

High Temperature X-ray Diffraction and TG-DTA Measurements of Pressure-Polymerized Fullerene

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Pressure-polymerized fullerenes (rhombohedral and amorphous phases) were synthesized by high pressure and high temperature treatment at 5 GPa and 800 - 1200 K. In-situ X-ray diffraction experiments of these two phases at high temperature were carried out. The structural phase transformation of the rhombohedral phase was observed at about 470 K with increasing temperature. The thermal expansion coefficients of the two phases were determined by using the change of the lattice parameters with temperature and thereby the in- and inter-layer bonding natures are discussed.

Key word: fullerene polymer, thermal analysis, XRD, TG-DTA

1. INTRODUCTION

Solid C_{60} is a molecular crystal in which C_{60} molecules are arranged in a face-centered cubic structure (lattice constant $a = 1.417$ nm) and bound together by weak van der Waals forces. In recent years, pressure-polymerized fullerenes, with two- or one-dimensional infinite carbon networks, which are synthesized from solid C_{60} (fcc C_{60}) by high pressure and high temperature treatment, have attracted considerable attention.[1][2] So far, at least three phases (rhombohedral, orthorhombic, and tetragonal phases) of pressure-polymerized fullerenes were synthesized. Among these three phases, the two dimensionally polymerized rhombohedral phase is of particular interest due to its layered structure like graphite, which is well known to be a host material for a wide variety of intercalated systems showing interesting physical properties.[3] In the rhombohedral phase, inter-cluster distance within the layer (~ 0.92 nm) is extremely shorter than that between adjacent layers (~ 0.97 nm) and that of fcc C_{60} (~ 1.0 nm). Such a small inter-cluster distance can be explained by the cycloaddition [2+2] mechanism between two adjacent C_{60} molecules in the layer. In other words, each C_{60} cluster is covalently connected with surrounding six C_{60} clusters in the layer while van der Waals force is dominant interaction between the layers. Goze et al. revealed the distortion from the spherical shape of the C_{60} molecules in the rhombohedral phase by high-resolution ^{13}C NMR experiments and attributed it to the cycloaddition reactions in the phase.[4] Núñez-Regueiro et al. proposed a model structure of the

rhombohedral phase giving excellent agreement with the X-ray diffraction pattern.[5] Okada et al. performed structural optimization by using the conjugated-gradient method in local density approximation calculation with this model and confirmed that the proposed geometry is stable.[6][7] However, the atomic positions are not determined experimentally because of the low crystallinity and lack of experimental evidence for the difference between in- and inter-layer bonding natures. In the present study, we performed high temperature X-ray diffraction experiments in order to determine the thermal expansion coefficients along and across the layer.

2. EXPERIMENTAL

C_{60} powder sample (fcc C_{60}) was purchased from Hoechst ("super gold grade" >99.78 %). The fcc C_{60} powder sample charged in a Pt capsule was inserted into the center of an MgO octahedron with a graphite heater. The sample was compressed by using a split-sphere type high pressure apparatus up to 5 GPa and then heated at 800 - 1200 K for 1 h. Subsequently, the sample was cooled down to room temperature at a cooling rate of >100 Ks $^{-1}$ followed by a release of the pressure.

In situ XRD measurements at high temperature were performed on a Rigaku RINT-2200 using Cu $K\alpha$ radiation. Pyrolytic graphite was used as a counter monochromator. The powder was sealed in a 0.3 mm diameter silica glass capillary. High temperature experiments were done with a home-made small furnace made of a 10 mm diameter ceramic tube

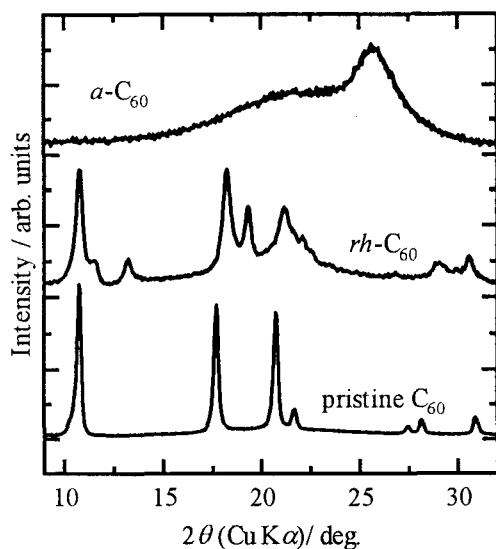


Fig. 1 XRD patterns observed for C_{60} treated at 5 GPa and the temperatures indicated.

wound by a Pt wire with windows for incident and diffracted beams. The sample in the capillary was set in the furnace. The sample temperature was monitored by a thermocouple at the top of the furnace. The distance from the sample to the thermocouple was about 20 mm. Prior to the XRD measurements, the temperature was calibrated by setting an extra thermocouple at the sample position.

