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Symmetric and Helical Growth of Polyacetylene Fibers over a Single Copper Crystal Derived from Copper Tartrate Decomposition

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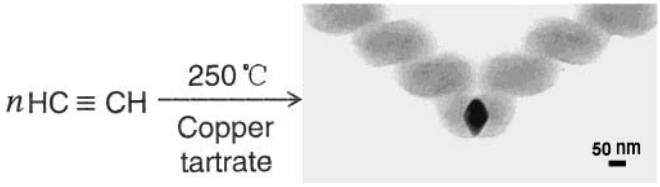
ABSTRACT



Helical polyacetylene fibers with absolutely symmetric structures were prepared by polymerization of acetylene using copper tartrate as a catalyst. There were always only two coiled polyacetylene fibers grown on a single copper nanocrystal. The two coiled fibers had absolutely opposite helical senses but were identical in cycle number, coil diameter, coil length, coil pitch, and fiber diameter.

Controlling the chirality of a molecule or polymer plays a vital role in chemical synthesis. Transition metal catalysts modified with chiral reagents (such as tartaric acid) are widely used in enantioselective hydrogenation to produce optically active organic molecules.[1,2] This is commonly referred to as "asymmetric catalysis". A few years ago, Green et al.[3,4] reported the amplification of chirality in the synthesis of polyisocynates. The macromolecular helicity of these polymers can be quantitatively controlled via the incorporation of asymmetric centers in the side chains. This falls under a term widely used in the literature: the "sergeants and soldiers" effect. Polymers of the same helical sense can be obtained by this method. Akagi et al.[5] studied the synthesis of helical polyacetylene by polymerization of acetylene under an asymmetrical reaction field consisting of chiral nematic liquid crystals. Schmid[6] reported that copper tartrate decomposed to produce copper particles when it was heated to 230 °C.

Herein we report novel coiled polyacetylene fibers with absolutely symmetric structures were prepared by polymerization of acetylene using copper tartrate as a catalyst under simple preparation conditions. The reaction was carried out at the low temperature of about 250 °C and gave good reproducibility and yield. No other introduced source gas (such as hydrogen, argon) was used.

These obtained polyacetylene fibers were regularly coiled and had a coil diameter of about 100 nm, a coil length of about 1 μm, and a dense coil pitch. It was observed by transmission electron microscope (TEM) that the catalyst particle, about 50 nm in grain size, was always located at the node of two coiled polyacetylene fibers (referred to as "coiled fibers" hereafter), as shown in Figure 1. By selected area electron diffraction, the particle was proved to be a

