



# Desorption and photopolymerization behavior of mixed and multilayered styrene–pyrrole nanofilms

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## Abstract

The molecular arrangement and polymerization of adsorbed styrene–pyrrole films were explored using two different dosing schemes: simultaneous dosing to form an intimately mixed film of the two monomers and sequential dosing to form films with distinct layers of styrene and pyrrole. It was found that the desorption of pyrrole was delayed until 175 K when either simultaneously dosed with styrene or in the presence of an overlying styrene layer, whereas it normally desorbs at 165 K when dosed alone. No such effects were observed with styrene in any dosing configuration. The polymerization rate of pyrrole was unaffected in the films when present as the top layer and was observed to decrease by 50% when beneath a styrene layer. Moreover, the rate of polymerization increased by two orders of magnitude in the case of the intimately mixed film. The rate of styrene polymerization was not found to change in any of the explored geometries. These effects are explained by considering the proximity of the components and the potential for screening UV radiation based on their molecular structure.

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## 1. Introduction

The formation of thin polymer films on various substrates is of growing interest in a number of fields, including electroluminescent films for flat panel

displays [1–3] and lubrication coatings for micro-electromechanical systems (MEMS) [4,5]. Thin polymer films play a vital role in the semiconductor industry for use as dielectric layers [6] and are of growing interest for the creation of organic light-emitting diodes, field effect transistors, photovoltaic cells and sensors [7,8].

Typically, thin polymer films are fabricated through spin coating. Unfortunately, this method can often

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generate films with less than desirable film morphology because of issues such as the “orange peel effect” and “pin hole defects” that arise during evaporation of the solvent [9]. Also, depending on the hygroscopic behavior of different solvents, the polymer can precipitate, causing nonuniformity in the film [9]. Finally, using spin coating, it can be difficult to control film thickness in the 10–100 nm region [10]. Perhaps the biggest disadvantage of traditional wet techniques lies in the fact that most conducting polymers are generally insoluble in organic solutions. This makes it very difficult to use spin coating to produce thin-film organic conductors.

It has been shown that ultrathin polymer films can be made using a two-step deposition polymerization process [11–18]. First, a substrate is placed in an ultra high vacuum (UHV) chamber and cooled to liquid nitrogen temperature. The monomer is then dosed into the chamber by backfilling through a leak valve. Liquid nitrogen cooling is necessary since, in UHV, most organic molecules on metal surfaces have desorption temperatures below 200 K. Once the desired exposure of monomer has been reached, the leak valve is closed, leaving behind a thin monomer film on the sample surface. Finally, the polymer film is formed by exposing the adsorbed monomer to ultraviolet radiation, which initiates polymerization. The resulting polymer film thickness can range from less than one nanometer up to several hundreds of microns, depending on the monomer dosage.

While the formation of single species polymer films using the deposition/polymerization method has been demonstrated, [11–18] the formation of multicomponent films with different components either mixed in a single layer or separated into individual layers has not. The construction of multicomponent films will allow for easier fabrication of complex devices, such as all-polymeric transistors, since both insulating and conducting layers could be formed simultaneously. Another motivation for this study is the synthesis of copolymers that are not easily formed via common wet chemical approaches. Typically, the formation of a specific copolymer is determined by the monomer reactivity ratios, [19] which come about from the ability of monomers in solution to diffuse and react preferentially with each other. However, in the fabrication method described here, the monomers are immobilized, giving rise to the possibility of forming

copolymers from monomers with large reactivity ratios. To the best of our knowledge, the adsorption and polymerization behavior and possible synergistic effects of multiple monomers coexisting on the same substrate has not been studied. For this reason, we chose to investigate the adsorption and polymerization behavior of styrene and pyrrole on a single crystal platinum (1 0 0) surface.

## 2. Experimental

All experiments were conducted in an ultra high vacuum (UHV) chamber with a base pressure below  $5 \times 10^{-9}$  Torr. A Pt (1 0 0) single crystal was mechanically polished using 0.5  $\mu\text{m}$  alumina micro-polish (Buehler) and spot welded to two tantalum wires, which allowed for resistive heating. The sample had a K-type thermocouple spot welded to the back and was attached to the head of a liquid nitrogen cryostat, which made it possible to control both the temperature and heating rate of the platinum sample between 93 and 1300 K. The cryostat was mounted on a manipulator that allowed translation in the  $x$ ,  $y$  and  $z$  directions as well as  $360^\circ$  rotation around the  $z$ -axis. The single crystal was cleaned using cycles of  $\text{Ar}^+$  sputtering at  $10^{-4}$  Torr, flash annealing at 1200 K, and oxidation at 920 K in  $10^{-6}$  Torr  $\text{O}_2$ .

Styrene and pyrrole were chosen for several reasons. From previous studies, it is known that their desorption temperatures are separated by several tens of Kelvin and they both undergo photoinitiated polymerization. Also, polystyrene is insulating while polypyrrole is conducting, leading to the possibility of using these two monomers to create electrical devices. Styrene (99%, Aldrich) was first prepared by passing it through an inhibitor removal column (Aldrich). Both styrene and pyrrole (98%, Aldrich) were stored in Schlenk tubes and subjected to several freeze–pump–thaw cycles before use.

Gaseous mixtures of styrene and pyrrole were created in a separate mixing chamber with a base pressure of  $10^{-5}$  Torr. The monomers were introduced individually through separate leak valves into the mixing chamber, where the pressure, and thus mixture composition, was measured using a capacitance manometer (MKS Baratron 627). This mixture was

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