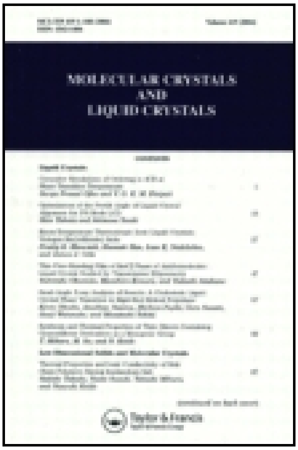

Molecular Crystals and Liquid Crystals

Regularly-Shaped Diacetylene Nano-Structures on Surfaces

Olga Franco [a] , Takashi Nemoto [a] , Toyonari Yaji [a] & Seiji Isoda [a]

[a] Institute for Chemical Research, Kyoto Univesity, Uji, Kyoto, Japan

To cite this article: Olga Franco, Takashi Nemoto, Toyonari Yaji & Seiji Isoda (2007): Regularly-Shaped Diacetylene Nano-Structures on Surfaces, Molecular Crystals and Liquid Crystals, 464:1, 73/[655]-81/[663]

To link to this article: http://dx.doi.org/10.1080/15421400601030316

Mol. Cryst. Liq. Cryst., Vol. 464, pp. 73/[655]–81/[663], 2007
Copyright © Taylor & Francis Group, LLC
ISSN: 1542-1406 print/1563-5287 online
DOI: 10.1080/15421400601030316

Regularly-Shaped Diacetylene Nano-Structures on Surfaces

Olga Franco
Takashi Nemoto
Toyonari Yaji
Seiji Isoda
Institute for Chemical Research, Kyoto Univesity, Uji, Kyoto, Japan

When 10,12-pentacosadiynoic acid (PENTA), dissolved in phenyloctane, is brought into contact with graphite, it immediately builds a film on the surface. The molecular arrangement of this ordered film has been characterized with an STM. The same packing was observed in a PENTA 2D-domain adsorbed from the solution into a small artificial hole scratched with an STM tip in a perylene-3,4,9,10-tetracarboxylic-dianhydride (PTCDA) layer formed in advance by vacuum-deposition. Thereby, a nano-scale domain of diacetylene molecules is embedded in the PTCDA film. In the posterior imaging scans, the original irregular scratched area becomes regular due to the readsorption of PTCDA into the gap.

Keywords: diacetylene; nano-structures; readsorption; STM

1. INTRODUCTION

Diacetylenes are known to polymerize in the solid state after heating or exposure to intense UV-light, X- or -ray sources [1]. The polydiacetylene backbone becomes a conductor when excess electrons or holes are supplied to it [2]. It also shows interesting optical and even nonlinear optical properties [3]. Furthermore, polydiacetylene builds highly ordered monomolecular films [4–10]. Thus, it is a promising candidate for the development of low-dimensional networks to transfer electrons (or holes) between sites in nano-electronic devices.

Our final objective is the nano-scale fabrication of one-dimensional molecular wires and two-dimensional domains of polydiacetylene on a

Address correspondence to Olga Franco, Dpto. Química Físca I, Facultad C. Químicas, Universidad Complutense, Ciudad Universitaria, 28040 Madrid, Spain. E-mail: franco@eels.kuicr.kyoto-u.ac.jp

surface. In a previous study, Takajo et al. succeeded in fabricating nano-scaled two-dimensional domains of diacetylene molecules embedded in an organic layer [9]. Firstly, they deposited a monolayer of perylene-3,4,9,10-tetracarboxylic-dianhydride (PTCDA, see insert of Figure 1(b) for its molecular structure) onto a highly oriented pyrolytic graphite (HOPG) substrate via vacuum-deposition (VD). Then the film was covered with a 17,19-dotetracontradiyne (DTDY) solution in phenyloctane. The next step consisted of the controlled scratching of the PTCDA layer with the tip of the scanning tunneling microscope (STM). Thereby, a two-dimensional region of bare HOPG surrounded by PTCDA was created. The STM-observation of the film showed that the scratched region was quickly coated with DTDY molecules from the solution. Unfortunately, however, the molecule could not be polymerized by UV-light irradiation.

Here, we follow the procedure described above using a polymerizable diacetylene. The main aim of the present study is to investigate the shape formation of the diacetylene domain embedded into PTCDA, since the shape may be correlated to the structural quality of the fabricated diacetylene domain. In the future, we will attempt the photopolymerization of the diacetylene domains.

