

Phototransformed C₆₀ Powder and Film Synthesized in Toluene, Benzene and Carbon Disulfide Solvents

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トルエン、ベンゼン及び二硫化炭素溶剤中での光化学反応 C₆₀ 粉末及び薄膜の合成

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C₆₀ dissolved in toluene, benzene and carbon disulfide respectively, yielded a brown precipitate upon exposure to ultraviolet radiation. A thin film was deposited on a silicon substrate when dipped in each of the solutions. Further examination of this deposit revealed: (1) the substance to be amorphous by TEM observation; (2) No oxygen was detected by Auger electron spectroscopy; (3) Absorption peaks produced by FT-IR differed from those of pristine C₆₀, solid-state photopolymerized C₆₀ and high-pressure polymerized C₆₀; (4) The same substance was obtained for each of the three solvents; (5) The substance obtained is presumably a new photopolymerized C₆₀ solid.

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1. Introduction

Rao et al. were first to report on the polymerization of C₆₀ by irradiation.¹⁾ Iwasa et al. synthesized bulk polymerized C₆₀ using a high-pressure technique.²⁾ The existence of C₆₀ polymer is well documented.³⁾⁻⁸⁾ These studies were carried out using solid specimens. However, very few attempts have been made to polymerize C₆₀ in solution.⁹⁾

In this study, C₆₀ solutions were irradiated with ultraviolet (UV) light following after the study of Rao et al. In each case a solid powder or film precipitated. We propose that this substance was photopolymerized. Transmission electron microscopy (TEM), Fourier transform infrared spectroscopy (FT-IR) and Auger electron spectroscopy (AES) measurements were taken for the precipitate from each solution. Results were compared with pristine C₆₀ as well as other C₆₀ polymers synthesized by solid-state photoreaction, and high-pressure techniques.

2. Experimental procedure

(1) C₆₀ powder (>99.98%) was dissolved in the three solvents toluene (>99.7%), benzene (>99.7%) and CS₂ (>99.9%), to a concentration of 0.5 g/l. A mercury-discharge lamp (100 W) was used as the UV-light source. Irradiation was carried out for 20 h, maintaining the temperature of the solutions between 26 and 29°C. The color of each solution was initially purple, later turning to wine red (Fig. 1 (a)). Pieces of Si wafer were suspended in each solution, to provide a surface for the precipitation of the photoreacted products (Fig. 1 (b)). The deposited films in toluene, benzene and CS₂ will be referred to as TF, BF and CF, respectively. Solid products were filtered from the irradiated solutions. The resultant brown powder obtained from each of the solutions will likewise be referred to as TP, BP and CP.

(2) TP and TF were alternately washed with pure toluene and acetone several times to remove unreacted C₆₀. BP/BF and CP/CF were similarly washed with benzene/acetone, and CS₂/acetone, respectively. It should be noted

that a considerable amount of solid was produced from the photoreaction in CS₂, and that this solid was soluble in alkali solution.¹⁰⁾ Hence, CP and CF were additionally washed with KOH (500 g/l) and pure water to remove as much of the CS₂ solid as possible. The preparation of purified CF was not successful because most of deposited film exfoliated-

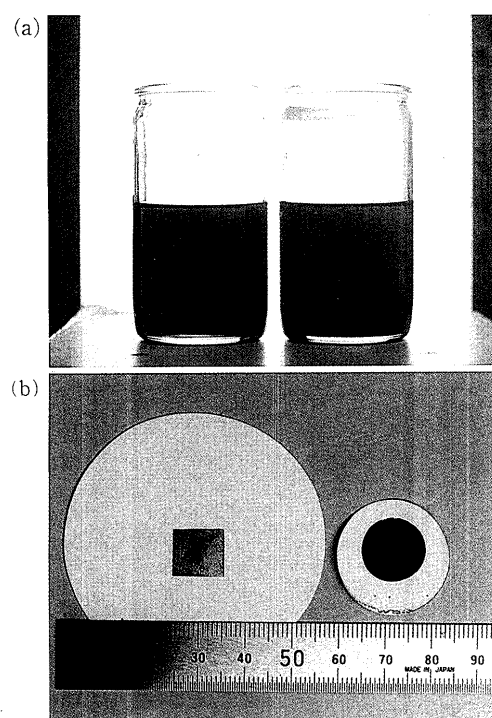


Fig. 1. (a) Change of color in C₆₀ solution (solvent: toluene). Left-side: initial solution, right-side: after the irradiation for 20 hours. (b) Resulting powder obtained by filtration (right-side) and a thin film precipitated on Si surface (left-side).

ed from the substrate during washing.