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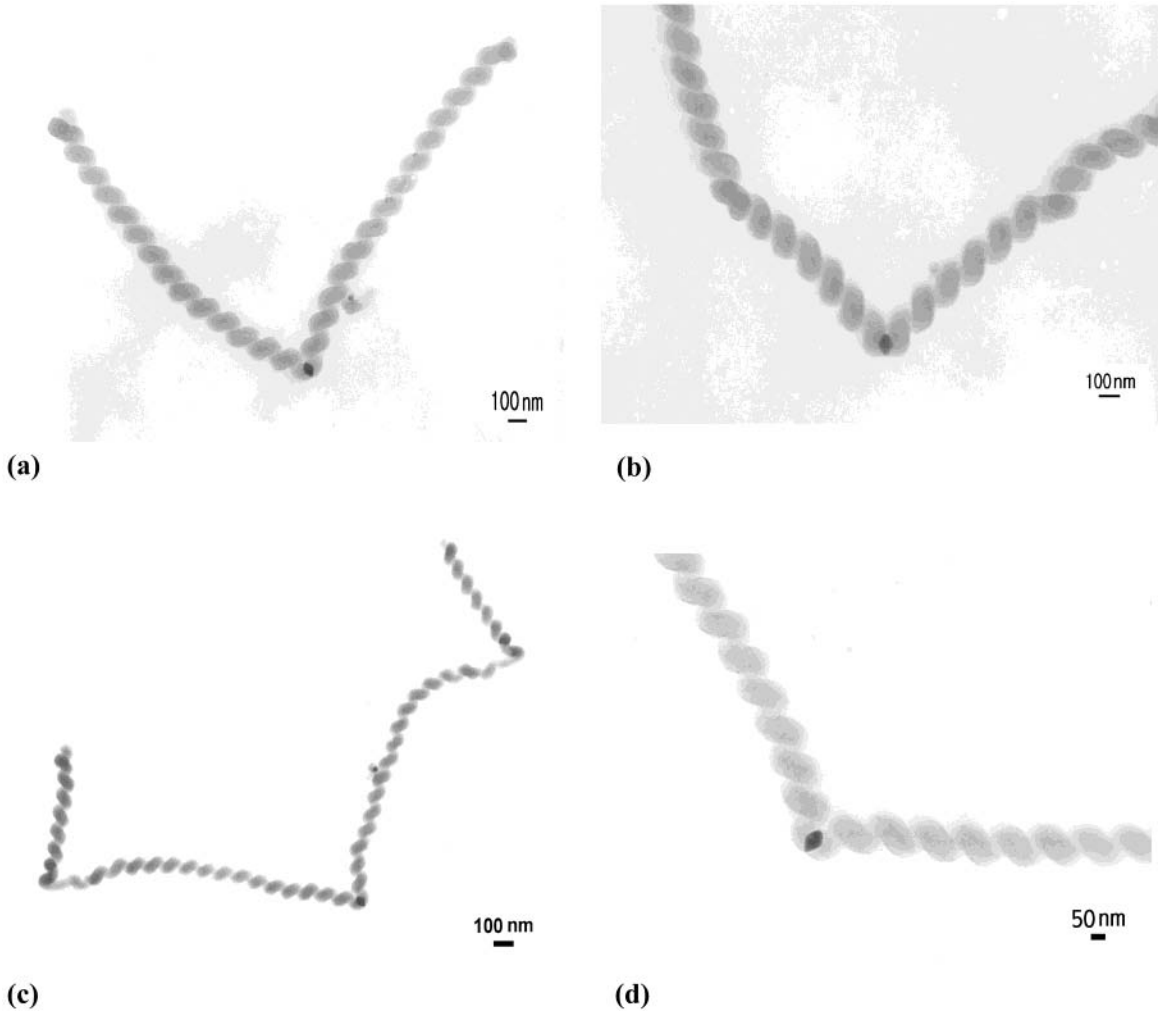

Figure 1. TEM images of regularly coiled fibers, symmetrically grown on a single copper crystal and prepared by polymerization of acetylene for 3 min at 253 °C. (a) Two symmetric coiled fibers with opposite helical senses, identical cycle number, and about a 70° angle; (b) two symmetric coiled fibers identically change helical senses at the sixth cycle; (c) two symmetric coiled fibers with the most apparent symmetric growth forms; (d) two symmetric coiled fibers with a 110° angle.

single copper crystal, which derived from decomposition of copper tartrate. Detailed studies manifested that these coiled fibers had grown absolutely symmetrically on a single copper crystal. First, there were always only two coiled fibers grown on a single copper crystal. Second, the helical senses of the two coiled fibers were absolutely opposite, namely, there were no two identical coiled fibers grown on the same copper crystal. Third, the cycle numbers of the two coiled fibers were absolutely identical, and interestingly, the two coiled fibers had almost an identical fiber diameter, coil diameter, coil length, and coil pitch. The fiber diameter of the two coiled fibers was approximately equal to the grain size of the single copper crystal on which the two coiled fibers were grown. Figure 1a shows the TEM image of two coiled fibers grown on a single copper crystal. It can be found that the coil of one fiber is left-handed and has 14 cycles, while the other one also has 14 cycles but is right-handed. Finally, surprisingly, if unknown factors interfered with the growth of the two coiled fibers and one fiber changed helical sense, the other also changed helical sense at the coil position of the same cycle number absolutely. There seemed to be a "mirror" between the two coiled fibers. As shown in Figure 1b, the two coiled fibers changed helical sense at the sixth cycle identically. Figure 1c most clearly shows the symmetric growth of two coiled fibers on a single copper crystal. This phenomenon suggested that the acetylene molecule always reacted on the surface of the catalyst particle and then extruded the fibers that had just been grown apart from the surface of the catalyst particle, namely, the single copper crystal was an exclusive growing point for the two coiled fibers. If an unknown factor around the single copper crystal particle, on which the two coiled fibers were growing, affected the surface properties of the particle, the two coiled fibers would possibly change helical senses together at the same time.

