JOURNAL OF THE AMERICAN CHEMICAL SOCIETY

Communication

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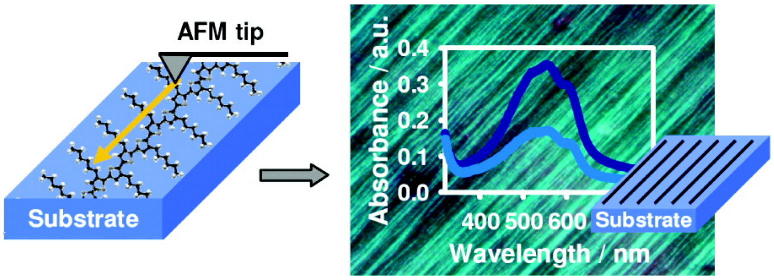
J. Am. Chem. Soc., **2005**, 127 (22), 8018-8019• DOI: 10.1021/ja0505806 • Publication Date (Web): 13 May 2005



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COMMUNICATIONS

Nanorubbing of Polythiophene Surfaces

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Conjugated polymers have been attracting much attention due to their use in semiconducting devices such as organic thin film transistors. As a typical example, poly(3-hexylthiophene) (P3HT) is intensively studied for field-effect transistor (FET) applications[1,2] because of its high charge mobility (up to 0.18 $cm^2/V{\cdot}s$).[3] The charge transport properties and the device performances are intimately related to the long-range order in the polymer films.[1] It is therefore essential to control the degree of structural order, in particular the chain orientation, in conjugated polymer thin films. Various methods exist to align the chains in thin films such as stretching,[4] Langmuir−Blodgett deposition,[5] or "friction-transfer" technique.[6] High degree of ordering can be achieved, leading to homogeneously organized films. In this communication, we describe a new orientation method suitable for conjugated polymers such as P3HT, which provides efficient orientation with precise control of the spatial localization of the oriented regions with a nanometric resolution, a feature that cannot be easily achieved with the "classical" techniques. This method combines in an original way two previously reported concepts: template growth[7] and nanorubbing.[8] We have recently shown that a crystallization process can be used to align the chains in semicrystalline rigid polymers. Upon rubbing amorphous polymer surfaces (e.g., poly(ethyleneterephthalate), PET), we observed on the surface the formation of crystalline aggregates, perfectly aligned along the sliding direction.[7] These aggregates then act as a template to propagate the chain orientation to the whole film when the polymer is heated to the crystallization temperature. This kind of template growth is clearly reminiscent of epitaxial growth.

The possibility to perform nanorubbing on polymers surfaces with an atomic force microscopy (AFM) tip, working in contact mode, has been demonstrated very recently. This method was used to prepare liquid crystal alignment layers made of polyimide with a complex texture.[9] The structural anisotropy induced by AFM nanorubbing was demonstrated to be sufficiently strong to induce efficient liquid crystal orientation even at a moderate load force.[10,11]

In the first part of this communication, we report the study of homogeneous rubbing followed by crystallization for P3HT thin films. On the basis of those results, we then focus specifically on the use of an AFM stylus to impart orientation to P3HT surfaces with a nanometric resolution.

For homogeneous rubbing, we prepared 30-nm-thick films of regioregular (>98%) P3HT (Aldrich) by dip-coating from chloroform solutions (10 mg/mL), on glass substrates, with advancing and retracting speed of 70 mm/min. The P3HT films were uniaxially rubbed with a velvet cloth (velocity of 1 cm/s) and subsequently crystallized in a Mettler hot stage at 170 °C for 30 min. The resulting chain orientation was investigated by polarized UV−visible absorption spectroscopy and by transmission electron microscopy (TEM). For P3HT, the transition dipole moment corresponding to the main electronic transition (peaking at 555 nm for regioregular P3HT) is parallel to the chain axis. Therefore, the dichroism observed with polarized UV−visible spectroscopy gives a direct estimate of the average chain orientation with respect to the rubbing direction. The absorption spectra recorded with the beam polarized either parallel or perpendicular to the rubbing direction yield a dichroic ratio of about 5, which illustrates the efficiency of the orientation process. The chains are aligned along the rubbing direction. TEM was also used to investigate the film organization: electron diffraction gives information about both azimuthal and planar orientation of the crystalline domains within the film. Dip-coated P3HT films were floated from the glass substrate on dilute hydrofluoric acid solution and picked up with copper grids.

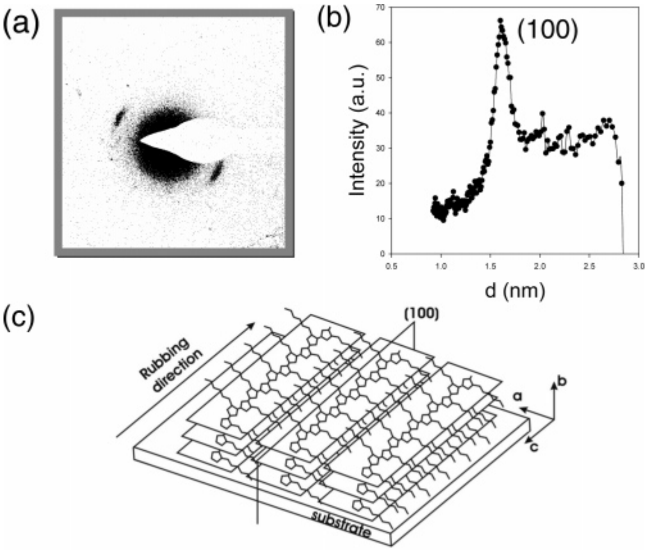

Figure 1. (a) Transmission electron diffraction pattern and (b) profile of a P3HT film rubbed with a velvet cloth. (c) Schematic structure of the arrangement of a rubbed P3HT film.

