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A Novel Approach for Synthesis of Carbyne by Electroreductive Polymerization of Diiodoacetylene Catalyzed by Ni Complex

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Diiodoacetylene was electropolymerized with Pt cathode at -2.0 V (vs. SCE) in the presence of Ni complex in dimethylformamide (DMF) under anaerobic conditions, giving an insoluble black powder which had a strong infrared absorption at 2050 cm^{-1} and a broad Raman peak around 2150 cm^{-1} due to conjugated polyyne structure. A compressed pellet of the as-prepared sample had an electrical conductivity of 3×10^{-5} S cm^{-1}.

Among various polymers composed of linear conjugated π-electron system, polyacetylene, $-(CH{=}CH)_n-$, has been extensively studied.[1] However, little is known about the simplest linear conjugated polymer, carbyne,[2] one of the allotropes of carbon. We now report a novel approach for synthesis of carbyne by electroreductive polymerization of diiodoacetylene catalyzed by a nickel complex (Eq. 1).

$$I-C{\equiv}C-I \xrightarrow[\text{DMF}]{\text{e / Ni cat}} \left(C{\equiv}C\right)_n \qquad (1)$$

Diiodoacetylene (100 mM) prepared by the reported method[3] was cathodically electrolyzed at a Pt plate at - 2.0 V (vs. SCE) in DMF-tetrabutylammonium iodide (200 mM) in the presence of diiodo[1,2-bis(diphenylphosphino)ethane]nickel(II)[4] (5 mM) for 15 h at room temperature under anaerobic conditions. A black swollen material was deposited on the Pt electrode. The insoluble product was washed with DMF and tetrahydrofuran several times, respectively, under ultrasonication and was dried under vacuum at room temperature, giving a black powder. The elemental analysis of this product showed 63% content of carbon,[5] suggesting that some

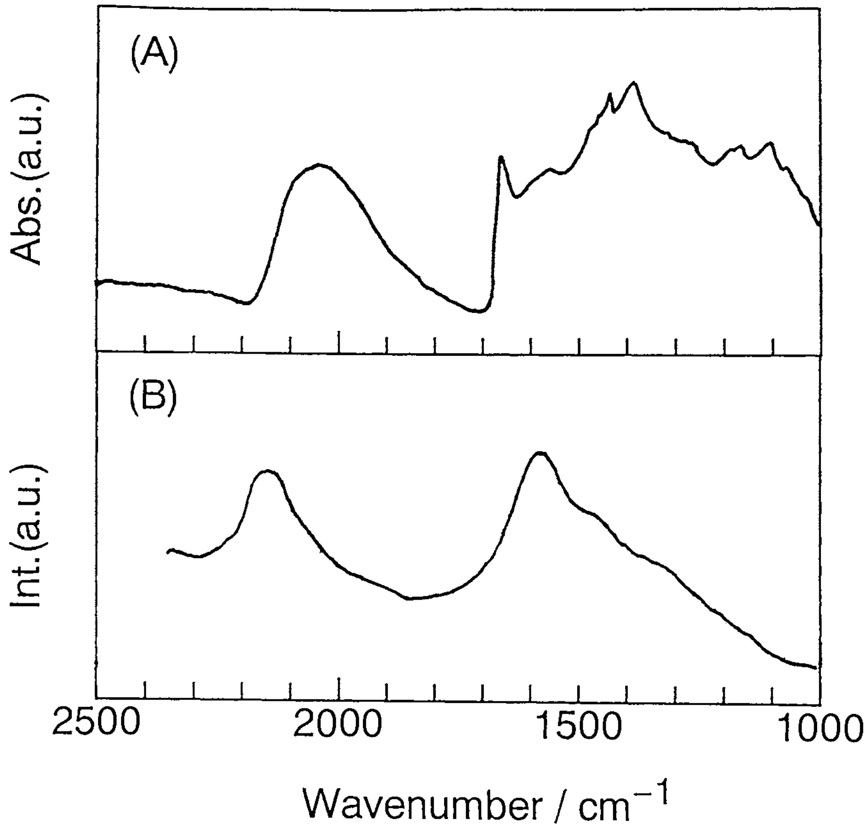

Fig. 1. Infrared (A) and Raman spectra (B) with Ar ion laser (488 nm) of the product .

impurities such as the Ni complex, the supporting electrolyte, the solvent, and halogen are contaminated in this product. The polymerization proceeded only in the presence of the catalyst under these conditions. Similar products were obtained under different conditions in which a different Ni complex is employed with the combination of supporting electrolyte and solvent. Infrared spectrum (2500-1000 cm^{-1}) (Fig. 1(A)) of the product was similar to those of carbyne reported previously.[6-9] Thus, a characteristic broad and strong absorption centered at 2050 cm^{-1} (ranging from 2200 to 1800 cm^{-1}) is corresponding to the stretching vibration of carbon-carbon triple bond. A broad absorption around 1700-1000 cm^{-1} is due to a mixed structure of various carbon skeletons such as cumulene[10] and polyene structures.[6,7] In addition, two weak but sharp absorptions at about 2900 cm^{-1} are assigned to C-H stretching vibrations in tetrabutylammonium cation that is incorporated into the product as a donor dopant during the cathodic reaction or contaminated as the remaining supporting electrolyte.[11] The broad absorption around 3500 cm^{-1} (O-H stretching vibration) is probably due to the terminal structure formed by the reaction of acetylide with DMF.[12] The Raman spectrum shown in Fig. 1(B) also supports that the product has polyyne (around 2150 cm^{-1}) and polyene (around 1550 cm^{-1}) structures. In general, the IR stretching vibration of carbon-carbon triple bonds of acetylenic compounds appears around 2200 cm^{-1}.13) Additionally, those of carbyne reported previously appears over 2100 cm^{-1}.6-9) The lower wavenumber of the band suggests6) that the triple-bond conjugation in this product is longer than those of reported ones. A similar product in a form of a black powder was obtained by either chemical condensation of diiodoacetylene by a Ni(0) complex14) or a catalytic polymerization with a Ni(II) complex.15) However, the infrared absorption of the C≡C stretching vibration in these products is very weak and appears at higher wavenumber than 2100 cm^{-1}, suggesting that the triple-bond conjugation is less than the product obtained by this electrochemical manner.

The powder XRD patterns of this product shows one broad peak at about $2\theta = 22^\circ$, which is typical of the amorphous carbon.16) When the sample is heated at 440° C under an argon atmosphere for 30 minutes, a weak but sharp peak appears at $2\theta = 27^\circ$ consisting with the value for the 002 reflection of graphite,16) the Raman intensity at about 1590 and 1350 cm^{-1} increases, and both infrared and Raman peak around 2100 cm^{-1} due to polyyne completely disappears. From these results, the polyyne structure in this product is unstable to heat, and the conversion of carbyne to graphite-like carbon9) occurs partially during the heat treatment. On the other hand, the infrared band at 2050 cm^{-1} gradually decreases on exposure to air at room temperature in contrast to the results of carbon-metal fluoride composite.9)

The electrical conductivity of pellet samples prepared from the as-prepared black powder under a pressure of 600 kg f cm^{-2} is 3×10^{-5} S cm^{-1}, which is comparable to those of I_2-doped samples. 7,8,17) Since the sample shows a negative thermoelectric power, the carbyne prepared by this manner is considered to be already n-doped by tetraalkylammonium cation.

In summary, we have demonstrated a novel approach for synthesis of carbyne by the electroreductive polymerization of diiodoacetylene catalyzed by a nickel complex. The results suggest that the product is consisted of long polyyne chains with a partially graphite-like cross-linked polyene structure containing the n-dopant.

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