Single-Crystal Synthesis and Structures of C_{60} Polymers

Xuean Chen and Shoji Yamanaka
Department of Applied Chemistry, Graduate School of
Engineering, Hiroshima University
Higashi-Hiroshima 739-8527 Japan

It is well known that fullerene C_{60} is easily polymerized by applying pressure. There are two kinds of two-dimensional C_{60} polymers, rhombohedral (2D-3R) and tetragonal (2D-T) phases. Most of the polymers were so far prepared using C_{60} powders, and thus the resulting polymers were not well crystalline for the single crystal structural analysis. Because of the poorly resolved X-ray profiles, even powder Rietveld analyses have not been attempted. In this study, we have succeeded in preparing the single crystals of the two types of C_{60} polymers, and determined the detailed structures.

C_{60} single crystals with submillimeter sizes were first grown from C_{60} powder by sublimation in a vacuum-sealed glass tube with a temperature gradient of 520-600 °C. The obtained C_{60} crystals were buried in hexagonal boron nitride (h-BN) powder in an h-BN crucible, which was placed in a cylindrical graphite heater. The sample assembly was in turn set in a pyrophyllite cube and subjected to a high-pressure treatment using a cubic multianvil type press. For the synthesis of the 2D-3R polymer, the sample was treated at a pressure of 5 GPa at 500 °C. For the synthesis of the 2D-T polymer, the condition was 2.5 GPa at 500 °C. Both samples were gradually cooled down to room temperature under pressure, followed by releasing the pressure very gradually. It was found that the crystal morphology was kept after the treatment. The X-ray intensity data of the single crystals were collected at room temperature on a Rigaku RAXIS diffractometer with an imaging plate area detector, using graphite monochromated MoKα radiation.

Structure of the 2D-3R polymer

The 2D-3R polymer was first prepared by Iwasa et al. [1] using high-pressure and high-temperature conditions. Núňez-Regueiro et al [2] proposed a structural model in which C_{60} units were polymerized within the plane of the fcc packing via [2+2] cycloaddition. The basic structure has been found to be the same, and the bond distances and bond angles were precisely determined by the structural refinements as shown in Fig. 1. Two types of the stacking models for the 2D polymer layers have been proposed as shown in Fig. 2. The present study revealed that the stacking (a) is correct, in which the hexagons of adjacent layers are facing each other, while in the other stacking (b) the pentagons are facing so as to form pentagonal antiprisms [3].

Structure of the 2D-T polymer

The so-called "tetragonal" (2D-T) phase was found to actually crystallize in an orthorhombic space group Immm rather than $P4_2/mmc$ as reported by other groups [4]. The lattice constants are a = 9.026(2), b = 9.083(2), c = 15.077(3) Å. The ORTEP representation of the C_{60} 2D network of the orthorhombic ("T") pahse is shown in Fig. 3 [5]. The calculated energy difference between the $P4_2/mmc$ and Immm stackings was estimated be be very small [6]. Although the $P4_2/mmc$ is considered to be energetically slightly favorable, the existence of the Immm phase will not be excluded.

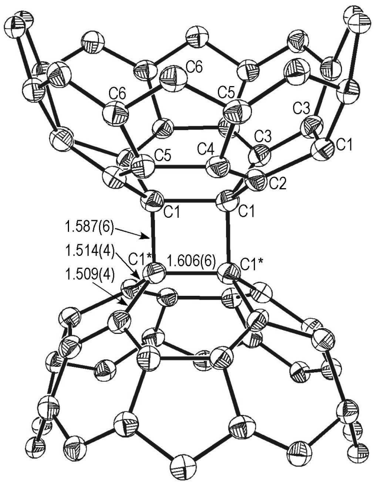

Fig.1. An ORTEP plot of the partial structure of the 2D-3R polymer via [2+2] cycloaddition.

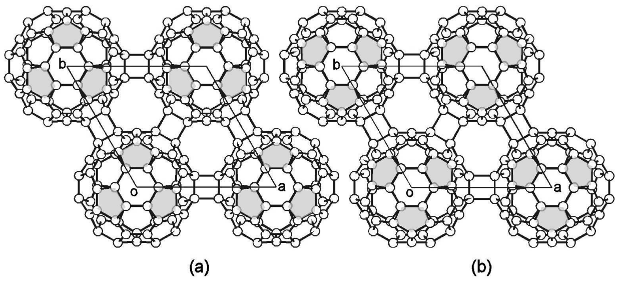

Fig. 2. Projection of the C_{60} 2D network of the 3R phasealong the [001] direction: present structural model (a) compared with that proposed by Núňez-Regueiro et al. (b).

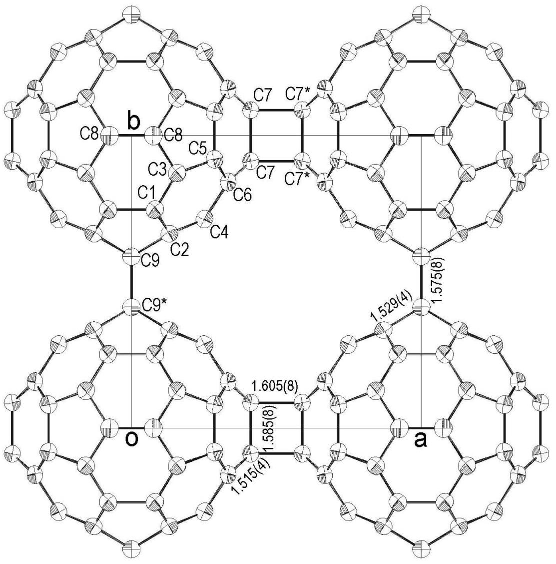

Fig. 3. An ORTEP plot of the C_{60} 2D network of the T phase.

Refererences
1. Y. Iwasa et al, *Science*, 264, 1570 (1994).
2. M. Núňez-Regueiro et al, *Phys. Rev. Lett.*, 74, 278 (1995).
3. X. Chen et al, *Chem. Phys. Lett.*, 356, 291 (2002).
4. R. Moret et al, *Eur. Phys. J.* B15, 253 (2000).
5. X. Chen et al, *Chem. Phys. Lett.*, 360, 501 (2002).
6. V. A. Davydov, et al, *J. Solid State Chem.*, 141, 164 (1998).