

## Orientation Control of *p*-Sexiphenyl Molecular Nanocrystals on Rubbed Polymethylene Surface

### Beamline

05B2 PEEM beamline  
17B1 W20 X-ray Scattering beamline

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*Highly oriented nanocrystals of *p*-sexiphenyl molecules were prepared by thermal evaporation of this material on a rubbed polymethylene surface. The polymethylene thin film, generated on a gold surface by the gold-catalyzed decomposition of diazomethane, was gently rubbed in a fixed direction with a flannel cloth to serve as the template for alignment, which induced the in-plane orientation as well as flat-lying geometry of the molecules in contact with the surface. Anisotropic growth from the aligned molecules resulted in oriented molecular crystals. Various techniques including reflection absorption IR spectroscopy (RAIRS), near-edge X-ray absorption fine structure (NEXAFS) spectroscopy, grazing incidence X-ray diffraction, and atomic force microscopy were used to elucidate the structural details at the rubbed polymethylene surfaces and the *p*-sexiphenyl crystals deposited on it.*

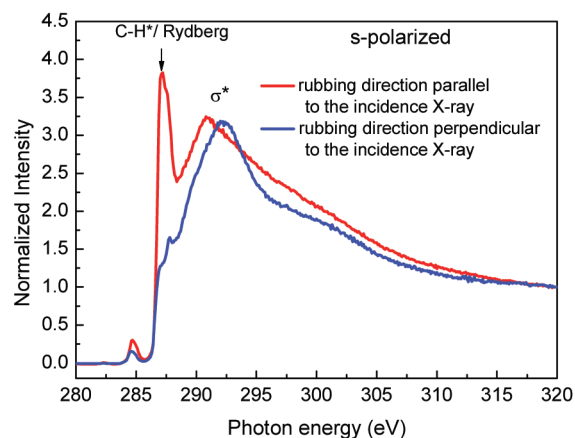
Molecular electronic devices based on organic semiconducting materials have attracted great attention because of their demonstrated potentials in areas such as light-emitting diodes (OLEDs), rectifier, solar cells and etc. The organic semiconducting materials offer the advantages of low cost and low-temperature processing, adaptability to large panel and flexible substrates, when compared with silicon-based materials. Depending on the application, different film materials and properties are desired. For example, in OLED applications, materials with high luminescent efficiency or charge transporting ability yet amorphous film-forming property are usually desired. In organic field-effect transistor (OFET) applications, a crystalline film with high field-effect charge mobility and on/off ratio is actively pursued. The charge conduction in semiconducting organic materials, although in general inferior to that of inorganic semiconductors, depends very much on the weak electronic interactions among discrete molecular components, so that the a strong  $\pi$ - $\pi$  stacking in an ordered array such as in a single crystal would most favor the charge migration. And the charge mobility is direction-dependent, that is, with the direction of  $\pi$ - $\pi$  stacking favored. In the case of deposited thin films, where polycrystalline films are usually obtained, numerous grain boundaries and discontinuities are introduced. The charge conduction is greatly retarded. While the size of the crystallites can be increased by choosing proper deposition condition, say, substrate temperature, a compromise between crystal size and grain boundary resistance may exist as the contact between larger crystals will decrease. For a field effect transistor utilizing polycrystalline organic thin film as the active channel material, an optimization in the film morphology as well as the uniform alignment of the crystallites will be desirable to achieve higher efficiency. Also, depending on the device structure, a control of the alignment of semiconducting molecules relative to the substrate surface and the electrodes is important.

In this work we studied the alignment effect of polymethylene,  $-(\text{CH}_2)_n-$  and rubbed polymethylene on the packing orientation of *p*-sexiphenyl molecular crystals. *p*-Sexiphenyl is examined as a representative of the long conjugate aromatic semiconducting molecules. The polymethylene used is structurally similar to that of polyethylene and is readily formed from diazomethane via gold-catalyzed polymerization. Reflection absorption IR spectroscopy (RAIRS), near-edge X-ray absorption fine structure (NEXAFS) spectroscopy, grazing incidence X-ray diffraction, and atomic force microscopy were used to characterize the structure of the vapor deposited *p*-sexiphenyl films. It is concluded that rubbing resulted in the alignment of the hydrocarbon chains near the surface, which induced the contacting molecules to align along the polymer chains. The crystallites nevertheless grow into rods with the long axes perpendicular to the polymer chains.

