Viewpoints

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Conductive Polymers
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Suppliers of Inherently Conductive Polymers

Why is this topic significant?

Areas to Monitor in the Technology Map identifies a variety of emerging applications for inherently conductive polymers, including optical displays, photovoltaic cells, lighting, transistors, capacitors, and sensors. This Viewpoints describes the major families of conductive polymers and the companies that produce these materials for the merchant market.

Inherently conductive polymers (ICPs)—macromolecules that are electrically conductive because they contain many carbon-carbon double bonds in series—are finding increasing use in optical displays, photovoltaic cells, and other applications. Commercial products that rely on ICPs include photographic film from Agfa-Gevaert, a new MP3 player from GoDot Technology, and the "magic mirror" cell phone and the Norelco Spectra 8894XL cordless shaver from Philips (see the December 2004/January 2005 Viewpoints). This category of materials includes light-emitting polymers—the polyfluorene, poly(*p*-phenylene), and poly(*p*-phenylenevinylene) families—as well as the polyacetylene, polyaniline, polypyrrole, and polythiophene families.

Currently, 11 companies produce ICPs for the merchant market (see Table 1). Three suppliers—American Dye Source, H. W. Sands, and Sigma-Aldrich—provide most families of ICPs in research-scale (milligram to kilogram) quantities. (Sigma-Aldrich is primarily a distributor of ICPs; however, the company will produce bulk quantities of ICPs on a custom basis.) The other 8 producers are targeting larger-scale commercial markets; their product portfolios are much narrower. Several ICP suppliers are forward integrated into formulated ICP products such as coatings, inks, additives, and compounding master batches; other suppliers have ongoing relationships with application developers.

Table 1
PRODUCERS OF INHERENTLY CONDUCTIVE POLYMERS

Company (Location)	Licensing	Manufacturing	Distribution	Comments
American Dye Source, Inc. (Baie D'Urfe, Quebec, Canada)		●		
Covion Organic Semiconductors GmbH (Frankfurt, Germany)		●		Produces LEPs and small-molecule OLED materials on a commercial scale at its Frankfurt plant
Dow Chemical Company (Midland, MI)		●		Produces LEPs on a commercial scale at its Midland production facility
DSM (Heerlen, Netherlands)		●		
H. C. Starck GmbH (Leverkusen, Germany)		●		Leading source of PEDOT/PSS dispersions
H. W. Sands Corporation (Jupiter, FL)		●		
Ormecon GmbH (Ammersbek, Germany)	●	●		Manufactures PAni and PAni-based products (corrosion-prevention coatings and finishes for printed circuit boards)
Panipol Oy (Porvoo, Finland)		●		Produces melt-processable PAni and PAni-based inks and coatings
Plextronics, Inc. (Pittsburgh, PA)		●		Manufactures highly regioregular P3ATs on a pilot-plant scale; also produces hole-injection-layer formulations
PolyOne (Avon Lake, OH)		●		Manufactures lignosulfonated PAni and PAni-based corrosion-control additives for protective coatings
Sigma-Aldrich (St. Louis, MO)		●	●	
TDA Research, Inc. (Wheat Ridge, CO)		●		

Note: LEP = light-emitting polymer; OLED = organic light-emitting diode; PAni = polyaniline; PEDOT/PSS = poly(3,4-ethylenedioxythiophene)/ polystyrene sulfonate; P3AT = poly(3-alkylthiophene).

Source: SRI Consulting Business Intelligence (SRIC-BI)

Light-Emitting Polymers

Light-emitting polymers (LEPs) are electroluminescent: They convert electricity into light. For example, the application of an electrical voltage across a cathode/LEP/anode sandwich causes this simple device to emit light. LEPs are critical components of polymer light-emitting diode (PLED) displays (see the August 2004 and October 2004 Viewpoints); they also enable the production of flexible light sources (see the November 2004 Viewpoints).

This group of materials includes three polymer families.

- *Polyfluorene* (PF). PF homopolymers and copolymers provide a Crayola-like palette of colors for display fabrication. The family includes blue, green, red, orange, and yellow emitters. PFs offer efficient electroluminescence, high charge-carrier mobility, and good perishability.

- *Poly(p-phenylene)* (PPP). The simplest member of this family, unsubstituted PPP, is intractable, but the addition of long-chain substituents to the polymer backbone increases solubility and usefulness. Commercial PPPs are blue emitters.

