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Atomic force microscopy and theoretical investigation of the lifted-up conformation of polydiacetylene on a graphite substrate

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Received 28th November 2007, Accepted 18th February 2008

First published as an Advance Article on the web 5th March 2008

DOI: 10.1039/b718402f

The structure of a single polydiacetylene compound on a graphite substrate was investigated using atomic force microscopy (AFM). The linear conjugated polydiacetylenes were obtained through chain polymerization of a monomolecular layer of diacetylene compound on a graphite substrate under ultraviolet light irradiation. AFM observations revealed that the polydiacetylenes were imaged higher than the unpolymerized monomer rows. This result supports the 'lifted-up' conformation model, in which the polydiacetylene backbone is geometrically raised. To investigate why the polymer backbone is lifted, we also carried out first-principles density-functional calculations in the local density approximation. These calculations suggested that the steric hindrance between the alkyl side-chains of the monomers and the oligomer caused the lifted-up conformation.

Introduction

With progress in nanotechnology, the chemistry and physics of single polymer chains have attracted considerable interest. The ability to characterize and understand the properties of individual single polymer chains is important because it will enable exploitation of potential new functions in the polymer and the development of novel devices such as single molecular devices.¹ There have already been many attempts to isolate single polymer chains on solid substrates and to characterize them. For instance, self-organization of polymer chains,² electrochemical epitaxial polymerization of polythiophene,³ and inclusion complex formation between single polymer chains with insulated cyclodextrins⁴ have been demonstrated for isolated single polymer chains on solid substrates.

We have also demonstrated that topochemical chain polymerizations on self-ordered films of diacetylene compounds (general formula $R-C\equiv C-C\equiv C-R'$, where $C\equiv C-C\equiv C$ is the diacetylene moiety and R and R' are substituent groups)⁵ can create single polymer chains on solid substrates.^{6–8} We used a 10,12-pentacosadiynoic acid [$CH_3(CH_2)_{11}-C\equiv C-C\equiv C-(CH_2)_8COOH$] molecule as the diacetylene compound and did the experiments on the monomolecular layers on a highly oriented pyrolytic graphite (HOPG) substrate at an air–solid interface. The chain polymerizations were initiated using ultraviolet irradiation or tunnelling electrons from the probe tip of a scanning tunnelling microscope (STM). Using this method,

we can create a long, linear, fully conjugated polydiacetylene (general formula $(=RC-C\equiv C-CR'=)_n$) at designated positions. This polydiacetylene provides an ideal sample for basic studies of single conjugated polymers and will also be useful as a nanowire for interconnecting future nanoelectronic devices. For instance, scanning tunnelling spectroscopy (SPS) investigations⁹ showed a polaron injection into the polydiacetylene backbone, and conductivity measurements using a double-probe STM¹⁰ on a polydiacetylene multilayer film indicated the high conductivity of polydiacetylene nanowires.

Despite its importance, however, the structure of this polydiacetylene on a graphite substrate has not yet been reported in detail. Fig. 1a shows a typical sub-molecular resolved STM image of the monomers and a polymer of 10,12-pentacosadiynoic acid on a graphite substrate (we can easily discern the polymer from the monomer row in STM images observed at higher sample biases⁷). Fig. 1b shows a model of the molecular arrangement in the monomer row, in which the alkyl side-chains of each molecule are oriented parallel to the main crystal axis of the graphite.⁷ STM images, such as in Fig. 1a, showed that the orientation of the alkyl side-chains of the polymer was maintained parallel to that of the alkyl side-chains of the monomers. Assuming that all carbon atoms in the polymer still lie on the same plane parallel to the surface of the graphite, the alkyl side-chains should show orientation changes as in the 'in-plane' model depicted in Fig. 1c. However, this is inconsistent with the experimental finding described above, which suggests that there is a change in conformation upon polymerization. Hence, we have proposed the 'lifted-up' conformation model⁷ shown in Fig. 1d, in which the innermost carbon atoms of the alkyl chains adjoining the polydiacetylene backbone and the polydiacetylene backbone itself were raised from the surface. When the polymer backbone is lifted, the alkyl side-chains tilt and the model satisfies the experimental observations.

Similar orientation changes in alkyl side-chains have been reported by Miura *et al.*¹¹ and Endo *et al.*¹² for other diacetylene compounds, and these also support the lifted-up conformation

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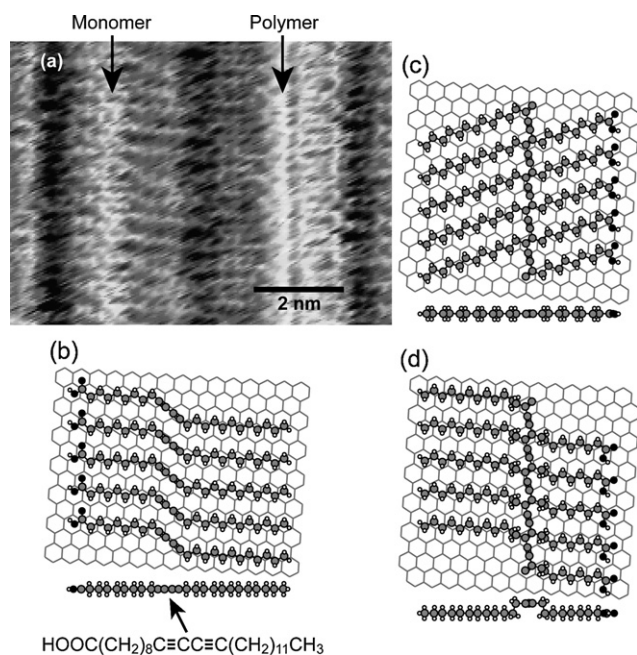