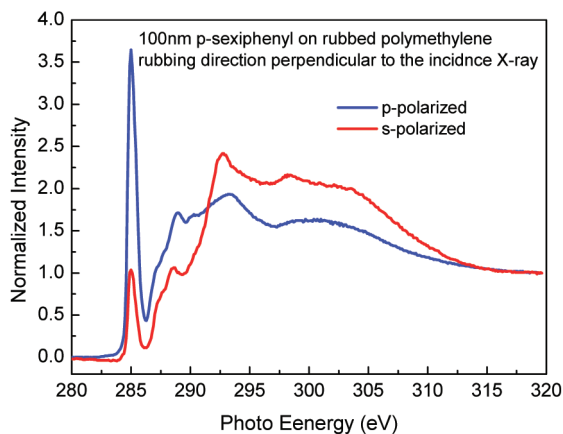
Firstly, the reflection absorption IR spectrum of  $\sim 250$  nm polymethylene film grown on a bare gold surface exhibits typical features expected for extended  $-(\text{CH}_2)_x-$  chains:  $725\text{ cm}^{-1}$  for  $\text{CH}_2$  rocking and  $1470\text{ cm}^{-1}$  for  $\text{CH}_2$  scissors deformation. The absorptions at  $2850\text{ cm}^{-1}$  and  $2919\text{ cm}^{-1}$  for symmetrical and asymmetrical  $\text{CH}_2$  stretching vibrations indicate the near crystalline state of the film obtained. The spectrum for the rubbed polymethylene is very similar to the un-rubbed one. In contrast to the NEXAFS results (*vide supra*), the reflection IR did not yield information on the structural change upon rubbing of the surface. Presumably because the greater probing depth of IR, and the very superficial change as a result of rubbing. The spectrum for 100 nm of *p*-sexiphenyl thermally deposited on the rubbed polymethylene was taken and compared with the isotropic KBr spectrum. The most prominent feature is the strong absorptions at  $760\text{ cm}^{-1}$  and  $816\text{ cm}^{-1}$  respectively, which are attributed to the out-of-plane bending vibrations of the phenyl ring C-Hs. These vibration modes have their transition dipoles aligned normal to the ring plane. The vibration modes associated with ring stretches (occurring at  $\sim 1481\text{ cm}^{-1}$  for mode **19a** and at  $1403\text{ cm}^{-1}$  for mode **19b**) and aromatic C-H stretches (at  $\sim 3061\text{ cm}^{-1}$  for mode **20a** and  $3027\text{ cm}^{-1}$  for mode **20b**), which have their transition dipole parallel to the ring plane along the long axis and

short axis respectively, are much weaker, compared with that of the isotropic KBr sample of *p*-sexiphenyl. The ratio of IR absorption intensity  $I_{816}/I_{1481} \approx 2.2$  and  $I_{816}/I_{1403} \approx 3.6$  for KBr-IR sample became 17.8 and 16.8 respectively for the 100 nm *p*-sexiphenyl sample. From the orthogonal relationship of these modes, the long axis of the molecule is estimated to be nearly parallel to the surface, and the short axis of the molecule is off more from the surface presumably due to the herringbone packing of the aromatic rings (*vide infra*).

