Surface Science Prospectives

# Covalently bonded networks through surface-confined polymerization

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## ARTICLE INFO

## ABSTRACT

The prospect of synthesizing ordered, covalently bonded structures directly on a surface has recently attracted considerable attention due to its fundamental interest and for potential applications in electronics and photonics. This prospective article focuses on efforts to synthesize and characterize epitaxial one- and two-dimensional (1D and 2D, respectively) polymeric networks on single crystal surfaces. Recent studies, mostly performed using scanning tunneling microscopy (STM), demonstrate the ability to induce polymerization based on Ullmann coupling, thermal dehalogenation and dehydration reactions. The 2D polymer networks synthesized to date have exhibited structural limitations and have been shown to form only small domains on the surface. We discuss different approaches to control 1D and 2D polymerization, with particular emphasis on the surface phenomena that are critical to the formation of larger ordered domains.

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## 1. Introduction

Molecular self-assembly is a fundamental process that can be harnessed for a variety of nanotechnology applications. The study of molecular epitaxial growth at surfaces may provide critical new insight for their integration in molecular electronics [1–3]. Various self-assembled structures held together by non-covalent bonds have been achieved based on different intermolecular interactions such as hydrogen bonds [4–9], van der Waals interaction [10], halogen bonds [11–13] and metal–organic coordination [14–16]. These types of interactions, which have the advantage of the reversibility of bonding on the surface, offer an opportunity for forming long range ordered structures in two dimensions. However, self-assembly does have some limitations, most notably that the intermolecular interaction is relatively weak and therefore leads to fragile structures. This challenge can be overcome by forming covalent bonds between molecules [17,18]. Various studies have been performed with the objective of creating macromolecular structures on a surface starting from small building blocks [19,20]. A major advantage provided by covalent bonding, in addition to the mechanical rigidity of the structures, is the effective charge transport through the bond [21]. Conjugated polymers are ubiquitous semi-conducting materials that are increasingly used in applications. Their integrated optoelectronic properties make them well-suited for use as active components in electronic devices [3,21,22], such as photovoltaic cells [23], organic light-emitting diodes [24–26] and organic field-effect transistors [27–29]. 1D or 2D conjugated polymer nanostructures, in which covalent bonds provide robust structural and thermal properties, are increasingly being synthesized using a bottom-up approach where monomers are deposited onto a surface and subsequently made to react. To date, such surface confined polymers have been synthesized using various routes including Ullmann dehalogenation [30,31], thermal cleaving of carbon-halide bonds [19,32,33] and dehydration reactions [34–38]. Although 1D polymer "lines" can be synthesized with reasonably high quality, 2D networks have so far exhibited small domains and a high defect density. Thus, the search for improved pathways to synthesize large covalently bonded 2D nanostructures with low defect densities is intensifying, as is the effort to probe and subsequently optimize their electronic properties.

The role of the substrate, specifically its orientation and chemical properties, in the polymerization process cannot be overemphasized. Depending on the synthesis approach employed, the surface can be used as both a catalyst and/or a template to confine the polymerization reaction. The resulting polymeric structures have been characterized using standard surface science techniques including STM and X-ray photoemission spectroscopy (XPS), complimented with density functional theory (DFT) calculations [20,30,35,39]. These characterization techniques provide information about both structural and electronic properties, critical for understanding and controlling the polymerization reaction on the surface [3,40–42].

In this prospective we describe recent work on 1D and 2D surface-confined polymerization reactions and discuss the surface phenomena that may play a key role in addressing the current limitations of polymerization reactions, particularly in two dimensions. These include the reactivity of monomers on the surface, the role of diffusion in the spatial extension of the network and the optimization of reaction intermediates.

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## 2. One-dimensional surface-confined polymerization

The simplest geometric examples of surface-confined growth of conjugated polymers have been demonstrated through the creation of 1D lines of polydiacetylene [43] and polyphenylene [30]. These structures were achieved using different chemical routes: photochemical activation, voltage pulsing with an STM tip and Ullmann coupling, respectively, and are discussed in more detail hereafter.

### 2.1. Diacetylene polymerization

Grim et al. first reported the photo-polymerization of diacetylene molecules on HOPG at the solution/solid interface [43]. The reactants and products of the polymerization reaction were characterized, with submolecular resolution, by STM. The structure adopted by the diacetylene-containing isophtalic acid (ISA) on HOPG comprises adjacent lamellae of diacetylene. Following irradiation with ultraviolet light (UV), a contrast change within the structure was observed, which was attributed to the polymerization of the diacetylene molecules. This interpretation was then confirmed by measuring the intermolecular spacing, which was found to expand from $9.44 \pm 0.09$ Å to $9.81 \pm 0.05$ Å, measured as the spacing between two adjacent ISA groups in the structure.

Okawa and Aono subsequently reported the creation of polymer nanowires through a polymerization chain reaction in diacetylene molecules initiated by applying a voltage pulse with the STM tip [44,45]. Two monomers, 10,12-pentacosadiynoic acid and 10,12-nonacosadiynoic acid, were self-assembled and made to react on the HOPG substrate. The authors demonstrated the ability to control the initiation and termination of the chain polymerization of the 10,12 pentacosadiynoic acid monomer [44]. This control was attained through the creation of a defect hole in the HOPG using the STM tip; the hole then acted as a topological termination site for the polymerization reaction [46]. The dependence of the polymerization probability with the duration of the applied voltage pulse was reported by Sullivan et al. [47]. They correlated increasing polymerization probability with increasing time of the voltage pulse. In addition, they suggested that pit edges terminate the polymerization reaction because topochemical conditions are interrupted at such a site. A similar effect was reported by Okawa and Aono, where the domains boundaries were found to interrupt the polymerization reaction [45].

