limits to ‘functional’ performance?

What are the prospects for improved process control?
Polymer functional properties:

Semiconductors:
- use in light-emitting diodes, LEDs
- use in thin-film Field-Effect Transistors
- use in solar cells

Metals:
- doped semiconductors – used as electrodes in diodes

Insulators:
- critical component for FETs

Substrates:
- plastic substrates with suitable flatness and suitable barrier properties

Optical materials:
- photonic structures via simple processing routes?
Light-emitting Transistors

Jana Zaumseil and Henning Sirringhaus
Advanced Materials, 2006

Gold electrodes used for both electron and hole injection...

F8BT: annealed above \( T_M \)
Channel length: 20 \( \mu \)m
Dielectric: PMMA (450 nm)
Light-emitting Transistors

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$V_S = 0V$
$V_G = V_{SD}/2$
$V_D = +V_{SD}$

Camera
Polymer Light-Emitting Diodes:

Ink-jet printing of red, green and blue for full color:

The competition:
Vacuum-sublimed ‘small molecules’ developed by Ching Tang, Kodak allow easier control of multilayer heterojunctions

Triplet-emitting (phosphorescent) Pt and Ir complexes (Forrest, Thompson) have increased efficiencies to very high levels

LED performance:

Semiconductor device architecture makes use of heterojunctions between different band-gap polymer semiconductors:

- stacked structures – CDT’s ‘interlayer’
- blended (and partly de-mixed) polymers
- copolymers

Developments in lifetime and efficiency are largely accomplished in industrial labs – open literature not a reliable guide..

Efficiencies are now high: 9 cd/A for blue, higher for red and green

Lifetimes are high: CDT results: at 400 cd/m$^2$ 150, 280 and 62 thousand hours to half brightness
Charge separation at a ‘heterojunction’ between different polymer semiconductors

**Photovoltaic diodes:**

- **Step 1**: Photon absorbed in polymer creates electron and hole on same polymer chain.
- **Step 2**: Electron drops down to lower energy site on the other polymer chain.

**Outcome of exciton at heterojunction = charge transfer when:**

Criterion for charge transfer:

\[ E_{\text{exciton}} < \Delta l_p, \Delta E_A \]
‘Dispersed Interface’ Photovoltaics

‘mixed’ polymers generally phase-separate due to low entropy of mixing – spinodal decomposition?


[ similar approach: Dye dispersed in TiO$_2$ nanoparticles (Grätzel) ]
Best organic solar cells:

Poly(3-hexyl thiophene) – hole acceptor

Fullerene – electron acceptor

Solar energy conversion efficiencies above 5%

Santa Barbara, Konarka

Improved efficiencies: ‘tandem’ cells – use of sol-gel TiO$_2$/PEDOT-PSS to enable the interlayer e-h recombination

‘plastic’ solar cells: prospects:

**Konarka** – US VC-backed start-up

Roll-to-roll manufacturing demonstrated.

Challenges: (a few ‘miracles’ still required?)

Efficiencies are too low. Silicon is close to 20%. Current levels near 6% can be improved in principle. This will require:

- new materials (better match with solar spectrum, towards near IR)
- better heterojunction architectures (control of molecular-scale structures at the heterojunction – may need to arrange a ‘cascade’ of steps to separate electron and hole far enough to avoid recombination (cf. photosynthesis)
- better ‘nanoscale’ structures for the ‘distributed heterojunction’ – (diblock copolymers, etc. ?)

Materials for the PV system are not all in place:

- polymer substrates with adequate barrier properties
- ITO replacement (transparent electrodes)
Polymer transistors:

- Field-effect mobility $\mu = 0.04 \text{ cm}^2/\text{Vs}$
- ON-OFF current ratio between 0V and -40V: $5 \cdot 10^5$
- sufficient for driving A5 100PPI electronic paper display

Active-matrix backplane for e-ink electrophoretic display:

Display with 600 x 800 pixels (100 dpi) or 900 x 1200 pixels (150 dpi) on flex using E Ink display media:

- multi-level patterning without mask alignment (needed for photolithography)
- active, real-time distortion correction for shape changes to substrate (PET film)
Transistors:

Field-Effect mobility is the favored ‘figure of merit’ – controls device switching speed and size. [a-Si about 1, crystalline silicon 100 cm$^2$/Vs]

Mobility, $\mu$, is strongly controlled by disorder in molecular/polymeric semiconductors:

Current polymer systems:

- Poly(3-hexyl thiophene), $\mu$ up to 0.1 cm$^2$/Vs
- New thiophene-based systems (Merck) $\mu$ up to 1 cm$^2$/Vs (better packing of alkyl side chains gives better crystallisation and chain order)

(note: thiophene-based systems do not yet give air-stable operation)
Transistors – limits to mobility?