To further explore the orientational details of the rubbed polymethylene as well as the deposited film, linear polarization-dependent near-edge X-ray absorption fine structure (NEXAFS) measurements were carried out on the films. The *s*-polarization of the incident X-ray was aligned either parallel or perpendicular to the rubbing direction. The NEXAFS spectra of *s*-polarized X-ray measured for rubbed polymethylene in both directions are shown in Fig. 1. A much enhanced C-H\*/Rydberg resonance at 287 eV was observed when the *s*-polarized incidence X-ray irradiated at the polymethylene surface along the rubbing direction. In this configuration, the *E* vector is perpendicular to the rubbing direction. The broad band appearing in the region 291–315 eV is characterized as  $\sigma^*$  resonances. In contrast, the C-H\*/Rydberg resonance was dramatically reduced when the *s*-polarized X-ray is directed perpendicular to the rubbing direction, a condition under which the *E* vector is parallel to the rubbing direction. The  $\sigma^*$  resonances gave similar intensity as the above. These NEXAFS results strongly suggest that the *trans* zigzag C-C-C backbone chains were highly oriented after rubbing and are aligned parallel to the rubbing direction. The C-H bonds of polymethylene chains were pointing



**Fig. 1:** The NEXAFS spectra of *s*-polarized X-ray measured for the rubbed polymethylene.



left and right or up and down and perpendicular to the C-C backbone chain. When the X-ray is directed along the rubbing direction and thus the backbone direction, the  $E_s$  is parallel to the C-H bonds and an enhancement in the C-H\* transition is expected. When the X-ray is directed perpendicular to the rubbing direction, the  $E_s$  is orthogonal to the C-H bonds and the C-H\* transition is minimized.

A prominent difference between the spectra for s- and p-polarization was observed when the incident X-ray is directed perpendicular to the rubbing direction, as shown in Fig. 2. The  $\pi^*$  resonance of phenyl rings at 285 eV was strongly enhanced in the p-polarization spectrum. In the s-polarization, the  $\pi^*$  resonance is reduced whereas the  $\sigma^*$  resonance at 293 eV is enhanced. The results can be rationalized by highly oriented p-sexiphenyl molecules with their long molecular axes aligned parallel to the rubbing direction and crystallized in a herringbone packing. With such an alignment in a multilayer film, the p-orbitals of the phenyl rings will point perpendicular to the rubbing direction yet alternate toward left and right along the layer direction due to the herringbone packing. The much reduced intensity for the  $\pi^*$  resonance in s-polarization mentioned above is due to a perpendicular relationship between the  $E_s$  and the p-orbitals.

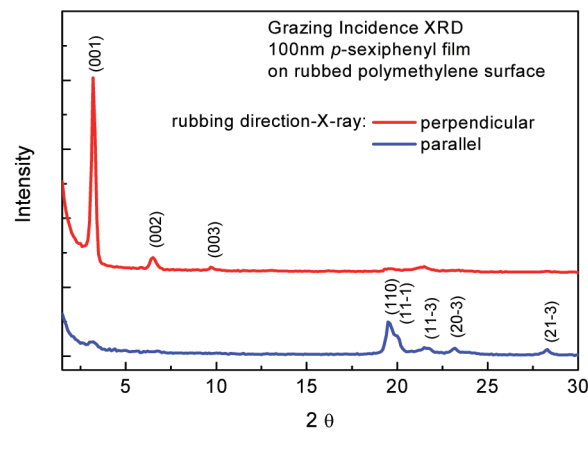
The results of in-plane X-ray grazing incidence diffraction are shown in the Fig. 3. The (001), (002), (003) diffraction peaks were found at  $2\theta$  values around  $3.2^\circ$ ,  $6.5^\circ$  and  $9.7^\circ$  respectively when the incidence X-ray is perpendicular to the rubbing direc-

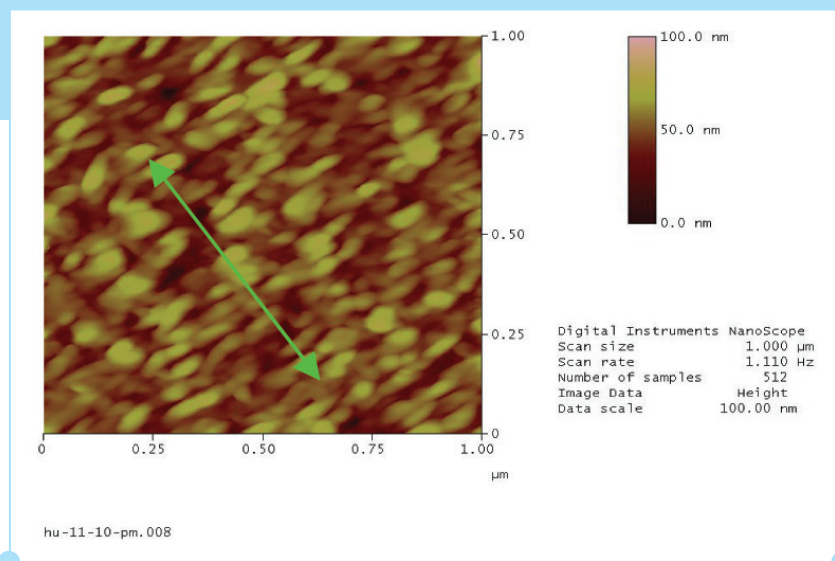
**Fig. 3:** The in-plane grazing incidence XRD pattern of 100 nm-thick p-sexiphenyl on rubbed polymethylene.

