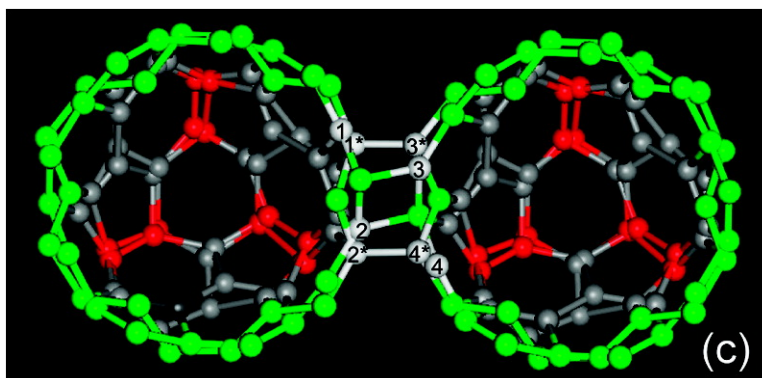


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## Topochemical 3D Polymerization of C<sub>60</sub> under High Pressure at Elevated Temperatures

Shoji Yamanaka,<sup>\*,†</sup> Nagesh S. Kini,<sup>†,§</sup> Akira Kubo,<sup>†</sup> Saeko Jida,<sup>†</sup> and Hideaki Kuramoto<sup>‡</sup>

Department of Applied Chemistry, Graduate School of Engineering, Hiroshima University, Higashi-Hiroshima 739-8527, Japan, Hiroshima City Industrial Promotion Center, Senda-machi 3-8-24, Hiroshima 730-0052, Japan, Present address: Chemistry and Physics of Materials Unit, Jawaharlal Nehru Centre for Advanced Scientific Research, Jakkur P.O., Bangalore-560 064, India

Received September 7, 2007; E-mail: syamana@hiroshima-u.ac.jp

**Abstract:** Fullerene C<sub>60</sub> monomer crystals were compressed to a face-centered cubic (fcc) phase with a lattice parameter of  $a = 11.93(5)$  Å and a micro-Vickers hardness of 4500 kg/mm<sup>2</sup> using high-pressure and high-temperature conditions of 15 GPa at 500–600 °C. The hardness is compatible with that of cubic boron nitride (c-BN), suggesting the formation of a 3D C<sub>60</sub> polymer. The single-crystal X-ray structural analysis revealed that each C<sub>60</sub> molecule in the polymer was linked to the 12 nearest neighbors by [2+2] cycloaddition between the common pentagon–hexagon (56) edges. However, *ab initio* geometry optimization and molecular dynamics calculations suggested that the 3D polymer should have a rhombohedral structure with the space group of  $R\bar{3}$  containing [3+3] cycloaddition between the pentagons of C<sub>60</sub> molecules within the plane perpendicular to the 3-fold axis. The higher apparent symmetry of fcc was observed as an averaged structure of different orientations of the rhombohedral structure. The  $R\bar{3}$  structure can be derived by only a slight rotation of each C<sub>60</sub> unit in the (111) plane of the fcc structure. The band-structure calculation suggested that the 3D polymer ( $R\bar{3}$ ) was a semiconductor; the activation energy for the electrical conductivity was experimentally determined to be 0.25 eV at 550 K.

### Introduction

Monomeric C<sub>60</sub> is easily polymerized into 2D polymers under high-pressure and high-temperature (HPHT) conditions:<sup>1</sup> tetragonal and rhombohedral 2D polymers are obtained at 2.5 and 5 GPa, respectively, at 500 °C.<sup>2–5</sup> In these 2D polymers, each C<sub>60</sub> unit is bonded two dimensionally within the {100} and {111} layers of the parent cubic monomer crystal to have four and six first neighbors, respectively, via [2+2] cycloaddition between the common hexagon–hexagon edges (double bonds) within the layer. Such layers are stacked on each other to form the 2D crystal structures with the space groups *Immm* or  $P4_2/mmc$  for the tetragonal phases and  $R\bar{3}m$  for the rhombohedral phase. Under much higher pressures ( $P > 13$  GPa) at elevated temperatures, 3D polymers are obtained.<sup>6</sup> In a previous study,<sup>7</sup>

we have compressed the 2D orthorhombic (pseudo tetragonal) polymer phase with the space group *Immm* at 15 GPa and at 550 °C, and found that the 2D C<sub>60</sub> layers are bonded three dimensionally by forming new C–C bonds between the layers by [3+3] cycloaddition, where each spherical C<sub>60</sub> monomer unit was substantially deformed to rectangular parallelepiped (cuboidal) shapes and bonded to eight cuboidal C<sub>60</sub> neighbors. It should be noted that in the 2D-to-3D conversion under high-pressure conditions, the orientation and the arrangement of C<sub>60</sub> molecules are kept and the *Immm* space group symmetry is preserved before and after the conversion.

Much attention has been paid to 3D C<sub>60</sub> polymers from two different points of view: (i) development of new superhard materials<sup>8,9</sup> and (ii) exploration of carbon clathrate compounds.<sup>10</sup> Although monomeric and 2D polymeric C<sub>60</sub> crystals are rather soft, owing to the weak van der Waals interaction between the monomers and the 2D layers, 3D polymers have been reported to be very hard due to the strong 3D covalent network. It was reported that some 3D C<sub>60</sub> polymers were so hard that they could scratch the surfaces of diamond and were called ultra-hard and

<sup>†</sup> Hiroshima University.

<sup>‡</sup> Hiroshima City Industrial Promotion Center.

<sup>§</sup> Present address: Jawaharlal Nehru Centre for Advanced Scientific Research.

