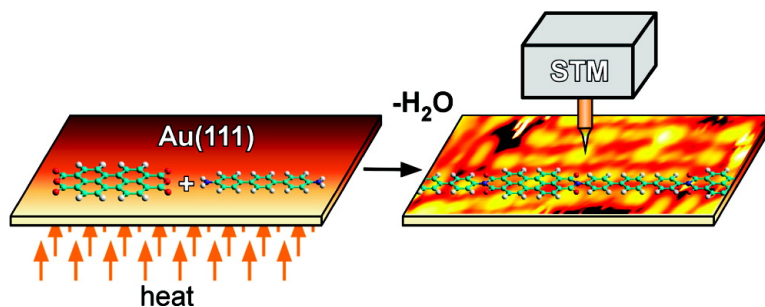


## Fabrication of Surface-Supported Low-Dimensional Polyimide Networks

Matthias Treier, Neville V. Richardson, and Roman Fasel

*J. Am. Chem. Soc.*, **2008**, 130 (43), 14054-14055 • DOI: 10.1021/ja805342n • Publication Date (Web): 01 October 2008

Downloaded from <http://pubs.acs.org> on February 8, 2009



### More About This Article

Additional resources and features associated with this article are available within the HTML version:

- Supporting Information
- Access to high resolution figures
- Links to articles and content related to this article
- Copyright permission to reproduce figures and/or text from this article

[View the Full Text HTML](#)



**ACS Publications**  
 High quality. High impact.

## Fabrication of Surface-Supported Low-Dimensional Polyimide Networks

Matthias Treier,<sup>†</sup> Neville V. Richardson,<sup>‡</sup> and Roman Fasel<sup>\*†</sup>

EMPA, Swiss Federal Laboratories for Materials Testing and Research, 3602 Thun, Switzerland, EaStCHEM, School of Chemistry, North Haugh, University of St. Andrews, St. Andrews, KY16 9ST, United Kingdom

Received July 10, 2008; E-mail: roman.fasel@empa.ch

A wide variety of highly regular supramolecular architectures, based on noncovalent bonds, has been realized on single crystal metal surfaces over the past decade.<sup>1</sup> In view of possible applications as templates, covalent bonding is however preferable to meet the optimal requirements of thermal and chemical stability. Attempts to fabricate covalently interlinked polymeric networks on single crystal metal surfaces have been reported only very recently.<sup>2</sup> Different types of chemical reactions have been found to proceed even though the reaction partners are confined to two dimensions,<sup>3</sup> while novel reaction pathways, which have no known equivalent in 3D chemistry, have also been reported.<sup>4</sup>

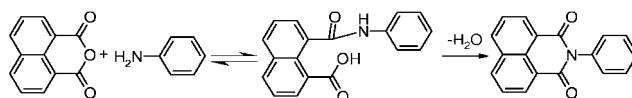
Polyimides represent a particularly important class of polymers which have found applications, inter alia, in electronic device insulation, X-ray windows, planar substrates for LCD displays, or cryogenics.<sup>5</sup> Synthesis of polyimide films has been achieved by various routes including physical vapor deposition of the precursor monomers<sup>6</sup> and spin casting<sup>7</sup> or Langmuir–Blodgett deposition of the intermediate polyamic acid.<sup>8</sup> Polyimides are generally chemically resistant, low-k dielectrics with a high decomposition temperature,<sup>5</sup> hence ideally fulfilling the requirements of thermal and chemical stability needed for potential technological applications of covalent surface-supported networks.

Here, we investigate the formation of ultrathin polyimide films on Au(111) using low temperature scanning tunneling microscopy (STM). According to textbook chemistry, imidization (Scheme 1) proceeds via rearside, out-of-plane nucleophilic attack of the amine on a carbonyl group, a mechanism which is expected to be strongly hindered when the two reactants are confined to two dimensions. We show, however, that the surface-confined imidization of aromatic amines and anhydrides readily takes place above ~570 K but that the temperatures needed for the different reaction steps are different from the corresponding reaction in solution or in bulk films. Covalently linked (sub)monolayer, one precursor molecule thick, polyimide films can be grown on Au(111) whose detailed structures can be tuned from parallel linear strands to an extended, 2D connected, porous network by varying the amine species used in the reaction.

