



Crystallization of Poly(3-hexylthiophene) on graphitic surfaces with different curvatures

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ABSTRACT

Graphitic substrates with different curvatures (i.e. carbon nanotubes, carbon nanofibers and graphene) are used to induce the crystallization of poly(3-hexylthiophene) (P3HT) on the surfaces. The effect of P3HT molecular weight (M_n) and the surface curvature on P3HT crystal structures is investigated. P3HTs with an M_n above the chain folding threshold M_n value form nanowires from all graphitic surfaces. P3HTs with an M_n below the chain folding threshold M_n value form nanowires from graphitic surfaces with a large curvature (e.g. SWCNTs) but produce nanoribbons from graphitic surfaces with smaller curvatures (e.g. MWCNTs, CFs, and graphene). The kinetic study of P3HT crystallizations on graphitic surfaces reveals that intermolecular interactions, specific surface area and curvature have major effects on P3HT crystallization rate on graphitic surfaces.

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1. Introduction

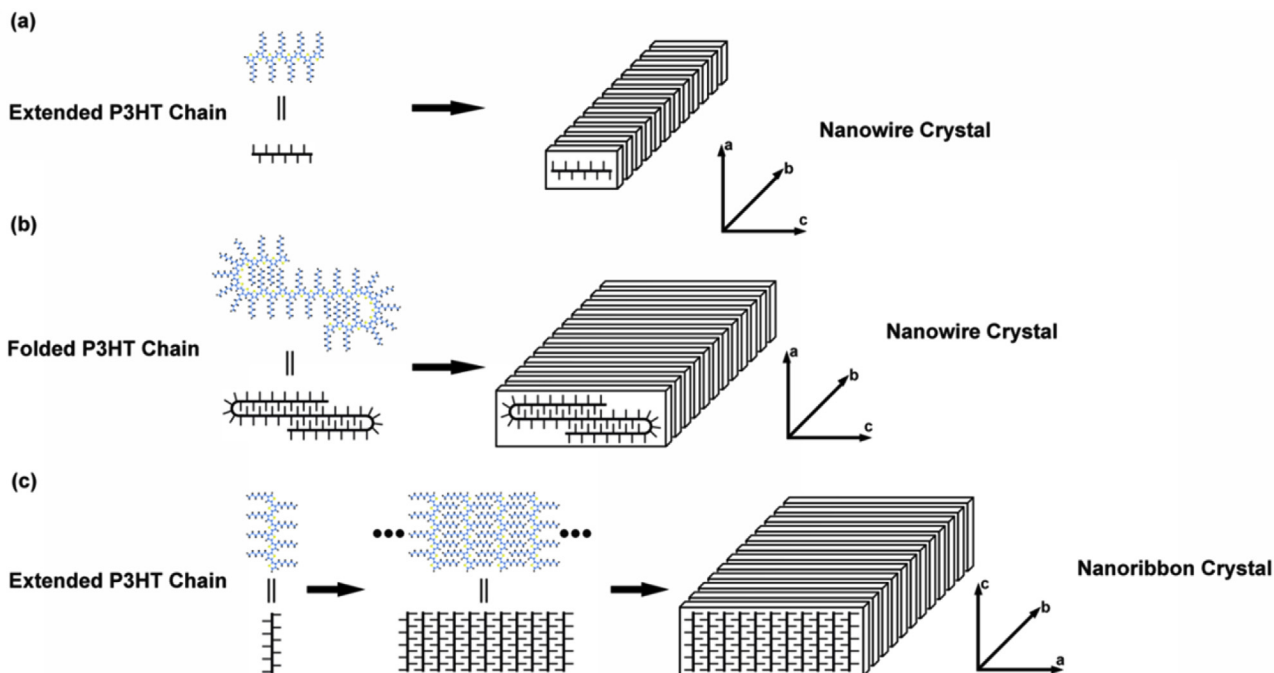
Solution processed organic electronic devices are of great interest for their potential applications in low cost electronics, optoelectronics and clean energy harvest because of their ease of processing, cost effective fabrication, light weight, flexibility, ability to cover large areas as well as the potential of constructing desired device using rationally designed molecules [1–3]. Conjugated polymers (CPs), containing conjugated chains with π -electrons delocalized along the polymer backbones, have numerous potential applications in solution processed organic electronics such as organic field-effect transistors (OFETs) [4–11], molecular electronics [12–14] and bulk heterojunction organic photovoltaics (BHJ-OPVs) [15–30]. The performance of CP based organic electronic devices is determined by two factors: the morphology of CPs and the interface between CPs and electrodes due to the anisotropic charge transport characteristics in these devices. The charge transport pathways in polycrystalline CP films include fast inter-chain and intrachain transport within crystals and slow inter-grain transport among CP crystals [31]. A recent study of the relationship between the disorder, aggregation and charge transport of CP films

suggests that the inter-grain charge transport is the rate determining step for charge transport. The key to improve the charge transport is eliminating the grain boundary [32]. The understanding of charge transport mechanisms in CPs leads to much effort in producing CP crystals with controlled orientation and improving the active material/electrode interfacial properties [33–38].