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super-hard fullerenes.<sup>8,9</sup> From the other view point, the covalent 3D network of 3D C<sub>60</sub> polymers containing carbon cages can be seen as carbon analogs of silicon clathrate compounds. Recently we have developed barium-containing silicon clathrate compound Ba<sub>8</sub>Si<sub>46</sub> isotopic with the type-I gas (G) hydrate G<sub>x</sub>·(H<sub>2</sub>O)<sub>46</sub>.<sup>11</sup> The silicon clathrate became a superconductor with a transition temperature (*T*<sub>c</sub>) of 8.0 K. This was the first superconductor having a Si-sp<sup>3</sup> 3D network. The mechanism of the superconductivity has been extensively studied by solid-state physicists,<sup>12,13</sup> and the superconductivity can be interpreted in terms of the usual phonon-mediated BCS mechanism. Therefore, it is expected that if we can obtain a similar structure composed of carbon instead of silicon, a much higher *T*<sub>c</sub> should be realized due to the much larger phonon-electron interaction.<sup>14</sup> A 3D network of polymerized C<sub>60</sub> appears to be a promising candidate for such carbon clathrate structures.

As mentioned above, in our previous study we succeeded in obtaining the 3D polymer single crystals by a two-step method;<sup>7</sup> the monomer single crystals were first converted to the 2D polymer (*Immm*) under a medium range of pressure of 2.5 GPa and at 500 °C, and then in the second step converted to the 3D polymer single crystals (*Immm*) under 15 GPa and at 550 °C. In the present study, we compressed the monomer single crystals directly to a high pressure of 15 GPa. We have obtained a new type of 3D polymer crystals with fcc symmetry. The structure has been determined on the basis of the X-ray diffraction (XRD) data, and some characteristic properties have been measured. Ab initio geometry optimization and molecular dynamic calculations have suggested that the structure determined by the XRD study is not stable, and some structural modification should be required to stabilize the structure determined by XRD analysis.

## Experimental Section

**Preparation of 3D Polymers.** Single crystals of monomeric C<sub>60</sub> were prepared from polycrystalline C<sub>60</sub> powder (MTR Ltd., 99.5+%) by sublimation in the temperature interval 500–600 °C in an evacuated and sealed glass tube. These single crystals were then embedded in hexagonal-BN (*h*-BN) powder and filled into an *h*-BN cell. The *h*-BN cell was then housed into a pierced CoO doped MgO octahedron, which was compressed in a Kawai-type<sup>15</sup> multi-anvil with a truncation edge length of 4 mm. A thin platinum tube surrounding the *h*-BN cell served as the heater. A ZrO<sub>2</sub> tube surrounding the platinum heater acted as a thermal insulator. The sample temperature was monitored and controlled using a chromel–alumel thermocouple. Several HPHT conditions were employed for polymerization. The optimized condition for obtaining good quality single crystals of 3D cubic (fcc) polymers was the following; the sample was first compressed to 15 GPa at room temperature and then heated up to 550 °C in 10 min. After keeping the sample at these conditions for 1 h, the crystals were cooled down to room temperature, followed by a gradual release of the pressure over the matrix. It was found that an addition of 2 mol of potassium azide (KN<sub>3</sub>) for every mole of C<sub>60</sub> monomer resulted in a better crystallinity. The electron probe microanalysis (EPMA) did not detect the presence

of potassium in the polymerized samples. The azide was thermally decomposed to potassium metal and nitrogen gas. It is well-known that C<sub>60</sub> monomer crystals form fullerenes with potassium metal such as KC<sub>60</sub> and K<sub>3</sub>C<sub>60</sub>.<sup>16</sup> In this study, however, C<sub>60</sub> crystals were first compressed to 15 GPa, and then KN<sub>3</sub> was decomposed to form potassium metal. The compressed C<sub>60</sub> crystals could not accept potassium metal into the structure. Although the role played by liquid potassium metal in the improvement of the crystallinity of the polymer is not clear, it is likely that potassium metal will act as a good thermal conducting media together with powder *h*-BN to provide uniform temperature and hydrostatic pressure conditions.

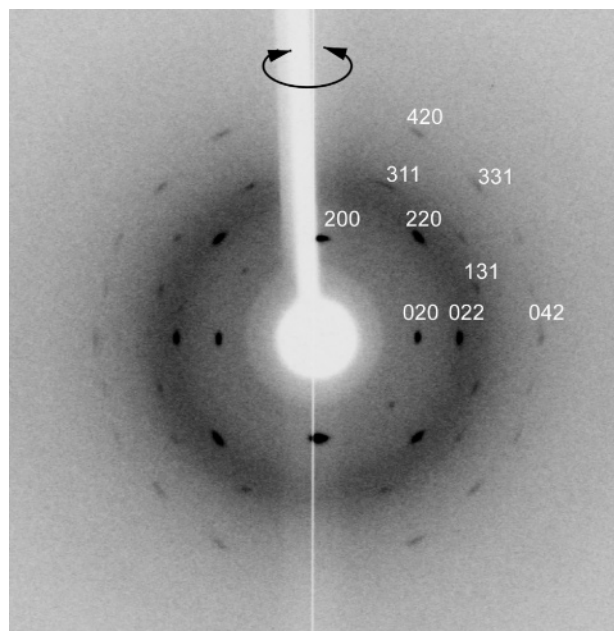
**Characterization.** The polymerized C<sub>60</sub> single-crystal samples were analyzed using an X-ray diffractometer (Rigaku-RAXIS) equipped with an imaging plate detector. About 100 crystals with dimensions of 0.3 × 0.2 × 0.2 mm<sup>3</sup> were scanned, and the best one was selected for the detailed analysis. The intensity data were collected at room temperature, employing a graphite monochromatized Mo Kα radiation ( $\lambda = 0.7107$  Å). The single-crystal structure was refined with the program *SHELX97*<sup>17</sup> and the *WinGX*<sup>18</sup> software package. The molecular dynamics (MD) and geometry optimization calculations were carried out using the quantum mechanical program, *DMol3 Solid State*, provided with the Materials Studio suite by Accelrys.<sup>19–21</sup> The band structure of the geometry optimized structure was calculated using the program *CASTEP*<sup>22</sup> with LDA-CA-PZ (Local density approximation, Ceperley and Alder-Perdew and Zunger) functional and ultrasoft potentials at the default fine setting. The densities of the crystals were measured using Archimedes principle in aqueous sodium polytungstate solutions with the densities in a range of 1.5 to 2.9 g/cm<sup>3</sup>. The micro-Vickers hardness (MVH) was measured using a load up to 500 g force for 10 s. The electrical resistivity of 3D polymer samples were measured in a temperature range of 100–650 K using a standard two-probe technique.

