C₆₀ Photo-Polymerization using Free Electron Laser

Hiroshi Yamamoto and Nobuyuki Iwata

College of Sci. & Technol., Nihon University, Narashinodai, Funabashi-shi, Chiba 274-8501, Japan

Fax: 81-47-469-5457, e-mail: hyama@ecs.cst.nihon-u.ac.jp

This paper is the review for the authors' works on Free Electron Laser (FEL) irradiation effects aiming at syntheses of 3-dimensional C₆₀ polymers. The used pristine was 99.5% C₆₀ powder or the mixture with iodine, and also C₆₀ precipitates prepared by a liquid-liquid interfacial precipitation (LLIP) method. The pristine was set in the vacuum and was compressed in the anvil with the pressure of 600 MPa~7 GPa. The third harmonics (@400-500 nm) FEL was irradiated with a macro-pulse (@20 μ s) containing very short micro-pulses (@200 fs). The Raman Ag(2) peak of C₆₀ molecules in the vicinity of 1469 cm⁻¹ becomes broad and shifts to the lower energy side as proceeding of polymerization. Under higher pressure the larger red-shift and the increment of the half width of the Raman peak were observed. The irradiated mixture with iodine revealed the more distinctive red-shift, above 10 cm⁻¹. Also the large peak red-shift *ca.* 10cm⁻¹ was observed in the LLIP specimen probably because of highly packing of C₆₀ molecules. The obtained results suggested that the C₆₀ molecular accession and/or the photon-assisted hole-doping from iodine were decisively effective to promote photo-polymerization.

Key words: C₆₀ polymer, Free Electron Laser, liquid-liquid interfacial precipitation, Raman peak

1. INTRODUCTION

Many researches on C₆₀ polymerization have been carried out^[1], such as electron beam irradiation, high-pressure, plasma-induced excitation and so on since the polymerization of C₆₀ films had been done by a photo-transformation first^[2]. Then a carbon double bond in a hexagon of a C₆₀ cage breaks and transforms into an inter-molecular four-fold ring with a neighbor molecule. As the result the two C₆₀ molecules are combined and change into the dimer or polymers. The polymerized fullerite structures based on a "2+2 cycloaddition" bonding are observed experimentally and theoretically as one-dimensional (1D) chains namely an orthorhombic phase, and two-dimensional (2D) planes include a tetragonal and a rhombohedral phase^[3-6]. A crystal structure of pseudo-tetragonal C₆₀ polymers, which were prepared by the polymerization of C₆₀ single crystals under a pressure of 2.5 GPa at 773 K, was studied^[7]. Although the possibility of a three-dimensional (3D) polymerized phase obtained under high pressure and temperature was discussed, only a few experimental data have been reported^[8, 9].

The polymerizations proceed usually by compressing at the order of GPa or heating above thousand degree^[10], and the C₆₀ cages partially collapse under stringent pressure conditions. These polymerization processes are not suitable to supply large samples enough for applications.

The our purposes are to develop a novel photo-assisted process for C₆₀ polymerization and to synthesize 3D C₆₀ polymers by irradiating Free Electron Laser (FEL) under not so high pressure. As a pristine C₆₀ powder or the mixture with

iodine was used, and also C₆₀ precipitates prepared by a liquid-liquid interfacial precipitation (LLIP) method^[11] were studied.

From several experimental approaches^[12-16] it was suggested that accession of C₆₀ molecules and/or the hole doping was effective to promote 3D C₆₀ photo-polymerization reaction under FEL irradiation with the wavelength of *ca.* 500 nm. In this review our experimental procedures and obtained remarkable results are demonstrated.

2. EXPERIMENTAL

Figure 1 shows the schematic apparatus system for syntheses of C₆₀ polymers. The vacuum chamber was evacuated to *ca.* 10⁻⁴ Pa by a turbo molecular pump.

Fig.1 The schematic apparatus system for syntheses of C₆₀ polymers.

The pristine C₆₀ powder or mixture with iodine was set in an anvil which was placed in the vacuum and was pressed via a bellows by a hydraulic press. The pressure, typically *ca.* 600 MPa, was applied to the sample powder by the

quartz window. In another case a compressed powder disk was set on substrates and irradiated by FEL. The laser was introduced to the surfaces of the specimen by Aluminum cold mirrors which reflect only lights with the wavelength less than ca. 700 nm.

Mid-infrared FELs (@ few tens μm) have been developed and applied to many researches of laser-solid interactions since the 1980^[17]. We adopted a newly developed FEL system which generated a tunable near-infrared laser and the higher harmonics. Figure 2 shows the schematic FEL system used. The details of the FEL system appeared in the elsewhere^[18]. About 20 μs macro-pulses which included about 200 fs micro-pulses were repeated in 2 Hz. The power of the fundamental macro-pulse was ca. 0.5 mJ/pulse. The irradiation time was typically 60-180 min.