(3) TEM observations were taken for all the specimens that were mounted on commercially available microgrids with a Hitachi H-9000 electron microscope accelerated at 300 kV. AES was performed for TF, using a Perkin Elmer PHI-650 operated at 3 kV and 50 nA, where argon sputtering before measurement was not employed so as to prevent the deterioration or decomposition of the deposited films by ion bombardment. Infrared spectra were measured by a Perkin Elmer SPECTRA2000 for TP, BP and CP incorporated in KBr disks.

3. Results

3.1 Transmission electron microscopy

Figures 2(a) and (b) show low-magnification images of TP and TF, respectively. The former shows the aggregation of many round particles, and the latter, film containing the particles. While the film is being deposited, particles may be taken up by the film.

The morphology of BP and BF were found to be essentially the same as TP and TF, respectively. CP was also an aggregation, but the shape of the particles was quite irregular.

The transmission electron diffraction (TED) pattern and a high-resolution image of TP are shown in Figs. 3(a) and (b).

(1) The halo pattern in Fig. 3(a) indicates the lack of long range order molecules, or the amorphous structure in the substance. A broad ring, R_1 exists about at $2 \text{ nm}^{-1} = (0.5 \text{ nm})^{-1}$. We believe that there is a ring inside of it (marked R_2), but it is not clear whether the R_2 is a diffracted halo ring from the specimen or only the tail of the main beam spot.

(2) TP, BP, BF and CP also showed halo patterns, where two rings R_1 and R_2 were observed. Although the existence of the latter rings was similarly in doubt, the former was certainly located at $\sim (0.5 \text{ nm})^{-1}$. Therefore, the TED patterns of the five specimens were identical. This suggests that the aggregation of the particles and also the film were of the same substance and that the synthesis of the substance was not solvent dependent.

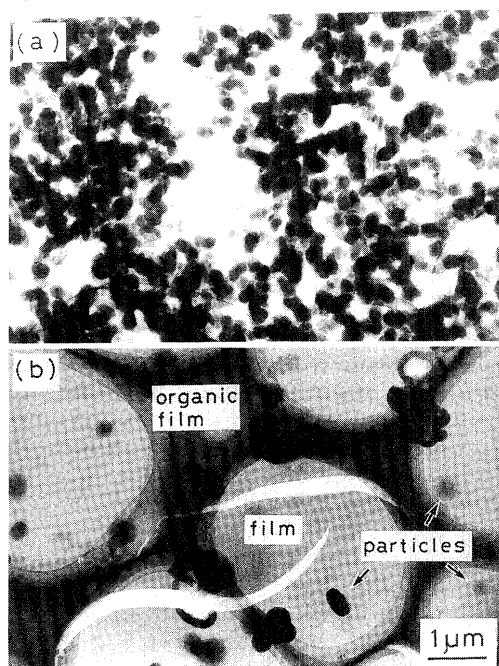


Fig. 2. TEM bright-field images of (a) TP and (b) TF. Specimens are supported on organic films full of holes.