Fig. 1 (a) STM image of 10,12-pentacosadiynoic acid molecular layer on graphite substrate obtained after ultraviolet irradiation (sample bias voltage $V_s = +0.1$ V and tunnelling current $I_t = 0.1$ nA). Molecules were partially polymerized so that polymer and remaining monomer rows were observed in same image. (b) Top and side views of model of molecular arrangement in monomer row. (c) 'In-plane' conformation model of polymer. (d) 'Lifted-up' conformation model of polymer.

model. Endo *et al.* also reported¹² that polymerization of 17,19-hexatriacontadiyne on a graphite substrate produced 'lifted-up' polymers, but they were transformed into 'in-plane' polymers by keeping them at room temperature or using further ultraviolet irradiation.

The basis for the lifted-up conformation model in these previous reports was, however, only the orientation of the alkyl side-chains of the polymer. Hence, further experimental evidence is desirable. Furthermore, there has been no explanation of why the polymer backbone is lifted.

Here, we show the results of observations made using atomic force microscopy (AFM). If the polymer backbones are imaged higher than the monomers in AFM images, this would support the lifted-up conformation model. Though numerous STM images of alkane layers on graphite substrates have been reported,^{6–8,11–15} only a few AFM images have been reported previously.^{16–18}

Theoretical calculations can also help us understand why polymerization produces the lifted-up conformation. Molecular dynamics or molecular mechanics simulations of long-chain alkanes adsorbed on a graphite substrate have been performed.^{19,20} In addition to such calculations using empirical potentials, here we employ first-principles density-functional calculations in the local density approximation. The first-principles calculations deal with the contributions of the electronic systems inside a molecule more precisely, enabling us to discuss the total energies of molecules that contain distorted chemical bonds in more detail.

Experimental

Sample preparation

10,12-Pentacosadiynoic acid (Tokyo Chemical Industry Co., Ltd) was used as received. The diacetylene monomer molecules were dissolved in chloroform at a concentration of 0.14 mg mL^{-1} and the solution was applied to the surface of purified water. After the evaporation of the chloroform, the thin film of molecules on the surface of the water was transferred to a freshly cleaved surface of HOPG (SPI Supplies SPI-2 grade) by nearly horizontal dipping. The sample was then stored overnight (about 18 hours) in a desiccator at room temperature in the dark for drying. Polymerization was performed by irradiation with ultraviolet light from a low-pressure mercury lamp (254 nm wavelength and 1 mW cm^{-2} power density at the sample position using a band-pass filter) at room temperature for a period of 10 min.

AFM observations

AFM experiments were performed using an Agilent 5500 SPM system under ambient conditions. Height, amplitude, and phase images were simultaneously recorded in acoustic alternating-current (AAC) mode with a typical scan rate of 1 Hz. Commercial silicon cantilevers (NanoWorld PPP-NCH) with a spring constant of $33\text{--}38 \text{ Nm}^{-1}$ and resonance frequency of $280\text{--}320 \text{ kHz}$ were used. Set-point amplitude was typically 75% of the free-oscillating amplitude.

Calculation

In the first-principles calculations to determine stable geometrical structures and self-consistent electronic ground states, a program package based on the real-space finite-difference method²¹ was employed, in which norm-conserving pseudopotentials and a time-saving double-grid technique were used to calculate the interactions between the electrons and the atomic nucleus. The exchange–correlation interaction was treated using the local density approximation of the density functional theory.

Results and discussion

AFM observations of diacetylene monomer layer

First, we examined AFM images of the molecular layer of 10,12-pentacosadiynoic acid monomers on a graphite substrate without ultraviolet irradiation. Fig. 2a shows a typical AFM height image of the layer. As the image shows, we were able to observe several domains, each of which consisted of parallel stripes. Fig. 2b is a magnified AFM height image of one of the domains, in which the parallel stripes run diagonally from top right to bottom left. The period of the stripes was measured at $6.5 \pm 0.4 \text{ nm}$.

From STM studies, we deduced the molecular arrangement shown in Fig. 2c.⁷ In this model, the molecules are aligned to form straight chains and the chains are arranged in pairs in such a manner that the carboxy end groups of one chain are opposite those of a neighboring chain. The period observed in the AFM images approximately corresponds to the repeating period of the pairs observed in the STM images (6.8 nm).