**Fig. 2:** The NEXAFS spectra of 100 nm-thick p-sexiphenyl on the rubbed polymethylene surface.

tion. The results strongly suggest that the (001) plane of the p-sexiphenyl nano crystals aligns parallel to the rubbing direction of the film. On the other hand, no (001) diffraction peak was found when incidence X-ray was parallel to the rubbing direction. Instead, diffraction peaks corresponding to much lower d spacings  $\sim 4.5\text{\AA}$  at  $19.5^\circ$ ,  $\sim 4.1\text{\AA}$  at  $21.5^\circ$ ,  $\sim 3.8\text{\AA}$  at  $23.2^\circ$ ,  $\sim 3.14\text{\AA}$  at  $28.3^\circ$  were observed, which are attributed to the diffraction planes of (110), (11-1), (11-3), (20-3) and (21-3). These results imply that the p-sexiphenyl nano crystals were aligned with their lower d-spacing planes perpendicular to the rubbing direction, with an interplanar spacing around  $3\text{\AA}$ . These results together strongly suggest that the flat-lying p-sexiphenyl molecules have a preferred orientation with their long molecular axis parallel to the rubbing direction.

The AFM micrographs of 100 nm-thick, thermally evaporated p-sexiphenyl film on the rubbed polymethylene are shown in Fig. 4. Rod-shaped crystallites of p-sexiphenyl with an average sizes about 110 nm long and 30 nm in width are observed. A clearly preferred orientation of the crystallites was found with their long crystal axes align *perpendicular* to the rubbing direction (the arrow direction). For comparison, a gold surface modified with a self-assembled monolayer of eicosanethiol was used as a reference substrate for depositing p-sexiphenyl film. The X-ray diffraction and reflection IR suggest that the p-sexiphenyl crystals are lying flat like on polymethylene surface. The AFM image shows similar rod-like crystallites that are randomly oriented on the SAM-covered Au surface.





**Fig. 4:** AFM images of 100 nm-thick *p*-sexiphenyl on rubbed polymethylene surface.

The polarization-dependent NEXAFS and X-ray diffraction above clearly suggest that the long molecular axes of *p*-sexiphenyl align with the rubbing direction. The AFM image shows that the long axes of the crystals align orthogonal to the rubbing direction. This concludes that the long axis of the crystal is different from the long axis of the molecule. It also suggests the crystal grow more in the lateral direction of the molecule rather than in the longitudinal direction.

In conclusion, we showed here that the orientation of a long conjugate aromatic molecule such as *p*-sexiphenyl within a thin film can be controlled in three directions, by using a rubbed polymethylene surface. The interaction between the  $\pi$ -surface and the stretched hydrocarbon chain locks the molecule into a flat-lying and parallel-to-the chain direction. The aligned molecules direct the growth of the crystals into highly oriented crystallites, with the long axes of the molecules parallel to the rubbing direction and the long axes of the crystal perpendicular to the rubbing direction. Integration of the orientation control into a device fabrication process and the possible direction-dependent electric conductance is being investigated.

### Experimental Station

Photoelectron Emission Microscopy end station

### Publications

- W. S. Hu, Y. T. Tao, Y. J. Hsu, and D. H. Wei, *Macromolecules* **38**, 9617 (2005).

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