

Creation of conjugated polymer nanowires through controlled chain polymerization

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To realize novel nanodevices beyond today's silicon-based transistors, a method is needed that will allow us to create nanowires at designated positions. In this review article, we introduce our method for creating a conjugated polymer nanowire by initiating a chain polymerization of organic molecules using the tip of a scanning tunneling microscope. We have demonstrated this method using a self-ordered monomolecular layer of amphiphilic diacetylene compound adsorbed on a graphite surface. The termination of the chain polymerization can also be controlled by making an artificial defect in advance. [DOI: 10.1380/ejsnt.2004.99]

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I. INTRODUCTION

Silicon-based transistors have become smaller and smaller, and the performance of computers has become better and better, following the empirical Moore's law. However, in the near future the laws of quantum mechanics and the limitations of fabrication techniques will prevent further improvement. A number of novel device concepts, which can be applied at the nanometer scale, have thus been proposed to enable further improvements in computer performance. The idea of single-molecule electronic devices, in which an individual organic molecule acts as an electronic device like a diode or a transistor, is one such proposal.

The history of single-molecule devices dates from Aviram and Ratner's 1974 proposal of a single-molecule rectifier [1]. Though the history of these devices is rather long, the study of molecular devices has become very active [2–16], for two main reasons. First, we feel a sense of crisis stemming from the belief that Moore's law will soon reach its limit. Second, the feasibility of single-molecule devices has increased because of the progress made in micro/nano-fabrication technology, improved scanning probe microscope technology, progress in organic synthesis chemistry, our better understanding of self-organization, and the appearance of attractive new materials such as carbon nanotubes.

However, even if we could make individual molecules which function as single-molecule electronic devices, we would still lack good methods by which to arrange them in a desired pattern and interconnect them with each other. Thus, we need to develop a way to fabricate conductive wires of nanometer width (nanowires) at designated positions.

At present, what kind of materials can be considered candidates for forming nanowires? We usually use metals for wires wider than the micrometer order. In the case

of nanowires, however, metal usage becomes much more difficult because of metal wires' poor stability and difficulties in their fabrication. Hence, many materials other than metals have been considered for nanowires, including silicon compounds and conductive organic materials, though we must conduct further basic studies before we can put any of these to practical use.

As one example of a silicon-compound nanowire, Chen *et al.* reported that an erbium disilicide (ErSi_2) nanowire can be automatically formed on a Si(001) surface through Er evaporation onto a clean Si surface followed by annealing [17]. The size of this ErSi_2 nanowire was 1 nm high, a few nanometers wide, and nearly 1 μm long, and high electrical conductivity was observed.

One of the best studied organic materials for nanowire use is carbon nanotubes [18]. Because of their size (a few nanometers in diameter and a few micrometers long) and their various electronic states, many studies have been done on carbon nanotubes [19, 20].

Of course, conductive organic polymers, such as polyacetylene, have also been considered as candidate materials for nanowires. It is difficult, however, to isolate a single conductive polymer chain for use as a nanowire because of the strong intermolecular interaction. Furthermore, a single conductive polymer chain in a free state, such as in a solution, generally has a coiled conformation that prevents the formation of the π -conjugation. For these reasons, the studies of conductive polymers for nanowire use have been restricted to short oligomers in most cases [21–24]. Thus, an important goal has been to develop a way to isolate or synthesize a single conductive polymer with good linearity.

Regarding this goal, we will introduce our method in this review article. In our method, we can create a single straight π -conjugated polymer nanowire at a designated position within a short time span [25, 26]. Our method is schematically illustrated in Fig. 1. First, appropriate monomer molecules are ordered on an appropriate substrate (Fig. 1(a)). The probe tip of a scanning tunneling microscope (STM) is then positioned on one of the monomer molecules, and a pulsed bias voltage is applied