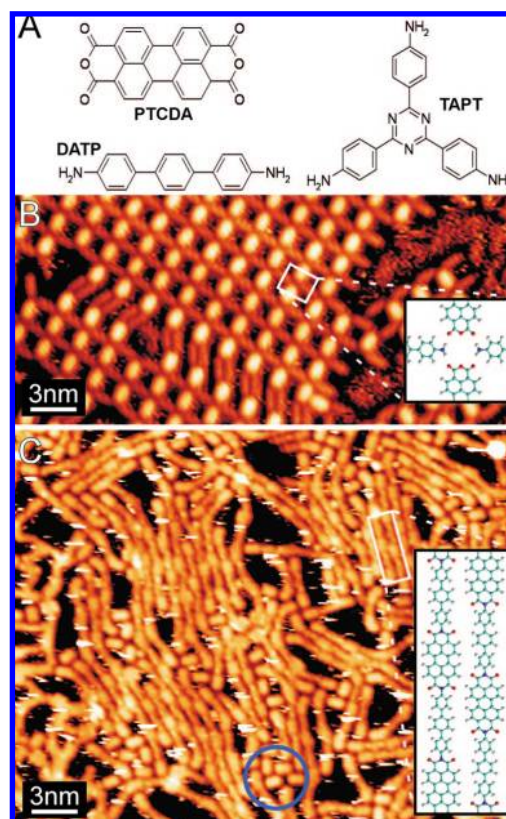
STM experiments were performed in an ultrahigh vacuum system using an Omicron low-temperature STM operated at 77 K. The Au(111) crystal was cleaned by sputtering and subsequent annealing to 700 K prior to adsorbate deposition. 4,4'-Diamino-*p*-terphenyl (DATP, 95%, ABCR), 2,4,6-tris(4-aminophenyl)-1,3,5-triazine (TAPT), and 3,4,9,10-perylenetetracarboxylic-dianhydride (PTCDA, 97%, Fluka) (Figure 1a) were deposited from resistively heated quartz crucibles held at 380, 470 and 510 K, respectively, resulting in deposition rates of ~0.2 ML/min. During deposition, the sample was kept at room temperature. To initiate the formation of polyimides, the sample was annealed to 570 K for 15 min before transfer to the STM.

Figure 1b shows the rectangular hydrogen-bonded superstructure formed by DATP and PTCDA on Au(111) at submonolayer coverage

### Scheme 1. Imidization Condensation Reaction



when approximately equal amounts of the two species are present. Both molecules adsorb in a planar geometry on this substrate as widely found for molecules containing polycyclic aromatic units.<sup>10</sup> In contrast to solution-based and solid-state polyimide formation, poly(amic acid) is not formed within the first monolayer at room temperature. The hydrogen-bonded structures are not modified by annealing the sample up to approximately 470 K for several minutes. At even higher annealing temperature (~470 to 540 K), few species ascribed to the amic acid intermediate are observed (see Supporting Information) but



**Figure 1.** (a) Chemical structure of compounds used for surface polyimide formation. (b) STM image<sup>9</sup> (−0.5 V, 20 pA) of hydrogen-bonded DATP-PTCDA superstructure on Au(111). The inset shows a junction of the rectangular network. Bright molecules are PTCDA and long, dimmer molecules are DATP. (c) STM image (−1.8 V, 50 pA) of parallel polyimide strands formed from DATP and PTCDA after annealing at 570 K. The blue circle highlights a small cluster of nonreacted PTCDA. The inset shows a model of two parallel oligomers.

<sup>†</sup> EMPA.

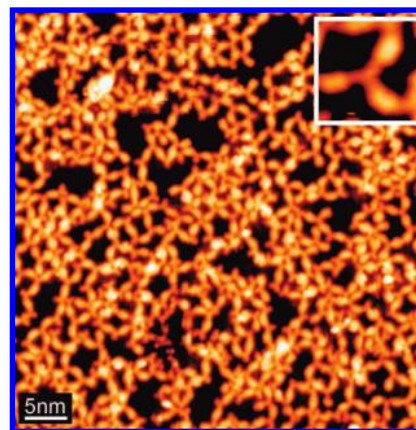
<sup>‡</sup> University of St. Andrews.