Fig. 2 The schematic FEL system used.

It was known that C_{60} thin films reveal typically large absorption peaks in 221 nm, 271 nm and 347 nm, or small absorption peaks in neighborhood 400-550 nm^[19]. These wavelengths necessary for give rise to photo-transformation. Since the FEL can supply a laser with a tunable wavelength, the fundamental wavelength was changed continuously in this work. The irradiated laser was the third harmonics of FEL with the fundamental wavelength, 1350-1500 nm. The wavelength of the harmonics mainly noticed was 450-500 nm.

The two kinds of pristine powder were used. The pure C_{60} (99.5%) was a commercial product. The C_{60} was also mixed with iodine in the mole ratio, 1:4. Here iodine was adopted for the enhancement of polymerization reactions expected from a "hole doping effect". We have noticed the hole doping effect which was demonstrated in the synthesis of a diamond from a graphite^[20]. This effect may be applicable to the polymerization of C_{60} molecules because of the resemble structure of carbon networks. Since the electron affinity of the C_{60} is high, we aimed to promote electron transfers from C_{60} to iodine atoms by the photon-excitation.

The obtained specimen was typically a disk

with a diameter of 5 mm and a height of less than 0.5 mm. For measurements it was brought with a vacuum case in order to prevent contamination from air.

On the other hand, C_{60} precipitates prepared by LLIP were also studied as the comparison with the powder pristine. The LLIP process conditions were as following. Isopropyl alcohol (20 ml) was added cautiously into the C_{60} supersaturated solution (10 ml). Then it was also left at 285 K for 7 days in the refrigerator. The precipitates were deposited on the substrate, gathered and compressed.

A crystal structures was studied by a reflective X-ray diffraction (XRD) (Rigaku RAD-C) with $\text{CuK}\alpha 1$ X-ray. The Micro-Raman spectroscope (Kaiser Corp.:Holo Lab 5000R) was used to investigate molecular vibration.

3. RESULTS AND DISCUSSION

Figure 3 shows the typical Raman peaks of the $\text{Ag}(2)$ -derived mode in the case of the compressed C_{60} powder by FEL@450 nm irradiation. The wave number of the peak of the non-irradiated compressed C_{60} was 1463 cm^{-1} of which the value was smaller by ca. 6 cm^{-1} than that of pure C_{60} powder. The FEL irradiated C_{60} revealed the peak at ca. 1460 cm^{-1} which was smaller by ca. 9 cm^{-1} compared with pure C_{60} . On the other hand, the irradiated mixture with iodine revealed the peak at 1455 cm^{-1} . The Raman peak red-shift attained to ca. 14 cm^{-1} . The half width of the peak also increased corresponding to the amount of the peak shift.

Fig.3 The typical Raman peaks of the $\text{Ag}(2)$ -derived mode: before and after FEL irradiation of the compressed pure C_{60} powder and the irradiated mixture with iodine. The wavelength of irradiated FEL was 450 nm.

Figure 4 shows the XRD patterns of the compressed C_{60} powder. After the FEL@450 nm irradiation XRD diffraction peaks became broad and the peak intensity decreased. The fcc lattice constant estimated from the XRD pattern decreased after FEL irradiation. In the case of mixture with iodine the d value of (111) planes decreased by ca. $6 \times 10^{-3}\text{ nm}$. The result revealed that molecular binding reactions took place and

the decline of the crystalline structure progressed according to the polymerization reactions induced by FEL irradiation.

Fig. 4 XRD patterns of the compressed C_{60} powder before and after FEL @450 nm irradiation.

Fig. 5 The optical microscope images and/or Raman peaks of C_{60} powder compressed by the press with grooves, (a) before and (b) after FEL@500 nm irradiation.

Figure 5 shows the optical microscope images and/or Raman peaks of C_{60} powder compressed by the press with grooves. At highly pressed area C_{60} powder was compressed by about 7 GPa. The color of the highly compressed area along the groove changed into gold from black to the naked eye as shown in the insets of Fig. 5. After FEL @500 nm irradiation the new Raman peak appeared at 1455 cm^{-1} with a large peak red-shift above 10 cm^{-1} , which suggested that the distinguished photo-polymerization reactions took place. The result was interpreted as the effect of the molecular accession caused by high pressure.

Fig. 6 The optical microscope images of the LLIP specimens from (a) toluene and (b) m-xylene.

Figure 6 shows the optical microscope images of the LLIP specimens obtained by using toluene and m-xylene. The needle-like precipitates with comparatively long size grew on all over the substrate surface in toluene solution. In the case of m-xylene solution precipitates obtained were also needle-like, but their length was short, less than about $100\mu\text{m}$.

The structures of the LLIP specimens were analyzed by XRD pattern and compared with that of the compressed C_{60} powder. The d-space values corresponding to the fcc phase are summarized in Table 1.