Crystalline molecular semiconductors do better…

- pentacene widely studied (and soluble derivatives are very promising (Anthony))
- rubrene gives highest values, $\mu$ above 15 cm$^2$/Vs

‘Inorganic’ carbon does even better…

- carbon nanobubes, graphene, $\mu$ well above 100 cm$^2$/Vs (even with disordered dielectric layers…)

Current ‘organic synthetic’ approaches to graphene-like structures do not yet give high mobilities (Mullen, MPI Mainz)

? Threshold for length scale of charge carrier delocalization

Delocalization reduces effects of local disorder, and allows better screening of disorder.

Requirements:
- $T_g, T_m$ sufficiently high, dimensional stability, avoidance of optical anisotropy (for LC displays)
- Surface flatness. Absolutely critical for semiconductor device manufacture!!

Coating layers for PET, PEN now developed

- Barrier properties (against water and oxygen)
  
  Water diffusion: Polymers 1-10 gm/m² day. OLED needs $< 10^{-6}$ gm/m² day

- Current approaches use inorganic layers: multilayer organic/inorganic coatings developed by Vitex Systems:
  - Polymer layer planarises and fills defects in inorganic layers
  - Provide tortuous path for molecules

Fig. 5. Surface smoothness of industrial grade polyethylene naphthalate (PEN) film.

Fig. 7. Surface smoothness of surface tailored Teonex® Q60 (poly-ethylene naphthalate (PEN) film).

SEM Photo courtesy of Vitex Systems
Conducting polymers:

PEDOT-PSS – developed by Bayer/H C Stark

- used as water-soluble anti-static (Agfa color film), and as conductor in high performance tantalum bead capacitors

- found to be a necessary ‘electrode modifier’ of ITO in both LEDs and solar cells. Reasons for this are not fully understood (desirable work function for hole injection/extraction, possible surface doping of adjacent semiconductor layer)

- relatively low conductivity (factor of at least 10 lower conductivity/transparency performance than ITO) [Agfa program of research]

Real need for ITO replacement – indium is scarce and increasingly expensive. Prospects for higher conductivity polymers now very important.

Recent advances with polyaniline: 

‘self-stabilized dispersion polymerisation’ gives \( \sigma \) (300K) > 1000 S/cm and metallic behavior to very low temperatures

Polymer Dielectrics

Dielectrics control the performance of FETs. Field-induced charge in semiconductor requires a thin and high dielectric strength insulator layer. [Silicon technology was made possible by the properties of thermal oxide grown off the Si surface]

Good news:

- high dielectric strengths, abrupt interfaces with semiconducting layers (non-polar dielectrics enable simultaneous n and p operation in LFETs)

Bad news:

- most polymer dielectrics cannot be prepared thin enough.
  - gate voltage for FET operation scales with gate thickness.
  - design rule for FETs – ratio between channel length and dielectric thickness should be about 10
progress:

(i) use of SAMs


Alkyl phosphonic acid SAMs grown on aluminum gate

(ii) cross-linking of thin films

Tobin Marks, JACS 127 10388 (2005)

thickness down to 10-20 nm

(iii) Direct growth off substrate (brushes)

Zhenan Bao, Wilhelm Huck
Optical Materials:

Non-linear optical properties:

Continued advances in performance, e.g. of electro-optical modulators. (Dalton, Univ Washington), and materials NLO properties (Georgia Tech)

Photonics:

**Full photonic band structures** hard to achieve with organics (contrast in refractive index > 2 is needed) [recent progress: Turberfield et al, Adv. Mater. 18, 1557 (2006)]

Current interest in organic lasers:

Easy to make if optically pumped

Extremely challenging to drive by electrical excitation…

Holographically-produced photonic crystal – (a) is SEM image (c) confocal optical image of dye activated by photoacid