no pure phases of this reaction intermediate can be obtained. Complete imide formation is possible even within the restricted geometry on the surface as observed by the formation of polyimide oligomers after annealing to 570 K as shown in Figure 1c. Individual oligimides agglomerate into patches of locally parallel strands. As can be seen by comparing Figure 1 panels b and 1c, the appearance of DATP and PTCDA is only weakly affected by the reaction with both precursors remaining easily identifiable within the polymeric units. Higher coverages can be achieved by repeating the deposition-annealing cycles. The sample shown in Figure 1c is richer in PTCDA resulting in most oligomers being terminated by PTCDA. Excess PTCDA, which has not reacted, can be found within voids of the polymeric structure as highlighted in Figure 1c. The chain termination can be changed to either PTCDA or DATP by simply providing an excess of the appropriate species during sample preparation. At coverages similar to or higher than the one shown in Figure 1c, no correlation between the orientation of the polyimide strands and the underlying substrate is observed. After annealing to 540 K, no unreacted DATP can be found on the substrate. Hence, the desorption temperature and the temperature needed for the onset of the reaction lie close together, suggesting that a high mobility of DATP is needed for reaction. This might be related to the known out-of-plane reaction geometry of the rearside nucleophilic attack, which might be achieved at temperatures close to the desorption temperature of DATP.

The periodicity along chains is 2.5 nm, in excellent agreement with the theoretical value of 2.56 nm obtained from relaxing an oligomer in the gas phase at the AM1 level of theory.<sup>11</sup> A hypothetical linear hydrogen-bonded structure would have a periodicity of  $\sim 3.0$  nm, further indicating that the observed structures do not result from unreacted molecules. Typical chain lengths are 5–10 nm corresponding to 4–8 reacted molecules. Patches of coparallel oligomers are densely packed with a strand-to-strand spacing of  $\sim 0.75 \pm 0.05$  nm stabilized by  $\text{CH}\cdots\text{O}$  hydrogen bonds (see inset of Figure 1c). Longer chains and better ordering of the chains are probably inhibited by the confinement to two dimensions and the high coverage. Also, chain lengths can vary on the same sample depending on the local coverage, indicating that the length might be limited by kinetics during the polyimide formation process. By this method, a second layer cannot be grown on top of the first polyimide layer, since both reaction partners will desorb before the reaction temperature. The preparation of a monolayer thin polyimide film based on DATP and PTCDA on Au(111) can hence be a self-limiting process.

To explore the potential use of this surface-supported condensation reaction for the fabrication of extended two-dimensional polymeric networks, the imidization between PTCDA and the 3-fold symmetric triamine species TAPT has also been investigated. At a stoichiometry of 2 TAPT to 3 PTCDA, a hypothetical hexagonal polyimide honeycomb network with a pore-to-pore distance of 3 nm could be expected (see Supporting Information). Figure 2 shows the covalently linked structures formed by PTCDA and TAPT after annealing to 600 K. Regularly spaced pores are not obtained under these sample preparation conditions even if the required stoichiometry is met, as is the case for the sample shown in Figure 2, where polyimide structures are terminated by either of the two molecules. However, compared to the structures formed by the linear DATP, the network formed from PTCDA and TAPT is highly porous and exhibits an extensive 2D connectivity although pore shapes different from the anticipated hexagonal pores are common.

While a highly regular network has not been realized with the preparation conditions chosen, the overall geometric properties of the submonolayer polyimide structures clearly depend on the choice of



**Figure 2.** STM image ( $-0.8$  V, 20 pA) of a porous polyimide network formed by TAPT and PTCDA at an approximate 3:2 stoichiometry. The inset shows a TAPT molecule at the center of a triangular arrangement connected by imidization to three PTCDA molecules.

precursors, which hence represents a means to tailor the properties of the resulting polyimide monolayer.

In summary, we have shown that the condensation reaction between diamines and dianhydrides, resulting in the formation of polyimides, can be thermally initiated on Au(111), giving rise to covalently linked subnanometer thick polymeric structures, whose geometric properties can be tuned by an appropriate choice of the reaction partners.