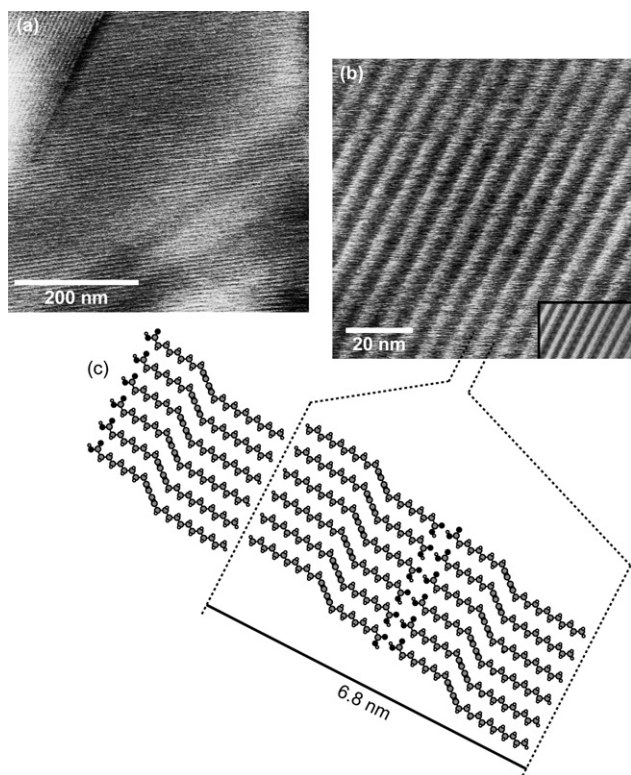


Fig. 2 (a) AFM height image of 10,12-pentacosadiynoic acid monomer layer on graphite substrate. (b) Magnified AFM height image of layer. Inset shows a corresponding STM image at same scale. (c) Model of molecular arrangement.

Note that each molecular chain can be observed in the STM images, as in the inset to Fig. 2b, but a pair of molecular chains is observed as a line in the AFM images. In previous AFM observations of normal alkane,¹⁶ alkanol,¹⁷ and alkanolic acid¹⁸ molecular films on graphite substrates, terminal methyl groups were imaged as dark lines^{16,17} and carboxy end groups were imaged as bright lines of bumps.¹⁸ Based on these reports, the bright and dark lines in our AFM images can be assigned to arrays of carboxy end groups and terminal methyl groups, respectively.

AFM observations of polydiacetylene

STM studies have shown that 10 minutes of irradiation with ultraviolet light on a 10,12-pentacosadiynoic acid layer induces partial polymerization of the layer and produces several polydiacetylene compounds in a $500 \times 500 \text{ nm}^2$ area.⁷ Fig. 3a shows an AFM phase image of such a surface. Several very bright, straight lines appeared in the monomer molecular stripes. Hence, these very bright lines can be assigned to polydiacetylene compounds created by photopolymerization. A magnified AFM height image of one of the polymers is shown in Fig. 3b. The polymer is clearly distinguishable from the monomers, even in the height image. The fact that the polymers were observed to be higher than the monomers in the AFM images supports the lifted-up conformation model.

Similarly to the case of STM,^{13,14} AFM scanning sometimes induced the desorption of polydiacetylenes, even in AAC mode. Fig. 3c is an AFM image of a polymer observed from

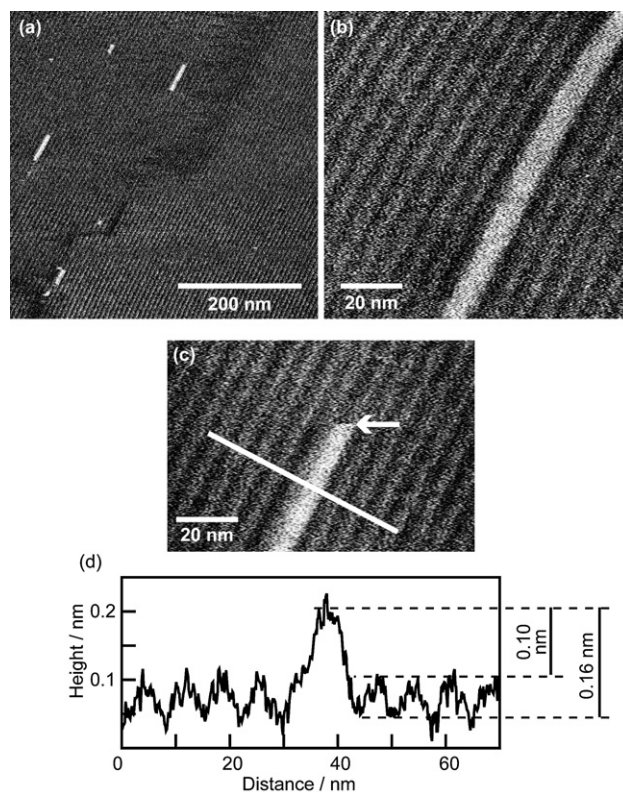


Fig. 3 (a) AFM phase image of partially polymerized 10,12-pentacosadiynoic acid layer obtained after ultraviolet irradiation. (b) Magnified AFM height image of polymer. (c) AFM height image of polymer observed from bottom to top. During scanning, the polymer was desorbed at the point indicated by the arrow. (d) Cross-sectional profile of polymer in (c).

