Mechanism of the Impact of the Air Atmosphere on the Photo-Induced Chain Polymerization of the Diacetylene on Graphite Surface

We statistically analyze the drastic impact of the air atmosphere on the photo-induced chain polymerization of the 10,12-pentacosadiynol (PCDYol) on the graphite. We find that the polymerization reaction is highly enhanced under high vacuum in comparison with the cases in air. The generation rate of polydiacetylene by UV-irradiation in vacuum is 3.1×10^3 times larger than that in air. The drastic increase of the reaction efficiency is interpreted in terms of the radical quenching by oxygen molecules in the photo-initiation process. We also find that the average polymerization degree for the polymers generated in vacuum is larger than those generated in air. This confirms that oxidation by oxygen is the dominant termination mechanism of the chain polymerization in air.
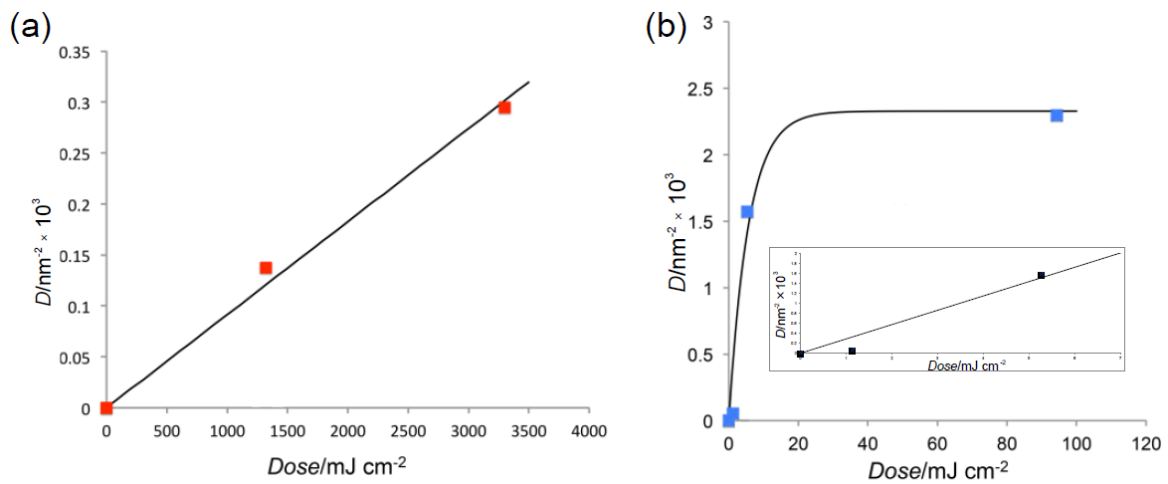
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Fig. 1. (a) The polymer number density vs. UV-dose plot for the P arrangement of the PCDYol monolayer obtained by STM after UV-irradiation (the power density of 1.1 mW/cm^2) at 23 °C in air. (b) The plot for the P arrangement after UV-irradiation (0.38 mW/cm^2) at 23 °C in vacuum. An arbitrary black curve is drawn for eye guide. The inset shows the enlarged plot near the origin suggesting the linear dependence of the polymer number density on the UV-dose.
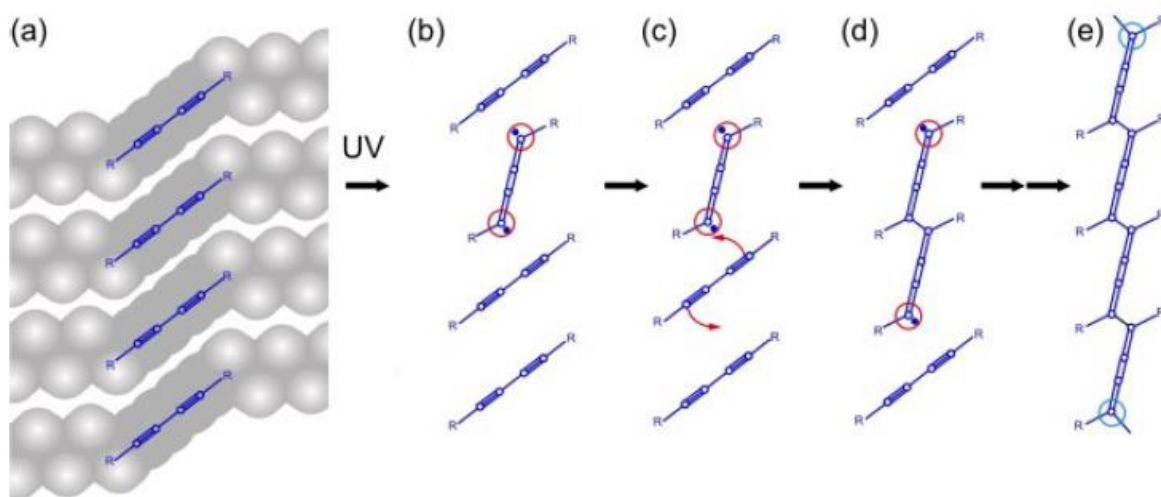
Fig. 2. The schematics of the solid-state polymerization model. (a) The DA array before UV-irradiation. (b) A DA monomer is optically excited by the UV stimulation. The radical species are located at the ends as suggested by red circles. (c,d) The chain growth involves the thermal excitation of the adjacent monomer to irreversibly form the chemical bond with the radical. The radical species is located at the end after the addition reaction of the monomer. The chain propagates toward both the sides in the same manner. (e) The chain growth is eventually terminated by the deactivation of the radical ends as suggested by blue circles.