It was also interesting to know that the angles between two coiled fibers grown on a single copper crystal were mostly about 70° (Figure 1a and 1b) and 110° (Figure 1d)

according to TEM observation. No angle less than 70° has ever been found in this study.

These single copper crystal particles, located at the node of these two coiled fibers, were usually faceted. Most of these particles had a rhombic projection as shown in Figure 2a. There were also quadrangular (Figure 2b), almost circular (Figure 2c), triangular (Figure 2d), polygonal (Figure 2e), and cone-shaped (Figure 2f) particles, although very few. Even though the single copper crystal particle was almost circular, the two coiled fibers grown on it were still helical and had a symmetric morphology (Figure 2c). Moreover, the angle between the two coiled fibers appeared not to be in close relation to the shape of the single copper crystal. As shown in Figure 2c, the angle between the two coiled fibers is 110° or so, although the single copper crystal has almost a circular projection. Therefore, the shape of the single copper crystal particle was not the determinating factor that caused the two coiled fibers to grow symmetrically in a helical morphology and at a certain angle.

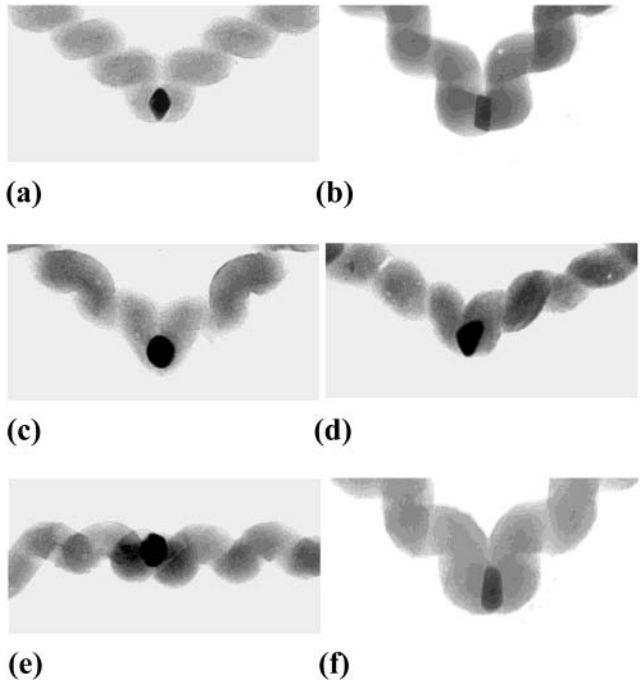

Figure 2. TEM images of single copper crystal particles with a grain size of 50−80 nm, located at the node of these two coiled fibers; (a) rhombic; (b) quadrangular; (c) almost circular; (d) triangular; (e) polygonal; (f) cone-shaped particle.

The observation reported here also suggested that the newly formed copper particle derived from copper tartrate had novel catalytic properties, in sharp contrast to the ordinary nm or μm copper powder, which could only catalyze acetylene to polymerize to produce irregular or ribbonlike polyacetylene fibers.

In summary, regularly coiled polyacetylene fibers, grown symmetrically on a single copper crystal, were prepared by polymerization of acetylene with copper tartrate catalyst. The reason for the helical and symmetric growth of these coiled fibers is not clear at present and requires further investigation.

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Supporting Information Available: Experimental section and characterization of the copper tartrate crystal used, coiled polyacetylene fibers obtained, and their nodes. This material is available free of charge via the Internet at http://pubs.acs.org.

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