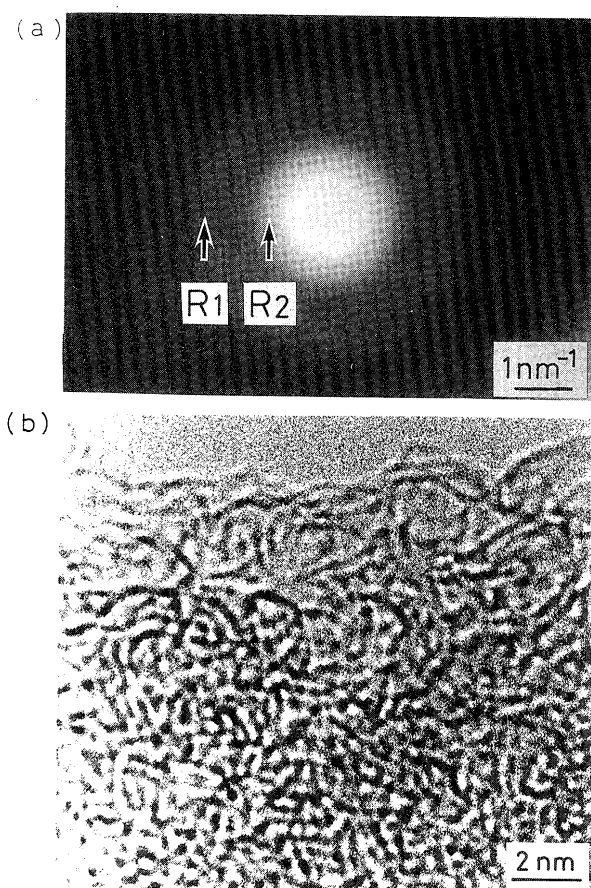


Fig. 3. (a) TED pattern and (b) high-resolution image of TP.

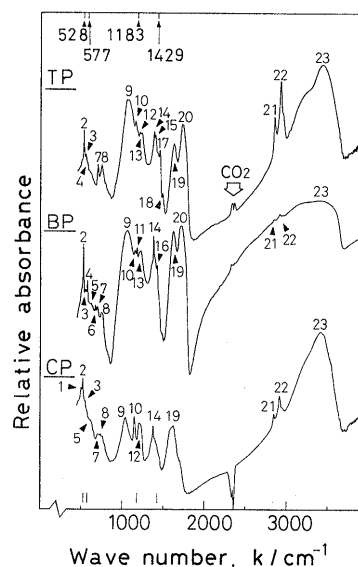


Fig. 4. FT-IR absorption spectra of TP, BP and CP.

(3) One of the high-resolution images is shown in Fig. 3(b). No lattice fringes were detected even across a region approximately 3 nm wide. The images for all the specimens are highly granular in pattern.

3.2 Fourier transform infrared spectroscopy

FT-IR spectra of TP, BP and CP are shown in Fig. 4. Their peaks are compared with other C_{60} polymers in Table 1.

(1) While the peak positions were almost identical for TP, BP and CP, the magnitudes of the peaks were not. This

Table 1. IR Absorption Peaks of C₆₀s. Values of Pristine, Solid-state Photopolymerized and High-Pressure Polymerized C₆₀s are Taken from Refs. 11), 1) and 8), Respectively. The Suffixes vs, s, m, w and b Characterize the Intensity of the Peaks as Very Strong, Strong, Medium, Weak and Broad, Respectively

Present study			Pristine	C ₆₀ polymers	
TP	BP	CP		photo-polymerized	high-pressure
		1. 506		484m	508s
2. 527	2. 526	2. 526	528vs	526vs	525s
3. 552	3. 553	3. 552		550m	549s
4. 574	4. 576		577s	569m	
	5. 621	5. 623		616w	607m
	6. 674				
7. 700	7. 698	7. 710		709m	
				727w	717s
8. 748	8. 748	8. 743		743w	741vs
				761w	761s
				769w	
				779w	776w
				796m	
9. 1049	9. 1062	9. 1046			
10. 1156	10. 1156	10. 1156	1183s	1183w	
	11. 1182				
12. 1209		12. 1215		1229w	1205w
13. 1233	13. 1228				
14. 1385	14. 1385	14. 1385			1382w
15. 1399					
	16. 1427		1429s	1424m	
17. 1454				1460w	
18. 1490					
19. 1627	19. 1625	19. 1629			1621w
20. 1724	20. 1721				
21. 2852	21. 2851	21. 2851			
22. 2923	22. 2921	22. 2921			
23. 3432	23. 3400	23. 3423			3438b

indicates that the same substance was obtained with toluene, benzene and CS₂.

(2) Absorption peaks were reported to be at 528, 577, 1183 and 1429 cm⁻¹ in pristine C₆₀.¹¹⁾ A very sharp peak was found at 526–527 cm⁻¹ in TP, BP and CP. Peaks at 577, 1183 and 1429 cm⁻¹, however, were almost undetectable in TP and CP, and weak in BP. Hence, the peak at 526–527 cm⁻¹ can be attributed not to unreacted C₆₀ but to the amorphous substance.

