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 [9] G. M. Sheldrick, SHELXS-86, Program for crystal structure determination, University of Cambridge in *Crystallographic Computing 3* (Eds.: G. M. Sheldrick, C. Kruger, R. Goddard), Oxford University Press, Oxford, 1985, p. 175.
 [10] G. M. Sheldrick, SHELXL-93, Program for crystal structure refinement, University of Göttingen, 1993.

Periodic Structure of a Single Sheet of a Clothlike Macromolecule (Atomic Cloth) Studied by Scanning Tunneling Microscopy**

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Recently we prepared a single sheet of a sashlike or clothlike macromolecule (atomic sash or atomic cloth) by photopolymerization of alkadiyne or alkatetrayne molecules that were laid flat and closely packed in a vapor-deposited monolayer on a cooled graphite substrate. The process was monitored by Penning ionization electron spectroscopy (PIES).^[1-3] Particularly the atomic cloth, which is composed of flatly lying alkyl chains cross-linked alternately by polydiacetylene (PD) and polyacetylene (PA) chains as shown in Figure 1, triggered our interest because of its molecular structure, electronic structure, and electrical properties. It is expected that the unit mesh of the atomic cloth is forced to have a parallelogram structure because of the peculiar clothlike configuration supported by the substrate. This is in spite of considerable strain mainly due to the overcrowding of hydrogen atoms at the crossing points of alkyl and PA chains.

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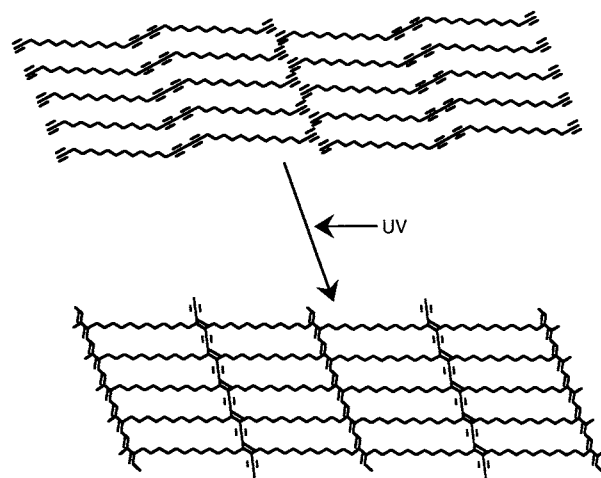


Figure 1. Schematic drawing of the atomic cloth prepared by photopolymerization of 1,15,17,31-dotriacontatetrayne molecules that were laid flat and closely packed in a monolayer.

The atomic cloth can also be regarded as a two-dimensional anisotropic sheet or an array of one-dimensional π -electron systems with fixed configuration, which cannot be easily obtained by ordinary preparative methods. Thus, it is of fundamental importance to prove and explain the periodic structure of the atomic cloth for studies on this fascinating material.

It was confirmed by PIES that 1) the graphite surface was just covered with the flatly lying alkyl chains, and the orientation was maintained throughout UV irradiation, 2) the π MOs of the diacetylene and acetylene units of the monomer (1,15,17,31-dotriacontatetrayne (DTTY)) were altered to the long conjugated systems of the PD and PA chains, and 3) unlike an unirradiated monolayer, the irradiated monolayer did not sublime under ultrahigh vacuum (UHV) upon heating to room temperature.^[2] To obtain direct evidence for the formation of the clothlike structure, scanning tunneling microscopy (STM) was applied. We found the unit vectors of the atomic cloth by analyzing the periodic modulation of the STM image contrast due to the coincidence of the structure of the atomic cloth and that of the graphite substrate.

The specimen was prepared on a cleavage plane of highly oriented pyrolytic graphite (HOPG) in an UHV electron spectrometer, as previously described.^[2,3] The atomic cloth did not show a different PIE spectrum after it was temporarily exposed to the air at room temperature and then returned to the spectrometer. The STM equipment (from WA Technology) was in another UHV chamber.^[4] An STM tip made of tungsten wire (diameter 0.5 mm) was sharpened by electrochemical etching. STM images were obtained at room temperature in the constant-current topograph mode and calibrated with the images of HOPG and Si(111) 7×7 surfaces obtained immediately before and after the measurements of the atomic cloth. The scanning time was about 30 s for one image of 256×256 points.

