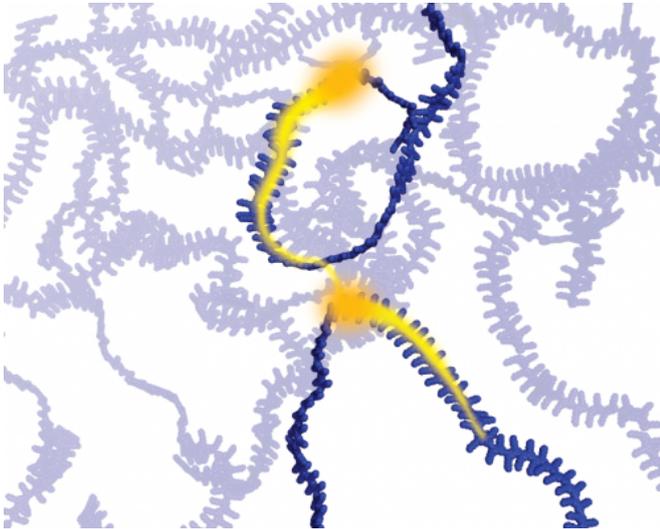


Researchers publish theory, formula to improve 'plastic' semiconductors

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The yellow electric charge races through a "speed-lane" in this stylized view of a polymer semiconductor, but pauses before leaping to the next fast path. Stanford engineers are studying why this occurs with an eye toward building flexible electronics. Credit: Professor Andrew Spakowitz

Anyone who's stuffed a smart phone in their back pocket would appreciate the convenience of electronic devices that could bend. Flexible electronics could spawn new products: clothing wired to cool or heat, reading tablets that could fold like newspaper, and so on.

Alas, electronic components such as chips, displays and wires are generally made from metals and inorganic semiconductors—materials with physical properties that make them fairly stiff and brittle.

In the quest for flexibility many researchers have been experimenting with semiconductors made from plastics or, more accurately polymers, which bend and stretch readily enough.

"But at the molecular level polymers look like a bowl of spaghetti," says Stanford chemical engineering professor Andrew Spakowitz, adding: "Those non-uniform structures have important implications for the conductive properties of polymeric semiconductors."

Spakowitz and two colleagues, Rodrigo Noriega, a [postdoctoral researcher](#) at UC Berkeley, and Alberto Salleo, a Stanford professor of Materials Science and Engineering, have created the first [theoretical framework](#) that includes this molecular-level structural [inhomogeneity](#), seeking to understand, predict and improve the [conductivity](#) of semiconducting polymers.

Their theory, published today in the *Proceedings of the National Academy of Sciences*, deals with the observed tendency of polymeric semiconductors to conduct electricity at differing rates in different parts of the material – a variability that, as the Stanford paper explains, turns out to depend on whether the [polymer strands](#) are coiled up like a bowl of spaghetti or run relatively true, even if curved, like lanes on a highway.

In other words, the entangled structure that allows plastics and other polymers to bend also impedes their ability to conduct electricity, whereas the regular structure that makes silicon semiconductors such great [electrical switches](#) tends to make it a bad fit for our back pockets.



MacDiarmid and Hideki Shirakawa, shared the Nobel Prize in Chemistry in 2000 for their co-discovery of polymeric semiconductors. In recent years, with increasing urgency, researchers have been trying to harness the finicky electrical properties of plastics with an eye toward fashioning electronics that will bend without breaking.

In the process of experimenting with polymeric semiconductors, however, researchers discovered that these flexible materials exhibited "anomalous transport behavior" or, simply put, variability in the speed at which electrons flowed through the system.

Stanford Professor Andrew Spakowitz has studied how the molecular structures that make polymers flexible also affect their usefulness as semiconductors. The research will help make bendable electronic devices possible. Credit: Tom Abate, Stanford University

One of the fundamental insights of the Stanford paper is that electron flow through polymers is affected by their spaghetti-like structure – a structure that is far less uniform than that of the various forms of silicon and other inorganic semiconductors whose electrical properties are much better understood.

The Stanford paper in *PNAS* gives experimental researchers a model that allows them to understand the tradeoff between the flexibility and conductivity of polymeric semiconductors.

"Prior theories of electrical flow in polymeric semiconductors are largely extrapolated from our understanding of metals and inorganic semiconductors like silicon," Spakowitz said, adding that he and his collaborators began by taking a molecular-level view of the electron transport issue.

Grasping how they created their model requires a basic understanding of polymers. The word "polymer" is derived from the Greek for "many parts" which aptly describes their simple molecular structure, which consists of identical units, called monomers, that string together, end to end, like so many sausages. Humans have long used natural polymers such as silk and wool, while newer industrial processes have adapted this same technique to turn end-to-end chains of hydrocarbon molecules, ultimately derived from petroleum byproducts, into plastics.

But it was only in the late 1970s that a trio of scientists discovered that plastics which, until then were considered non-conductive materials suitable to wrap around wires for insulation could, under certain circumstances, be induced to conduct electricity.

The three scientists, Alan Heeger, Alan



A mathematical model created by Stanford researchers identifies key variables affecting the conductivity of

polymer semiconductors. Credit: Tom Abate, Stanford Engineering

Provided by Stanford University

In essence, the variability of electron flow through polymeric semiconductors owes to the way the structure of these molecular chains creates fast paths and congestion points (refer to diagram). In a stylized sense imagine that a polymer chain runs relatively straight before coming to a hairpin turn to form a U-shape. An electric field moves electrons rapidly up to the hairpin, only to stall.

Meanwhile imagine a similar U-shape polymer separated from the first by a tiny gap. Eventually, the electrons will jump that gap to go from the first fast path to the opposing fast path. One way to think about this is a traffic analogy, in which the electrons must wait for a traffic light to cross from one street, through the gap, before proceeding down the next.

Most importantly, perhaps, in terms of putting this knowledge to use, the Stanford theory includes a simple algorithm that begins to suggest how to control the process for making polymers – and devices out of the resulting materials - with an eye toward improving their electronic properties.

"There are many, many types of monomers and many variables in the process," Spakowitz said. The model presented by the Stanford team simplifies this problem greatly by reducing it to a small number of variables describing the structural and electronic properties of [semiconducting polymers](#). This simplicity does not preclude its predictive value; in fact, it makes it possible to evaluate the main aspects describing the physics of charge transport in these systems.

"A simple theory that works is a good start," said Spakowitz, who envisions much work ahead to bring bending [smart phones](#) and folding e-readers to reality.

More information: Chain conformations dictate multiscale charge transport phenomena in disordered semiconducting polymers, *PNAS*, www.pnas.org/cgi/doi/10.1073/pnas.1307158110

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