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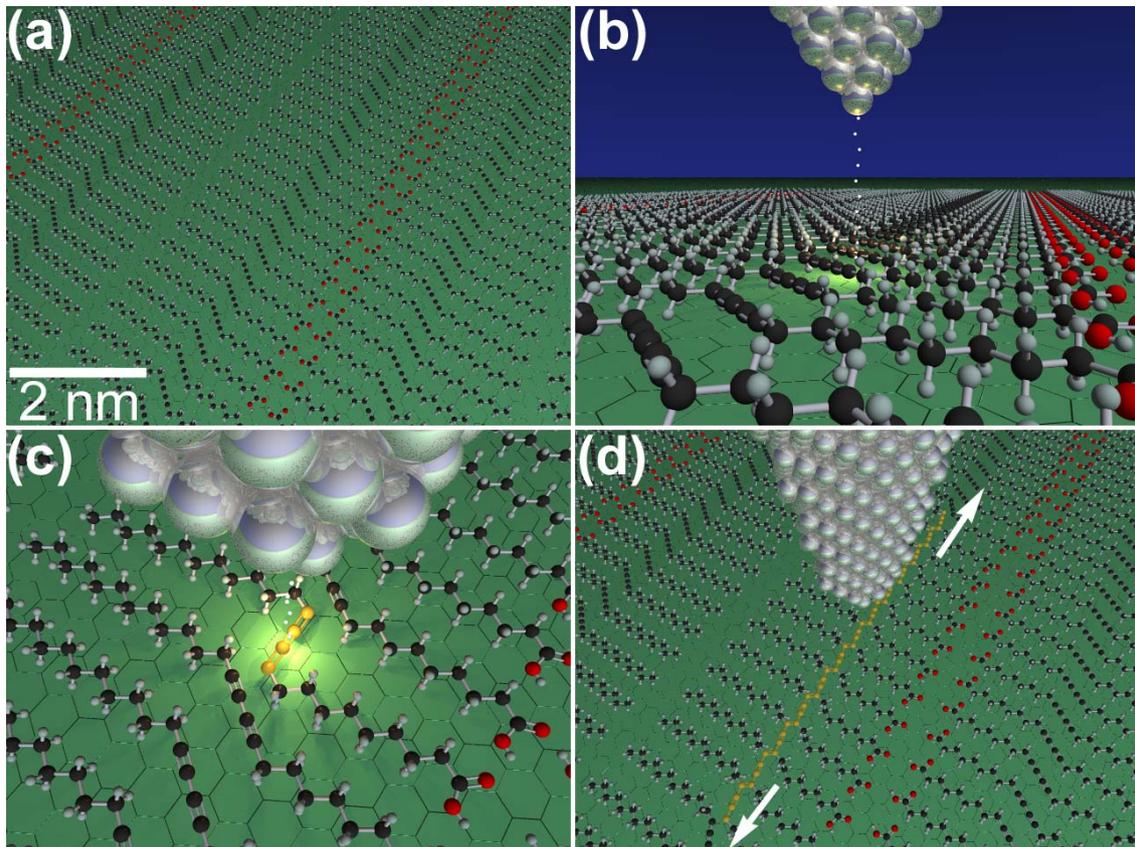


FIG. 1: Nanowire fabrication procedure: On the molecular film in (a), a stimulus is applied to a molecule through an STM tip (b), causing excitation (c), which initiates a chain polymerization reaction, resulting in formation of a polymer nanowire (yellow line) (d).

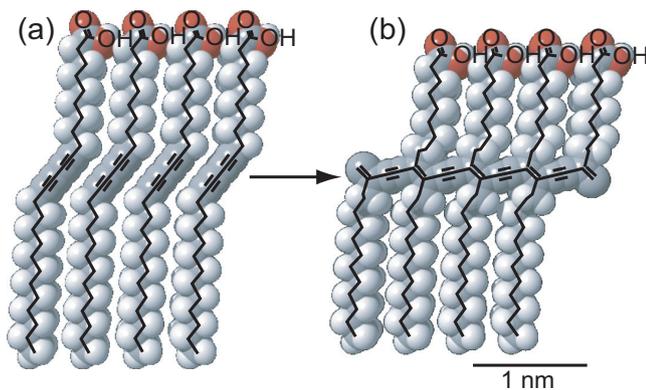


FIG. 2: (a) A model of 10,12-pentacosadiynoic acid molecules. (b) Polydiacetylene compounds formed through chain polymerization.

(Fig. 1(b)). The stimulated molecule is excited (Fig. 1(c)) and initiates a chain polymerization reaction. As a result, a long straight single-polymer chain can be created (Fig. 1(d)) by applying only one pulsed bias voltage at one point.