the bottom to the top. We can see that the polymer was abruptly desorbed and disappeared at the point indicated by the arrow. By imaging the same area from which Fig. 3c had just been obtained, we confirmed that the polymer had completely disappeared from the scanning area and only the monomer stripes could be observed. The polymer was replaced by well-ordered monomer molecules within the time that elapsed between subsequent line scans (about 1 s) in Fig. 3c, as pointed out by Giridharagopal *et al.*¹⁴

The averaged cross-sectional profile across the polymer in Fig. 3c is shown in Fig. 3d, which was obtained by averaging 20 cross-sectional profiles along the same polymer. In Fig. 3d, the polymer is observed to be 0.10 and 0.16 nm higher than the top and bottom, respectively, of the monomer stripes. As mentioned before, the top and bottom of the monomer stripes correspond to the carboxy and terminal methyl groups, which should be imaged higher and lower than the alkyl chains, respectively. Hence, the observed height of the polymer backbone from the alkyl side-chains should be between 0.10 and 0.16 nm in Fig. 3c, although the alkyl side-chains themselves are not resolved in the image. The heights of the polymers depended on the AFM probes and the measuring parameters. The measured heights of several polymers from the top of the monomer stripes varied from 0.05 to 0.10 nm, and the heights from the bottom of the monomer stripes varied from 0.11 to 0.16 nm.

As mentioned above, carboxy end groups were imaged as bright lines of bumps,¹⁸ which implies that not only the atomic position but also the electronic structure may be factors in the origin of the height difference in the AFM. Deformation of the polymers by the AFM probe might also affect the heights of the AFM. Indeed, the observed height of the polymer backbone from the alkyl side-chains in some images was lower than the calculated value, 0.146 nm, which will be described in the next section. This discrepancy might be due to the influence of the electronic states of conjugated systems, or to deformation of the polymers by the AFM probe.

Calculations of polymers of infinite length

To investigate why the backbones of polydiacetylenes are lifted, we performed first-principles density-functional calculations in the local density approximation.²¹ We first optimized the structures of polydiacetylenes of infinite length for both in-plane and lifted-up conformations, and estimated their total energies. To calculate the in-plane conformation model, the *z*-coordinates of all the carbon atoms were fixed in the same plane, and the *x*- and *y*-coordinates of the carbon atoms and the positions of the hydrogen atoms were optimized so as to minimize the total energy. To optimize the lifted-up conformation model, the position of the polymer backbone and the four innermost methylene groups (carbon atoms numbered 6 to 17 in Fig. 4b) were set free, while the *z*-coordinates of the outer carbon atoms (numbered 1–5 and 18–25 in Fig. 4b) were fixed in the same plane. The periodic length was fixed to be 0.474 nm, which was the experimentally determined value,⁷ for both models.

As a result, both in-plane and lifted-up conformations were obtained as stable structures with local energy minimums, as shown in Fig. 4. In the lifted-up conformation, the height of the polymer backbone from the alkyl side-chains was calculated to be 0.146 nm, as shown in Fig. 4b. The cohesive energy, which is defined as the difference in energy between the total energy of individual monomer molecules and that of the polymer, was calculated at 1.282 eV per unit for the in-plane conformation model and 1.171 eV per unit for the lifted-up conformation model. Hence, the in-plane conformation was calculated to be slightly (0.111 eV per unit) more stable than the lifted-up conformation.

Since the above calculations did not include the graphite substrate, we next estimated the interaction energies between the adsorbed molecules and the substrate. When the polymer backbone is lifted, the innermost methylene groups adjoining the polydiacetylene backbone (numbered 9 and 14 in Fig. 4) are also lifted, so that the polymer loses their adsorption energy. The orientations of the methylene groups numbered 8 and 15 in Fig. 4 are also completely changed by being lifted. The rest of the alkyl side-chains (total of 16 methylene groups per unit, which are numbered 2–7 and 16–25 in Fig. 4b) adsorb parallel to the main crystal axis of the graphite in the lifted-up conformation model, but 20 methylene groups adsorb on random sites with an inclined orientation in the in-plane conformation model. Since the alkyl side-chains of the monomer molecules are always oriented parallel to the main crystal axis of the graphite, as shown in Fig. 1b, the parallel orientation should be more stable than the inclined orientation. Thus the adsorption energy per