**Acknowledgment.** We would like to thank N.R. Champness and S. Argent for providing the TAPT sample.

**Supporting Information Available:** STM images of amic acid; hydrogen-bonded superstructure and potential polyimide honeycomb network between TAPT and PTCDA. This material is available free of charge via the Internet at <http://pubs.acs.org>.

## References

- (1) (a) Theobald, J. A.; Oxtoby, N. S.; Phillips, M. A.; Champness, N. R.; Beton, P. H. *Nature* **2003**, *424*, 1029. (b) Barth, J. V. *Annu. Rev. Phys. Chem.* **2007**, *58*, 357. (c) Stepanow, S.; Lingenfelder, M.; Dmitriev, A.; Spillmann, H.; Delvigne, E.; Lin, N.; Deng, X.; Cai, C.; Barth, J. V.; Kern, K. *Nat. Mater.* **2004**, *3*, 229.
- (2) (a) Weigelt, S.; Busse, C.; Bombis, C.; Knudsen, M. M.; Gothelf, K. V.; Laegsgaard, E.; Besenbacher, F.; Linderroth, T. R. *Angew. Chem., Int. Ed.* **2008**, *47*, 4406. (b) Zwaneveld, N. A. A.; Pawlak, R.; Abel, M.; Catalin, D.; Gignes, D.; Bertin, D.; Porte, L. *J. Am. Chem. Soc.* **2008**, *130*, 6678.
- (3) (a) Matena, M.; Riehm, T.; Stöhr, M.; Jung, T. A.; Gade, L. H. *Angew. Chem., Int. Ed.* **2008**, *47*, 2414. (b) Weigelt, S.; Schnadt, J.; Tuxen, A. K.; Masini, F.; Bombis, C.; Busse, C.; Isvoranu, C.; Atman, E.; Laegsgaard, E.; Besenbacher, F.; Linderroth, T. R. *J. Am. Chem. Soc.* **2008**, *130*, 5388. (c) Grill, L.; Dyer, M.; Laffert, L.; Persson, M.; Peters, M. V.; Hecht, S. *Nat. Nanotechnol.* **2007**, *2*, 687. (d) In't Veld, M.; Iavicoli, P.; Haq, S.; Amabilino, D. B.; Raval, R. *Chem. Commun.* **2008**, 1536. (e) Gourdon, A. *Angew. Chem., Int. Ed.* **2008**, *47*, 6950.
- (4) Weigelt, S.; Busse, C.; Bombis, C.; Knudsen, M. M.; Gothelf, K. V.; Strunskus, T.; Wöll, C.; Dahlbom, M.; Hammer, B.; Laegsgaard, E.; Besenbacher, F.; Linderroth, T. R. *Angew. Chem., Int. Ed.* **2007**, *46*, 9227.
- (5) (a) Ding, M. *Prog. Polym. Sci.* **2007**, *32*, 623. (b) Halasa, E. *Polimery* **2005**, *69*, 179.
- (6) (a) Jou, J. H.; Cheng, C. L.; Jou, E. C. Y.; Yang, A. C. M. *J. Polym. Sci., B* **1996**, *34*, 2239. (b) Salem, J. R.; Sequeda, F. O.; Duran, J.; Lee, W. Y.; Yang, R. M. *J. Vac. Sci. Technol., A* **1986**, *4*, 369.
- (7) Meyer, W.; Grunze, M.; Lamb, R.; Ortega-Vilami, A.; Schrepp, W.; Braun, W. *Surf. Sci.* **1992**, *273*, 205.
- (8) Ghosh, M. K.; Mittal, K. L. *Polyimides: Fundamentals and Applications*; Taylor & Francis: London, 1996.
- (9) STM-images have been analyzed and processed using WSxM: Horcas, I.; Fernandez, R.; Gomez-Rodriguez, J. M.; Colchero, J.; Gomez-Herrero, J.; Baro, A. M. *Rev. Sci. Instrum.* **2007**, *78*, 013705.
- (10) Ruffieux, P.; Gröning, O.; Fasel, R.; Kastler, M.; Wasserfallen, D.; Müllen, K.; Gröning, P. *J. Phys. Chem., B* **2006**, *110*, 11253.
- (11) Dewar, M. J. S.; Zoebisch, E. G.; Healy, E. F.; Stewart, J. J. P. *J. Am. Chem. Soc.* **1985**, *107*, 3902.

JA805342N