II. CHAIN POLYMERIZATION OF DIACETYLENE COMPOUNDS

The monomer molecules we used are diacetylene compounds with the 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. A variety of substituent groups can be considered as R and R' , and we chose to use 10,12-pentacosadiynoic acid [$CH_3(CH_2)_{11}-C\equiv C-C\equiv C-(CH_2)_8COOH$] (Fig. 2(a)) and 10,12-nonacosadiynoic acid [$CH_3(CH_2)_{15}-C\equiv C-C\equiv C-(CH_2)_8COOH$] in our work. These are amphiphilic molecules which contain a hydrophobic alkyl group on one side and a hydrophilic carboxy group on the other side.

It is well known that diacetylene compounds in the form of solid crystals [27] or Langmuir-Blodgett films [28] polymerize into polydiacetylene compounds upon appropriate stimulation such as heating or ultraviolet irradiation (see Fig. 2). Polydiacetylene compounds are a π -conjugated polymer with the general formula $\left[RC\equiv C-CR'\right]_n$, and contain double bonds and triple bonds alternately in their backbone. We therefore expected the polydiacetylene compounds to be conductive if there was a charge transfer between the polymer and its surroundings.

An important property of diacetylene compounds is that the polymerization reaction proceeds topochemically. That is, both the monomer and the polymer crystals belong to the same crystal system, and their lattice constants are almost the same. This property is a reason why we chose to use the diacetylene compounds; if the monomer and the polymer have different lattice constants, the polymerization will be unable to proceed for long, because the distance between the reactive edge of the polymer and the adjacent monomer molecule will not remain suitable for the reaction.

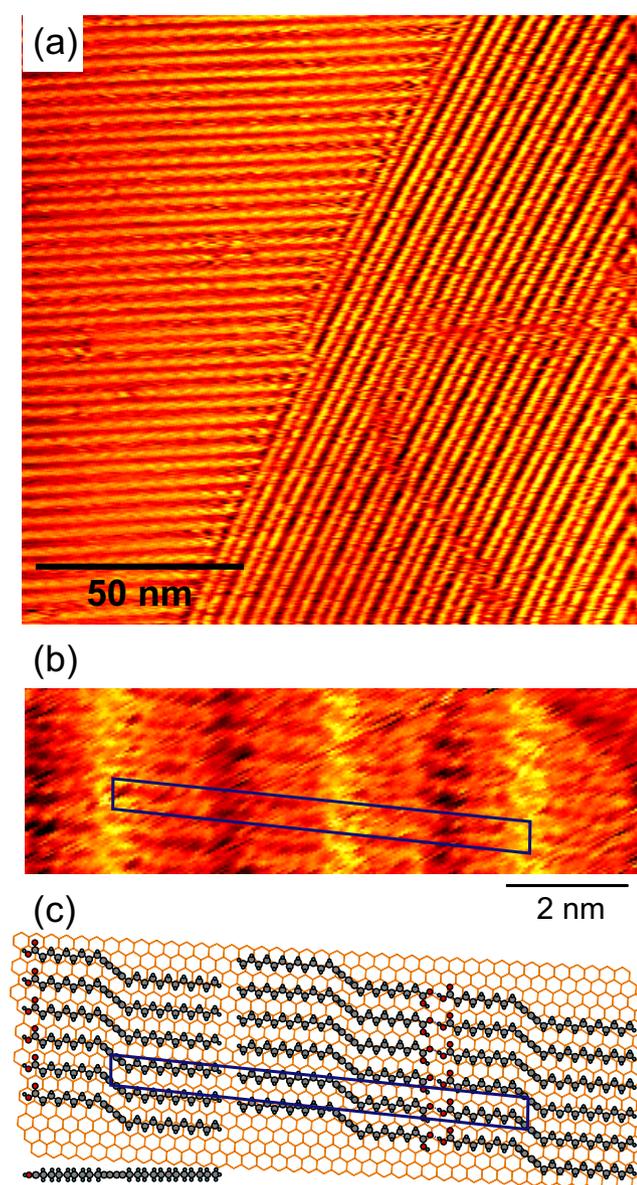


FIG. 3: (a) Typical STM image of 10,12-pentacosadiynoic acid layer on a graphite surface. (b) Magnified STM image of the layer. (c) Top and side views of a model of the molecular arrangement. Parallelograms in (b) and (c) represent the unit cell.

