Photopolymerization of C$_{60}$ Crystal Synthesized from Organic Solution

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Abstract. We have been developing a novel process to synthesize C$_{60}$ polymers as superior functional materials. Polymerization reactions of C$_{60}$ precipitated from organic solution were investigated under Free Electron Laser (FEL) irradiation. The two processes: a liquid-liquid interfacial precipitation (LLIP) method and an evaporation technique from supersaturated solution, were studied with a respect of crystal structure and/or Raman spectrum for the precipitates before and after FEL irradiation. It was found that the photopolymerization reaction took place effectively in the LLIP precipitate because of its highly packed molecular crystal structure.

1. Introduction
Since C$_{60}$ polymers were found first by phototransformation [1], many studies have been done for many C$_{60}$ polymerization processes. It can be expected that C$_{60}$ polymers become marvelous super-materials accompanying with very low-density, flexibility, and ultra-hardness etc. We have studied photo-assisted polymerization processes for synthesis of 3-dimensional polymers from pressed C$_{60}$ powder by irradiation of Free Electron Laser (FEL) which has the features of wavelength variability and extremely sharp pulse width [2-5]. The specimen after FEL irradiation revealed a characteristic red-shift of Raman $A_{1g}(2)$ peak. The obtained results suggested that FEL irradiation with wavelength of 400–500nm was effective for photo-polymerization reactions and/or smaller C$_{60}$ intermolecular distance was more proper to promote polymerization reactions.

The purposes of this work are to study the crystal structure of C$_{60}$ precipitates grown by a liquid-liquid interfacial precipitation (LLIP) method [6] and an evaporation technique from supersaturated solution using organic solvents: toluene and m-xylene, and to investigate FEL irradiation effects for the obtained precipitates with a respect of crystal structure and/or Raman spectrum. The result of the precipitates is discussed compared with that of photopolymers synthesized from C$_{60}$ pressed powder.

2. Experimental
Fig. 1 shows the schematic process of the evaporation technique from supersaturated solution. Commercial C$_{60}$ powder (99.5%) was dissolved to organic solution with 50ml test tube (inner diameter 35xheight 115mm, surface area 491mm$^2$). At first C$_{60}$ was dissolved into toluene or m-xylene. After an ultrasonic dispersion was done for 5 minutes to prepare saturated solution, C$_{60}$ (0.1g) was putted into the saturated solution (10ml) to make supersaturated solution. Then SiO$_2$ substrates attached to
fluorine strings were soaked into the supersaturated solution and were preserved at 12ºC in a refrigerator to suppress evaporation speed. The substrates appeared out of the solution after about 7 days.

The LLIP process conditions were as following. Isopropyl alcohol (20ml) was added cautiously into the C60 supersaturated solution (10ml). Then it was also left at 12 ºC for 7 days in the refrigerator.

The used FEL has the following features: a variable wavelength from 800nm to 3000nm as a fundamental and a macro-pulse (@20μs) containing very short micro-pulses (several hundreds fs) [7]. As reported 400–500 nm-FEL irradiation effectively promoted C60 polymerization reactions. The 500nm FEL, which was the 3rd harmonics of fundamental 1500nm FEL, was irradiated through a band pass filter for 60 min and pressure was 10⁻⁴ Pa. The power of the fundamental FEL was ca. 3.0 mJ/pulse cm².

The crystal structure of the obtained specimens was analyzed by X-ray diffraction (XRD) (Rigaku International Corp.: RAD-C). The Micro-Raman spectroscopy (Kaiser Corp.: Holo Lab 5000R) was used to investigate molecular vibrations. The Raman A_g(2) mode of C60 molecules in the vicinity of 1469cm⁻¹ is defined as contracting vibration of pentagon rings. It is known that the A_g(2) pentagonal pinch mode peak is broaden and shifts to the lower-energy side; e.g. the photo-polymerization results in a peak red-shift by approximately 10cm⁻¹. Then the A_g(2)-derived mode has been therefore noted as an index of the polymerization reaction progress.[8]

3. Results and discussion
Fig. 2 shows the optical microscope images of the evaporation method specimens grown from supersaturated toluene solution. Precipitates with the rectangular shape grew on the substrate which was set up at the angle of 60°. The shape of the precipitate was plate-like rather than needle-like probably because blemishes or scratches became nuclei of growth. The precipitates hardly grew on the substrates set up at the angles of 0° and 30° and short needle-like precipitates on the substrate at the angle of 90°. The contact area between the substrate and solution was an important factor for the growth of precipitates during evaporation. This is the reason why the shape or the amount of the precipitates drastically changed according to the substrate set up angle. Fig. 3 shows the optical microscope images of the evaporation method specimens grown from supersaturated m-xylene solution. Characteristic needle-like precipitates were obtained, not depending on the substrate set up angle. Especially very long precipitates grew up at the angle of 60°. It should be noticed that the
crystal growth using the m-xylene solution took place preferably with a hexagonal close-packed (hcp) phase and the obtained shape of the precipitate became needle-like as the result [9].

Fig. 2. Optical microscope images of the evaporation method specimens grown from supersaturated toluene solution on the substrate set up angle of 0° (a), 30° (b), 60° (c) and 90° (d).

Fig. 3. Optical microscope images of the evaporation method specimens grown from supersaturated m-xylene solution on the substrate set up angle of 0° (a), 30° (b), 60° (c) and 90°(d).