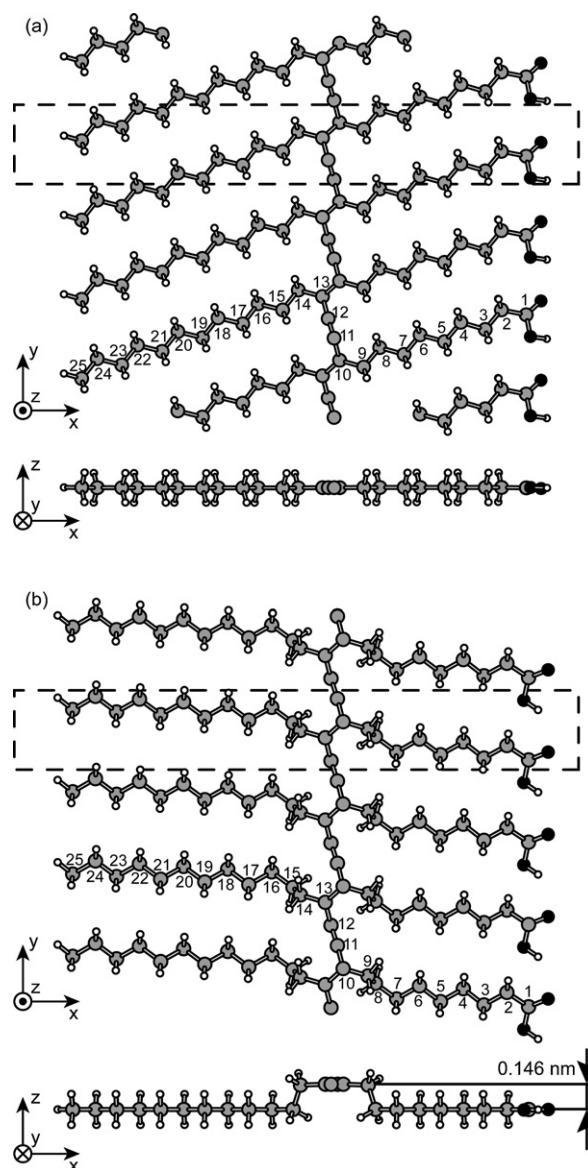


Fig. 4 Optimized structures by first-principles density-functional calculations for (a) in-plane and (b) lifted-up conformation models.

unit of the polymer for the in-plane and lifted-up conformation model, $V_{\text{in-plane}}$ and $V_{\text{lifted-up}}$ respectively, can be represented as

$$V_{\text{in-plane}} = 20v_{\text{inclined}}, \quad (1)$$

$$V_{\text{lifted-up}} = 16v_{\text{parallel}} + 2v_{\text{vertical}}, \quad (2)$$

where v_{inclined} and v_{parallel} describe the averaged adsorption energies per CH_2 of the outer alkyl side-chains for the in-plane and lifted-up conformation models, respectively, and v_{vertical} describes the adsorption energies per CH_2 of the methylene groups numbered 8 and 15 in Fig. 4b.

Yin *et al.* performed molecular mechanics calculations of long-chain alkanes on a graphite substrate.²⁰ According to their calculations, the adsorption energies for C_8H_{18} , $\text{C}_{24}\text{H}_{50}$, and $\text{C}_{34}\text{H}_{70}$ molecules in a flat orientation are -1.028 , -2.955 , and -4.140 eV, respectively. In the case of C_8H_{18} , the methylene hydrogens

are located above hollow sites in the graphite hexagon. Hence, the adsorption energy of methylene groups on a hollow site can be estimated to be $-1.028 \text{ eV}/8 = -0.1285 \text{ eV}$ per CH_2 . The methylene hydrogens at both ends of $\text{C}_{34}\text{H}_{70}$ are, on the other hand, located near bridge sites of the graphite. Accordingly, the difference in adsorption energies between $\text{C}_{34}\text{H}_{70}$ and $\text{C}_{24}\text{H}_{50}$ molecules can be ascribed to the adsorption energy of the 10 methylene groups near the bridge sites. The adsorption energy of methylene on a bridge site can thus be estimated to be $\{(-4.140 \text{ eV}) - (-2.955 \text{ eV})\}/10 = -0.1185 \text{ eV}$ per CH_2 . As an over estimation, we assume that v_{incline} is less than the adsorption energy of the methylene group on the bridge site, and v_{parallel} is larger than that on the hollow site:

$$-0.1285 \text{ eV} < v_{\text{parallel}} < v_{\text{incline}} < -0.1185 \text{ eV}. \quad (3)$$

Yin *et al.* also calculated the adsorption energy for a $\text{C}_{34}\text{H}_{70}$ molecule in a vertical orientation, in which the carbon zigzag plane of the alkane is oriented perpendicular to the substrate, as -3.628 eV . Since 17 methylene groups in a $\text{C}_{34}\text{H}_{70}$ molecule are attached to the graphite substrate, the adsorption energy of methylene in the vertical orientation is estimated to be $-3.628 \text{ eV}/17 = -0.213 \text{ eV}$ per CH_2 . We assume that v_{vertical} is larger than this value:

$$-0.213 \text{ eV} < v_{\text{vertical}} < 0 \text{ eV}. \quad (4)$$

From eqn (1) to (4), we obtain:

$$-0.11 \text{ eV} < V_{\text{lifted-up}} - V_{\text{in-plane}} < 0.51 \text{ eV}. \quad (5)$$

We can thus conclude that the difference in adsorption energy between the lifted-up and in-plane conformation models is very small.