III. SELF-ORDERED MOLECULAR LAYER

To prepare the diacetylene compound thin films, we dissolved the monomer molecules (10,12-pentacosadiynoic acid or 10,12-nonacosadiynoic acid) in chloroform and applied the solution onto a surface of purified water. After evaporation of the chloroform, the thin films of monomer molecules on the water surface were transferred to a freshly cleaved surface of highly oriented pyrolytic graphite (HOPG) by nearly horizontal dipping.

The STM images were recorded using the Digital Instruments NanoScope STM system under ambient conditions in the constant-current mode. A sample bias voltage V_s of -1.0 V and a tunneling current I_t of 0.1 nA were typically used for the observation.

Several studies have dealt with STM observations of physisorbed layers of various diacetylene compounds on

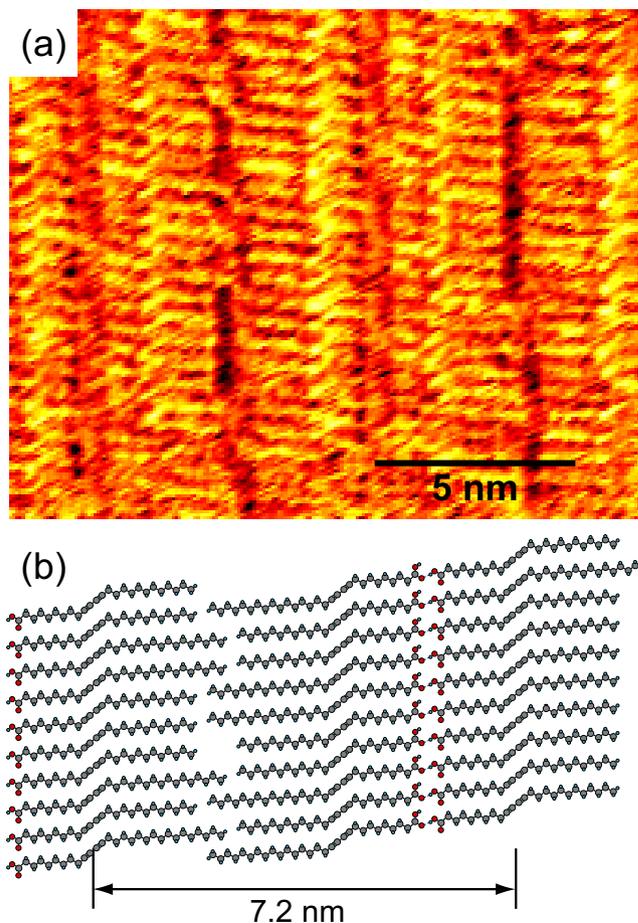


FIG. 4: (a) STM image of a coadsorbed layer of 10,12-pentacosadiynoic acid and 10,12-nonacosadiynoic acid. (b) Proposed model of the molecular arrangement of the mixed layer.

graphite surfaces [29–35]. According to these studies, various molecular arrangements are formed depending on the species of substituent groups, the method of film preparation, and the incorporation of foreign molecules. In our 10,12-pentacosadiynoic acid and 10,12-nonacosadiynoic acid monomolecular layer described above, the molecular arrangement was as follows.

A typical STM image of the 10,12-pentacosadiynoic acid layer is shown in Fig. 3(a). The image in Fig. 3(a) consists of parallel bright lines separated by two different alternate spacings of about 3.0 and 3.8 nm, indicating that the 10,12-pentacosadiynoic acid molecules on the graphite surface were self-ordered. A magnified STM image of the layer is shown in Fig. 3(b), in which individual molecules are resolved. On the basis of such STM images, we can deduce the molecular arrangement shown in Fig. 3(c), where the molecules are aligned to form straight chains and the chains are arranged in a manner such that the COOH end groups of a chain are opposite those of a neighboring chain. In Figs. 3(a) and (b), each bright line corresponds to the linear array of diacetylene moieties.