2. EXPERIMENTAL PROCEDURE

2.1. Materials

The diacetylene molecule we investigated was 10,12-pentacosadiynoic acid (PENTA, see insert of Figure 1(a) for its chemical formula). This molecule polymerizes under UV-irradiation [6].

2.2. Vacuum Deposition

A layer of PTCDA was deposited onto freshly cleaved HOPG via VD in a bell jar. Prior to the deposition, the substrates were heated for several hours above 373 K to liberate their surfaces from possible contamination, e.g., condensed water. The deposition was performed at a pressure of 3×10^{-5} Pa and at a substrate temperature of 333 K. The thickness of the deposited film, monitored with a quartz crystal microbalance, was chosen to correspond to a monomolecular PTCDA layer.

2.3. Scanning Tunneling Microscope

For the imaging and scratching of the organic layers we used a Nanoscope III-a STM (Digital Instruments). The STM was operated in a liquid medium at room temperature. We poured a drop of a phenyloctane solution, onto the substrate in the vicinity of the tip, immersing the tip in the liquid. The liquid prevents the contamination of the sample during the measurement and other possible disturbances such as atmospheric humidity and, more essentially, it serves as a solvent for the diacetylene molecules. The films were imaged with tunnel current and voltage bias values of 10 to 20 pA and of 100 to 200 mV. For the scratching, the tip was approached very close to the surface by increasing the current and decreasing the voltage to around 60 to 80 pA and 10 to 20 mV. If the tip-surface distance is small enough, the tip removes the organic molecules of the surface and the HOPG substrate appears at the scratched area.

3. RESULTS AND DISCUSSION

3.1. Self-Assembled PENTA Film on HOPG

Immediately after the solution of PENTA ($c = 10^{-3}$ mol/l, in phenyloctane) is dropped onto bare HOPG, a PENTA film is formed on the surface. This layer has domains with sizes in each direction which range from few tens of nanometers up to around two hundred nanometers as already reported in [6]. The relative orientation between the different domains is approximately 60°.

Figure 1(a) shows a high resolution image of such a PENTA layer. Alternating bright and dark parallel lines can be recognized indicating columnar packing of molecules. The bright bands correspond to the diacetylene groups of PENTA. They appear bright in the STM image because they contain two triple bonds and have therefore a higher density of states than other zones (with only simple or double bonds). The aliphatic chains of the PENTA molecules can be seen nearly perpendicularly (92.7°) to the bright lines. A given bright line is closer to one of its neighbors (2.9 nm) than to the other one (3.8 nm). The distance between the dark lines is constant (3.2 nm), as expected, because it corresponds to the molecular length. Therefore, the carboxyl end group of one PENTA molecule (which is attached to the short aliphatic chain, see chemical formula in Figure 1(a)) is next to the carboxyl group of the molecule of the adjacent column and the methyl end group of one molecule (which is attached to the long aliphatic chain) is close to the methyl group of a molecule of the neighbor stack, as sketched in Figure 1(a). This arrangement may be induced by hydrogen bonds between the carboxyl moieties of adjacent columns. The aliphatic chains show a contrast modulation: four bright chains are followed by three dark chains, along the column axis. The Moiré

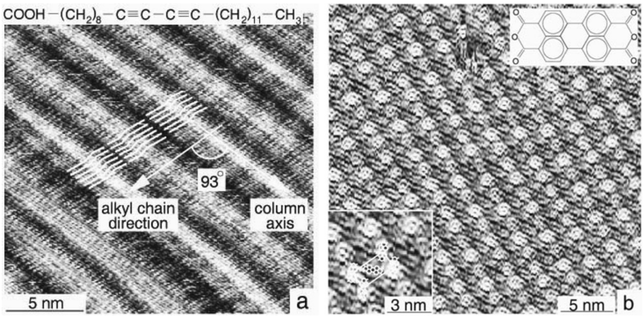

FIGURE 1 STM images and models for the molecular packing of (a) a PENTA film adsorbed from a solution in phenyloctane on HOPG and (b) a PTCDA film deposited via VD on HOPG. Scan size: (a) $20 \times 20\,\mathrm{nm}^2$ and (b) $30 \times 30\,\mathrm{nm}^2$ (insert in the lower left: $7 \times 7\,\mathrm{nm}^2$); scan rate: (a) 6.10 Hz and (b) 7.04 Hz; bias voltage: (a) 200 mV and (b) 100 mV; current: (a) 10.0 pA and (b) 20.0 pA. The inserts in the upper part show the chemical structures of (a) PENTA and (b) PTCDA.

analysis of this modulation gives an spacing between aliphatic chains of approximately 0.46 nm.