- *Poly(p-phenylenevinylene)* (PPV). PPV homopolymers and copolymers combine good mechanical and processing properties with excellent luminescence. The addition of substituents to the polymer backbone increases the solubility and tunes the optical properties of the material. For example, MEH-PPV (poly[2-methoxy-5-(2´-ethylhexyloxy)-1,4-phenylenevinylene]) often serves as the electroluminescent layer in PLED displays; a related cyano-substituted polymer, CN-PPV (poly[2-methoxy-5-(2´-ethylhexyloxy)-1,4- phenylene(1-cyanovinylene)]), can serve as the electron-accepting material in LEP heterojunctions. The PPV family includes blue, green, red, and orange emitters.

Cambridge Display Technology (CDT; Cambridge, England), which controls much of the intellectual property related to LEPs, does not manufacture the materials (see the March Viewpoints); it licenses its technology to Covion Organic Semiconductors, Dow Chemical, H. C. Starck, and Sumitomo Chemical. At present, two CDT licensees—Covion and Dow—are producing LEPs on a commercial scale for the merchant market. Other LEP suppliers include American Dye Source and H. W. Sands (see Table 2).

- Covion Organic Semiconductors GmbH produces both polymer and small-molecule OLED (organic light-emitting diode) materials on a commercial scale. The company's Frankfurt, Germany, plant can produce more than 40 000 liters of LEPs per year; the product line includes PPPs and PPVs. The company continues to develop new LEPs as part of a joint-development project with CDT. Covion LEPs are a critical component of Philips's PolyLED products. Recently, Merck KGaA (Darmstadt, Germany) agreed to purchase Covion from Avecia (see the March Viewpoints).

- Dow Chemical Company has manufactured red-, green-, and blue-emitting PFs at a multireactor production facility in Midland, Michigan, since October 2003. The company markets its LEPs under the Lumation trade name. Dow has signed long-term supply agreements with OSRAM Opto Semiconductors and MicroEmissive Displays.

Table 2
LIGHT-EMITTING POLYMERS*

Polymer Family	Acronym	Suppliers
Polyfluorene	PF	American Dye Source, Covion, Dow Chemical, H. W. Sands
Poly(*p*-phenylene)	PPP	American Dye Source, H. W. Sands
Poly(*p*-phenylenevinylene)	PPV	American Dye Source, Covion, Dow Chemical, H. W. Sands

* Sigma-Aldrich supplies gram-scale quantities of most of these polymers for research purposes.

Source: SRIC-BI

Polyacetylene

From a historical perspective, polyacetylene is among the most important conductive polymers; from a commercial perspective, its significance is minor. The entire field of conductive polymers is the result of fundamental research on doped polyacetylene films by the research groups of Alan J. Heeger (University of California, Santa Barbara), Alan MacDiarmid (University of Pennsylvania), and Hideki Shirakawa (University of Tsukuba). The three professors shared the 2000 Nobel Prize in Chemistry for their work in this area.

Unsubstituted polyacetylene is of limited utility. This material degrades in air, is chemically stable only in solution, and is brittle and difficult to process. In contrast, alkylthio-substituted polyacetylenes (polythioacetylenes) are soluble and processable. Upon irradiation with laser light, polythioacetylenes exhibit conductivities of 10 to 200 S/cm (siemen/centimeter). These hole-transport materials appear to have limited commercial use at present. Sources include H. W. Sands and Sigma-Aldrich (see Table 3).

Table 3
CONDUCTIVE POLYMERS*

Polymer Family	Acronym	Suppliers
Polyacetylene, alkylthio-substituted	PAc	H. W. Sands
Polyaniline	PAni	American Dye Source, Ormecon, Panipol, PolyOne
Polypyrrole	PPy	American Dye Source, DSM
Polythiophene	PT	
Poly(3-alkylthiophene)	P3AT	American Dye Source, H. W. Sands, Plextronics
Poly(3,4-ethylenedioxy-thiophene)	PEDOT	H. C. Starck, TDA Research (through Sigma-Aldrich)

* Sigma-Aldrich supplies gram-scale quantities of most of these polymers for research purposes.