Fig. 4 shows the optical microscope images of the LLIP method specimens obtained by using toluene and m-xylene. The needle-like precipitates with comparatively long size grew on all over surfaces of the substrate in toluene solution. In the case of m-xylene solution obtained precipitates were also needle-like, but their length was short, at most about 100μm. Since the amount of C\textsubscript{60} dissolved for toluene was larger than that for m-xylene, comparatively long precipitates of the maximum of about 10mm and/or much precipitates were grown up from m-xylene solution.

Table 1. The fcc lattice d-space value of the typical samples. The upper and the lower values are the result before and after FEL irradiation, respectively.

| fcc plane | Evaporation of supersaturated solution | LLIP method | C\textsubscript{60} powder |
|-----------|---------------------------------------|-------------|--------------------------|
|           | Toluene | m-xylene | toluene | m-xylene | - |
| d-space of the lattice plane [Å] |
| (111)     | 8.3     | 8.3      | 8.3     | 8.2      | 8.3 |
| (220)     | 5.1     | 5.1      | 5.1     | 5.0      | 5.1 |
| (311)     | 4.4     | 4.4      | 4.4     | 4.3      | 4.4 |

Fig. 4. Optical microscope images of the LLIP method specimens obtained by using toluene (a) and m-xylene (b).

The structures of the specimens obtained were analyzed from XRD patterns. The d-space values corresponding to the face centered-cubic (fcc) phase are summarized in Table 1. The typical XRD pattern of the toluene and m-xylene LLIP specimen before and after FEL irradiation is shown in Figs. 5, 6 and Figs. 7, 8, respectively. As the general tendency the intermolecular distances of the precipitates from organic solution were smaller than those of C\textsubscript{60} powder pressed under 600 MPa. In the both evaporation method specimens from the supersaturated toluene and m-xylene, the intermolecular distance changed not so much by FEL irradiation. On the other hand, the intermolecular distance of the LLIP specimens before irradiation was smaller than that of C\textsubscript{60} powder. And the lattice constants of the fcc phase obviously decreased by FEL irradiation. The higher dense
C_{60} packing was attained 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.[9] 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 in the specimens and additional diffraction peaks assigned to the hcp phase appeared in Figs. 6 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 C_{60} molecules is shorter by about 10% than the average intermolecular length of a monomer state. Since the average lattice constants expand in amorphous structure as a general argument, the polymeric C_{60} bonds result in the expanding distortion of the crystal structure as proceeding polymerization. The similar discussion appeared in elsewhere[8]. So the conflicting two mechanisms worked in the polymerization process. It was understood that the large decrease in the lattice space observed may be caused by polymerized bonding effects were so large.

Fig. 5. XRD pattern of the toluene LLIP specimen before FEL irradiation. The index appeared in the figure means the each planes from the fcc phase.

Fig. 6. XRD pattern of the m-xylene LLIP specimen before FEL irradiation. The index appeared in the figure means the each planes from the fcc phase and the dots correspond to the diffraction peaks assigned as the hcp phase.
Fig. 7. XRD pattern of the toluene LLIP specimen after FEL irradiation. The index appeared in the figure means the each planes from the fcc phase.

Fig. 8. XRD pattern of the m-xylene LLIP specimen after FEL irradiation. The index appeared in the figure means the each planes from the fcc phase and the dots correspond to the diffraction peaks assigned as the hcp phase.

Fig. 9. Raman spectrum of the toluene LLIP specimen before and after FEL irradiation. The dotted lines mean the decomposed peaks.

Fig. 10. Raman spectrum of the m-xylene LLIP specimen before and after FEL irradiation. The dotted lines mean the decomposed peaks.

The Raman spectra of the pressed powder and/or the toluene and m-xylene LLIP specimens are shown in Figs. 9-10, comparing with the each result before and after FEL irradiation. The peak at 1469 cm\(^{-1}\) identified as \(\text{A}_g(2)\)-derived mode of \(\text{C}_{60}\) was confirmed in all specimens. In the case of the pressed powder obvious red-shift of \(\text{A}_g(2)\) peak was not observed even after FEL irradiation because not so high pressure, 600 MPa resulted in small changes of intermolecular distances. The main peak at 1469 cm\(^{-1}\) and the small red-shifted 1454 cm\(^{-1}\) peak, which indicated partial strong photo-polymerization, were observed in the toluene LLIP specimen after FEL irradiation. On the other hand, the main peak shifted to ca. 1463 cm\(^{-1}\) in the m-xylene LLIP specimen. Furthermore it revealed the characteristic peak tails in the lower energy side, which suggested the 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 each obtained precipitate as discussed in the results of XRD. These results strongly suggested that the photo-polymerization was promoted as C_{60} intermolecular distances decreased.

4. Conclusion
The C_{60} precipitates were grown from organic solution by two methods: the evaporation from supersaturated solution and the LLIP method. The polymerization reaction by FEL irradiation was investigated by the crystal structure and/or Raman spectroscopic analysis. It was found that the intermolecular distances decreased and the polymerization was promoted especially in the LLIP specimens. Conclusively the LLIP method was useful to get raw materials for the effective synthesis of C_{60} polymers.

Acknowledgments
The authors are grateful for the financial support of the Grant-in-Aid for the Futaba Foundation. The authors are also grateful for the financial support of an Interdisciplinary General Joint Research Grant (Nihon University). This work was supported by the Ministry of Education, Culture, Sports, Science and Technology through a Scientific Grant-In-Aid (No. 20360145).

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