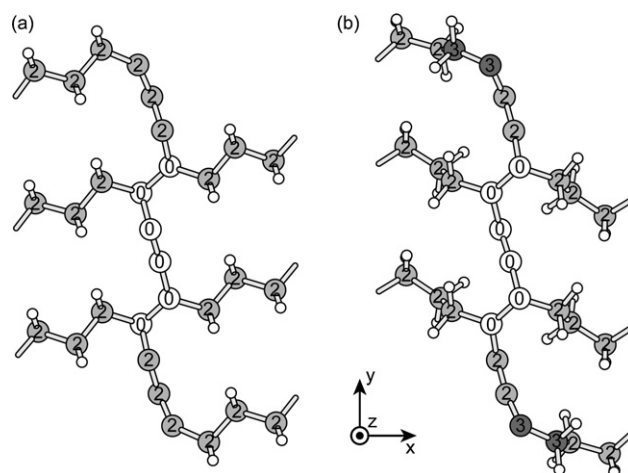
As mentioned before, our first-principles calculations of the cohesive energies showed that the in-plane conformation was 0.111 eV per unit more stable than the lifted-up conformation. Hence, the difference in total energy including the interaction with the substrate, $\Delta E_{\text{lifted-up}} - \text{in-plane}$, should be in the range of

$$0.00 \text{ eV} < \Delta E_{\text{lifted-up}} - \text{in-plane} < 0.62 \text{ eV per unit}. \quad (6)$$

Accordingly, the in-plane conformation model should be more stable than the lifted-up conformation model, even if we consider the effect of the interaction with the graphite substrate. MM2 calculations of oligomers of $\text{H}(\text{CH}_2)_n\text{C}\equiv\text{C}-\text{C}\equiv\text{C}-(\text{CH}_2)_n\text{H}$ ($n = 6$ to 8) on a graphite substrate by Suhara *et al.*²² also showed the same tendency. Their calculations suggested that the in-plane conformation model was 0.15 eV per unit more stable than the lifted-up conformation model.

Calculations of oligomers

As discussed above, the total energy calculations for polymers of infinite length cannot explain why a lifted-up conformation is always produced by chain polymerization. We therefore considered the stability of the oligomers as intermediates of the chain polymerization. To reduce the size of the calculation, we considered a trimer of the $\text{H}(\text{CH}_2)_n\text{C}\equiv\text{C}-\text{C}\equiv\text{C}-(\text{CH}_2)_n\text{H}$ molecule located between the two monomer molecules and calculated



Scheme 1 To optimize trimer structure, x -, y - and z -coordinates were fixed for carbon atoms labelled '0', z -coordinates were fixed for carbon atoms labelled '2', and all coordinates were set free for carbon atoms labelled '3' during calculation. (a) In-plane and (b) lifted-up conformation models.

the total energies $E_{\text{in-plane}}$ and $E_{\text{lifted-up}}$ for the in-plane and lifted-up conformation model, respectively; the length of the alkyl side-chains n was varied from 5 to 9. The position and structure of the monomer molecules were fixed during the calculations, and the central part of the polymer backbone (carbon atoms labelled '0' in Scheme 1) was also fixed. To calculate the in-plane conformation model, the z -coordinates of the rest of the carbon atoms, which are labelled '2' in Scheme 1a, were fixed in the same plane, and the x - and y -coordinates of the carbon atoms and the positions of the hydrogen atoms were optimized. Similarly, to optimize the lifted-up conformation model, the z -coordinates of the carbon atoms labelled '2' in Scheme 1b were fixed, and the carbon atoms labelled '3' were set free. Fig. 5 shows the optimized structure of the in-plane and lifted-up conformation models when $n = 9$.

In Fig. 6, the calculated energy differences, $E_{\text{lifted-up}} - E_{\text{in-plane}}$, are plotted against the length of the alkyl side-chains. As we can see, the in-plane conformation model is more stable than the lifted-up conformation model when the alkyl side-chains are

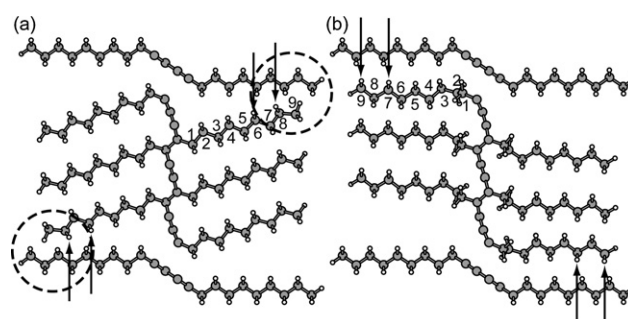


Fig. 5 Optimized structures of trimers between two monomer molecules for (a) in-plane and (b) lifted-up conformation models with C_9H_{19} alkyl side-chains. Dashed circles in (a) indicate the collision of alkyl chains and arrows indicate hydrogen atoms which are close to neighboring monomers.