The comparative Fourier analysis of the PENTA image of Figure 1(a) and an HOPG image taken immediately afterwards, reveals that the bright lines in Figure 1(a) align nearly perpendicularly (92.4°) to one of the principal axes of HOPG. Therefore, the alkyl chains align nearly parallel to a symmetry axis of HOPG, as reported for many aliphatic chain molecules.

Our results agree quite well with those of Okawa and Aono [5]. They found distances of 3.8 and 3.0 nm for the bright lines. Their films were transferred from an aqueous subphase via Langmuir-Schaeffer deposition. Thus, water molecules may be transferred to their films, in particular participating in H-bonding between carboxyl groups. These could be the reason for the slightly larger value found by Okawa and Aono for the shorter distances between the bright lines, in comparison to our results. Those authors report a value of 0.47 nm as spacing between the aliphatic chains.

3.2. PTCDA Layer Vacuum-Deposited on HOPG

It was observed that the deposition at substrate temperature of 333 K enhances the quality of the film and in particular the size of its domains. At this substrate temperature the PTCDA molecules which reach the substrate gain enough energy to move along the surface until they find the energetically most favorable arrangement, i.e., they approach an already existing nucleus. Thus, few nuclei are built and the film is composed by large domains of at least 300 × 300 nm^2.

Figure 1(b) shows a high resolution STM image of a PTCDA film where the two dimensional lattice can be recognized. In the unit cell, four molecules with the same orientation place at the corners and a fifth one with a different orientation is located in the center of the cell. The relative orientation between the two kinds of molecules could not be determined precisely. The lattice parameters are $a = 1.142\,\mathrm{nm}$, $b = 1.921\,\mathrm{nm}$ and $\Gamma = 81.7°$ which agree reasonably well with those reported by Hoshino *et al.* [11] for the type-II structure. The b-axis of the unit cell forms an angle of 6.2° with one of the symmetry axes of HOPG, as could be determined from the analysis of the PTCDA image together with an image of HOPG acquired immediately after it.

3.3. Nanolithography via STM on a PTCDA Layer

First, we scratched a region of 10 × 10 nm^2 of a PTCDA layer in a phenyloctane medium in order to obtain a small area of bare HOPG. Despite the fact that the scratching took place in a small squared region, the images taken afterwards show a large irregular hole in the PTCDA layer. Figure 2(a) may serve as an example, where the artificial hole is approximately 37 nm long and 14 nm wide, i.e., it enlarges mainly horizontally (along the main scan direction). In posterior imaging scans the cavity becomes longer but not wider. These effects can be explained by the tip crashing into the step created at the boundary HOPG/PTCDA and removing PTCDA molecules, which

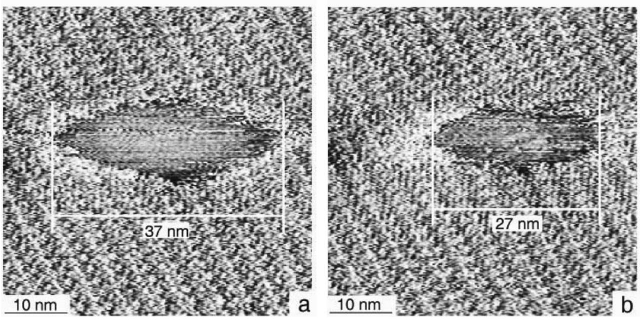

FIGURE 2 50 × 50 nm^2 STM images of a PTCDA film; (a) immediately after the scratching and (b) after another two imaging scans. Scan rate: 7.04 Hz; bias voltage: 100 mV; current: 20.0 pA.

may happen when scanning from the HOPG zone (the hole) to the more elevated PTCDA zone. The hole growth was observed in analogous experiments and can be reduced by decreasing the scan rate and/or increasing the gain parameters. However, if the latter are too high, it is difficult to acquire a good image and both film and tip could be further damaged.

