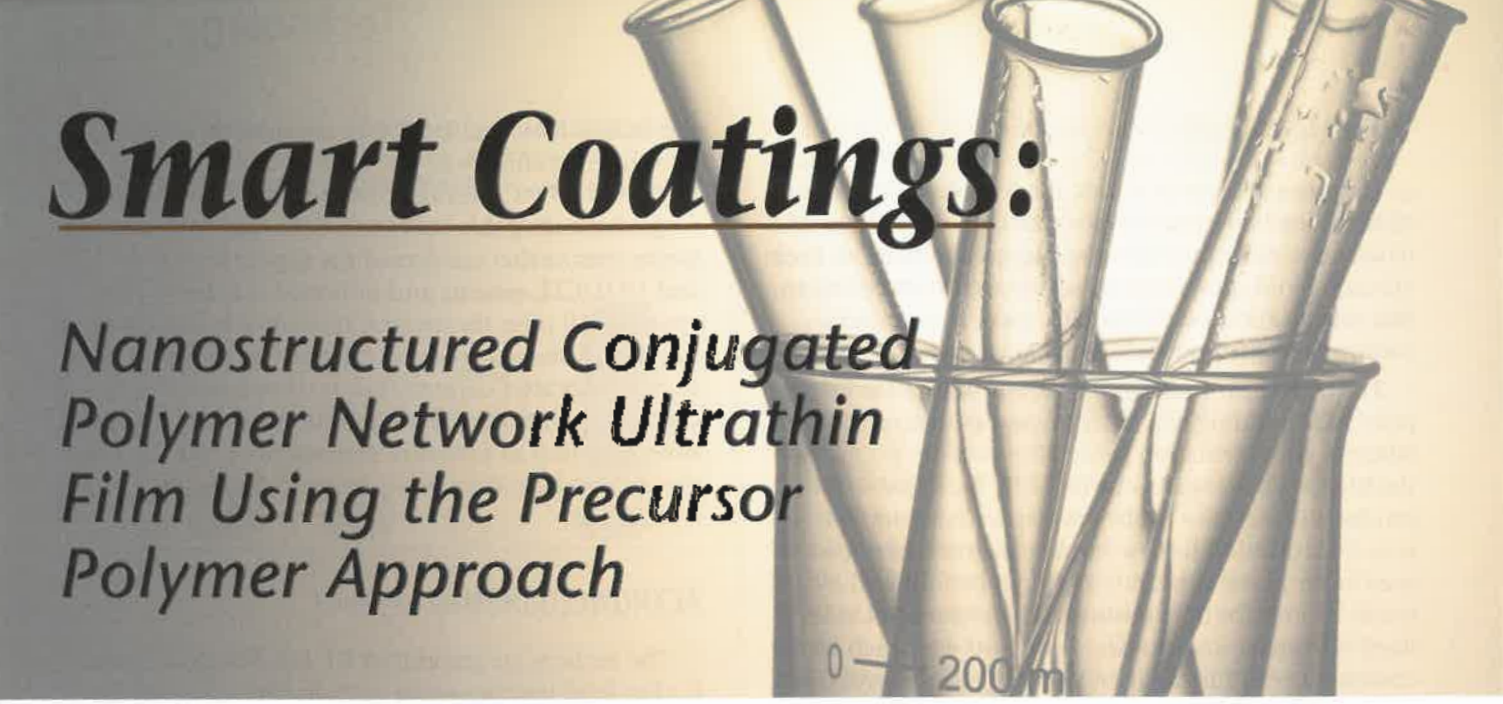
Smart Coatings:

Nanostructured Conjugated Polymer Network Ultrathin Film Using the Precursor Polymer Approach



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The coatings industry has had a fascination with "smart coatings" for some time. Smart coatings are not new in the sense that they take into account everyday applications using new materials and mechanisms to improve the performance of existing coatings. On the other hand, because of fundamental discoveries made in the field of polymeric and inorganic materials there is a potential to generate new and "smart applications." The use of so-called macromolecular assemblies in ultrathin films provides new ways of assembly of ultrathin film coatings even through a layer-by-layer approach.

