

## Thin Film Construction and Characterization and Gas-Sensing Performances of a Tailored Phenylene–Thienylene Copolymer

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**Abstract:** An alternating copolymer, poly(2,5-dioctyloxy-1,4-phenylene-*alt*-2,5-thienylene), has been synthesized and used in this research. The behavior of the floating film at the air–water interface has been investigated by measuring surface pressure versus area Langmuir isotherms and contemporaneously by reflection spectroscopy and Brewster angle microscopy. The floating films were transferred by the Langmuir–Schäfer (horizontal lifting) method onto various substrates. It is apparent from these analyses that the effective conjugation length is larger than those in other electroactive polymers and that a strong coplanarity and interchain association takes place above all in the floating film on the water surface and in the transferred multilayers. Such films were used as the active layers in resistive chemical gas sensor devices, thus revealing excellent sensitivity toward NO<sub>2</sub>, reversibility, and time stability of the response.

### Introduction

In past decades, conjugated polymers have been paid considerable attention because of their academic importance and capability in technological applications. Their electrical and optical properties are utilized in functional device preparation such as large flat-panel displays, light emitting diodes,<sup>1</sup> and chemical sensors.<sup>2</sup> However, the correlation between such properties and the structural characteristics of these materials has rarely been performed.<sup>3</sup>

The rationale for the utilization of soluble polymeric derivatives in such apparatuses is connected to the possibility of modulating materials' characteristics and economical processing requirements. The variation of materials' properties can be obtained through the chemical modification of unsaturated chain units. In this light, the vinylene moiety of PPVs has been replaced by a thiophene ring, thus inducing in some instances improvement of chemical and physical characteristics, such as solubility, adhesion for film formation, and electrical properties.<sup>1,4</sup> Moreover, the presence of suitable pendant groups allows processible alkoxy substituted copolymers, such as poly(2,5-

dialkoxy-1,4-phenylene-*alt*-2,5-thienylene), to preserve their solubility during conversion procedures, thus making available further chances of easy processibility. Ballauff compared the behavior of lateral substituents to bound solvent molecules, inducing the macromolecules' solubility and fusibility.<sup>5</sup> Additionally, these rigid main chain materials behave as mesogenic moieties in which the liquid-crystalline characteristics are intimately connected to the optical and electrical properties.<sup>3</sup> Upon being heated above their melting points, such electroactive polymers undergo a phase transition, producing a nematic phase.

Unlike the construction of devices containing the inorganic counterpart, usually demanding severe conditions, polymeric coatings could be prepared by different techniques such as spin-coating, casting, Langmuir–Blodgett, self-assembly, or printing methods.<sup>6</sup>

Microelectronics apparatuses are becoming more and more small-scale and elaborate, and consequently the standard of control over orientation and arrangement of molecules becomes more exigent and pressing. The method of deposition univocally considered well fitting with molecular engineering is the Langmuir–Blodgett technique that in this research has been used for the deposition of poly(2,5-dioctyloxy-1,4-phenylene-*alt*-2,5-thienylene), POPT (Scheme 1, Supporting Information). The control over the film thickness is of paramount importance to

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