The zones adjacent to the hole, especially on both lateral sides, appear bright in Figure 2 and in images from other scratching experiments. They correspond to elevated areas compared to the rest of the PTCDA film. Such elevation may be built by PTCDA molecules which come from the scratched area and accumulate on the hole's edge. However, a reverse process was often observed depending on the imaging conditions. The hole of Figure 2(b) is as wide as that of Figure 2(a) (two scans later) but around 10 nm shorter in length. Therefore some PTCDA molecules readsorb in the hole. Since this happens principally in the lateral edges of the scratched area, we propose that the STM tip sweeps the PTCDA molecules piled up on the lateral sides of the hole into it. Thus, the hole's size results from the competition of two effects both favored by the tip: the enlargement of the hole due to the crash of the tip into the step hole/PTCDA and the readsorption into the cavity of the scratched out PTCDA molecules which accumulated close to the hole's edges.

3.4. Adsorption of PENTA in the Scratched Area

When the scratching was performed under a PENTA solution in phenyloctane ($c = 10.3\,\mathrm{mol/l}$), the scratched area (originally $50 \times 50\,\mathrm{nm}^2$) was immediately covered by a PENTA film. Figure 3 shows the

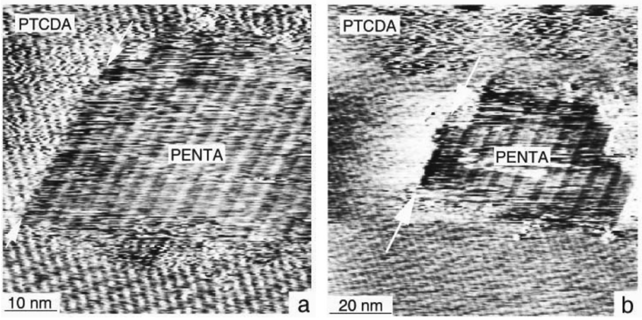

FIGURE 3 STM images of a scratched PTCDA film. Scan size: (a) $60 \times 60\,\mathrm{nm}^2$, (b) $100 \times 100\,\mathrm{nm}^{2;}$ scan rate: 6.10 Hz; bias voltage: 100 mV; current: 20.0 pA.

PTCDA layer and a region where PTCDA is replaced by PENTA. The typical columns of a PENTA layer can be recognized in the image. Our results corroborate the statement by Takajo et al. about a similar diacetylene molecule, that the alkyl chains align parallel to the principal axis of HOPG which is nearest to the scanning direction [9].

Remarkably, the artificial hole created by the scratching of the PTCDA layer differs in size and shape depending on whether PENTA is adsorbed in it or not. As it is described above, with pure phenyloctane as liquid medium, that is, when the scratched zone exposes bare HOPG during the whole imaging process, the hole size first increases and then decreases. In addition, the scratched area is irregular in shape. Contrarily, when PENTA deposits into the cavity, the cavity immediately adopts a regular shape and maintains its size. Figure 3(a) clearly shows that there are no gaps at the edges between the PTCDA and the PENTA zone, as indicated with the arrows. Moreover, the boundary between these two regions is straight and parallel to the diacetylene columns built by the PENTA molecules. The upper corners of the PENTA domain in Figure 3(b) show a stair-wise geometry. The bases of the steps are perpendicular to the diacetylene columns and, therefore, parallel to the alkyl chains of PENTA. Their length equals that of two PENTA molecules, which suggests a pair-wise structuring through hydrogen bonding [12].

These surprising facts can be explained as follows. Firstly, the scratching of the PTCDA layer produces an irregular hole due to disturbances generated by possible PTCDA molecules attached to the STM tip and/or to molecules dragged by the tip to the edges of the cavity, where they accumulate in irregular shapes (see Fig. 4(a)). The

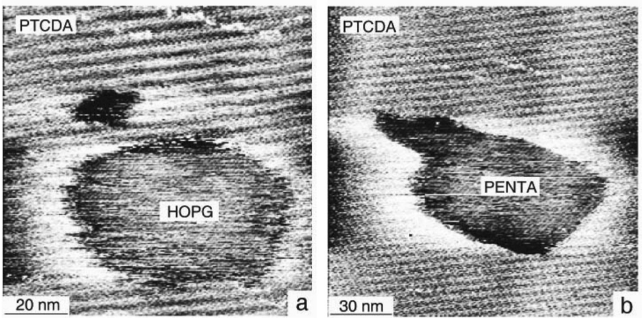

FIGURE 4 STM images of two scratched PTCDA films. The medium in (a) pure phenyloctane and (b) a PENTA solution in phenyloctane. Scan size: (a)$100 \times 100\,\mathrm{nm}^2$ and (b) $150 \times 150\,\mathrm{nm}^2$, scan rate: 6.10 Hz, bias voltage: 100 mV, current: 20.0 pA.