By comparing the images of the molecular layer with an image of the graphite substrate for the same area observed at an appropriately small sample bias and large tunneling current, we found that the alkyl side chains of each molecule were oriented parallel to the main crystal

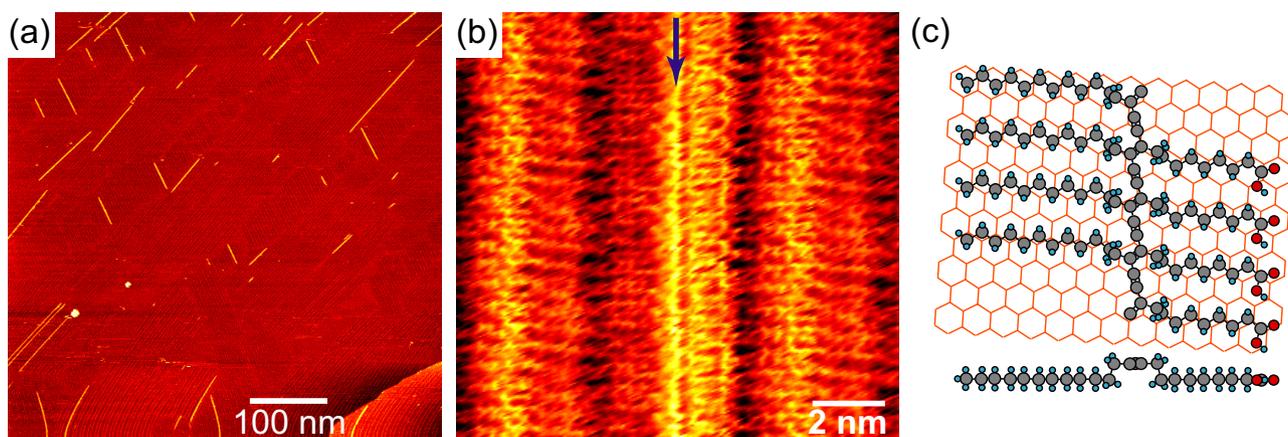


FIG. 5: (a) STM image obtained after ultraviolet irradiation on a 10,12-nonacosadiynoic acid layer. (b) Magnified STM image of a 10,12-pentacosadiynoic acid polymer (indicated by an arrow). The adjacent rows are the unreacted monomer rows. (c) Top and side views of the proposed structural model of a polymer.

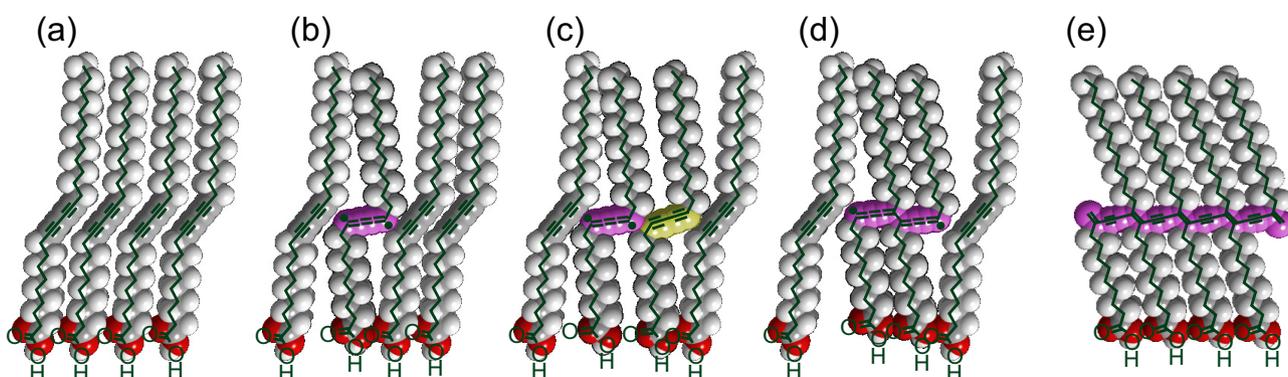


FIG. 6: Illustration of the photopolymerization mechanism. (a) Array of the monomer molecules. (b) Diradical formation by optical excitation. (c) Approach of a neighboring diacetylene moiety because of vibrational excitation. (d) Radical dimer formation through an addition reaction. (e) Extended polymer formation through a chain propagation reaction.

axis in the basal plane of graphite, $\langle 1 \frac{1}{2} \frac{1}{2} 0 \rangle$.