Thermogravimetry – differential thermal analysis (TG-DTA) measurements were performed with a differential thermal analyzer (TG-DTA2020S, MAC Science Co.). The measurements of the pressure-polymerized fullerene powder were conducted in Ar gas atmosphere (flow rate: 200 ml min^{-1}) while heated at 10 K min^{-1} .

4. RESULTS AND DISCUSSION

Figure 1 shows the observed X-ray diffraction patterns of pressure-polymerized fullerenes. Two phases were synthesized by the high pressure treatment. It was found by the XRD experiments that rhombohedral (hexagonal-system parameters: $a = 0.917$ nm, $c = 2.456$ nm) and amorphous phases are synthesized in the synthesis temperature ranges of 823 – 883 K and 903 – 1223 K, respectively. For convenience sake, the rhombohedral and the amorphous phases are abbreviated as $rh-C_{60}$ and $a-C_{60}$, respectively.

Figure 2 shows the change in the diffraction patterns

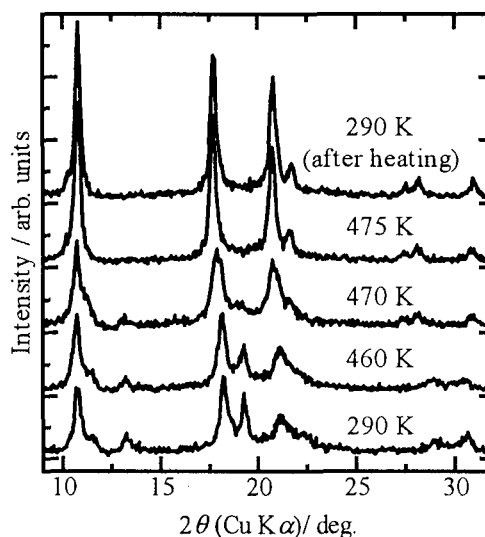


Fig. 2 Change in XRD patterns of $rh-C_{60}$ polymer with temperature.

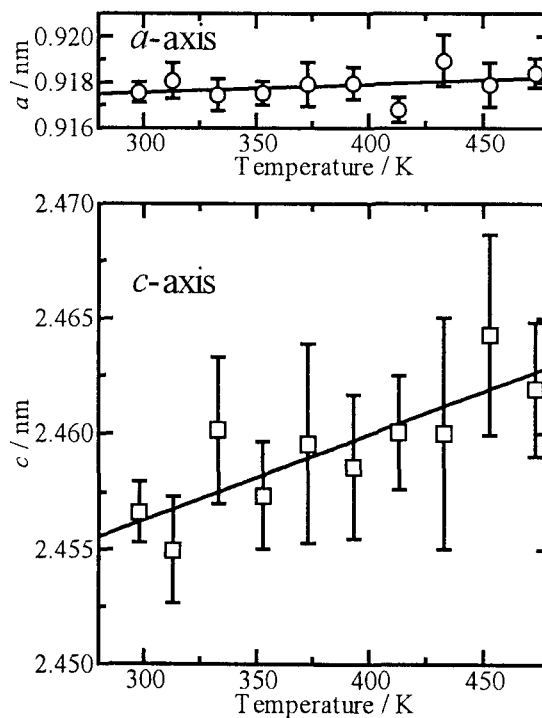


Fig. 3 The temperature dependence of the lattice parameters (hexagonal axes) of the $rh-C_{60}$ polymer.

of $rh-C_{60}$ with temperature. As shown in Figure 2, the diffraction pattern begins to change at about 470 K. The phase at high temperature is a face centered cubic. This rhombohedral to cubic transformation of $rh-C_{60}$ is

