How Many [2 + 2] Four-Membered Rings Are Formed on a C_{60} Molecule when Photopolymerization Is Saturated?

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The saturation number of the [2 + 2] four-membered cross-link between adjacent C_{60} molecules in a photopolymerized C_{60} film has been determined using the intensity of the C 1s shake-up satellite, which originates from the π-π^* transition of π electrons of C_{60}, by x-ray photoelectron spectroscopy. It was found that six [2 + 2] rings were formed on a C_{60} molecule when polymerization was saturated. A possible configuration of the C_{60} polymer was postulated on the basis of the saturation number and the structure of a pristine C_{60} film. [S0031-9007(97)04330-5]

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Since the first report on C_{60} photopolymerization by Rao *et al.* [1], there have been many reports on C_{60} polymers produced by various methods such as (1) photoirradiation, (2) high pressure and high temperature, and (3) alkali-metal doping [2]. In the polymers formed by methods (1) and (2), it is well established that C_{60} molecules are bound to each other via the [2 + 2] cycloadditional four-membered ring structure shown in Fig. 1 [3,4]. In this figure, the designed atoms represent those including intermolecular C—C bonds. These carbon atoms form C═C double bonds between hexagons in a C_{60} cage before photopolymerization.

In the study of the photopolymerized C_{60} film, it is of great interest to determine how many [2 + 2] rings can be formed on a C_{60} molecule when photopolymerization is saturated. However, no attempt to examine this subject has been made so far. Wang *et al.* discussed the kinetics of the C_{60} photopolymerization reaction by examining the time dependence of the relative intensity ratio (I_{1459}/I_{1469}) of the $A_g(2)$ pentagonal pinch mode upon photoirradiation, and estimated an activation energy of 1.25 eV using Raman spectroscopy [5,6]. However, it is difficult to estimate the number of [2 + 2] rings, because the molecular absorption coefficient of the mode (I_{1459}) associated with the photopolymerized phase is still unknown. In addition, the molecular absorption coefficient of the Raman-active mode of 118 cm^{-1} arising from the four-membered ring is not known. Consequently, Raman spectroscopy cannot be used to estimate the number of [2 + 2] four-membered rings formed on a C_{60} molecule in the photopolymerized C_{60} film at this stage. For a similar reason, infrared spectroscopy is also not suitable for such an estimation.

In a recent paper [7], we successfully demonstrated that the intensity of the C 1s shake-up satellite is a good indicator for estimating the average degree of photopolymerization between adjacent C_{60} molecules. However, we could not recognize the saturation number of the [2 + 2] rings formed on a C_{60} molecule in that paper, since this reaction was unsaturated even for 200 h of photoirradiation of the pristine C_{60} film. In this Letter, we evaluate the saturation number of the [2 + 2] rings formed on a C_{60} molecule, by examining the change in the intensity of the C 1s shake-up satellite of the C_{60} film irradiated for more than 200 h.

C_{60} films were formed on a gold-coated (about 1 μm in thickness) stainless steel substrate by sublimation at 400 °C for 90 min in a stainless steel vacuum chamber [8]. During the deposition of C_{60} molecules, the substrate was heated to and maintained at 100 °C in order to obtain good crystallinity (fcc structure) of the C_{60} film [9]. The thickness of the C_{60} film thus formed was about 100 nm. After the C_{60} film was deposited on the substrate, this sample was taken out of the vacuum chamber and exposed to air prior to introducing it into an x-ray photoemission spectroscopy (XPS) apparatus (VG: ESCALAB Mk-II) equipped with an ultrahigh-vacuum (UHV) system through a liquid N_2 trap (the base pressure was 5×10^{-10} Torr), an x-ray source (Mg$K\alpha = 1253.6$ eV, 300 W), a high-resolution cylindrical energy analyzer ($\Delta E = 10$ meV), and a five-axis sample manipulator (X, Y, Z, rotation, tilt). XPS data analyses such as smoothing, background removal, and peak fitting (deconvolution of unresolved lines) were carried out using a Fisons analysis software package (ECLIPS). The binding energy of the Au4$f_{7/2}$ transition (83.7 eV) was used as a reference. A 500 W mercury (Hg) lamp (Ushio Electric Co.: Model HB-50110AA) was used as a light source

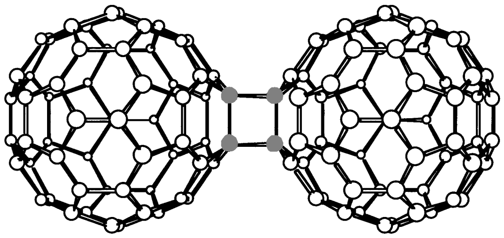


FIG. 1. C_{60} dimer structure formed via a [2 + 2] cycloadditional four-membered ring. The designed atoms are those including intermolecular C—C bonds.

for photopolymerization. Since infrared light from the lamp causes an undesirable rise in substrate temperature, the IR light was removed using a colored glass filter (Toshiba: IR-25S). Thus only UV-visible light from the Hg lamp (emission lines in the range of 2–4 eV, and the power density = 0.15–0.20 W/cm^2) was used. The C_{60} film was irradiated with the focused UV–visible light beam through a sapphire optical window (40 mm in diameter and 4 mm thick) at room temperature. The details of XPS experiments have been described in Ref. [7].