We also studied a coadsorbed layer of the two species, 10,12-pentacosadiynoic acid and 10,12-nonacosadiynoic acid, and found that the coadsorbed layer gave a novel mixed structure [36]. Figure 4(a) shows an STM image of the coadsorbed layer, in which individual molecules are resolved. This image shows that the two species formed a mixed structure, as shown in Fig. 4(b), in which the alkyl side chains of 10,12-pentacosadiynoic acid and 10,12-nonacosadiynoic acid molecules form a pair between the neighboring chains. As a result, the period of the molecular arrangement became 7.2 nm, as shown in Fig. 4(b). This period, 7.2 nm, is an intermediate value between 6.8 nm of 10,12-pentacosadiynoic acid and 7.9 nm of 10,12-nonacosadiynoic acid, indicating that we can control the separation of molecules by mixing more than two molecular species.

IV. PHOTOPOLYMERIZATION

First, we examined whether such chain polymerization could be induced by ultraviolet irradiation in the monomer film described above, and how the created polymers were observed in STM images. For this purpose, the molecular layer was irradiated with ultraviolet light

from a low-pressure mercury lamp (254 nm wavelength and 1.3 mW/cm^2 power density at the sample position) for a period of 20 minutes.

Figure 5(a) shows a typical STM image of the 10,12-nonacosadiynoic acid layer after the ultraviolet irradiation. As we can see, very bright lines appeared. The number density of the very bright lines increased almost linearly with increasing duration of the ultraviolet irradiation. Hence, we assigned these very bright lines to polydiacetylenes created by the photopolymerization of the linear array of diacetylene moieties.

Figures 5(b) and (c) show, respectively, a magnified STM image and the structure model of a polymer of 10,12-pentacosadiynoic acid. If we examine Fig. 5(b) carefully, we can observe periodic changes in the contrast of the alkyl side chains of both the monomer arrays and the polymer. This modulation of the image contrast followed a moiré pattern due to the interference between the molecular layer and the graphite substrate. An important point is that the period of the moiré pattern on the polymer was the same as that on the monomer arrays. Since the period of a moiré pattern is very sensitive to the molecule-molecule distance, this means that the distance between the alkyl side chains along the lamella direction remained constant before and after the polymerization. In other words, the polymerization reaction proceeded topochem-

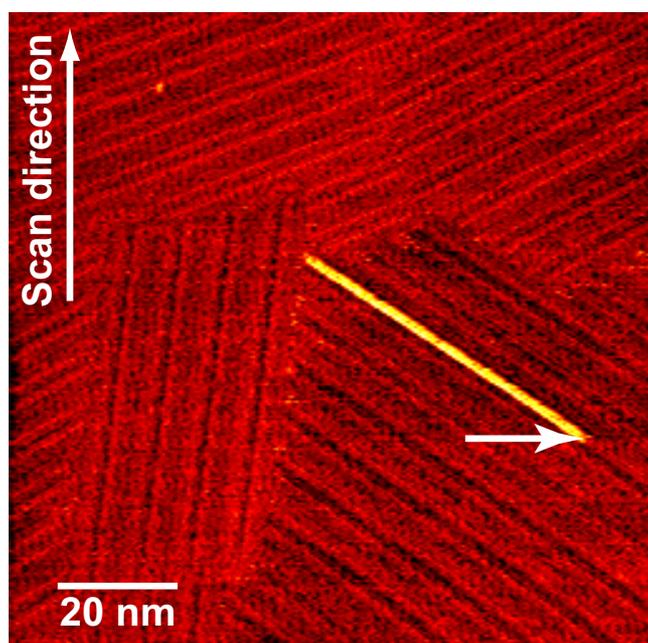


FIG. 7: STM image of a 10,12-nonacosadiynoic acid layer observed from the bottom to the top, with a pulsed sample bias voltage applied at the point indicated by the arrow.

ically, as we expected.

For a chain reaction proceeding in a large domain without any defects, polymers longer than 500 nm have been observed. In contrast with our case, Miura *et al.* reported that in the case of a layer of isophthalic acid derivative diacetylene compound (ISA-DIA) on a graphite substrate, the polymerization results in an increase of 4 % in the molecule-molecule distance along the lamella direction, and the length of the polymer is restricted to less than 100 nm [35].