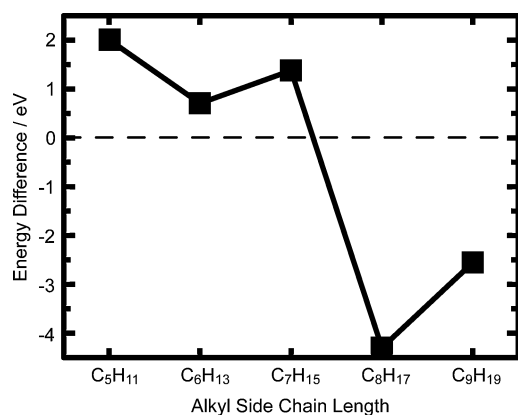


Fig. 6 Plots of calculated energy differences, $E_{\text{lifted-up}} - E_{\text{in-plane}}$, against length of alkyl side-chains.

short ($n \leq 7$). With increasing alkyl side-chain length n , however, $E_{\text{lifted-up}} - E_{\text{in-plane}}$ rapidly decreases, while it oscillates alternately in response to even and odd numbers of n . When the alkyl side-chains are C₈H₁₇ or longer, $E_{\text{lifted-up}} - E_{\text{in-plane}}$ becomes negative, so that the lifted-up conformation model becomes more stable than the in-plane conformation model. Hence, the lifted-up conformation will also be more stable for the oligomers of 10,12-pentacosadiynoic acid, the side-chains of which are C₁₂H₂₅ and C₈H₁₆COOH.

The reason why the lifted-up conformation model is preferable for oligomers that have long alkyl side-chains can be explained by the steric hindrance between the alkyl side-chains of the monomers and the oligomer. As shown in Fig. 5, the oligomer is restricted between the two neighboring monomers, which will form chemical bonds with the oligomer in the process of further chain polymerization. In the case of the in-plane conformation model, the alkyl side-chains of the oligomer are not parallel to those of the neighboring monomers. Hence, the long alkyl chains of the oligomer will collide with those of the monomers on both sides, as indicated by the dashed circles in Fig. 5a. In contrast, in the case of the lifted-up conformation model, the alkyl side-chains of the oligomer are parallel to those of the neighboring monomers, so that they will not collide even when they are long.

The even-odd oscillation in Fig. 6 can be explained as follows: when an even-numbered methylene group is added to the alkyl side-chains, its hydrogen atoms collide with the neighboring monomers in the in-plane conformation model, as indicated by the arrows in Fig. 5a. This results in an increase in $E_{\text{in-plane}}$. In contrast, $E_{\text{lifted-up}}$ becomes larger when an odd-numbered methylene group is added, as shown by the arrows in Fig. 5b. As a result, $E_{\text{lifted-up}} - E_{\text{in-plane}}$ becomes smaller or larger when n is even or odd, respectively.

In the above calculations, the position and structure of the two neighboring monomers were fixed to reduce the size of the calculation, though these monomers must have high mobility. Hence, the calculations are a very rough estimation and the actual energy differences are likely to be smaller than those in Fig. 6. Nevertheless, the above calculations indicate that the energy of the in-plane conformation model will become higher as the length of the alkyl side-chains increases, and that the

energy difference will be in the order of 1 eV. It should also be pointed out that the collision of alkyl side-chains will induce vibrational excitations of the monomer molecules, even in the lifted-up conformation model. These vibrational excitations might help the propagation of the chain polymerization, since the monomers have to 'jump' to the reactive site of the lifted-up oligomer to propagate the chain reaction.

Conclusion

We investigated the structure of a single polymer of 10,12-pentacosadiynoic acid on a graphite substrate. We found that the polymers were imaged higher than the unpolymerized monomer rows in AFM images. This result supports the lifted-up conformation model, in which the polymer backbone is raised from the surface. The fact that we can distinguish polymers from monomers in AFM images is extremely interesting because it opens up the possibility of creating and investigating single polymers also on insulating substrates. Making polymer nanowires on insulating substrates will be an important step in investigating the intrinsic charge-transport properties of single π -conjugated nanowires and in developing single molecular devices.²³

To investigate why the polymer backbone is lifted up, we also carried out first-principles density-functional calculations in the local density approximation. These calculations suggested that the stability of an oligomer as an intermediate, not the stability of a long polymer as a final product, determines the conformation of the polymer. The steric hindrance between the alkyl side-chains of the monomers and the oligomer caused the lifted-up conformation.

Acknowledgements

This work was supported by KAKENHI (19510121).