The STM topograph of the atomic cloth is shown in Figure 2. This image was obtained at a sample bias voltage of +0.2 V, which corresponds to the unoccupied states. Sixteen bright lines running diagonally from the upper left to the lower right are observed; their brightness changes alternately.^[5-7] The distance between the adjacent brighter and darker

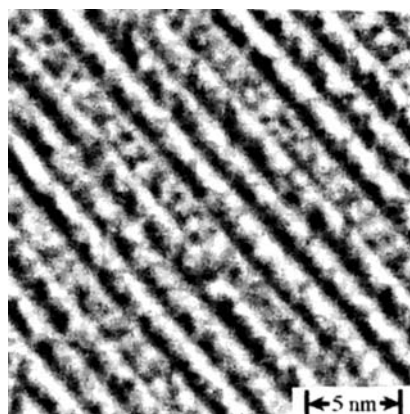


Figure 2. UHV-STM image of the atomic cloth on graphite. Sample bias voltage: +0.2 V, tunneling current: 0.1 nA, image sizes: 20.0 × 20.0 nm.

lines is 1.7 ± 0.1 nm. Taking into account the chemical structure of the atomic cloth, it is natural to ascribe this value to the distance between the neighboring PD and PA chains; this results in a distance D of 3.4 nm between two nearest PD or PA chains. It is noteworthy that there is a modulation in the STM image contrast at every fourth lines, that is, with a periodicity of $2D = 6.8$ nm. Moreover, an internal structure is observed between two of the four lines: runglike features are placed at an average rung – rung separation of $d = 1.4$ nm. This value is close to three times the width of an alkyl chain (0.47 nm). The peak – peak height of the topograph is about 0.4 nm, which is in agreement with the thickness of the atomic cloth. However, the real thickness cannot be estimated by STM.

Figures 3a and 3b show a Fourier-transformed power spectrum of the STM image (Figure 2) and its schematic interpretation, respectively. From the analysis of the Fourier transform we can make the following four findings: First, intense spots in Figure 3a (large spots in Figure 3b) result in the main interval in Figure 2 ($D/2 = 1.7$ nm), the distance between a PD chain and its neighboring PA chain. Second, additional spots in Figure 3a (small spots in Figure 3b) are

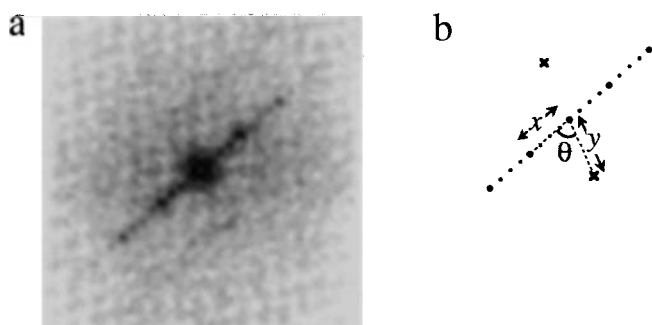


Figure 3. a) Fourier-transformed power spectrum of the STM image shown in Figure 2; b) schematic interpretation of the power spectrum.

lined up with the quartered interval of distance $2D = 6.8$ nm. This periodicity is observed as the four-line modulation pattern of the STM image contrast in Figure 2. Third, two diffuse spots (crosses in Figure 3b) are also observed in Figure 3a. Half of the distance between the diffuse spots corresponds to the spacing for the twisted features in Figure 2 ($d = 1.4$ nm), which is three times the width of the alkyl chain.

Fourth, angle θ between the two lines drawn on the spots in Figure 3b is 71.7° , and ratio y/x is 1.18.

These results are explained by lattice matching between the atomic cloth and graphite according to Equation (a);

$$p \cdot \mathbf{a} = i \cdot \mathbf{a}_g + j \cdot \mathbf{b}_g, \quad q \cdot \mathbf{b} = k \cdot \mathbf{a}_g + l \cdot \mathbf{b}_g \quad (\text{a})$$

\mathbf{a}_g and \mathbf{b}_g are the unit vectors of graphite, \mathbf{a} and \mathbf{b} vectors for the repeating units of the atomic cloth along a PD or PA chain and $-(\text{C}=\text{C}-\text{C}_{12}\text{H}_{24})_{2n}$ – chain, respectively, and $p\mathbf{a}$ and $q\mathbf{b}$ the unit vectors of the total system comprising the atomic cloth and graphite. Periodicities $2D$ and d (corresponding to $x/4$ and y in the Fourier transformation) imply $q = 2$ and $p = 3$. Using the values of $2D$, d , and θ , we can find the approximate commensuration $\begin{pmatrix} i \\ k \end{pmatrix} = \begin{pmatrix} 7 \\ 13 \end{pmatrix}$, as shown schematically in Figure 4. Furthermore, if the one-dimensional modulation of

