

## Feature article

## Backbone orientation in semiconducting polymers

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## ABSTRACT

Charge carrier transport is one of the most important functions of semiconducting polymers when they are used in organic electronic devices. Due to the transport path limited in two directions, i.e., along the  $\pi$ -conjugated backbone and intermolecular  $\pi$ - $\pi$  stacking, the backbones are required to be oriented in the desired motifs with respect to the substrate, such as “edge-on” and “face-on” in order to maximize the device performances. In this Feature Article, we focus on how the orientation of semiconducting polymer backbones are influenced by the chemical structure, e.g., backbone structure, molecular weight, and side chains, and processing conditions. Implications of the backbone orientation for the performance of organic devices such as transistors and solar cells are also discussed.

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## 1. Introduction

$\pi$ -Conjugated polymers, often called semiconducting polymers [1–3], are important class of materials for organic electronics such as organic field-effect transistors (OFETs) [4–6], organic photovoltaics (OPVs) [7–10], and organic light-emitting diodes (OLEDs) [11–13], which enables low-cost, large-area, and flexible devices. In the last two decades, we have seen the significant evolution of semiconducting polymers in terms of design, synthesis, physical properties, and device performances in particular in the field of OFETs and OPVs.

One of the most important functions of semiconducting polymers is charge carrier transport, which largely influences the device performances. Charge carrier transport in semiconducting polymer thin films is apparently governed by an intramolecular pathway along the  $\pi$ -conjugated backbone and an intermolecular pathway along the  $\pi$ - $\pi$  overlaps between the face-to-face  $\pi$ - $\pi$  stacked backbones [14]. Therefore, in order to promote the efficient charge carrier transport, the backbones must be as co-planar as possible and as closely  $\pi$ - $\pi$  stacked each other as possible [15,16], which is referred to as a high crystalline structure. On the other hand, since the above devices require different charge carrier transport direction, i.e., in-plane transport for OFETs [14] and out-of-plane transport for OPVs [17], one must further take into account the

orientation of the backbones or crystallites of semiconducting polymers. If one expects the high in-plane charge carrier mobility, the polymer backbone axis (*c*-axis) is desired to extend within the substrate plane and the backbone plane (*ac* plane) is desired to orient normal to the substrate surface, namely “edge-on” orientation (Fig. 1a) [14]. In contrast, in the case of out-of-plane charge carrier mobility, both the backbone axis and plane are desired to be parallel to the substrate surface, or the axis is desired to extend normal to the substrate surface, where the former is typically called “face-on” orientation [17] (Fig. 1b) and the latter “end-on” orientation [18] (Fig. 1c).

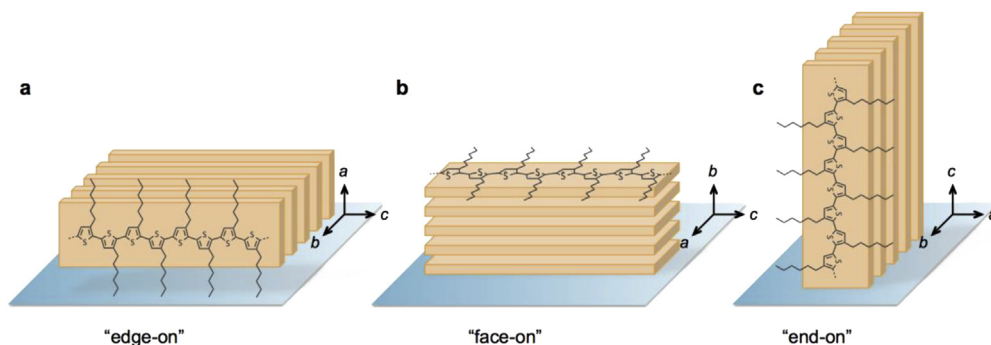
Indeed, a number of studies on the backbone orientation and the influence on the device properties have been reported to date. In this Feature Article, we summarize the correlation of the orientation with the polymer structure, such as the backbone and side chain, and processing methods. Although the end-on orientation certainly facilitates the out-of-plane transport, it is very difficult to construct this orientation motif and the reports are limited [19–23], and thus we here focus on edge-on and face-on.

## 2. Determination of the orientation motifs

Grazing incidence wide-angle X-ray diffraction (GIXD) measurement with a two-dimensional (2D) detector is often used to determine the backbone orientation in thin films deposited on substrates, such as Si/SiO<sub>2</sub>, glass, ITO coated glass, which are often treated with surfactants or coated with interlayers depending on the devices. Since the details of 2D GIXD measurements and

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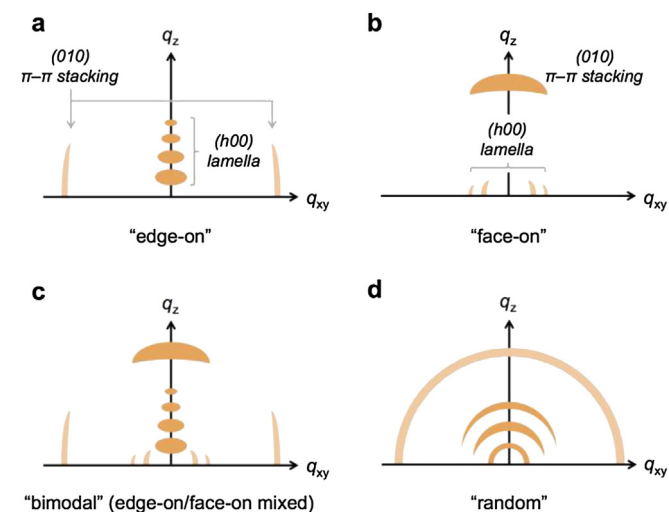