We consider the photopolymerization mechanism to be as follows based on the case of three-dimensional crystals of diacetylene compounds [37]. In the array of monomer molecules (Fig. 6(a)), the diacetylene moiety of one of the molecules is excited by photoabsorption into a diradical with an unpaired electron at either end (Fig. 6(b)), which is a reasonable representation of the lowest excited $\pi\pi^*$ singlet or triplet state located at 3.7 and 3.1 eV above the $\pi\pi$ ground state, respectively [38, 39]. Within the lifetime of the diradical, if a neighboring diacetylene moiety on either side approaches the diradical because of thermal vibration (Fig. 6(c)), an addition reaction will occur, forming a dimer of diacetylene (Fig. 6(d)). The created dimer of diacetylene is still in an excited state as a diradical, so a similar addition reaction occurs on both sides; the repetition of such addition reactions finally results in the extended chain polymerization (Fig. 6(e)).

We therefore expected that if the diradical shown in Fig. 6(b) can be created by stimulation with an STM tip instead of ultraviolet irradiation, extended chain polymerization would be induced via the processes illustrated in Figs. 6(c)–(e).

V. CHAIN POLYMERIZATION INITIATED WITH AN STM TIP

Figure 7 shows an STM image of the 10,12-nonacosadiynoic acid layer observed from the bottom to the top at a sample bias of -1 V, but with a large sample bias of -4 V applied for $5 \mu\text{s}$ when the scanning tip passed the point indicated by the arrow. A very bright line appeared starting from the point where the pulsed sample bias was applied. The structure of this very bright line was identical to those in the images of photopolymerized polymers, so we concluded that stimulation with the STM tip did indeed initiate the chain polymerization and create a polymer with polydiacetylene as its backbone. Since the pulsed sample bias was applied during scanning from the bottom to the top, the created polymer was observed in only the upper side from the point of stimulation in Fig. 7. Chain polymerization, however, occurred on both sides of the point of stimulation. In Fig. 7, we can also see that the chain polymerization was terminated when it reached a domain boundary where the orientation of the monomer molecules changed.

We also investigated how the frequency of the chain polymerization occurrence changed when we varied the height of the pulsed sample bias voltage. We found that the reaction probability was almost symmetric with respect to the polarity of the pulsed sample bias with a threshold of $\pm 2.9 \pm 0.2$ V. This threshold value is close to the energy separation between the $\pi\pi$ ground state and the lowest excited $\pi\pi^*$ triplet state of the diacetylene moiety, 3.1 eV [39]. This suggests that electrons tunneling from the tip to the substrate (for a positive pulsed sample bias) or from the substrate to the tip (for a negative pulsed sample bias), passing through the intermediate molecular layer, inelastically excited a diacetylene moiety into the diradical state (as shown in Fig. 6(b)) and initiated the chain polymerization.

As seen in Fig. 7, the chain polymerization reactions were usually terminated at domain boundaries. In other words, the chain polymerization initiated by the STM tip propagated in the domain without any additional energy other than thermal energy and terminated when it encountered the domain boundary which acted as a kind of structural defect. Exploiting the fact that the chain reaction is terminated by a structural defect, we can also control the termination of the chain polymerization by forming an artificial structural defect in advance. We demonstrated this in a monomolecular layer of 10,12-nonacosadiynoic acid on a graphite surface, as shown in Fig. 8. First, we created an artificial defect in the form of a 6-nm-wide hole at a predetermined position in the monomolecular layer, as shown in the center of Fig. 8(a), using a reported method [40]. That is, we placed an STM tip at that position and applied a high pulsed sample bias ($+5$ V in height, $10 \mu\text{s}$ in width). After that, a pulsed sample bias (-4 V in height, $5 \mu\text{s}$ in width) was applied at the point indicated by arrow 1 in Fig. 8(b). As is evident in the figure, a very bright line appeared, indicating that chain polymerization started at the indicated point and ended at the artificial defect. Next we stimulated the adjacent molecular array indicated by arrow 2 in Fig. 8(c), by applying another pulsed bias. In this case as well, chain polymerization started at the point of stimulation