(3) For C₆₀ polymers prepared by solid-state photoreaction and high-pressure methods, it is characteristic that many new peaks appear in the range 700–800 cm⁻¹.^{1),2)} This is in contrast to the above substance, for which new peaks appeared at 1000–1700 cm⁻¹.

From the results of FT-IR, we can assert the following: (a) The four peaks in pristine C₆₀ correspond to intramolecular vibration modes. Many more peaks were exhibited by the substance. This indicates a lowering in the degree of icosahedron symmetry in the C₆₀ molecule, and that new intramolecular bonding (or most likely photopolymerization) occurred. (b) The nature of the intermolecular bonding differed from that of the other C₆₀ polymers.

3.3 Auger electron spectroscopy

The AES measurement of TF identified the three elements C, Si and O. The Si signal can be attributed to the silicon substrate. The very weak signal of O may be due to the contamination by O₂ or CO₂ gases adsorbed on the film surface. The film itself was pure carbon. It should be noted that interaction between C₆₀ and O is much enhanced under exposure to light,^{6),12)} and that oxygen diffusion occurs in the solid state.^{4),5)} In the present case, however, since oxygen is almost insoluble in toluene, an oxygen-free film could be obtained.

4. Discussion

(1) From TEM and AES, the substance was character-

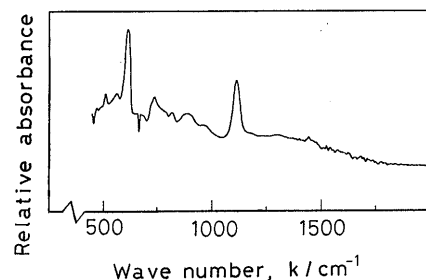


Fig. 5. FT-IR absorption spectra of an amorphous carbon film deposited by arc-discharge on Si substrate.

ized as amorphous and composed of carbon. Initially, it might be considered that C₆₀ molecules were decomposed by the UV irradiation and that amorphous carbon was produced by this photolysis.

However, for comparison, we prepared an amorphous carbon film by conventional arc-discharge method and obtained the following: (a) TED showed halo patterning, but there was no ring at $\sim(0.5 \text{ nm})^{-1}$. Halo rings of the amorphous carbon were much larger (about $(0.21 \text{ nm})^{-1}$ and $(0.11 \text{ nm})^{-1}$). (b) Two strong peaks were found at 612 and 1108 cm⁻¹ in the FT-IR measurement of the amorphous carbon (Fig. 5). The absorption peaks could not be assigned, but were clearly distinct from those of the present substance as shown in Fig. 4.

From these comparisons, we consider it to be phototransformed C₆₀ rather than the photolysis product of decomposed fragments of C₆₀.

(2) To show how solutions were more reactive for the phototransformation than solid-state, we prepared a C₆₀ solid film on Si substrate by evaporation, and irradiated it for 40 hours in air. No trace of phototransformation was evident in X-ray diffraction and FT-IR measurements.

When the C₆₀ solutions were exposed for several hours, however, readily apparent transformations were found as previously described. Two factors may account for the difference between solid and solution; (a) The photopolymerization of C₆₀ is disturbed by the presence of oxygen in the solid state.^{3),4)} This influence is greatly reduced in solution, because oxygen is almost insoluble in the three chosen solvents. (b) The interaction between C₆₀ and solvent molecules enhances the reactivity of C₆₀.¹³⁾ Thus, the reaction between C₆₀ molecules in solution is significantly promoted by the assistance of UV light.¹⁴⁾

(3) It has been reported that the bonding is of the [2+2] cyclo-additive type for all C₆₀ polymerization.^{1),2)} The FT-IR measurements, however, suggest a different case for the present substance.

This observation is corroborated by other experimental evidence. Polymeric C₆₀s synthesized by solid-state photoreaction and high-pressure techniques are not very stable and revert to the pristine C₆₀ phase during heat treatment.^{2),5),8)} The present substance, however, remained unchanged even after annealing at 1000°C for 3h in a vacuum of $\sim 10^{-3}$ Pa.

These results indicate that the linkage between C₆₀ molecules in this substance is different from that of the other C₆₀ polymers, and that it is chemically very strong. It is, however, hard to classify the bonding from the present FT-IR measurements only. Further investigation is in progress to exploit techniques in X-ray photoelectron spectroscopy and nuclear magnetic resonance.

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