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Self-Forming Microtubes of Polypyrrole: Reaction Conditions and Physical Properties

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Abstract

Polypyrrole microtubes have myriad promising technological applications. The known synthetic routes for preparing the microtubes involve a shape-guiding template which needs to be removed at final stage of the synthesis. We have recently discovered a new synthetic method, by which polypyrrole microtubes spontaneously form during the electropolymerization of pyrrole without any shape-guiding template. Here the reaction conditions for self-formation of polypyrrole microtubes were examined and the favorable conditions to repeatedly synthesize the microtubes were determined. The reaction processes were also traced by a microscope with a CCD camera. The microtubes were found to grow near the free end of microtubes. In addition a small bubble of hydrogen gas, which was attached at the free end of microtube, was suggested to have an important role in the growth of microtubes. The temperature dependence of electrical resistance suggests that the conduction mechanism of microtubes is similar to that of the conventional polypyrrole films.

Keywords: Polypyrrole and derivatives / Electrochemical polymerization / Self-organization in macromolecules / Conductivity / Infrared and Raman spectroscopy / Graphite and related compounds

1. Introduction

Polypyrrole is known as one of the most popular intrinsically conductive polymers and has attracted great attention because of its unique electrical properties, good thermal stability, and easy production in a film form. Since the discovery of carbon nanotubes [1], nanotubes as well as microtubes have also attracted considerable attention because of their unique properties and potential applications in various fields. The template-synthesis method using commercial membranes as templates, proposed by Martin et al. [2, 3], has successfully been applied to the syntheses of micro- or nano-tubes of polyacetylene, polypyrrole, and polyaniline [4-6].

In contrast, we have unexpectedly found template-free formation (self-formation) of polypyrrole microtubes during electrochemical polymerization of pyrrole in an aqueous solution [7]. Independently, Wan et al. reported the formation of polypyrrole nanotubes without templates [8]. The polypyrrole microtubes we have found are as large as a few hundreds μm in diameter and a few mm in length, and have a high electrical conductivity and large anisotropy in electrical conductivity [7], as well as strong emission of visible light accompanied by increase of surface temperature [9].

Here we have precisely examined the reaction conditions in order to increase the reproducibility of the self-formation of polypyrrole microtubes and get information on the formation mechanism. The formation process of microtubes was traced by a microscope with a CCD camera. The electrical properties of the self-forming polypyrrole microtubes were measured at various temperature in order to get information on the mechanism of electrical conductivity.

2. Experimental

2.1. Preparation of Polypyrrole Microtubes

The typical standard preparation procedure of polypyrrole microtubes is as follows: The electrochemical polymerization of pyrrole was performed in an aqueous solution of 0.1 mol dm^{-3} of pyrrole and 0.4 mol dm^{-3} of sodium *p*-toluenesulfonate using a platinum electrode potentiostatically at 800 mV vs. Ag/AgCl at room temperature without any shape-guided template. The microtubes were carefully taken off from the electrode, and washed with deionized water and acetonitrile to remove

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non-reacting pyrrole and sodium *p*-toluenesulfonate adsorbed on the microtubes, and finally dried under a reduced pressure to eliminate adsorbed water.

2.2. Observation of Growing Process of Polypyrrole Microtubes

The growing process of polypyrrole microtubes were observed in-site with a microscope attached by a CCD camera from the outside of the reaction vessel.

2.3. Measurements

Raman spectra of the microtubes were collected in backscattering geometry using a Renishaw Ramascope System 1000 equipped with Olympus microscope. An excitation light at 785 nm from a diode laser was focused on the sample surface through the microscope. The wavenumber was calibrated by comparing the Raman band at 1332.3 cm^{-1} of diamond.

The electrical resistance was measured by a four-point contact method with direct current using the samples jointed to gold wire (0.1 mmΦ) with gold paste and silver-epoxy resin. The temperature dependence of the electrical resistance was observed by the measurement in a cryostat chamber of a SQUID magnetic flux meter from 300 K to 1.8 K.