Organic π-conjugated polymers and intrinsically conducting polymers (ICPs) have shown very promising behavior as alternative electrical conducting, nonlinear optical, and electroluminescent materials.[1] Other applications include: energy storage, electrochromic displays, sensors, charge-dissipation, and anticorrosion coatings. Both doped and undoped forms are being investigated for these applications with the idea of replacing their inorganic material counterpart. A wealth of synthetic techniques leading to novel molecular, macromolecular, and microstructural design has been reported.
Electrochemical methods have been utilized to control the oxidation potential for polymerization and investigate the resulting electronic properties of these polymers. In this case, the conjugated polymers are formed in-situ as the monomers are polymerized (radical cation mechanism) and deposited on a conductive electrode. Recently, the importance of optical film qualities of these materials has been emphasized for electrochromic applications. For non-doped film applications such as polymer light-emitting diode (PLED) and field effect transistor (FET) devices, the optical dielectric constants, charge carrier properties, thickness, morphology (crystallinity or aggregation), and layer order of the films are deemed to be important.

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We have demonstrated previously the deposition of high optical quality ultrathin film coatings of conjugated polymers through the Precursor Polymer approach (*Figure* 1). We have reported the synthesis and electrochemical deposition of "passive" polysiloxane-precursor derivatives (by cyclic voltammetry or potentiostatic methods) of thiophene and pyrrole to form crosslinked polythiophene and polypyrrole, respectively.[2] These polymers can be directly deposited from an electrolyte solution or spin-coated to the electrode substrate first and electrochemically oxidized. We have also reported the electrodeposition and electrochemical grafting to indium tin oxide (ITO) substrates of a precursor polymer (copolymer) with an "active" conjugated polyfluorene backbone.[3] The electro-active carbazole side group facilitated electrodeposition, forming oligocarbazole links. Recently, we have also investigated the use of poly(vinyl carbazole) or PVK as precursor polymer materials for polycarbazole thin films.[4]

In all these cases, film formation was accomplished by electrochemically crosslinking and polymerizing the precursor polymers through the electro-active monomer side group as they deposited to the surface of the electrode. We believe that the reason the films were of such good quality is because the mechanical strength is "built in" at the precursor stage. The films are held together by the entanglements between chains due to the inter- and intra-molecular polymerization pathways resulting in crosslinks. It is also possible to increase the amount of linear conjugated polymer chains simply by introducing non-polymer bound electro-active monomers as we have demonstrated in the case of precursor polypyrroles with polysiloxane and polymethacrylate backbones.

In this article we report methods of coating and patterning of precursor polymers electrochemically. We will also present several strategies for the synthesis, fabrication, and characterization of these unique conjugated polymer ultrathin films. The application of these crosslinked materials is towards electro-optical devices, e.g., polymer light-emitting diode (PLED) devices will also be described. Micro-contact printing (μCP) is a soft-lithographic approach that has been used for creating micron-sized patterns on flat surfaces. By controlling the deposition site using micro-contact printing, patterns on the electrode surface can be formed prior to electropolymerization. This resulted in light-emitting regions from the selectively deposited sites containing carbazole-modified polyfluorenes. Furthermore, we will also demonstrate the possibility of sequential electrochemical deposition of two different precursor polymers based on precursor polycarbazole and polythiophene derivatives. Electrochemical Nanolithography (ECN) is a technique in which a pattern is created by applying a potential between the AFM tip and the substrate (conducting AFM set-up) during "writing."