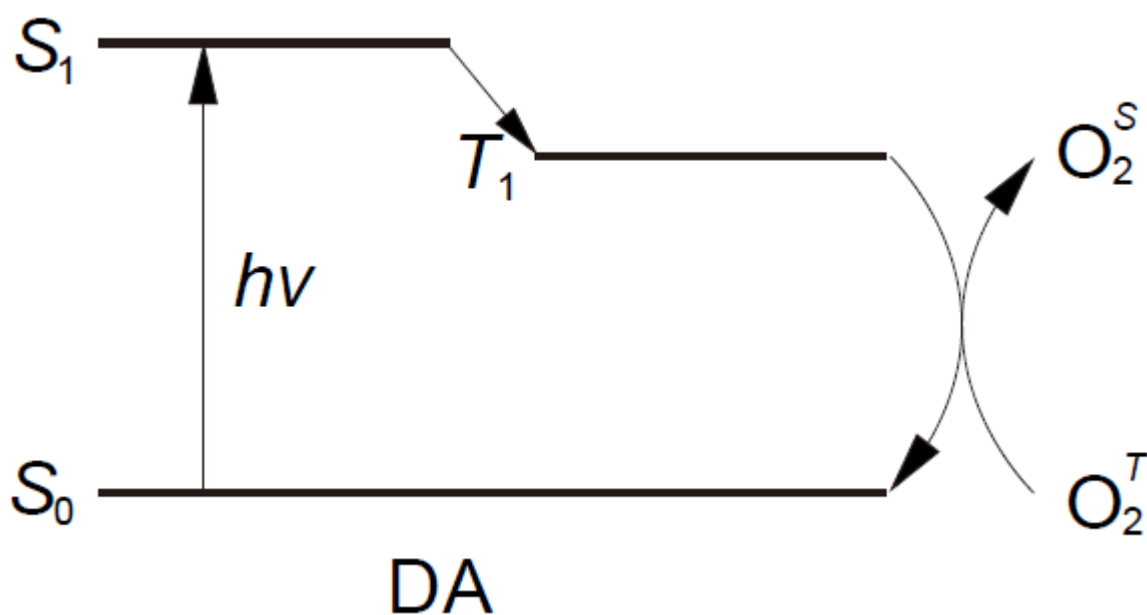

Fig. 3. The schematic energy diagram showing the main energy transfer during the phosphorescence quenching of the DA radial by the collision with the oxygen molecule. S_0, S_1, and T_1 represent the ground state, the excited singlet state, and its triplet state for the DA monomer, respectively.
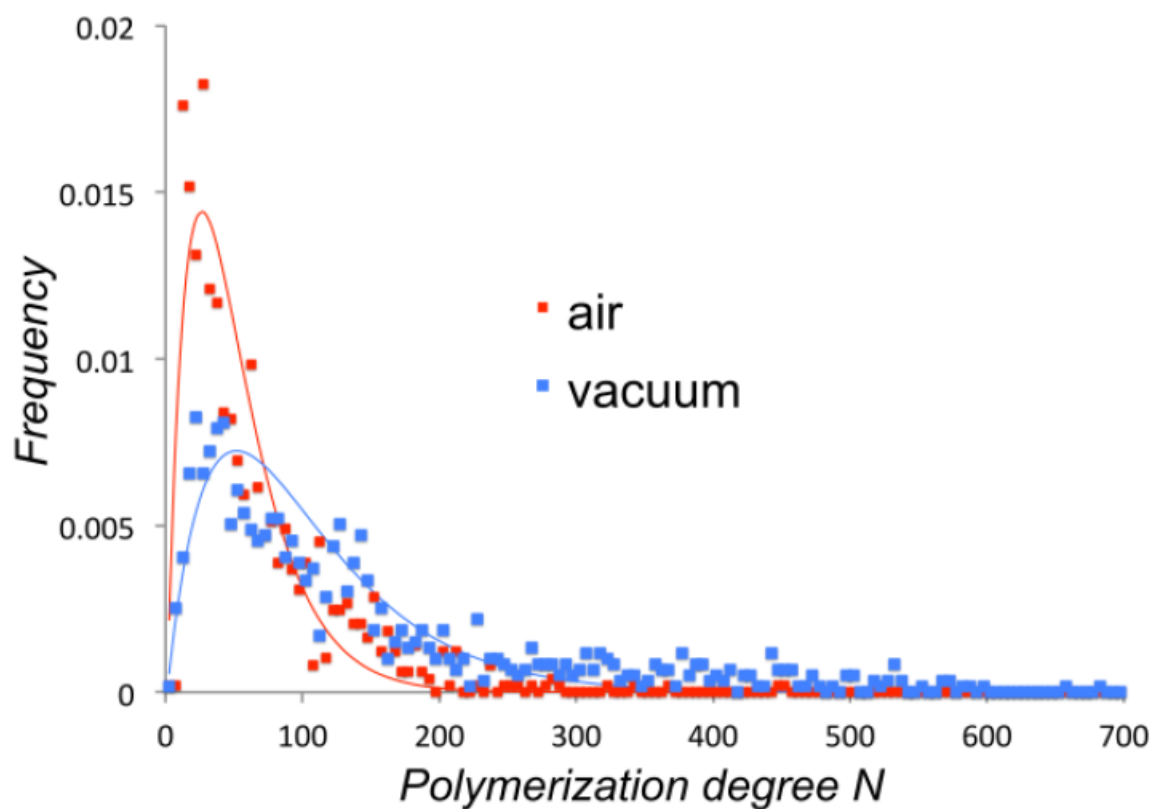
Fig. 4. The probability density distributions of the polymerization degree for the P arrangement obtained by STM after UV-irradiations at 23 °C in vacuum and air. The solid lines suggest the best fit by $(N-1)p^{N-2}(1-p)^2$, where p represents the addition reaction probability.