As shown in Figure 1a, the electron diffraction pattern obtained in TEM for rubbed and crystallized P3HT shows the presence of arcs, which attests to a global orientation of the crystalline domains. The diffraction profile (Figure 1b) reveals the presence of a (100) reflection, which corresponds to the intermolecular distance between two adjacent P3HT chains in the orthorhombic crystal form (a = 1.66 nm, b = 0.77 nm, and c = 0.8 nm).[12] The presence of this reflection confirms that the polymer chains are aligned along the rubbing direction. The degree of polymer orientation, expressed in terms of Herman's orientation function f, defined as $f_{\mathrm{cryst}} = (3\langle\cos^2\sigma\rangle - 1)/2$, was directly computed from the integration of

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10.1021/ja0505806 CCC: $30.25

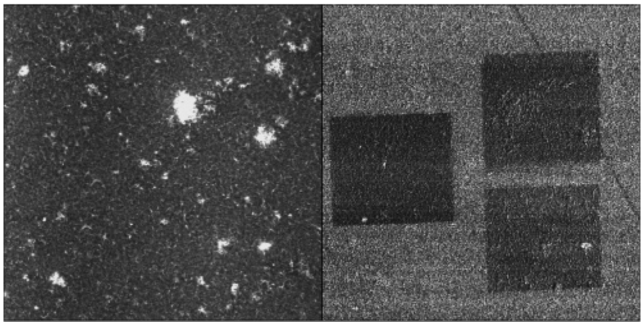

Figure 2. (30 × 30) μm^2 tapping-mode AFM height (left) and phase (right) images of a nanorubbed P3HT film. The vertical gray scale is 30 nm for the height image and 15° for the phase image.

the diffraction intensity profile. In our case, $\langle \cos^2 \sigma \rangle = 0.90$ and $f = 0.85$, which means that 85% of the crystalline domains is aligned along the rubbing direction. In addition, the absence of a (010) reflection, by far the most intense reflection for P3HT,[1] clearly demonstrates the high quality of the planar orientation obtained by rubbing. As reported for the "friction-transferred" thin films,[6] we find that the orientation induced by rubbing for anisotropic molecules (such as P3HT) corresponds to a single-crystal orientation. This orientation results from two effects: (i) the shear of the surface during rubbing, which aligns the chains along the sliding direction, and (ii) the compression of the surface by the loading force, which orients the molecular planes parallel to the surface. Figure 1c schematically represents the polymer chain orientation after rubbing.

By comparison, rubbing has also been carried out on thin films of regiorandom P3HT, which cannot crystallize. In that case, rubbing induces no orientation, which clearly indicates that chain orientation is related to the regioregularity and consequently to the polymer ability to crystallize.

Using the stylus of an AFM working in contact mode, we can perform the nanorubbing process locally on an area of defined size, down to the nanometer scale. As an example, (10 × 10) μm^2 areas were unidirectionally nanorubbed on regioregular P3HT thin films. Afterward, the morphology of the rubbed regions was investigated by AFM in tapping mode. Figure 2 shows height and phase images of three squares nanorubbed with an AFM tip on P3HT thin films.

Surprisingly, the rubbed areas are not visible in the height image but are well-defined in the phase image. This is most probably due to the relaxation of the P3HT surface above the glass transition ($T_g \approx 10$ °C).[14] Indeed, at room temperature, the polymer chains have enough mobility to relax after the shear induced by the AFM stylus and consequently any modification to the surface topography is strongly attenuated. In marked contrast, the phase image reveals three well-resolved (10 × 10) μm^2 areas. Phase contrast in tapping-mode AFM originates from differences in energy dissipation related to local differences in tip−sample interaction due to, for instance, differences in local stiffness. The contrast we observe in the phase images therefore indicates that the rubbed areas have been modified with respect to the pristine surface. On the basis of the results obtained when rubbing the whole surface, we suggest that nanorubbing induces local chain orientation and polymer crystallization, which modifies the local response of the surface to the oscillating AFM tip. To confirm this hypothesis, the nanorubbed films were crystallized at 170 °C during 30 min and the propagation of the surface orientation toward the bulk was followed by optical microscopy between crossed polars (Figure 3).

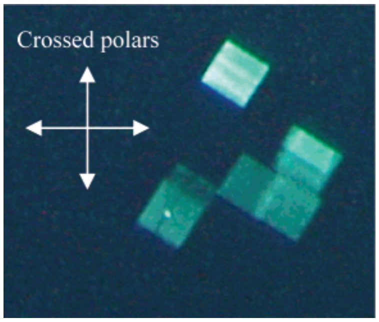

Figure 3. Optical micrograph between crossed polars for a P3HT film with five (10 × 10) μm^2 nanorubbed areas. The crossed polars are oriented as shown by the arrows.

As shown by the optical micrograph, the nanorubbed domains appear with a high birefringence after crystallization. In addition, a complete extinction of the nanorubbed squares is observed when the scanning direction is either parallel or perpendicular to the polarization directions, testifying to the orientation of the polymer chains.

We have demonstrated the possibility to realize modifications on P3HT surfaces with spatial and geometrical control of the nanorubbing using the stylus of an AFM. These chain-aligned structures can be permanent thanks to the crystallization process, which propagates the orientation obtained at the surface to the bulk.

Acknowledgment. This work was supported by the Belgian National Fund for Scientific Research (FNRS) and by the Belgian Federal Science Policy Office in the framework of the "Pôle d'Attraction Interuniversitaire en Chimie Supramoléculaire et Catalyse Supramoléculaire (PAI 5/3)". P.D. and P.L. are Research Associates of the FNRS. G.D., S.C., and M.S. are grateful to FRIA for a doctoral fellowship.

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JA0505806