RESULTS AND DISCUSSION

Precursor Polymers

The synthesis of the polymers was done either by polymer analogous reactions or through direct polymerization of vinyl monomers containing electropolymerizable side-groups. Several synthesis strategies have been reported. One such copolymer is shown in *Figure* 2, where the presence of carbazole and thiophene side groups provided a crosslinking unit for electrochemical deposition. We have also utilized extensively polyvinylcarbazole (PVK), which functions as very good hole-transport layers and can be crosslinked to form polycarbazole thin films. All of these polymers have the common design feature of tethered electropolymerizable monomers, which can be varied in composition.

The precursor polymers were then crosslinked by electropolymerization and monitored by cyclic voltammetry at various solvents, substrates, solution concentrations, and counter electrolytes. The crosslinking can also be done by potentiostatic methods. Crosslinking occurs to form very uniform and optically clear films which are essentially insoluble once formed. Most of the films investigated showed reversible color changes (electrochromism) during the redox process and CV cycling. The use of surface plasmon spectroscopy (SPS) electrochemical quartz crystal microbalance (E-QCM), X-ray photoelectron spectroscopy (XPS), and FTIR spectroscopy and AFM revealed interesting deposition, doping, morphology, and crosslinking chemistry for these conjugated polymer films.

Figure 1—Precursor Polymer approach to conjugated polymers with different polymeric backbones.

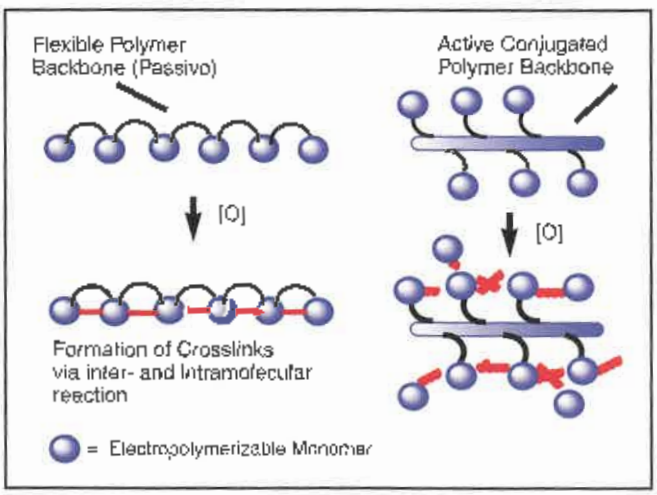
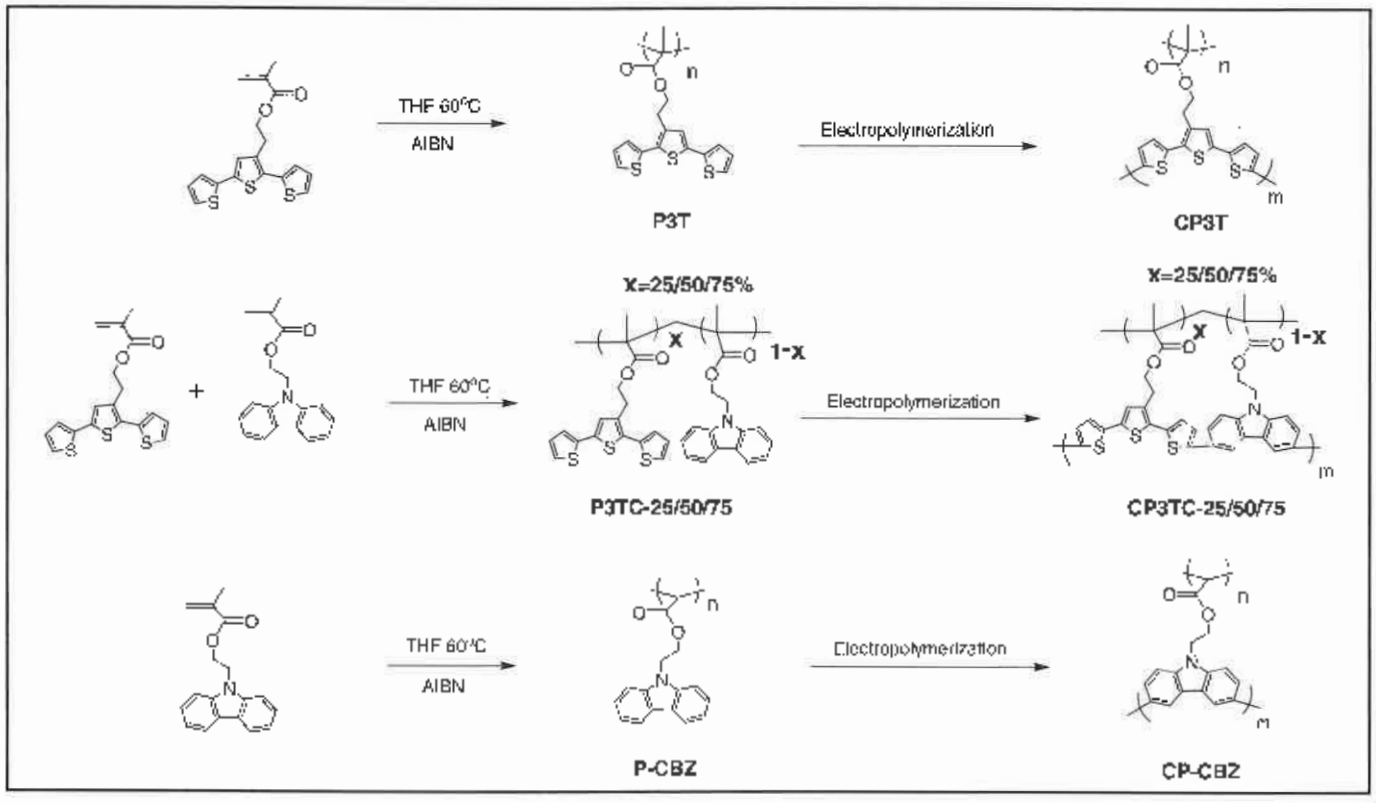