## Results and Discussion

**Structure Analysis.** When the fcc monomeric C<sub>60</sub> single crystals embedded in *h*-BN powder were compressed to a high pressure of 15 GPa and then heated up to 550 °C, a new cubic polymer phase with a lattice parameter of about 12 Å was obtained but it was difficult to find single crystals suitable for the structural analysis. A similar high-pressure polymerization was performed by Marques et al.<sup>23,24</sup> using C<sub>60</sub> powder in a toroid-type chamber of 13 GPa at 547 °C. They also reported the formation of a compressed phase with the face-centered cubic unit cell of *a* = 12.05 Å, showing a powder diffraction pattern with a large atomic thermal Debye–Waller factor. In this study, we mixed potassium azide (KN<sub>3</sub>) powder with *h*-BN powder, and C<sub>60</sub> single crystals similarly embedded in the mixture were compressed at 15 GPa and 550 °C. The crystallinity of the so obtained polymers was much improved and served the purpose of X-ray structural analysis. As mentioned in the Experimental Section, EPMA analysis showed that the resulting polymer crystals did not contain any potassium. The XRD oscillation photograph measured on the single crystal is shown in Figure 1. The diffraction pattern can be indexed on

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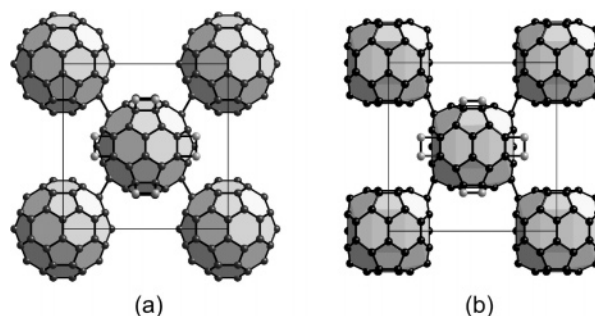


**Figure 1.** Oscillation photograph of the fcc 3D C<sub>60</sub> polymer crystal around the *a* axis.

the basis of the fcc system with a lattice parameter  $a = 11.93(5)$  Å, which is significantly smaller than the 14.17 Å of the parent monomeric crystals. As can be seen from the diffraction pattern shown in Figure 1, the polymer sample is not highly crystalline, and only 21 unique reflections for  $I \geq 2\sigma(I)$  were observed in the data collection. The number of reflections is not sufficient for the direct structural analysis, and then it was tentatively assumed that the basic structure of the monomer crystal would be kept in the polymer crystal as found in the 2D-to-3D conversion of the *Immm* polymer.<sup>7</sup>

At room temperature, C<sub>60</sub> molecules can rotate freely as homogeneous spheres in the monomeric fcc crystals, and form an average structure with space group *Fm* $\bar{3}$ *m*.<sup>25</sup> On cooling, the molecules are orientationally ordered and the symmetry is lowered from *Fm* $\bar{3}$ *m* to *Pa* $\bar{3}$  with a restricted rotation around one of the four [111] axes of the crystal. In the resulting ordered structures, electron-rich double bonds on the molecule face the electron-poor centers of hexagons (*H* orientation) and pentagons (*P* orientation) on its neighbor. Although the energy difference is very small, the *P* orientation is more stable, and at a lower temperature the fraction of the *P* orientation increases. The molecular volume of the *H* orientation is slightly smaller than that of *P*-orientated state. Under high pressure, the *H*-orientated state is preferred.<sup>26</sup> Under extremely high pressures of this study ( $P > 13$  GPa), it is reasonable to assume that C<sub>60</sub> molecules would have the ordered phase with all of the molecules having the same orientation close to the *H* orientation with the space group *Fm* $\bar{3}$ , which is the minimal non-isomorphic klassengleiche supergroup of the space group *Pa* $\bar{3}$ .<sup>27</sup>

To estimate the polymerized structure, which will be obtained by one-step compressing of the monomer crystal, a crystallographic operation was carried out to reduce the lattice parameter of the monomer crystal from 14.17 to 11.93 Å,



**Figure 2.** Structural models of the 3D C<sub>60</sub> polymer with the fcc symmetry. (a) Model C, the compressed monomer structure, and (b) model X, the X-ray refined structure. Carbon atoms marked by gray balls belong to the adjacent C<sub>60</sub> units above the plane of this paper, forming 56/65 [2+2] cycloaddition with the C<sub>60</sub> molecules at the center.