**Fig. 1.** Representative motifs of backbone orientation for semiconducting polymers with respect to the substrate surface. (a) edge-on, (b) face-on, (c) end-on.

analyses are reviewed elsewhere [24], here we simply show the typical textures observable in 2D GIXD for the respective orientation motifs [25,26]. In Fig. 2a, diffractions appear in the smaller angle region along the  $q_z$  axis as spot, and in the wider angle region along the  $q_{xy}$  axis as short arc. Assuming that the unit cell of the polymer crystallites is orthorhombic, the former corresponds to ( $h00$ ), lamella, and the latter corresponds to (010),  $\pi$ - $\pi$  stacking, which represents the edge-on orientation. In Fig. 2b, the ( $h00$ ) diffractions appear along the  $q_{xy}$  axis and the (010) diffraction appears along the  $q_z$  axis. This corresponds to the face-on orientation. Textures comprising diffractions for both edge-on and face-on crystallites (bimodal) are often seen (Fig. 2c), meaning that both crystallites co-exist in the film. The ratio of the crystallites can be determined by using the pole figure analysis [24,27] or by simply calculating the peak intensities in the profiles along the  $q_z$  and  $q_{xy}$  axes [28,29]. In some cases, the diffractions appear as arc or ring (Fig. 2d). This indicates that the crystallites are misoriented or randomly oriented.

### 3. Influence of backbone conformation

The backbone is the basic structure of semiconducting polymers, which determines the ordering structure, namely crystallinity and orientation, as well as the electronic structure.

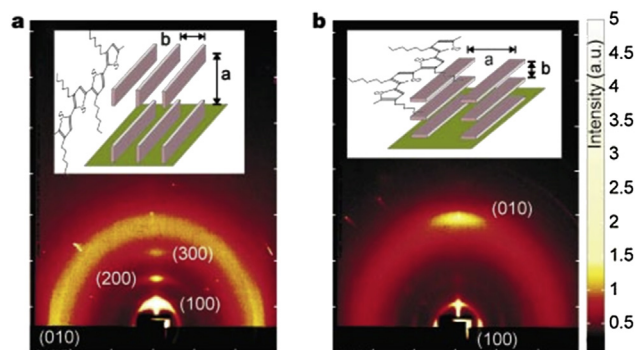


**Fig. 2.** Typical textures that can be observed in the grazing incidence wide-angle X-ray diffraction (GIXD) study with a 2D detector, which correspond to edge-on (a), face-on (b), bimodal (coexistence of edge-on and face-on) (c), and random orientation (d).

Combination of building unit and side chain distribution largely influence their regioregularity, coplanarity, or shape and thus the ordering structure.

Sirringhaus and co-workers reported that poly(3-hexylthiophene) (P3HT), a most widely used semiconducting polymer, can alter the edge-on and face-on orientation depending on the regioregularity and processing conditions on a Si/SiO<sub>2</sub> substrate for OFETs [14]. Whereas the spin-coated samples with lower regioregularity (81%) exhibited face-on orientation, those with higher regioregularity (>91%) exhibited edge-on orientation (Fig. 3). Notably, the solution-cast film of P3HT with the regioregularity of 81% had increased population of the edge-on crystallite. They also established a direct correlation between the orientation, i.e., direction of  $\pi$ - $\pi$  stacking, and the in-plane OFET mobility. The mobility of OFET with high-regioregularity P3HT, with edge-on orientation, was as high as  $0.1 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$  (Fig. 4). In contrast, the mobility of OFET with spin-coated film of low-regioregularity P3HT, with face-on orientation, was lower by three orders of magnitude, namely,  $2 \times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$  (Fig. 4). This value was increased for more than an order of magnitude by using solution-cast film with increased edge-on fraction (Fig. 4). These results have clearly demonstrated that the OFET mobility is limited by  $\pi$ - $\pi$  interchain rather than intrachain transport, and that the charge carrier transport reflects the transport in ordered polymer domains.

A number of studies regarding polythiophene-like semiconducting polymers, such as poly(3,3'-dialkylquaterthiophene) (PQT; Fig. 5a) [30,31], and poly(2,5-bis(3-alkylthiophen-2-yl)thieno[3,2-*b*]thiophene) (PBTTT; Fig. 5b) [32,33], revealed that these



**Fig. 3.** Two different orientations of ordered P3HT domains with respect to the OFET substrate. 2D GIXD images of 70–100 nm thick P3HT films with regioregularity of 96% (a) and 81% (b) on SiO<sub>2</sub>/Si substrates. Reprinted with permission from Ref. [14] Copyright 1999 Nature Publishing Group.

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