Figure 2—Synthesis of precursor homopolymers/copolymers and their electropolymerization.



Patterning by Microcontact Printing

To investigate in-situ the growth of conjugated polymers on patterned conducting surfaces, we have employed an electrochemical surface plasmon microscopy (EC-SPM) technique. The patterns on the electrode surface were first defined by micro-contact printing (*Figure 3*). Upon electrodeposition of the monomer on the surface by cyclic-voltammetry (or potentiostatically), the polymer was observed to grow only on the bare Au surfaces which have not been insulated by the ODT layers used under a particular potential. We observed that the contrast of the images where the conjugated polymer has grown varied with the "height" of the deposited polymer, the refractive index contrast, and the angle of observation for microscopy. These changes were also correlated with the specific redox stages of the potential on the CV. The in-situ EC-SPM technique emphasizes the sensitivity of these patterns to optical reflectivity changes, which can have possible applications in micro-displays and sensors.

Grafting of Carbazole-Modified Polyfluorenes on Electrode Surfaces

We have reported previously the grafting of carbazole-modified polyfluorenes. Using the precursor polymer shown in *Figure 3*, we grafted the polymers directly to an ODT microcontact printed surface. The grafting was done electrochemically by CV or by potentiostatic methods from solution. Different morphologies and deposition behavior were observed. Interestingly, the polymer preferentially deposited on the hydrophobic SAM modified surfaces. This underscores the importance of matching the particular surface energies of the electrodeposited organic polymer materials to the substrate surface. Since the electrochemical activity was limited to the carbazole side groups, the absorption and fluorescence properties of the polyfluorene backbone remained intact. That is why patterned fluorescence was observed on these dots using fluorescence microscopy. This selective electropolymerization and electrodeposition is an interesting method for preparing thermally stable and mechanically robust conjugated polymer patterns and should be useful for a number of electro-optical applications including PLEDs.