**Table 1.** Crystallographic Parameters of the Structures of C<sub>60</sub> Polymers, Model C, the Compressed Structural Model of C<sub>60</sub> with *Fm* $\bar{3}$  symmetry, and Model X, the X-ray Refined Structure<sup>a</sup>

Model C: $a = 11.93$ Å, Space group: <i>Fm</i> $\bar{3}$ (No. 202)					
	site	<i>x</i>	<i>y</i>	<i>z</i>	
C1	96 <i>i</i>	0.060	0.193	0.283	
C2	96 <i>i</i>	0.098	0.119	0.246	
C3	48 <i>h</i>	0	0.059	0.209	
Model X: $a = 11.93(5)$ Å, Space group: <i>Fm</i> $\bar{3}$ (No. 202)					
	site	<i>x</i>	<i>y</i>	<i>z</i>	$U_{eq}$
C1	96 <i>i</i>	0.082(2)	0.190(5)	0.287(4)	0.81(3)
C2	96 <i>i</i>	0.078(5)	0.121(6)	0.245(3)	1.02(4)
C3	48 <i>h</i>	0	0.065(9)	0.210(4)	1.18(7)

<sup>a</sup> *R* index [ $I \geq 2\sigma(I)$ ]:  $RI = 0.0586$ ;  $wR = 0.1342$ . *R* index (all data):  $RI = 0.2326$ ;  $wR = 0.2341$ . GOF on  $F_o^2$ : 0.979; unique no. reflns: 21; observed no. reflns: 124; parameter: 13. (The structure factor table is attached as Supporting Information.)

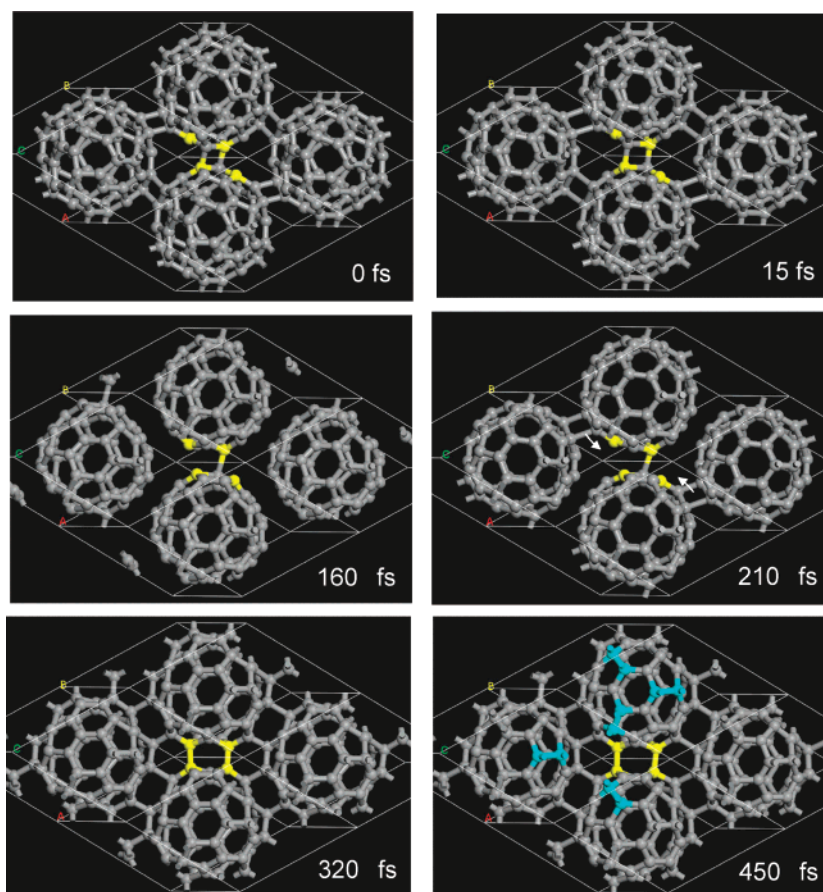
leaving the orientation, the arrangement, and the dimensions of C<sub>60</sub> molecules unchanged, but only the van der Waals radius of C<sub>60</sub> molecules was reduced. The resulting compressed structure is referred to as model C (space group *Fm* $\bar{3}$ ), hereafter, where each C<sub>60</sub> molecule is coordinated by 12 neighbor units and the C–C bonds at the common pentagon–hexagon (56) edges can face each other with a distance of only 1.574 Å to form [2+2] cycloaddition (part a of Figure 2). A similar polymerized model has been proposed by Berber et al.<sup>28</sup> as one of the possible 12 rigid crystalline models for polymerized fullerenes in their theoretical exploration of new hard materials. This is a new type of cycloaddition between C<sub>60</sub> molecules, which is different from the cycloaddition between the common hexagon–hexagon (66) edges found in 2D C<sub>60</sub> polymers. After Berber et al., the new cycloaddition bonding is represented as 56/65[2+2] in contrast to the cycloaddition formed between the common hexagon–hexagon edges found in the 2D C<sub>60</sub> polymers, 66/66[2+2]. The crystallographic parameters of model C are listed in Table 1, which were used as the starting structure in a *SHELX*-97 refinement system by full-matrix least-squares methods on  $F_o^2$ . After the refinement of the structure with the reflection data with  $I > 2\sigma(I)$  for 13 variables including isotropic atomic displacement parameters ( $U_{eq}$ s), the reliability factors converged to  $R_1/wR_2 = 0.0586/0.1342$ . The X-ray refined structure is referred to as model X, whose crystallographic parameters are compared with those of model C in Table 1, and the structures are compared in Figure 2. Note that the two