### 2.2. Polythiophene

Using the electrochemical epitaxial polymerization (ECEP) technique [48], based on step-by-step electro-polymerization of monomers using a voltage pulse, Sakaguchi et al. demonstrated the formation of linear polythiophene wires up to 75 nm in length on the surface of an iodine-terminated Au(111) electrode [48,49]. The polymers were formed after the Au(111) electrode was introduced into a cell containing both iodine and 3-butoxy-4-methylthiophene (BuOMT) monomers and a step-function voltage pulse was applied. By using the ECEP technique in a solution containing different-types of monomers, the authors demonstrated the formation of polythiophene chains as diblocks, triblocks and multiblocks [49]. The structures of these polymers were reproduced using a second method, in which the I-Au(111) electrode was moved between two cells that each contained a single monomer species (3-octyloxy-4-methylthiophene (C8OMT) or 3-octyl-4-methylthiophene (C8MT)). In both cases, the authors differentiated the blocks using the contrast of the structures in STM images; the polythiophenes formed from C8OMT appear bright and solid whereas the C8MT appear as discrete elements.

### 2.3. 1D Ullmann-coupled structures

The success of the ECEP method, which is predicated on the presence of the Au(111) surface as electrode, stimulated interest in identifying

other methods for on-surface polymerization. Ullmann coupling, a reaction based on catalyzed dehalogenation, was identified more than 100 years ago [50]. More recently, each of the Ullmann reaction steps was achieved using an STM tip on Cu(111) [51], when Hla et al. reported the synthesis of biphenyls from iodobenzene molecules in three steps. First, tunneling electrons from the STM tip were used to induce the dissociation of iodobenzene to iodine and phenyl. Second, the STM tip was used to move two phenyls close to one other. Finally, conjugated coupling was accomplished through application of a voltage pulse.

Lipton-Duffin et al. also translated Ullmann polymerization to a single crystal copper surface [30], leading to the formation of two different polyphenylenes: *meta*-polyphenlene (PMP) and *para*-polyphenylene (PPP). PPP and PMP were synthesized on the Cu(110) surface, under UHV conditions, by Ullmann dehalogenation from 1,4 diiodobenzene (*para*-dIB) and 1,3 diiodobenzene (*meta*-dIB) precursors, respectively [30]. These results clearly illustrate that the geometry of the polymerized structures is dependent on the position of the halogen substituent on the molecule. The PPP chains represent the end result of polymerizing *para*-dIB monomers by annealing at 500 K for 5–10 min. In STM images, the PPP chains appear as discrete elements oriented along $\begin{bmatrix} 1 & 1 & 0 \end{bmatrix}$ and separated laterally by lines of iodine atoms (Fig. 1a). The periodicity of PPP was measured at 4.1 Å (profile on Fig. 1a). Approximately the same value was found between two covalently bonded phenyls in the gas phase using DFT calculations (SI of reference [30]). Thus, the adsorption of *para*-dIB on Cu(110) followed by annealing at 500 K led to the formation of aligned polymer chains.

On the other hand, the polymerization of *meta*-dIB on Cu(110) produced two structures: zigzag lines and macrocycles (Fig. 1b). The formation of the zigzag polymer chains can be explained by the presence of kinks introduced by the symmetry of the *meta*-dIB monomers [30]. In addition to PMP, circular macrocycles were found on the surface as shown in the inset of Fig. 1c. Both pentagonal and hexagonal structures were identified.

Lipton-Duffin et al. later reported the formation of ordered poly (3,4-ethylenedioxythiophene) (PEDOT) chains directly on the Cu(110) surface, which was again used as both a template and a catalyst [31]. Different structures like monomers, dimers and trimers were observed on the surface (Fig. 2a) following the deposition of 2,5-diiodo 3,4-ethylenedioxythiophene) (DIEDOT). These structures are surrounded by regions with $c(2 \times 2)$ symmetry, ascribed to iodine atoms adsorbed on hollow sites of the Cu(110) surface [31], confirming the dehalogenation of the molecules. In combination with DFT calculations, the experimental results show that the dehalogenated molecules reside above the long bridge sites of Cu(110), oriented with the sulfur atoms pointing toward the surface. Three interactions stabilize the EDOT elements: C–Cu, Cu–S bonds with the surface and the van der Waals interaction between adjacent molecules.

Increasing the DIEDOT coverage led to the formation of bonded lines formed from dimeric and trimeric structures (Fig. 2a). These structures appear as discrete elements in $\begin{bmatrix} 1 & 1 & 0 \end{bmatrix}$ and a continuous element in [001]. Surfaces saturated by DIEDOT show the formation of PEDOT oligomers and I-c$(2 \times 2)$ structures (supporting information of reference [31]). The oligomer chains are the result of an extended polymerization reaction between EDOT monomers along the [001] direction (supporting information in reference [31]). It was thus shown that the strong molecule-surface interaction dictates the formation of the cis configuration of the polymer chains. This occurrence was surprising and unexpected, since in the gas phase only the trans configuration is present.

Identifying the intermediate state of the Ullmann coupling reaction on the surface is a crucial step to understanding the mechanism of the reaction. McCarty and Weiss proposed that the radicals, in an intermediate state, are linked by molecule-molecule and surface-mediated interactions [52,53]. Lipton-Duffin et al. and Walch et al. proposed that the copper atoms link two adjacent radicals based on