Source: SRIC-BI

Polyaniline

The emeraldine salt form of polyaniline (PAni) is the workhorse of ICPs. The material—which consists of the emeraldine base form of PAni plus an organic sulfonic acid (the dopant)—is highly conductive, thermally stable, and dispersible in aqueous solution and organic solvents. When the dopant is an organic sulfonic acid, the concentration of emeraldine salt in the dispersion is low (1 to 10 weight%); when the dopant is lignosulfonic acid, higher concentrations are possible (up to 20 weight% in water). Films made from the emeraldine salt are green (as the name suggests), transparent, and conductive. Various research groups have reported that PAni nanowires are also highly conductive.

Suppliers of PAni include Ormecon, Panipol, and PolyOne. In addition, American Dye Source offers gram to kilogram quantities of PAni, various alkyl-substituted polyanilines, and PAni copolymers.

- Ormecon GmbH owns much of the fundamental intellectual property related to PAni. The company has patented the PAni technology that it developed in-house; in addition, Ormecon acquired key PAni patents from Monsanto and AlliedSignal. Currently, Ormecon manufactures PAni dispersions, sells PAni-based products (corrosion-prevention coatings and finishes for printed circuit boards), and licenses PAni technology to other companies, including Bayer AG (the parent of H. C. Starck), Covion Organic Semiconductors GmbH, DuPont, Nissan Chemical Industries, and Panipol Oy. Panipol is the only licensee that produces PAni; Bayer's license provides freedom to manufacture dispersions of another conductive polymer, poly(3,4-ethylenedioxythiophene) (PEDOT). Ormecon is a subsidiary of Zipperling Kessler & Co. (Ammersbek, Germany).

- Panipol Oy, a licensee of Ormecon, supplies melt-processable grades of PAni for use as static-dissipative additives in thermoplastic blends. Melt-processable PAni has sufficient thermal stability for use in polyolefins (low-density polyethylene, high-density polyethylene, polypropylene, ethylene-propylene-diene rubber, and ethylene methyl acrylate) and some styrenics (high-impact polystyrene and styrene-ethylene-butadiene-styrene). In addition, Panipol supplies PAni-based inks and coatings (solutions or dispersions of doped emeraldine salt in an organic solvent or water) and (undoped) emeraldine base PAni. Panipol is a spin-off of Neste, which is now a subsidiary of Fortum Corporation (Espoo, Finland).

- PolyOne manufactures and markets Teslart lignosulfonated PAni under exclusive license from GeoTech Chemical LLC (Tallmadge, Ohio). To make Teslart, PolyOne polymerizes aniline to form PAni, then grafts lignin to the polymer chains in the presence of acid. The lignin improves the ability of Teslart ICPs to disperse in water and other solvents; the acid improves conductivity. Applications for Teslart include corrosion-resistant coatings; antistatic fabrics, coatings, and packaging; and conductive inks and adhesives. Teslart is also a key component of PolyOne's Catize corrosion-control additives for protective coatings.

Polypyrrole

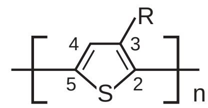
Polypyrrole (PPy) exhibits good stability and—in combination with organic sulfonic acids and similar dopants—high conductivity. Commercial uses for doped PPy and PPy derivatives include conductive coatings and low-ESR (equivalent-series-resistance) capacitors. (In the 1980s, Bridgestone, Seiko, and Varta produced flexible batteries that incorporated PPy, but the companies have since withdrawn these products from the market.) Merchant sources of PPy include DSM, which supplies PPy and polymer-supported PPy, and American Dye Source, which produces gram to kilogram quantities of PPy on a custom basis.

Polythiophene

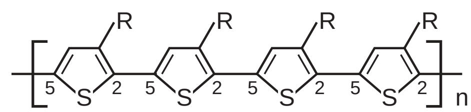
Unsubstituted polythiophene (PT) is completely insoluble and thus has essentially no commercial utility. In contrast, substituted PTs such as poly(3-alkylthiophene) (P3AT) and poly(3,4-ethylenedioxythiophene) are soluble (or at least dispersible) and thus find use in a variety of applications. Poly(3-alkylthiophene) serves as a hole-injection layer in PLEDs and a p-type semiconductor in organic solar cells; poly(3,4-ethylenedioxythiophene) finds use as a hole-injection layer in PLEDs and a flexible, transparent electrode in lighting applications.

Poly(3-alkylthiophene). Poly(3-alkylthiophenes) are very stable, highly conductive, and—because of their alkyl substituents—readily soluble in organic solvents. Both regioregular (head-to-tail) and regiorandom P3ATs are commercially available (see Figure 1). Regioregular P3ATs provide higher electrical conductivity (greater charge mobility) than their regiorandom counterparts provide. Photovoltaic cells are an emerging application for this family of ICPs (see the February Viewpoints).