small size of the PTCDA molecules and their low resistance against scratching are determinant factors which favor the irregularity of the hole shape. Immediately after the scratching (probably, even before the scratching of the whole area had finished), PENTA adsorbs onto the cavity. As we mentioned before, the alkyl chains of the PENTA molecules align along one of the symmetry axes of graphite and their diacetylene groups join together building columns basically composed of dimers. The hydrogen bond between the carboxyl ending groups is as strong as to stabilize the PENTA double column on the HOPG surface. Such geometrical restrictions and the large length of PENTA unavoidably induce the appearance of some voids at the boundaries between the PTCDA and the PENTA areas. During the next imaging scans these voids disappear thanks to the readsorption of some PTCDA molecules. This adsorption is aided by the tip motion, as it was already pointed out. The complete covering of the hole with PENTA and PTCDA after the scratching determines the stabilization of the PENTA area's size. Since there are no voids, and consequently no steps, between the PENTA and the PTCDA areas, the STM tip approximately maintains the same height during the scan. Therefore, it does not laterally crash into the PTCDA area as it occurred when bare HOPG was exposed in the hole.

Thus, the large length and ordered deposition of the PENTA molecules combined with the small size and readsorption mechanism of the PTCDA molecules enables to obtain stable well-shaped PENTA nanoareas embedded in a PTCDA layer by the STM scratching technique.

4. CONCLUSIONS

We have studied the controlled replacement of PTCDA molecules by PENTA molecules in nano-scale areas. Paying special attention to the shape of the artificial PENTA zone, we have found a "shape-correction" mechanism which ensures a regularly shaped and stable PENTA domain embedded in PTCDA. The process is as follows. The first stage consists in the scratching with the STM tip of a PTCDA layer in a liquid medium with PENTA molecules solved in it. This step produces an irregular hole. Rapidly, in the second step, the cavity is covered with PENTA molecules from the solution. The PENTA molecules arrange in columns of dimers connected by strong H-bonds. The third stage is the "shape-correction" stage. It consists in the STM-favored readsorption of PTCDA into the voids at the PTCDA/PENTA boundaries. Thus, the PTCDA/PENTA edges become straight and consequently the shape of the PENTA domain emerges as regular. The final form of the PENTA zone is determined by the length of a PENTA dimer.

REFERENCES

[1] Wegner, G. Z. (1969). *Naturforschung*, *24B*, 824.

[2] Donovan, K. J., Sudiwala, R. V., & Wilson, E. G. (1992). *Thin Solid Films*, *210–211*, 271.

[3] Messier, J. (1990). *Organic molecules for nonlinear optics and photonics*, Volume 194, NATO ASI series.

[4] Tachibana, H., Yamanaka, Y., Sakai, H., Matsumoto, M. (2002). *Colloid Surf. A*, *198–200*, 83.

[5] Okawa, Y. & Aono, M. (2002). *Surf. Sci.*, *514*, 41.

[6] Qiao, Y. H., Zeng, Q. D., Tan, Z. Y., Xu, S. D., Wang, D., Wang, C., Wan, L. J., & Bai, C. L. (2002). *J. Vac. Sci. Technol*. B, *20*, 2466.

[7] Menzel, H., Horstmann, S., Mowery, M. D, Cai, M., & Evans, C. E. (2000). *Polymer*, *41*, 8113.

[8] Takajo, D., Fujiwara, E., Irie, S., Nemoto, T., Isoda, S., Ozaki, H., Toda, N., Tomii, S., Magara, T., Mazaki, Y., Yamamoto, G. (2002). *J. Cryst. Growth*, 237–239, 2071.

[9] Takajo, D., Nemoto, T., Kurata, H., Isoda, S., Ozaki, H., & Mazaki, Y. (2003). *Thin Solid Films*, *438–439*, 428.

[10] Irie, S., Isoda, S., Kobayashi, T., Ozaki, H., & Mazaki, Y. (2000). *Probe Microsc.*, *2*, 1.

[11] Hoshino, A., Isoda, S., Kurata, H., & Kobayashi, T. (1994). *J. Appl. Phys.*, *76*, 4113.

[12] Takajo, D., Nemoto, T., Franco, O., Kurata, H., & Isoda, S. (2006). *Jpn. J. Appl. Phys.*, *45*, 2091.