Atomic Force Microscope Study of the Polydiacetylene Conformations for Two-Dimensional Topochemical Reactions of 10,12-pentacosadiyn-1-ol on a Graphite Substrate

Previously, we demonstrated that two polymorphs are formed for self-assembled 10,12-pentacosadiyn-1-ol layers on graphite substrates, a “parallel” molecular arrangement and a “herringbone” molecular arrangement. The linear conjugated polydiacetylenes are obtained through chain polymerization of the diacetylene monomer compound in the two-dimensional crystal phase under ultraviolet light irradiation. Here, the polydiacetylenes conformations are investigated using atomic force microscopy (AFM). AFM observations reveal that the conformations of polydiacetylenes formed from the parallel and herringbone arrangements are different. For the parallel arrangement, the backbone is lifted up from the side alkyl-chain level, while the backbone is in plane with the side chains for the herringbone arrangement. This relationship between the ordering of the monomer arrangement and the structure of the produced polymer is supported by the principle of least motion.

(by D. Takajo & K. Sudoh)

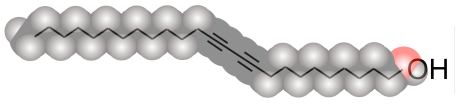

Fig. 1 Molecular structure of PCDYol.

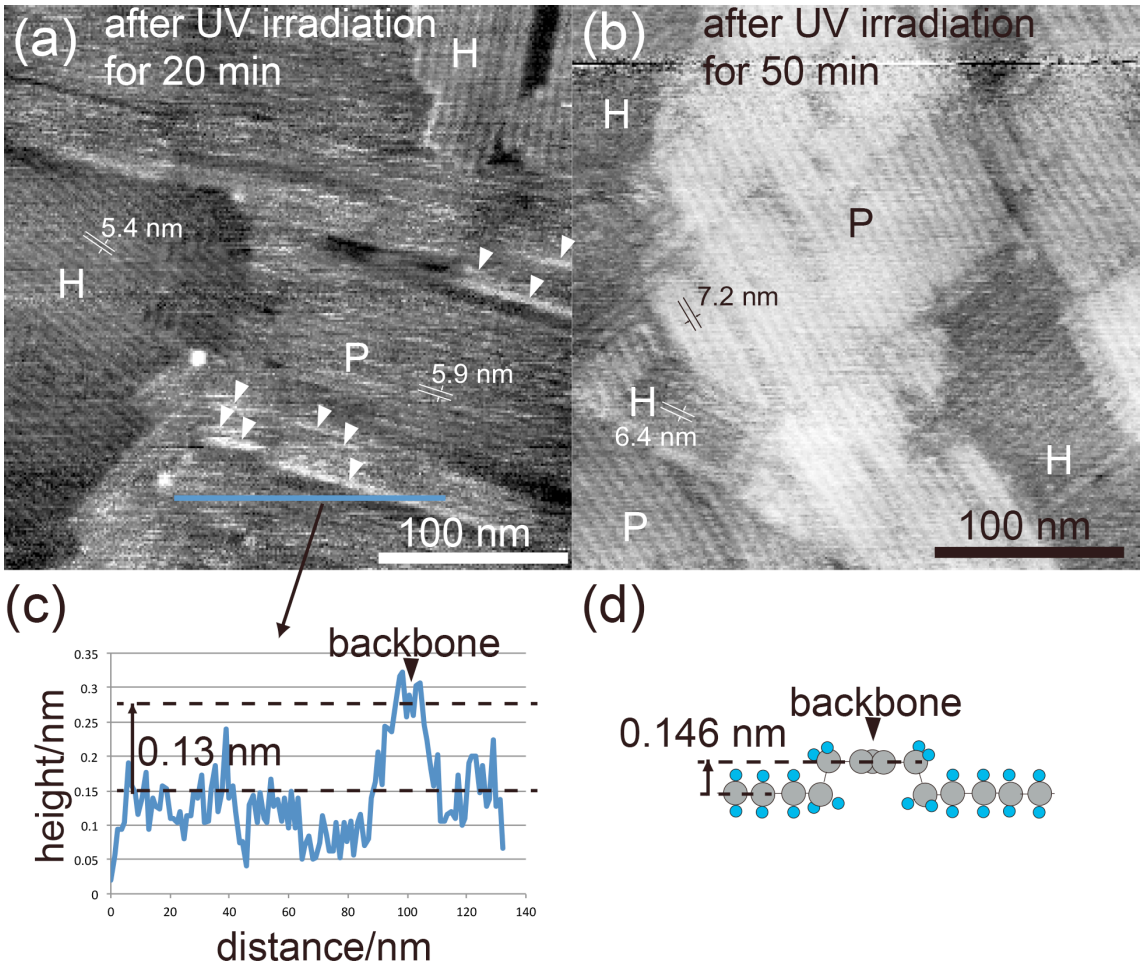

Fig. 2 AFM height image of partially polymerized PCDYol layer obtained after UV irradiation for 20 min. Very bright lines assigned to polydiacetylenes appeared in the monomer molecular stripes as suggested by white arrowheads in the P domains. (b) AFM height image of the PCDYol layer after additional irradiation with UV light for 30 min (total 50 min). The number density of the very bright lines (polymers) increased with increasing the duration of UV irradiation in the P domain. In contrast, the contrast of the H domains is still dark. (c) The cross-sectional profile across the polymer on the P arrangement along the blue line in (a). (d) The side view of the polydiacetylene model with the lifted-up conformation after the reaction.

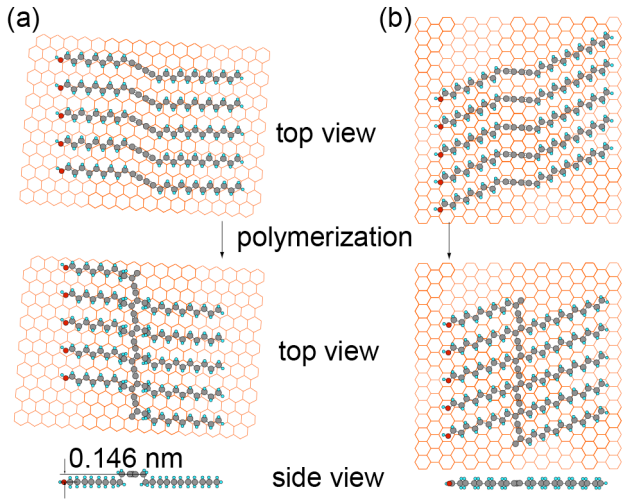

Fig. 3 (a) PCDYol molecular adsorption model for the P arrangement on the HOPG surface (top) and the lifted-up conformation model for the polydiacetylene formed after the polymerization (middle). The side view of the polydiacetylene indicates the backbone is lifted up after the reaction (bottom). (b) PCDYol adsorption model for the H arrangement (top) and the in-plane conformation model for the polydiacetylene (middle). The side view of the polydiacetylene shows the backbone is in plane with the side alkyl-chain after the reaction (bottom).