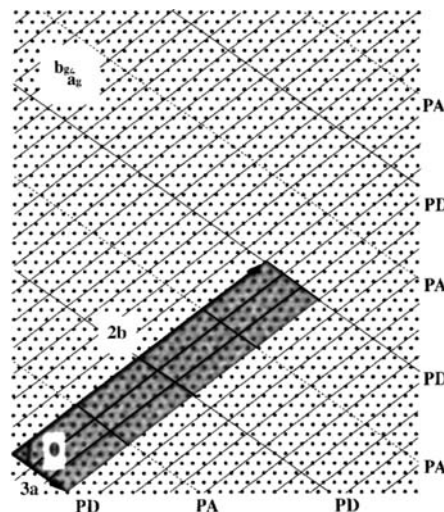


Figure 4. Proposed periodic structure of the atomic cloth on a graphite lattice (black circles). Solid and dashed lines show the PD and PA chains, respectively.

the STM image contrast with periodicity $2D$ is ascribed to the point-on-line coincidence,^[8] which occurs when only j and l (or i and k) are integers and places all the lattice points of the organic layer on the (1,0) (or (0,1)) lines of graphite, values i and k are modified as 7.01 and 12.9 by introducing $m = |\mathbf{b}|/|\mathbf{a}| = (1/|\mathbf{a}|)/(1/|\mathbf{b}|) = (3y \sin \theta)/(x \sin \theta/2) = 6y/x = 7.07$ in Equation (b).

$$\begin{pmatrix} \frac{i}{p} \\ \frac{\sqrt{3}k}{2mq} \end{pmatrix} = \frac{1}{\sin \theta} \begin{pmatrix} -\sin\left(\theta + \frac{\pi}{3}\right) & 1 \\ -\frac{3}{4} & -\sin\left(\theta - \frac{\pi}{3}\right) \end{pmatrix} \begin{pmatrix} \frac{j}{p} \\ \frac{\sqrt{3}l}{2mq} \end{pmatrix} \quad (\text{b})$$

Equation (b) can be derived from the geometry of an adlayer whose structure on a hexagonal substrate is expressed by Equation (a). Thus, one obtains $|\mathbf{a}| = 0.499$ and $|\mathbf{b}| = 3.54$ nm; the former is comparable to the length of the repeating unit of various PDs (ca. 0.49 nm).^[9]

Eichhorst-Gerner et al. prepared a one-dimensional hydrogen-bonded network with a donor – acceptor complex of 5-alkoxyisophthalic acid and 2,5-dimethylpyrazine at a liquid – graphite interface, and obtained the STM image with submolecular resolution.^[10] In this network, the hydrogen bonds were introduced without altering the alkyl skeletons, and the methyl ends remained free. As a consequence, the direction of the zigzag coincides with that of vector \mathbf{a}_g , and the

length of the repeating unit nearly matches $|a_g|$, which is responsible for the resolved STM pictures of the chains. This is usually the case for STM images of, for example, alkanes, alkanols, fatty acids, and dialkylbenzenes adsorbed on HOPG and observed with submolecular or atomic resolution.^[11–13] In contrast, we introduced the new covalent bonds among molecules in a vapor-deposited monolayer and prepared a single sheet of a two-dimensional macromolecule: The centers and ends of chain molecules were transfixed with PD chains and stitched with PA chains, respectively, to afford condensed parallelograms without free methyl ends but with changes in the bond lengths and angles of the alkyl chains (see Figure 1). We consider that the drastic rearrangement of the covalent bonds detected by PIES^[2] leads to the following results.

First, the atomic cloth is not commensurate with graphite in all directions. In fact, since i is very close to an integer (7)—to say nothing of j —the atomic cloth is almost point-on-point coincident with graphite along the a axis. On the other hand, since k is considerably different from an integer (13), there is no point-on-point but only point-on-line coincidence along the b axis. In other words, the periodicities of the PD and PA chains are approximately commensurate with that of graphite, while that of the $-(C=C-C_{12}H_{24})_{2n}-$ chains is not. It should be noted that neither the direction nor the periodicity of $-C_{12}H_{24}-$ matches that of graphite (a_g and $|a_g|$). Second, the two-dimensionality of the atomic cloth may bring about slight local fluctuation or irregularity in the periodicity: The two-dimensional macromolecular network on a graphite lattice probably distorts the flexible portions in order to reduce the total energy of the system. Third, it is likely that these situations lead to the obviously observed periodicity $2D$ ($x/4$), but rather ambiguous periodicity d (y) in Figure 2 (Figure 3). It is surprising that the commensuration between PD/PA and graphite is present after such a drastic reaction. Studies on the structure of the DTTY monolayer are desired to elucidate the details. However, they are difficult, because the monomer monolayer is very liable to sublime under UHV at room temperature; furthermore, DTTY undergoes photopolymerization in the room light.