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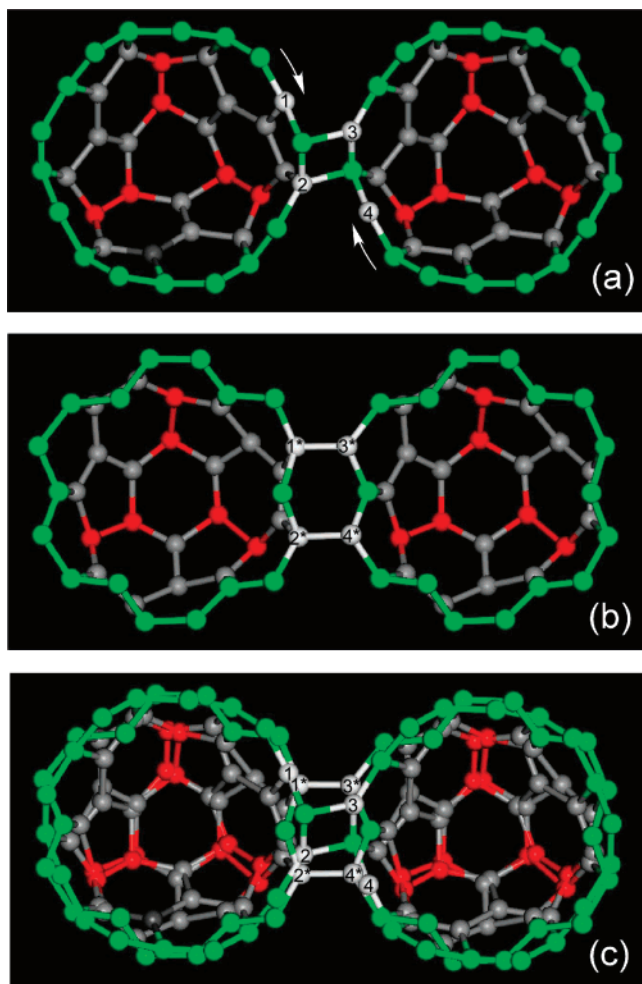
**Figure 3.** Time course of the relaxation of the polymer structure in the MD calculation at a temperature of 1000 K on NVT ensemble. The carbon atoms marked by yellow color show how the 56/65 [2+2] cycloaddition bonds on the equatorial zone are changed into the [3+3] cycloaddition bonds by a few degrees of rotation around the three-fold axes perpendicular to the plane of this sheet. The carbon atoms marked by blue color can keep the 56/65 [2+2] bonding with the  $C_{60}$  units from the next layer before and after the rotation.

sets of crystallographic parameters for model X do not deviate very much from those of model C, although the isotropic displacement parameters  $U_{\text{eq}}$ s are unusually large. This result also supports the conclusion in the previous study<sup>7</sup> that the  $C_{60}$  polymerization under high pressure proceeds topotactically, maintaining the orientation and arrangements of the molecules in the parent crystal structure. It would be difficult to develop a more detailed discussion on the polymer structure based on such insufficient structural data. It is only evident here that the polymer crystals obtained by one-step compression to 15 GPa with heating has the fcc symmetry, which is very different from the orthorhombic 3D polymer phase derived by the two-step polymerization and conversion of the 2D polymer.<sup>7</sup>

**Molecular Dynamics and Geometry Optimization.** To evaluate the stability of the structure determined by the XRD analysis using the insufficient number of reflection data, we performed the geometrical optimization and MD calculations using the *DMol3 Solid State* program. Because the fcc unit cell is too large for the calculation of the periodic system, we employed a rhombohedral reduced cell. MD calculation has been performed on the two starting structures given in Table 1: X-ray determined (model X) and the van der Waals compressed model (model C). The calculation was made on a NVT (constant volume and temperature) ensemble using a step of 1 fs at 1000 K on a Nose–Hoover thermostat. As shown in Figure 3, in the course of the MD calculation on model X, the first 15 steps (15 fs) were used to relax the deformed  $C_{60}$  structures so as to

have regular hexagons; the bond lengths between the  $C_{60}$  units via the cycloaddition, 56/65 [2+2], repeatedly became shorter and longer than 1.6 Å, and suddenly after about 200 steps (200 fs), the molecules slowly began to rotate to have different modes of cycloaddition [3+3] between the adjacent molecules. The rotation of the  $C_{60}$  units changed the space group of the polymer crystal from  $Fm\bar{3}$  to  $R\bar{3}$ . A similar MD calculation with the structural model C also experienced a similar rotation to have [3+3] cycloaddition in earlier stages of the calculation of ~100 steps (100 fs). We have had another type of [3+3] cycloaddition in the *Immm* 3D polymer prepared under 15 GPa from the 2D polymer.<sup>7</sup> It is likely that [3+3] addition is a characteristic bonding formed under extremely high pressures, which can reduce the separation of  $C_{60}$  molecules to realize a dense phase without serious stress.

A part of the structure of model X with the [2+2] cycloaddition bonding and its MD transient structure at 450 steps (450 fs) with the [3+3] cycloaddition bonding are compared in Figure 4. The overlapping of the two structures (part c of Figure 4) clearly shows that only a slight movement of carbon atoms on the equatorial zones is required to convert the bonding from [2+2]- to [3+3]-type cycloaddition. Note that the carbon atoms (colored green and white in Figure 4) located on the equatorial zones are shifted by only 0.5–0.6 Å between the two structural models, which corresponds to a rotation of 4–5 degrees around the three-fold axis of each  $C_{60}$  molecule. The carbon atoms at 5:6 joins marked by red color in Figure 4 are forming 56/65



**Figure 4.** Comparison of the coordinates of the carbon atoms located in the half hemispheres of the 3D  $C_{60}$  units in the polymers shown in Figure 3. (a) Model X, (b) model MD (450 fs), and (c) overlapped two structures, (model X + model MD), showing the resemblance of the two sets of coordinates. Note that the carbon atoms marked by white color ([1, 2, 3, and 4] and [1\*, 2\*, 3\*, and 4\*]) can be changed from [2+2] cycloaddition to [3+3] cycloaddition with a very small degree of rotation. The carbon atoms marked by red and gray colors near the three-fold axes are hardly moved by the rotation.