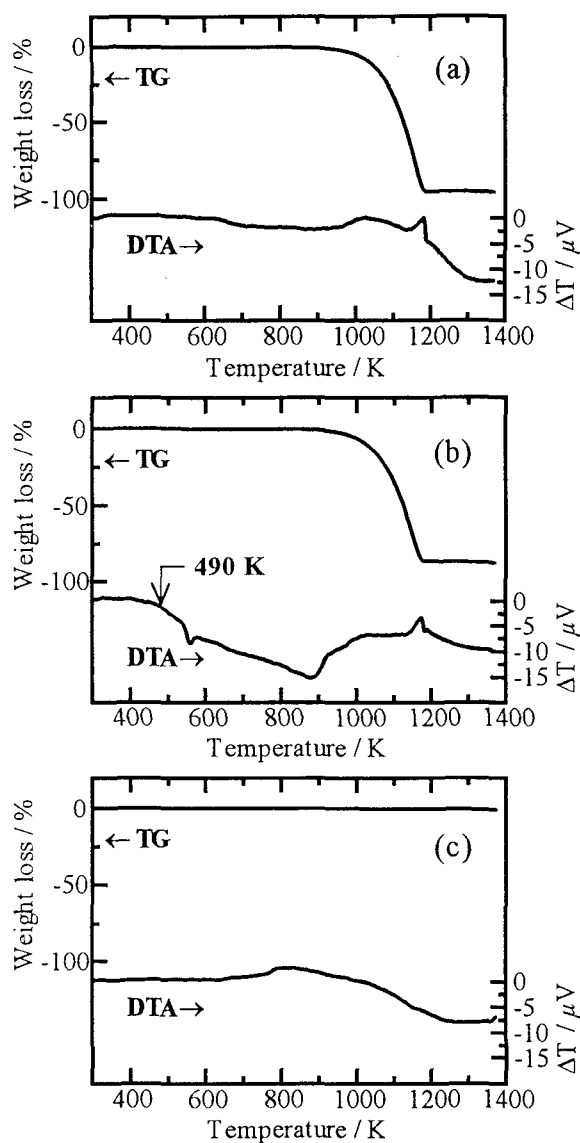


Fig 4 TG - DTA profiles of (a) pristine C_{60} , (b) $rh-C_{60}$ and (c) $a-C_{60}$.

irreversible, since the sample after the high temperature measurements showed the pattern of fcc C_{60} . On the other hand, no remarkable change was observed in the diagrams of $a-C_{60}$. For convenience' sake, we express the lattice parameters of the rhombohedral phase by using the hexagonal-system parameters. It should be noted that the inter-cluster distance is a and that the interlayer distance is $c/3$. Figure 3 shows the lattice parameters of $rh-C_{60}$ as a function of temperature. The linear expansion coefficients along the a - and c -axes are determined to be $4.0 \times 10^{-6} K^{-1}$ and $1.5 \times 10^{-5} K^{-1}$, respectively. The facile expansion along the c -axis is

confirmed by the positive slope of the temperature dependence of ca , and this phenomena can be explained by the difference between the bonding natures along the a - and c -axes.

Figure 4 shows the TG-DTA curves of fcc C_{60} , $rh-C_{60}$ and $a-C_{60}$. It was observed that fcc C_{60} begins to sublime at about 1181 K. On the other hand, it was found that $a-C_{60}$ does not sublime up to 1373 K. Although the structural details of $a-C_{60}$ have not been well known, it is considered that a three-dimensional network of inter-molecular bonds is formed in $a-C_{60}$. The formation of such network explains why $a-C_{60}$ does not sublime. In the DTA curve of the $rh-C_{60}$, an endothermic peak attributed to the rhombohedral to cubic phase transformation was observed at about 530 K. The transition temperature (about 490 K) observed by the DTA measurement is higher than that by the XRD measurement. The temperature of the DTA measurement is probably more accurate. It was observed that $rh-C_{60}$ begins to sublime at about the same temperature as fcc C_{60} does. However, the weight loss of $rh-C_{60}$ after the sublimation is a little smaller than that of fcc C_{60} . It indicates the possibility that the synthesized $rh-C_{60}$ includes a small amount of $a-C_{60}$.

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