Mechanism of Chain Polymerization in Self-Assembled Monolayers of Diacetylene on Graphite Surface

We have studied the mechanism of the photo-induced chain polymerization in the self-assembled monolayer of a diacetylene (DA) compound, 10,12-pentacosadiyn-1-ol (PCDYol, Fig. 1), on the graphite surface. We statistically analyze the polymerization degree N of the polydiacetylene (PDA) chains using scanning tunneling microscopy as shown in Fig. 4. The chain propagation towards one direction is modeled by a sequence of Bernoulli trials, where the addition of a monomer molecule and deactivation are two possible outcomes as shown in Fig. 5. Considering the trials at the both ends of the PDA, we obtain the probability density function $P(N) = (N-1)p^{N-2}(1-p)^2$. Figure 4 shows that the distributions of the polymerization degree agree well with the prediction from the simple probabilistic model.

(by D. Takajo & K. Sudoh)

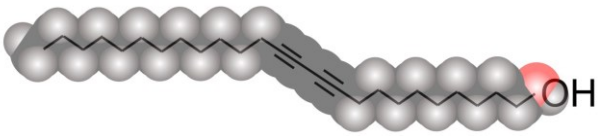

Fig. 1. Molecular structure of PCDYol.

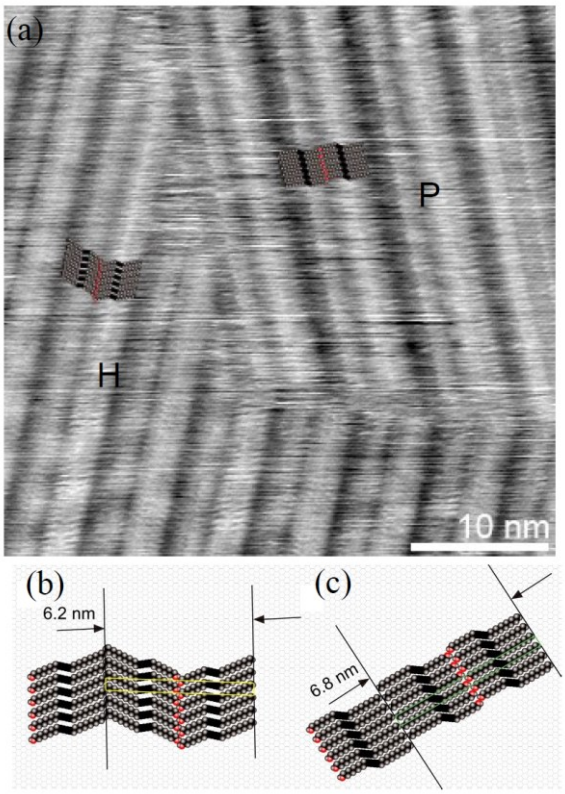

Fig. 2. (a) STM image of the adjacent herringbone (H) and parallel (P) arrangement domains that cover the left and right parts, respectively. The molecular adsorption models on the graphite surface for (b) H- and (c) P-arrangements are shown.

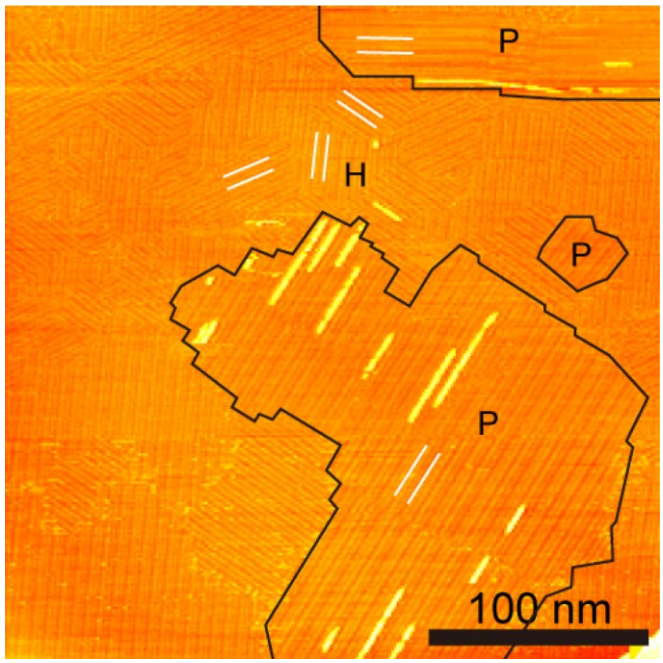

Fig. 3. STM image of the polydiacetylenes arising as bright lines obtained after the UV irradiation at 20 °C. The polydiacetylenes (PDA) are generated in domains of both P- and H-arrangements. The domain boundary is suggested by black lines. The intervals of the lamellar structures are indicated by pairs of white lines.