[2+2] cycloaddition with the next neighbors. These carbon atoms are located near the three-fold axis and hardly shifted by the small angle rotation. As mentioned above, the isotropic atomic displacement parameters ( $U_{eqs}$ ) estimated by the XRD structural analysis are unusually large. Such low-resolution XRD data cannot distinguish the two structural models shown in Figure 4.

The 3D  $C_{60}$  polymer with the space group  $R\bar{3}$  obtained by the MD calculation was geometrically optimized including coordinates and lattice parameters, using the quantum mechanical software package *CASTEP*; a  $3 \times 3 \times 2$  Monkhorst–Pack mesh was used for  $k$ -point sampling with the Brillouin zone for the reduced cell of the rhombohedral unit cell. The crystallographic parameters of the optimized structure with the space group  $R\bar{3}$  are given in Table 2, and the schematic structural model is shown in Figure 5 with some selected bond lengths. Each  $C_{60}$  unit is bonded to six  $C_{60}$  neighbor units via [3+3] cycloaddition horizontally in a plane perpendicular to the three-fold axis, and three  $C_{60}$  units are bonded by 56/65 [2+2] cycloaddition from the top, and another three  $C_{60}$  units from

**Table 2.** Crystallographic Parameters of 3D  $C_{60}$  with the  $R\bar{3}$  Symmetry Determined by Geometry Optimization by *CASTEP*;  $C_{60}$ ,  $a = 8.4097$ ;  $c = 21.3932$  Å;  $Z = 3$ ; Space group,  $R\bar{3}$  (No. 148)

atom	x	y	z
C1	0.47203	0.24286	0.17658
C2	0.57494	0.43193	0.18654
C3	0.36675	0.1921	0.11567
C4	0.41030	0.08908	0.07247
C5	0.36016	0.35623	0.02519
C6	0.33394	0.32639	0.08486
C7	0.48855	0.1582	0.00829
C8	0.48932	0.32664	−0.00991
C9	0.31467	−0.09557	0.07378
C10	0.51319	0.52015	0.22217

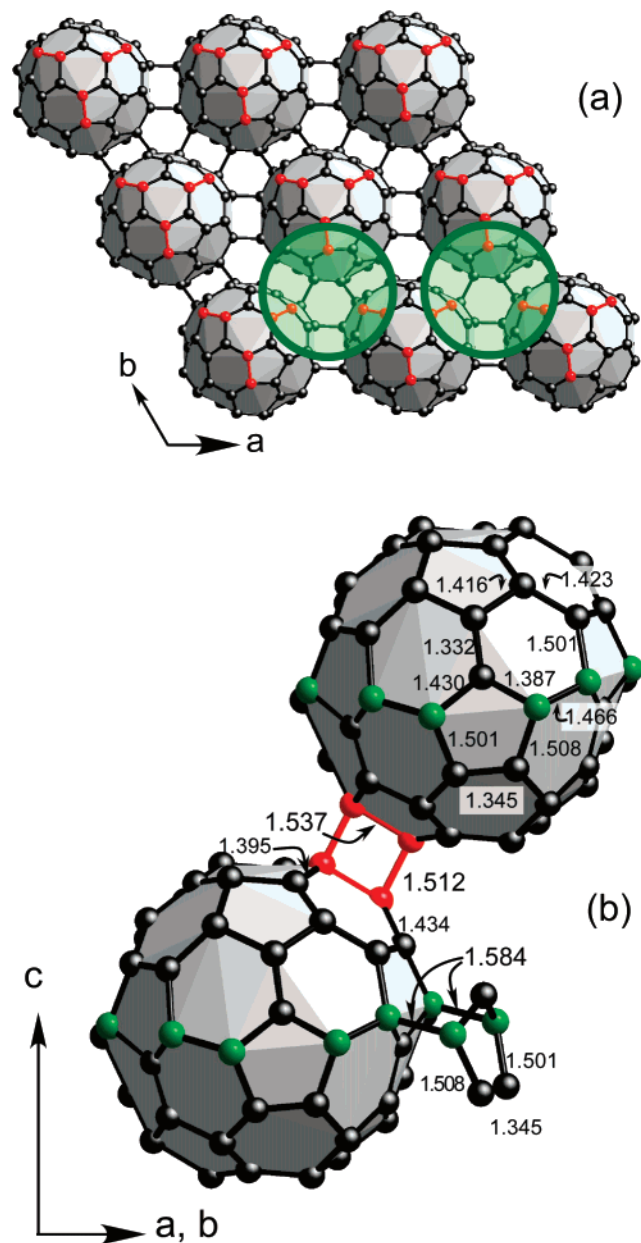
the bottom of the horizontal plane to have a 12 coordination. The lattice parameters for the trigonal setting for model X (fcc) were  $a = 8.44$  Å,  $c = 20.67$  Å, and  $c/a = 2.449$ . The optimized lattice parameters were  $a = 8.4649$  Å,  $c = 21.3932$  Å, and  $c/a = 2.5438$ , which are very close to the cubic rhombohedral setting parameters. In model X (fcc), there are four equivalent three-fold axes, each of which is associated with an equatorial plane with carbon atoms to rotate to convert the [2+2] cycloaddition to the [3+3] one. Because only a small angle rotation is enough for the conversion, such rotation can occur around the four equivalent axes, and the crystal has an average, or disordered structure with the apparent  $Fm\bar{3}$  symmetry. The unusually large atomic displacement parameters ( $U_{eqs}$ ) should reflect such average structures.