Electrochemical Nanolithography (ECN)

A negative voltage bias is applied to the AFM tip (anode) and electrochemical oxidation occurs on a dielectric material coated on a conducting electrode (cathode). This voltage bias (constant potential) in the presence of the right condition for an electrochemical reaction will

result in crosslinking of the precursor. The patterns are formed and the conductivity will differ, i.e., direct electropolymerization of patterns by the AFM tip. Control of patterning will involve varying the potential, writing speed, film thickness, and specific sites. While previous work has described FCN based on direct introduction of electroactive monomers from the AFM tip to the substrate, here we emphasize the preparation of nanopatterns on polymer films through electrochemical polymerization/crosslinking of a precursor polymer film. The method has been demonstrated recently on PVK, spin-coated on a conducting substrate. In our experiment, the application of a biased potential from the AFM tip resulted in the oxidation of carbazole followed by polymerization or crosslinking under ambient conditions (23°C, in air with 75% humidity). A pattern "NUS-CHE" was written on the spin-coated PVK film. Test lines showed that the pattern varied in thickness and resolution as a function of voltage and writing speed. The control of thickness was not explored at that time. Recently, we have demonstrated electrochemical nanolithography on polyelectrolyte layer by layer films of polyfluorene precursors with controlled nm thicknesses.

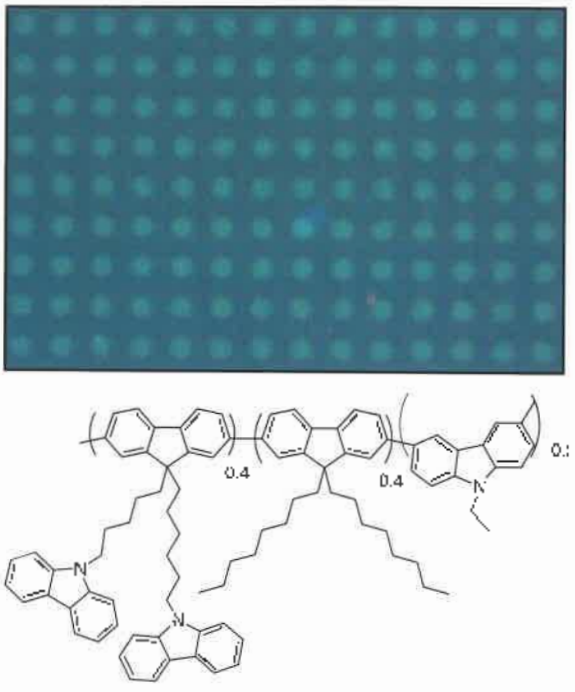
PLED Devices

Our recent investigations on the application of these crosslinked films to the fabrication PLED devices showed dramatic improvements towards lower turn-on-voltages and greater efficiencies. For example, the application of crosslinked polyvinylcarbazole (PVK) as a hole transport material for a heterojunction bilayer PLED device with polyfluorene or Alq_3 showed significant improvements and tenability with doping. These interesting results show that crosslinked conjugated polymer films play an important role in the development of these display devices and their application to other types of semiconductor devices. In principle, electrical or band gap tuning is possible with the right choice of a conjugated or non-conjugated polymer backbone. The difference is that these films are very robust both thermally and mechanically. Other applications of these films to sensors, dielectric materials, nonlithographic patterning, etc., are currently being investigated by our group.

Future Applications

The previous methods and applications have shown the potential for ultrathin film applications based on the precursor approach for conjugated polymer networks. It is obvious that bulk or thick film coatings applications have yet to be demonstrated. The crosslinking and electropolymerization leads to the formation of conjugated/conducting and electrochromic or even fluorescent coatings. It is possible that applications involving anticorrosion, electrochromic windows, antistatic, and even "sensing" coatings will be fully exploited in the near future.

Figure 3—Blue emitting polyfluorene precursor polymer as applied to electrodeposition on a microcontact printed electrode pattern.



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