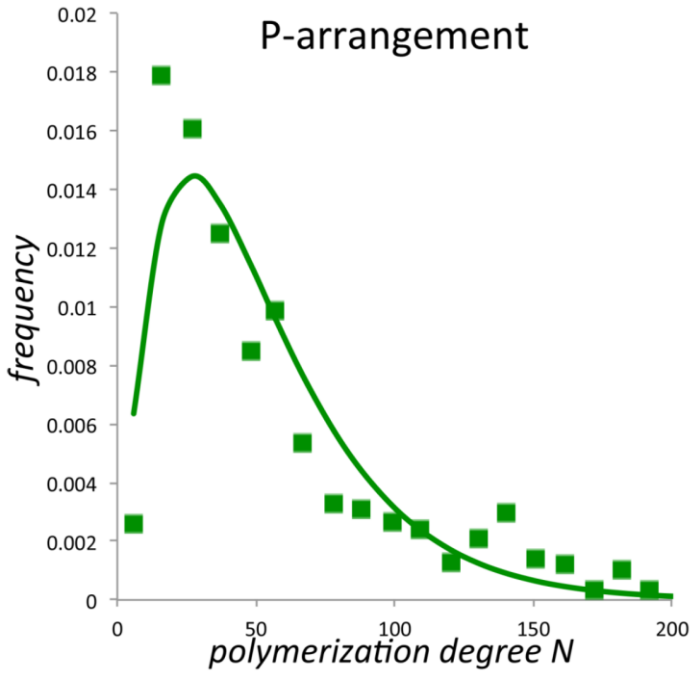

Fig. 4. Frequency distribution of the polymerization degree N for PDA chains formed at 23 °C in the P-arrangement extracted from STM images. The values of the frequency are normalized so that its sum is equal to unity. The solid line represents the fitted curve with the formula $P(N) = (N-1)p^{N-2}(1-p)^2$ (p; the probability that the addition reaction will occur).

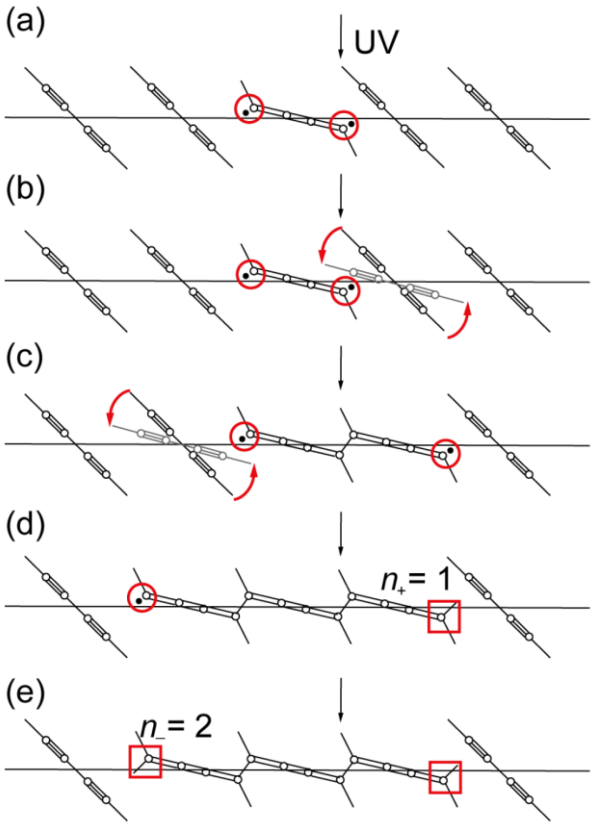

Fig. 5. Model for the conventional solid-state polymerization of DA crystals. The polymer chain grows in a domino-like fashion. (a) An array of DA molecules. The DA moiety of one of the monomers (M) is excited by UV-stimulation. Both ends of the DA group are activated as a diradical monomer (R_1) as indicated by red circles. (b) An addition reaction of the neighboring M can occur through the thermal process as suggested by red arrows. (c) The diradical dimer (R_2) is produced as the source of the PDA chain. The extended PDA chain grows through a chain propagation reaction towards the both sides. (d,e) Reactive species are deactivated as suggested by red squares.

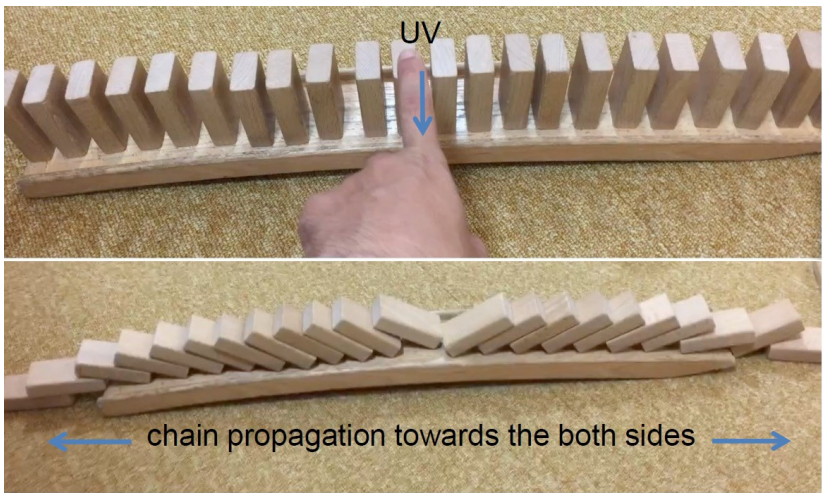

Photo 1. Schematic demonstration of DA molecular domino by using wooden blocks. The PDA chain propagates towards the both sides after UV-stimulation. The contact between blocks represents the chemical bond formation.