Table 1. The fcc lattice d-space of the typical specimens. The upper and the lower value in the column is the result before and after FEL@500 nm irradiation, respectively.

fcc plane	LLIP C_{60} @toluen	LLIP C_{60} @m-xylene	C_{60} Powder compressed by 600 MPa
(111)	0.83 nm 0.81 nm	0.82 nm 0.81 nm	0.83 nm 0.82 nm
(220)	0.51 nm 0.50 nm	0.50 nm 0.50 nm	0.51 nm 0.51 nm
(311)	0.44 nm 0.43 nm	0.43 nm 0.43 nm	0.44 nm 0.44 nm

The typical XRD patterns of the toluene and m-xylene LLIP specimen before and after FEL@500 nm irradiation are shown in Figs. 7 and 8, respectively. As the general tendency the average intermolecular distance of the LLIP specimen was smaller than that of C_{60} powder pressed under 600 MPa before FEL irradiation. By FEL irradiation the lattice constant of the fcc phase obviously decreased. The higher dense of C_{60} packing was achieved by using the LLIP method probably because of large internal compressive stress in the precipitating process via liquid-liquid interfacial region. Especially the m-xylene LLIP specimen revealed a large halo pattern, which indicated the existence of large crystalline distortion. M. Sathish et al.^[21] reported that the LLIP precipitate showed the tendency to form the hcp phase in the solution though its phase was not so stable in air. The result of m-xylene specimen was the case. The similar mechanism took place and additional

diffraction peaks assigned to the hcp phase appeared in Figs. 7 and 8. The reason why the intermolecular distortion of the precipitate from toluene was comparatively smaller than that from m-xylene was not clear, but which may be related to the number of hydroxyl terminals.

After FEL irradiation the halo diffraction pattern appeared also in the both LLIP specimens and the lattice space became almost same. The polymerized bond length between C₆₀ molecules is shorter by about 10% than the average intermolecular length of pure C₆₀. Since the average lattice constants expand in amorphous structure as a general argument, the polymeric C₆₀ bonds result in expanding distortion of the crystal structure as proceeding polymerization. The similar discussion appeared in elsewhere^[1]. So the conflicting two mechanisms took place in the polymerization process. The obvious decrease in the lattice space observed is understood from the reason why a polymerization bonding force is stronger than an expanding force caused from a structural distortion.

(a) Before FEL irradiation

(b) After FEL@500 nm irradiation

Fig. 7 XRD pattern of LLIP C₆₀ precipitate from toluene solution.

The Raman spectra of the toluene and m-xylene LLIP specimens are shown in Figs. 9 and 10, comparing with the each result before and after FEL irradiation, respectively. The toluene LLIP specimen showed the main peak at 1469 cm⁻¹ and the red-shifted 1454 cm⁻¹ peak which indicated progress of photo-polymerization after FEL@500 nm irradiation. On the other hand, the main peak shifted to *ca.* 1463 cm⁻¹ in the m-xylene

(a) Before FEL@500 nm irradiation

(b) After FEL@500 nm irradiation

Fig. 8 XRD pattern of LLIP C₆₀ precipitate from m-xylene solution: closed circles are hcp peaks.

Fig. 9 Raman spectra of LLIP C₆₀ precipitate from toluene solution.

Fig. 10 Raman spectra of LLIP C₆₀ precipitate from m-xylene solution.

LLIP specimen. Then characteristic peak-tails in the lower energy side were also observed, which suggested the strongly promoted photo-polymerization. So the polymerization reactions took place more effectively in the m-xylene specimen rather than in the toluene specimen. It was thought that the difference of the polymerization was caused by the different crystalline structure of the each obtained precipitate as discussed in the results of XRD. These results suggested that the more photo-polymerization was promoted as C₆₀ intermolecular distance decreasing.

3. CONCLUSION

The FEL with the wavelength of typically 450 nm or 500 nm was irradiated to the surfaces of compressed C₆₀ powder and LLIP C₆₀. The Raman peak of the Ag(2)-derived mode clearly shifted to the lower energy side and/or the half width of the peak became broad. These characteristic changes were well interpreted as the results of the photo-polymerization. Furthermore the average distance between C₆₀ molecules decreased after FEL irradiation. These distinct changes of the structure suggested that various kinds of inter-molecular combinations took place. It was also found that the intermolecular distances decreased and the polymerization was promoted especially in the LLIP C₆₀. The LLIP method was useful to get pristine materials for the synthesis of C₆₀ polymers. Conclusively the 3D polymerization of C₆₀ was effectively promoted by the FEL @450-500 nm irradiation under the condition of the C₆₀ molecular accession and/or the effect of

the photon-assisted hole-doping from iodine to C₆₀ molecules. The detailed characterization of the obtained specimens is a subsequent work.

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