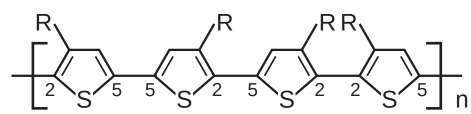
Figure 1
REGIOREGULAR AND REGIORANDOM POLY (3-ALKYLTHIOPHENES)



Numbering Convention for Poly (3-Alkylthiophenes)
(R = Any Alkyl Group)



Regioregular Poly (3-Alkylthiophene)
Head-to-Tail (2–5) Linkages Only



Regiorandom Poly (3-Alkylthiophene)
Head-to-Tail (2–5), Head-to-Head (2–2), and Tail-to-Tail (5–5) Linkages

Source: SRI Consulting Business Intelligence

Suppliers of P3ATs include American Dye Source, H. W. Sands, and Plextronics.

- American Dye Source supplies a variety of regioregular and regiorandom P3ATs. The company’s product line also includes a water-soluble polythiophene derivative (the alkyl side chain incorporates a sulfonic acid group) and several fluorene/thiophene copolymers.

- Plextronics, Inc., offers a variety of highly regioregular P3ATs in research and larger quantities. In addition, the company produces formulated products, such as hole-injection layers for optical displays. Plextronics has also developed technology for the production of block copolymers of P3AT and various nonconductive polymers, including polystyrene (PS), polymethylacrylate (PMA), and polyurethane (PU). These diblock and triblock copolymers are inherently conductive; the level of conductivity depends on the ratio of conductive P3AT blocks to nonconducting PS, PMA, or PU blocks. The different blocks of the copolymers are immiscible in one another and separate into nanoscale domains in the solid state. As a result of this spontaneous phase separation, cast films of the block copolymers contain networks of conductive P3AT nanowires in a matrix of the nonconductive polymer.

Poly(3,4-ethylenedioxythiophene). Poly(3,4-ethylenedioxythiophene)/ polystyrene sulfonate (PEDOT/PSS)—a doped, conductive form of PEDOT—is in large-scale commercial use as an antistatic coating for photographic film. The material is also finding application as a hole-injection layer in PLEDs (see the September 2004 Viewpoints), a transparent electrode in luminescent films (see the December 2004/ January 2005 Viewpoints), and a cathode material in tantalum and aluminum low-ESR capacitors.

H. C. Starck, a subsidiary of Bayer AG, is the leading source of aqueous PEDOT/PPS dispersions. TDA Research offers doped PEDOT block copolymers and PEDOT oligomers with reactive end caps.

- H. C. Starck GmbH supplies regular and OLED grades of Baytron P PEDOT/PSS dispersions. Agfa-Gevaert N.V. (Mortsel, Belgium) is perhaps the largest single user of Baytron P; the company employs the material as an antistatic coating for photographic film and as a component of its Orgacon conductive film.

- TDA Research, Inc., has developed PEDOT block copolymers that are soluble or dispersible in organic solvents. The conductivity of the company's Aedotron polymers—block copolymers of PEDOT and a flexible polymer, such as polyethylene glycol, polypropylene glycol, or polydimethylsiloxane—is tunable; the ratio and length of the PEDOT and flexible-polymer segments determine the conductivity of the block copolymer as a whole. TDA Research has also developed oligomeric PEDOT copolymers that contain reactive methacrylate end groups. The oligomers cure (crosslink) upon exposure to ultraviolet light. TDA Research distributes its products through Sigma-Aldrich.

CURRENTLY AVAILABLE TECHNOLOGY AREAS

Advanced Silicon Microelectronics/ULSI
Biocatalysis
Biomaterials
Biopolymers
Biosensors
Conductive Polymers
Engineering Polymers
Fiber-Optic Sensors
Flat-Panel Displays
Fuel Cells
Genomics
Internet Commerce
Knowledge-Based Systems
Knowledge-Management Tools
Membrane Separation
Micromachining
Mobile Data
Nanobiotechnology
Nanoelectronics
Nanomaterials
Novel Ceramic/Metallic Materials
Optoelectronics/Photonics
Pervasive Computing
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RFID Technologies
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Solid-State Microsensors
Virtual Environments
Web Services