In a previous study,<sup>7</sup> we have also made similar geometry optimization on the *Immm* 3D polymer structure determined by X-ray refinement and showed that the calculation can reproduce the experimental structure. The accuracy of the density functional theory method was also confirmed in another application to the rhombohedral 2D polymer.<sup>29</sup> The binding energies for various types of polymers were calculated using the program *DMol3 Solid State* (LDA-PWC functional) and are summarized in Figure 6. It should be noted that the 3D ( $R\bar{3}$ ) polymer derived by the MD calculation is the most stable phase compared to model X and model C. The higher-density phases have smaller binding energies, and could be prepared under high pressure, which is necessary to overcome the activation energy for the structural transition to the higher-density phases.

The band structures of  $R\bar{3}$  polymer were calculated using the program *CASTEP*. The obtained density of states (DOS) profile is shown in Figure 7. The DOS profile has a semiconducting band gap of  $\sim 0.5$  eV at the Fermi level. This is a striking contrast to the DOS distribution of the *Immm* polymer, which shows metallic nature with no band gap at the Fermi level.<sup>7</sup> The electrical conductivity of the 3D  $R\bar{3}$  polymer crystal was measured in the temperature interval of 100–650 K and shown in Figure 8. The activation energies for the electrical conductivity were determined to be 0.08, 0.12, and 0.25 eV at 150, 300, and 550 K, respectively. Half of the gap energy corresponds to the conductivity activation energy from the valence to the conduction bands. The activation energy (0.25 eV) for the highest temperature range appears to be in good agreement with the calculated gap value of 0.5 eV. However, the LDA calculation usually underestimates the gap value;<sup>30</sup> it is reason-

(29) Miyake, T.; Saito, S. *Chem. Phys. Lett.* **2003**, *380*, 589–594.

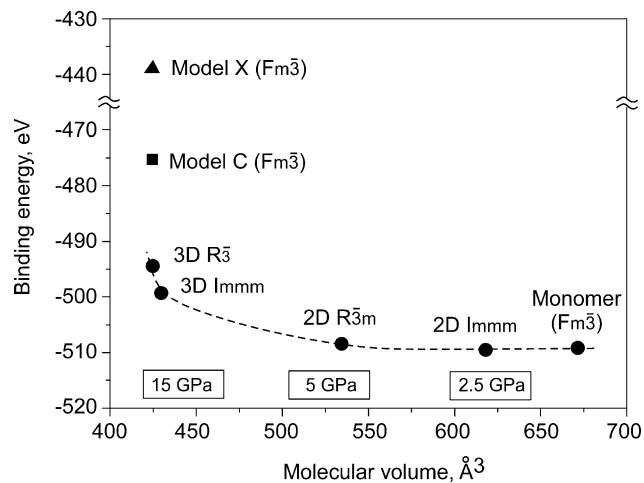
(30) Saito, S.; Oshiyama, A. *Phys. Rev. B* **1995**, *51*, 2628–2631.



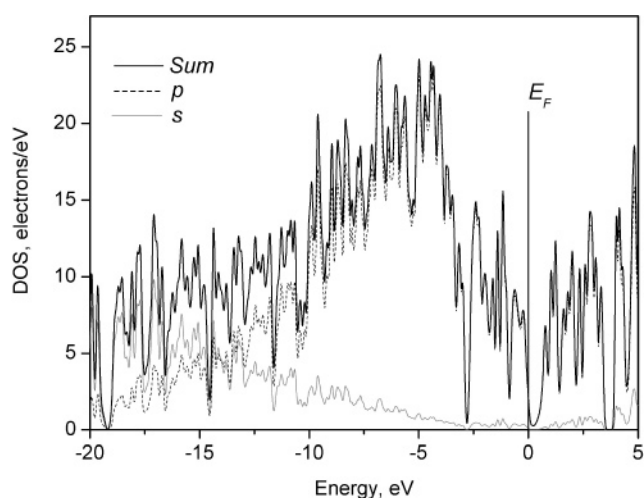
**Figure 5.** Schematic illustration of the 3D polymer structure with the  $R\bar{3}$  symmetry. (a) The structure in the plane, where  $C_{60}$  units are linked by [3+3] cycloaddition. The carbon atoms marked by red color are bonded with the adjacent balls (green circles) by 56/65 [2+2] cycloaddition from the next layer as shown in (b). Typical bond lengths are shown in (b).

able to estimate a band gap larger than 1 eV for this polymer. It is likely that the above measurement should be still in the impurity conductivity temperature range. The conductivity of the 3D  $R\bar{3}$  polymer is about  $10^{-4} \text{ Scm}^{-1}$  at room temperature, which is three orders-of-magnitude smaller than that of 3D  $Immm$  polymer reported elsewhere.<sup>7</sup> Note that 3D  $C_{60}$  polymers having different arrangements of  $sp^2$ - and  $sp^3$  carbon atoms show very different electrical properties.