3. Results and Discussion

3.1. Reaction Conditions

The electrochemical polymerization of pyrrole was carried out for 0.5~2 h under various conditions. The total number of the microtues and the length of the longest microtube under a certain condition were measured to determine the favorable conditions for the reproducible preparation of microtubes. For example the dependence of pyrrole concentration was observed by the experiments under various concentrations (from 0.007 to 1.0 mol dm^{-3}) of pyrrole at a constant concentration (0.6 mol dm^{-3}) of sodium *p*-toluenesulfonate under constant potential (800 mV vs. Ag/AgCl) at room temperature putting a platinum plate as a working electrode at the distance of 1.0 cm from the Pt mesh as a counter electrode. By these experiments the favorable concentration of pyrrole was determined as 0.1 mol dm^{-3}, in which 40 microtubes with the longest length of 10 mm formed.

The similar experiments showed that the favorable reaction conditions are 0.4 mol dm^{-3}. of sodium p-toluenesulfonate at constant potential of 800 mV vs. Ag/AgCl or constant current density of 6 mA cm^{-2} at the distance of two electrodes of 10 mm at temperature of 20℃. As the working electrode Pt plate gave the favorable results among Pt, Au, Ni and Fe plate. Sodium *p*-toluenesulfonate was the favorable supporting electrolyte among lithium chloride, lithium tetrafluoroborate, lithium perchlorate, methanesulfonic acid, sodium methanesulfonate, *β*-naphthalenesulfonic acid, and sodium *p*-toluenesulfonate. Thus, the favorable reaction conditions were those as shown in the experimental section as typical standard conditions.

The results of the examination on reaction conditions suggest that the role of sodium p-toluenesulfonate is not to form the rod-shaped micelle, which may work as templates to produce the microtubes, but to work only as the electrolyte. Thus, the micelle template mechanism proposed by Wan for the explanation of 2 μmΦ-sized microtubes formed in their experiments [8] cannot be applied to the present system of a few hundred μmΦ-sized microtubes.

3.2. Characterization

The microtube obtained under the conditions mentioned in the previous session has a shape of tubes with the diameter from ca. 0.1 to 0.5 mm and the length from a few to 10 mm by the observation with a microscope attached by a CCD camera or a scanning electron microscope. The elemental analyses, Raman spectra (cf. Fig. 1), and X-ray photoelectron spectra indicated that the microtubes have the structure similar to doped polypyrrole films prepared by a conventional electrochemical method [7, 10-13].

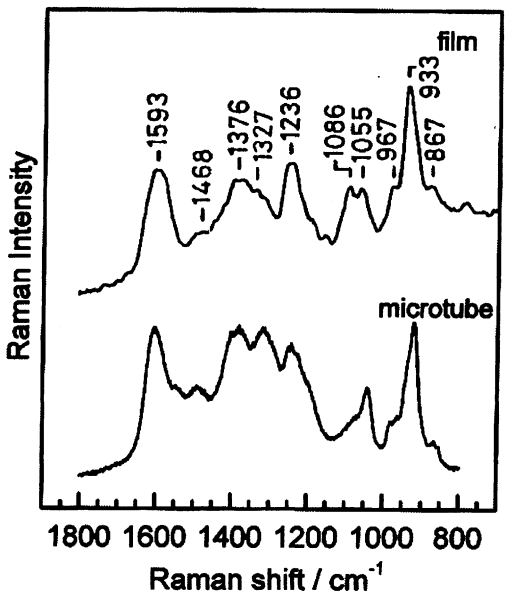

Fig. 1 Raman spectra of polypyrrole microtube and film.

3.3. Reaction Processes

The importance of gaseous bubbles became clear from the experiments on reaction conditions. The distance between two electrodes should be near 10 mm. If they were too close, too much amount of hydrogen bubbles produced from the counter electrode could attack the working electrode. Then too much polypyrrole were produced as a