Regioregular poly(3-hexyl thiophene) (P3HT) is one of the most extensively studied CPs due to its high charge mobility and tendency to assemble into crystals (i.e. nanowires and nanoribbons) [33–36,39–46]. The research has been focused on the formation of P3HT crystals in solutions and on substrates include carbon nanotubes [8,36,39,47], graphene [48] and derivatives [49–53], and polymer assemblies [54,55]. The most reported P3HT supermolecular assemblies are nanowires, which are formed through π - π interactions among polymer backbones (Scheme 1 a–b) [43–46,53,56–59]. The investigation of P3HT crystallization process in solutions by changing molecular weight (M_n), crystallization temperature and polymer concentration suggested that P3HT polymer chains transit from extending to folding in nanowhiskers when the M_n is above a critical value (10 kDa). The folding length can be controlled by crystallization temperature, and extended P3HT chains can further grow into highly ordered two-dimensional (2D) nanoribbons by the combination of π - π interactions among polymer backbones and alkyl side chain Van der Waals interactions (Scheme 1c) [33].

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Scheme 1. Schematic illustrations of (a) nanowire crystals formation from extended P3HT chains, (b) nanowire crystals formation from folded P3HT chains, and (c) nanoribbon crystals formation from extended P3HT chains.

CNTs and graphene have been used as electrodes in organic electronic devices for replacing indium tin oxide (ITO) [60]. CNT electrodes are known to have superior charge injection than metal electrodes in OFETs [61–65]. Graphene has extraordinary room-temperature carrier mobility ($20000 \text{ cm}^2/\text{V}$) [66–71], conductivity, and high optical transmittance (97.7% at 550 nm), making it a viable candidate for electrodes. CNTs and graphene are ideal for guiding the crystallization of CPs to improve charge transport and providing optimum CP/electrode interfaces for efficient charge injection. The π - π intermolecular interactions between graphitic surfaces (i.e. surfaces of CNT and graphene) and CPs such as poly(3-hexylthiophene) (P3HT) have been used to guide the growth of CP supramolecular assemblies (i.e. nanowires) on graphitic surfaces [34,39,48,72–76], and fabricate efficient organic electronics with optimized CP crystal orientation and CP assembly/electrode interfacial contact.

In this article, we report the investigation of the crystallization of P3HT on graphitic surfaces with different curvatures (i.e. SWCNTs, MWCNTs, carbon fibers, and graphene) from the solutions. The crystals of P3HT with M_n above and below the folding threshold M_n , referred as large molecular weight P3HT (LM-P3HT) and small molecular weight P3HT (SM-P3HT), respectively, on the graphitic surfaces were examined. The crystallization kinetics of P3HT on graphitic surfaces was investigated using in situ UV-Vis spectroscopy and quartz crystal microbalance (QCM). Computational simulations of single P3HT molecule on carbon materials were used to understand the preferential orientation of P3HT nanocrystals on graphitic surfaces. It is discovered that P3HT intermolecular interactions and surface curvature have major effect on P3HT crystallization behavior and crystal structures on graphitic surfaces.

2. Materials

Poly(3-hexylthiophene) (P3HT) were synthesized using a procedure previously reported [77]. P3HT molecules with different

molecular weight were synthesized by controlling polymerization time, and their molecular weight was determined by gel permeation chromatography (GPC). P3HT with molecular weight larger than the chain folding threshold (around 10 kDa) was denoted as “LM-P3HT” ($M_n = 13.8 \text{ kDa}$, $\text{PDI} = 1.51$), and P3HT with molecular weight smaller than the chain folding threshold was denoted as “SM-P3HT” ($M_n = 4.8 \text{ kDa}$, $\text{PDI} = 1.70$).

Single-walled carbon nanotubes (SWCNTs) with 1.5 nm diameters and multi-walled carbon nanotubes (MWCNTs) with 10–20 nm diameters were purchased from NanoLab Inc. (Fig. S1). Carbon fibers (CFs) with 160–180 nm diameters were purchased from Sigma Aldrich (Fig. S2). Highly Ordered Pyrolytic Graphitic (HOPG) and silicon wafers were purchased from SPI. Anisole (HPLC grade) and N, N-dimethylformamide (DMF) (HPLC grade) were purchased from Fisher. Hydrogen and Methane were purchased from Air Liquide. All materials were used as received without further purifications.

Graphene flakes were synthesized by a chemical vapor deposition (CVD) method similar to previous reports [78–80]. Mixed gases of hydrogen and methane were reacted at 1000°C , and graphene flakes were formed on copper foils. After etching copper foils by the iron nitrate aqueous solution, graphene flakes were transferred onto desired substrates (TEM grids and QCM probes) by a wet transfer process.

3. Experimental procedures

3.1. P3HT crystallizations on graphitic carbon materials with different curvatures

To form P3HT crystals on SWCNTs, MWCNTs and CFs, these graphitic carbon materials were added into 95°C P3HT marginal solutions (0.05 mg/mL and 0.3 mg/mL) with a concentration of 0.005 mg/mL. The mixtures contained graphitic carbon materials and P3HT were sonicated for 30 min by a horn sonifier to produce uniform bright yellow dispersions. Dispersions were then heated to

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