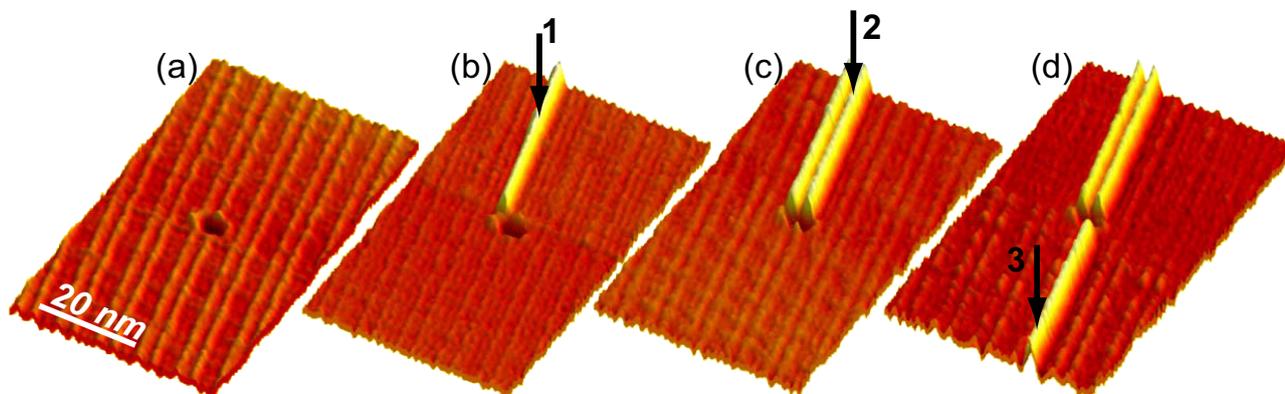


FIG. 8: (a) STM image of the original monomolecular layer of 10,12-nonacosadiynoic acid in which an artificial defect was created in advance using an STM tip. (b)–(d) STM images obtained after applying a pulsed bias voltage on the molecular arrays indicated by arrows 1–3. Polymer nanowires were created through these stimulations.

and ended at the artificial defect. In a similar manner, as shown in Fig. 8(d), we created one more polydiacetylene nanowire by stimulating a molecular array indicated by arrow 3. Figure 8 shows that we can control the initiation and termination of the chain polymerization with a spatial precision on the order of 1 nm. Furthermore, this result indicates that we can connect at least three nanowires to an object as small as 6 nm; thus, we could wire up the three electrodes (source, drain, and gate) of a transistor, for example, even one that is nanometer sized.

VI. CONCLUSION

It is well known that we can manipulate individual atoms or molecules with an STM tip [41], so we should be able to create nanowires using such atom-by-atom crafting. It is also known that if a thin molecular film is stimulated by a biased STM tip, a local chemical reaction or reorientation is sometimes induced [42–46], so that continuous modification will be possible through scanning with a biased STM tip. Although such work is essential to fundamental advances, the chain polymerization technique used in our work has several advantages.

First, the nanowires obtained are guaranteed to have perfect structures without any defects. If defects exist, the chain reaction itself will be terminated, as discussed above. Hence, if the chain reaction proceeds, the obtained nanowire is guaranteed to have a perfect structure. Furthermore, a single conducting polymer chain in a free state generally has a coiled conformation which prevents the occurrence of π -electron conjugation, as mentioned. In our method, we can obtain defect-free polydiacetylene

nanowires with good linearity because of the self-ordering of monomer molecules due to the interaction between the molecules and the substrate. The obtained nanowires can therefore be considered ideal π -conjugated systems.

Second, the obtained nanowires are stable at room temperature, because they are products of a room-temperature reaction. In contrast, if nanostructures are fabricated by atom-by-atom crafting, they are stable only at low temperature in many cases.

Third, we can create a long nanowire by applying only one pulsed bias voltage at one point; the propagation speed of the chain reaction is high, so we can create a nanowire in a short time with high efficiency. We roughly estimated the propagation speed of the chain polymerization to be 0.1 to 1 m/s, and are now planning to measure the propagation speed directly.

Finally, the process requires no additional energy for the chain propagation reaction, other than the initial stimulation.

Because the obtained polymer is a long, linear, conductive nanowire with high structural perfection, it will be an ideal system for basic studies of the physics and chemistry of one-dimensional conductive polymers. From such studies, we believe that much important information can be obtained about the basic properties of nanowires and nanodevices. Furthermore, we expect that our method will be useful for interconnecting future nanoelectronic devices, and also expect that the obtained polydiacetylenes themselves will be applicable as novel molecular devices or sensors. Of course, many more basic and applicatory studies still need to be performed before we can turn our method to practical use.

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