References

- 1 A. Aviram and M. A. Ratner, *Chem. Phys. Lett.*, 1974, **29**, 277; C. Joachim, J. K. Gimzewski and A. Aviram, *Nature*, 2000, **408**, 541; C. P. Collier, E. W. Wong, M. Belohradský, F. M. Raymo, J. F. Stoddart, P. J. Kuekes, R. S. Williams and J. R. Heath, *Science*, 1999, **285**, 391; Z. J. Donhauser, B. A. Mantooth, K. F. Kelly, L. A. Bumm, J. D. Monnell, J. J. Stapleton, D. W. Price Jr, A. M. Rawlett, D. L. Allara, J. M. Tour and P. S. Weiss, *Science*, 2001, **292**, 2303.
- 2 E. Mena-Osteritz, A. Meyer, B. M. W. Langeveld-Voss, R. A. J. Janssen, E. W. Meijer and P. Bäuerle, *Angew. Chem., Int. Ed.*, 2000, **39**, 2679; B. Grévin, P. Rannou, R. Payerne, A. Pron and J. P. Travers, *J. Chem. Phys.*, 2003, **118**, 7097.
- 3 H. Sakaguchi, H. Matsumura and H. Gong, *Nat. Mater.*, 2004, **3**, 551; H. Sakaguchi, H. Matsumura, H. Gong and A. M. Aboulwafa, *Science*, 2005, **310**, 1002.
- 4 K. Yoshida, T. Shimomura, K. Ito and R. Hayakawa, *Langmuir*, 1999, **15**, 910; T. Shimomura, T. Akai, T. Abe and K. Ito, *J. Chem. Phys.*, 2002, **116**, 1753; F. Cacialli, J. S. Wilson, J. J. Michels, C. Daniel, C. Silva, R. H. Friend, N. Severin, P. Samori, J. P. Rabe, M. J. O'Connell, P. N. Taylor and H. L. Anderson, *Nat. Mater.*, 2002, **1**, 160.
- 5 G. Wegner, *Makromol. Chem.*, 1972, **154**, 35; B. Tieke, G. Lieser and G. Wegner, *J. Polym. Sci.: Polym. Chem. Ed.*, 1979, **17**, 1631.
- 6 Y. Okawa and M. Aono, *Nature*, 2001, **409**, 683.
- 7 Y. Okawa and M. Aono, *J. Chem. Phys.*, 2001, **115**, 2317.
- 8 D. Takajo, Y. Okawa, T. Hasegawa and M. Aono, *Langmuir*, 2007, **23**, 5247.
- 9 M. Akai-Kasaya, K. Shimizu, Y. Watanabe, A. Saito, M. Aono and Y. Kuwahara, *Phys. Rev. Lett.*, 2003, **91**, 255501; M. Akai-Kasaya,

- Y. Yamamoto, A. Saito, M. Aono and Y. Kuwahara, *Jpn. J. Appl. Phys.*, 2006, **45**, 2049.
- 10 K. Takami, J. Mizuno, M. Akai-kasaya, A. Saito, M. Aono and Y. Kuwahara, *J. Phys. Chem. B*, 2004, **108**, 16353; K. Takami, Y. Kuwahara, T. Ishii, M. Akai-Kasaya, A. Saito and M. Aono, *Surf. Sci.*, 2005, **591**, L273.
- 11 A. Miura, S. De Feyter, M. M. S. Abdel-Mottaleb, A. Gesquière, P. C. M. Grim, G. Moessner, M. Sieffert, M. Klapper, K. Müllen and F. C. De Schryver, *Langmuir*, 2003, **19**, 6474.
- 12 O. Endo, H. Ootsubo, N. Toda, M. Suhara, H. Ozaki and Y. Mazaki, *J. Am. Chem. Soc.*, 2004, **126**, 9894.
- 13 S. P. Sullivan, A. Schnieders, S. K. Mbugua and T. P. Beebe, Jr., *Langmuir*, 2005, **21**, 1322.
- 14 R. Giridharagopal and K. F. Kelly, *J. Phys. Chem. C*, 2007, **111**, 6161.
- 15 J. P. Rabe and S. Buchholz, *Phys. Rev. Lett.*, 1991, **66**, 2096; G. C. McGonigal, R. H. Bernhardt and D. J. Thomson, *Appl. Phys. Lett.*, 1990, **57**, 28; J. P. Rabe and S. Buchholz, *Science*, 1991, **253**, 424; J. P. Rabe, S. Buchholz and L. Askadskaya, *Synth. Met.*, 1993, **54**, 339; P. C. M. Grim, S. De Feyter, A. Gesquière, P. Vanoppen, M. Rücker, S. Valiyaveetil, G. Moessner, K. Müllen and F. C. De Schryver, *Angew. Chem., Int. Ed. Engl.*, 1997, **36**, 2601; T. Takami, H. Ozaki, M. Kasuga, T. Tsuchiya, Y. Mazaki, D. Fukushi, A. Ogawa, M. Uda and M. Aono, *Angew. Chem., Int. Ed. Engl.*, 1997, **36**, 2755.
- 16 S. N. Magonov and N. A. Yerina, *Langmuir*, 2003, **19**, 500.
- 17 T. Nakada, S. Miyashita, G. Sazaki, H. Komatsu and A. A. Chernov, *Jpn. J. Appl. Phys.*, 1996, **35**, L52.
- 18 G. Mao, W. Dong, D. G. Kurth and H. Möhwald, *Nano Lett.*, 2004, **4**, 249; W. Dong, R. Wang, G. Mao and H. Möhwald, *Soft Matter*, 2006, **2**, 686.
- 19 R. Hentschke, B. L. Schürmann and J. P. Rabe, *J. Chem. Phys.*, 1992, **96**, 6213.
- 20 S. Yin, C. Wang, X. Qiu, B. Xu and C. Bai, *Surf. Interface Anal.*, 2001, **32**, 248.
- 21 T. Ono and K. Hirose, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 2005, **72**, 085115.
- 22 M. Suhara, O. Endo, H. Ozaki, T. Ishida, H. Katagiri, T. Egawa and M. Katouda, Abstract of Bunshi Kouzou Sougou Touronkai, Tokyo, 2005 (in Japanese), http://www.molsci.jp/discussion_past/2005/papers/1P177_w.pdf.
- 23 B. Grevin and P. Rannou, *Nat. Mater.*, 2004, **3**, 503.