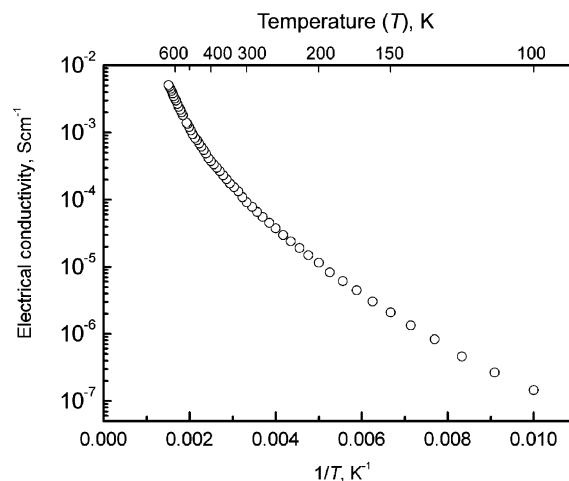
**Micro-Vickers Hardness.** 3D  $C_{60}$  polymers contain strong covalent bonds between  $C_{60}$  units and should be very hard. Blank et al.<sup>8,9</sup> reported that fullerides prepared under high pressure were extremely hard and could scratch the surfaces of diamond. We have measured the micro-Vickers hardness (MVH) of the 3D polymers as well as 2D polymers and monomer  $C_{60}$ . As shown in Figure 9, the logarithm of the MVH gave a linear



**Figure 6.** Binding energies of various  $C_{60}$  phases as a function of molecular volume in the corresponding crystals. Approximate pressure regions for the polymerizations are shown together.

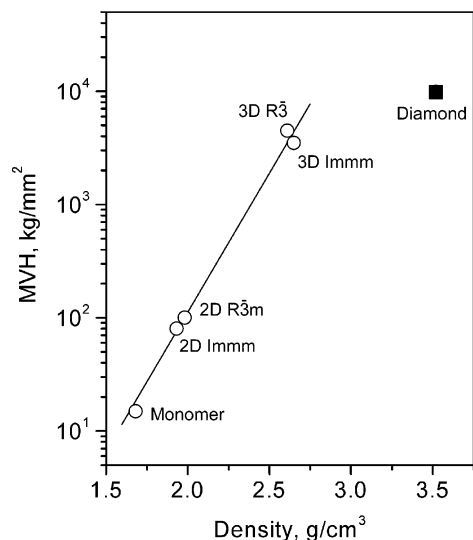


**Figure 7.** Density of states (DOS) of the 3D  $C_{60}$  polymer with the  $R\bar{3}$  structure. A band gap of about 0.5 eV is located at the Fermi level.



**Figure 8.** Electrical conductivity of the 3D  $R\bar{3}$   $C_{60}$  polymer as a function of temperature.

relationship with the observed densities of various  $C_{60}$  phases including the polymers and the monomer. The densities were measured using a heavy aqueous solution of sodium polytungstate and the Archimedes method. As shown in Table 3, the observed and calculated densities agreed very well. The MVH



**Figure 9.** Micro-Vickers hardness (MVH) of various C<sub>60</sub> phases as a function of the observed density. The value for diamond is taken from ref 31 for comparison.

**Table 3.** Micro-Vickers Hardness (MVH) and the Density of Various C<sub>60</sub> Phases in Comparison with Those of *c*-BN and Diamond

C <sub>60</sub> phase	no. of covalently bonded neighbors	MVH, kg/mm <sup>2</sup>	<i>d</i> <sub>calcd</sub> g/cm <sup>3</sup>	<i>d</i> <sub>obs</sub> g/cm <sup>3</sup>
monomer	0	15	1.684	1.68
2D <i>Immm</i>	4	80	1.936	1.93
2D <i>R3m</i>	6	100	2.004	1.98
3D <i>Immm</i>	8	3,500	2.78	2.65
3D <i>R3</i>	12	4,500	2.81	2.61
Diamond <sup>a</sup>		10,000	3.52	
<i>c</i> -BN <sup>a</sup>		5,000		

<sup>a</sup> MVHs of diamond and *c*-BN were taken from ref 31.

of C<sub>60</sub> monomer crystals is only 15 kg/mm<sup>2</sup>, and those of 2D polymers are in a range of 80–100 kg/mm<sup>2</sup>. The MVH of the 3D *Immm* polymer with a higher density jumped to 3500 kg/mm<sup>2</sup>, and the 3D *R3* polymer had a MVH of 4500 kg/mm<sup>2</sup>, comparable with that of *c*-BN. Diamond (density, 3.5 g/cm<sup>3</sup>) has a MVH of 10000 kg/mm<sup>2</sup>.<sup>31</sup> The 3D polymers obtained in

this study were not super- or ultra-hard phases, unlike the phases reported by Blank et al.<sup>8,9</sup> They obtained polymer phases with much higher densities of 2.9–3.3 g/cm<sup>3</sup> using much higher reaction temperatures. Those phases should be partially graphitized and different from the polymers obtained in this study.

## Conclusions

Fullerene C<sub>60</sub> monomer single crystals have been transformed to the 3D polymer single crystals with an apparent symmetry of fcc under 15 GPa at 550 °C in the presence of potassium metal. Single-crystal structural analysis with the aid of ab initio MD calculations suggested that the 3D polymer should have a rhombohedral structure with the space group *R3*, where each C<sub>60</sub> unit is bonded to 12 adjacent units. Six units are bonded by [3+3] cycloaddition between adjacent pentagons in the plane perpendicular to the three-fold axis and another six units are bonded by 56/65 [2+2] cycloaddition from the bottom and top of the plane. The polymerization proceeded topochemically in a one-step compression starting from the monomer. The resulting polymer structure is very different from the 3D C<sub>60</sub> polymer with the space group *Immm* reported earlier, which was prepared by a two-step topochemical reaction. It can be concluded that the polymerization of C<sub>60</sub> molecules occur topochemically, keeping the basic arrangements of the lower dimensional parent crystal structures. This is due to the strong restriction of the molecular movements under high pressure. The 3D polymers were very hard and had MVHs comparable to that of *c*-BN.

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**Supporting Information Available:** Table of observed and calculated structure factors for 3D C<sub>60</sub> (fcc). This material is available free of charge via the Internet at <http://pubs.acs.org>.

JA076761K

(31) Andrievski, R. A. *Int. J. Refract. Met. Hard Mater.* **2001**, *19*, 447–452.