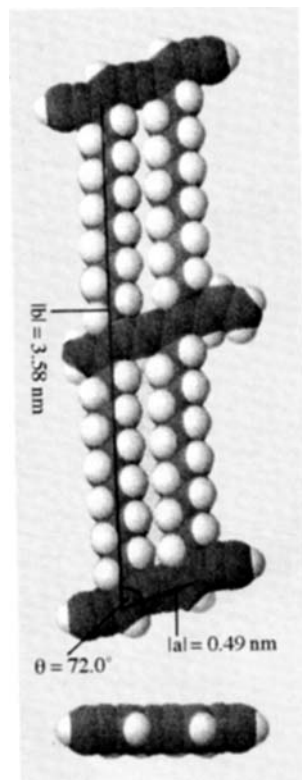


Figure 5. Structure of a model oligomer corresponding to the unit mesh of the atomic cloth obtained by MM2 calculation.

The periodic structure of the atomic cloth determined by STM can be supported by an MM2 calculation. Figure 5 shows the calculated structure of a model oligomer molecule corresponding to the unit mesh of the atomic cloth. The values of $|a|$, $|b|$, and θ are in good agreement with those observed.

We have observed the atomic cloth, a single sheet of a clothlike macromolecule, by STM. The periodic features

and contrast modulation of the STM images are explained by lattice matching between the atomic cloth and graphite. The lengths of the unit vectors of the atomic cloth are 0.499 and 3.54 nm, and the angle between the vectors is 71.7° . These results show the great promise of STM in determining the structure of a two-dimensional macromolecule (organic monoatomic layer) prepared on a crystallographical surface.

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- [1] H. Ozaki, T. Funaki, Y. Mazaki, S. Masuda, Y. Harada, *J. Am. Chem. Soc.* **1995**, *117*, 5596–5597.
- [2] H. Ozaki, M. Kasuga, T. Tsuchiya, T. Funaki, Y. Mazaki, M. Aoki, S. Masuda, Y. Harada, *J. Chem. Phys.* **1995**, *103*, 1226–1228.
- [3] H. Ozaki, *J. Electron Spectrosc. Relat. Phenom.* **1995**, *76*, 377–382.
- [4] T. Takami, D. Fukushi, T. Nakayama, M. Uda, M. Aono, *Jpn. J. Appl. Phys.* **1994**, *33*, 3688–3695.
- [5] We carried out ab initio calculations on some oligomeric models of the atomic cloth. The results showed that the LUMO is mainly distributed on the PD chains, whereas the HOMO is on the PA chains. If the picture presented in Figure 2 is assumed to be due to the LUMO, the brighter lines correspond to the PD chains, and the darker lines to the PA chains. However, this tentative assignment does not matter for the following discussion on the structure of the atomic cloth.
- [6] We compared our STM images with the artifact images reported in C. R. Clemmer, T. P. Beebe, Jr., *Science* **1991**, *251*, 640–642 and H. Chang, A. J. Bard, *Langmuir* **1991**, *7*, 1143–1153, which were ascribed to the cleavage steps, strands, and small particles of HOPG. Our STM image, however, has a long periodicity and is different from the artifact images.
- [7] Reversed STM images were observed upon changing the bias voltage; that is, PD and PA chains were dark, and alkyl chains bright. Nevertheless, there was no distinct feature corresponding to the latter chains but the undulation of contrast due to the former chains with periodicity $2D$. The image due to graphite was not observed either.
- [8] A. Hoshino, S. Isoda, H. Kurata, T. Kobayashi, *J. Cryst. Growth* **1995**, *146*, 636–640.
- [9] "Polydiacetylenes": V. Enkelmann in *Advances in Polymer Science*, Vol. 63 (Ed.: H.-J. Cantow), Springer, Berlin, **1984**, pp. 91–136.
- [10] K. Eichhorst-Gerner, A. Stabel, G. Moessner, D. Declercq, S. Valiyaveetil, V. Enkelmann, K. Müllen, J. P. Rabe, *Angew. Chem.* **1996**, *108*, 1599–1602; *Angew. Chem. Int. Ed. Engl.* **1996**, *35*, 1492–1495.
- [11] G. C. McGonigal, R. H. Bernhardt, D. J. Thomson, *Appl. Phys. Lett.* **1990**, *57*, 28–30; G. C. McGonigal, R. H. Bernhardt, Y. H. Yeo, D. J. Thomson, *J. Vac. Sci. Technol. B* **1991**, *9*, 1107–1110.
- [12] J. P. Rabe, S. Buchholz, *Science* **1991**, *253*, 424–427; S. Buchholz, J. P. Rabe, *Angew. Chem.* **1992**, *104*, 188–190; *Angew. Chem. Int. Ed. Engl.* **1992**, *31*, 189–191; J. P. Rabe, D. Buchholz, L. Askadskaya, *Synth. Met.* **1993**, *54*, 339–349, and references therein.
- [13] M. Hibino, A. Sumi, I. Hatta, *Jpn. J. Appl. Phys.* **1995**, *34*, 3354–3359.