XPS provides information on the surface layers of materials. We estimate the escape depth of the C 1*s* photoelectrons, using a modified Bethe equation derived by Tamura *et al.* [10], to be about 18 Å. Since C_{60} film forms a fcc structure with a lattice constant of 14.17 Å [11] at room temperature and the mean ball diameter of a C_{60} molecule is 7.10 Å [12], the present XPS spectra provide information from more than one unit cell below the film surface. Although a C_{60} film was exposed to air for a few hours prior to measuring its XPS spectra, O_2 or H_2O was removed from the surface layers (18 Å) after 20 h of photoirradiation. Since no peak corresponding to O 1*s* was observed in the C_{60} film after further irradiation, the effect of these molecules on C_{60} polymerization was negligible [7].

Figure 2 shows the average number of [2 + 2] cycloadditional four-membered rings formed on a C_{60} molecule as a function of irradiation time for a photopolymerized C_{60} film. When S_0 and S_t represent the intensity of the C 1*s* shake-up satellite before and after t hours of photoirradiation, respectively, the number of π electrons on a C_{60} molecule after t hours of photoirradiation can be evaluated by calculating $60 \times S_t/S_0$ (S_0 corresponds to the C 1*s* shake-up satellite intensity due to 60 π electrons). In addition, two π electrons of a C_{60} molecule are necessary to form one [2 + 2] cycloadditional four-membered ring between adjacent C_{60} molecules, as shown in Fig. 1. Thus we can estimate the average number of [2 + 2] rings formed on a C_{60} molecule from the intensity of the C 1*s* shake-up. The details of this procedure have also been described in Ref. [7]. Figure 2 shows that the average number of photopolymerized C_{60} molecules increased with irradiation time and photopolymerization was saturated after about a 350-h photoirradiation. From the result in Fig. 2, the saturation number of the [2 + 2] four-membered rings formed on a C_{60} molecule is estimated to be approximately 6.

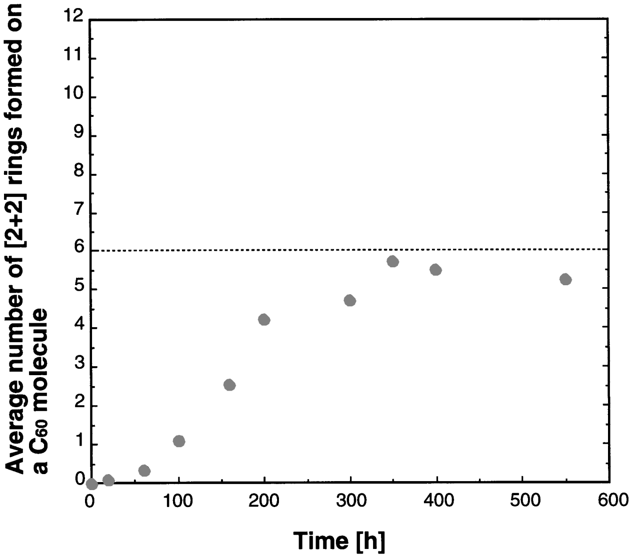
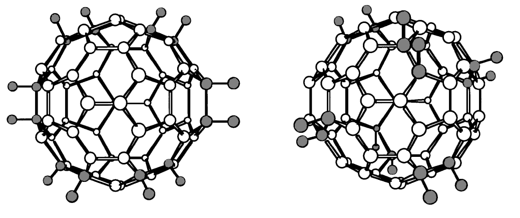


FIG. 2. The average number of [2 + 2] four-membered rings formed on a C_{60} molecule as a function of irradiation time.

What does this value imply? We next consider a physical picture to explain the saturation value. Since the present experiments were carried out at room temperature, the pristine C_{60} film has fcc crystal structure [13]. Based on the fact that photopolymerization proceeds via the [2 + 2] cycloadditional four-membered ring formation between adjacent C_{60} molecules (see Fig. 1) [3], two possible configurations can be considered. As shown in Fig. 3, one possible configuration is the 2D-rhombohedral structure, and the other one is the 3D-octahedral structure. In these figures, the designed atoms are those with intermolecular C—C bonds. Another configuration with six [2 + 2] rings per C_{60} molecule is not considered with respect to the steric size of a C_{60} molecule. The information on the crystal growth of the C_{60} film is useful for speculating the C_{60} polymer configuration. In the present study, the pristine C_{60} film was deposited on a Au-coated stainless steel substrate. Previous work [14–20] on C_{60} film growth by scanning tunneling microscopy (STM) has shown C_{60} to exhibit a preference for the formation of close-packed hexagonal overlayers, (111) fcc structure, on gold surfaces such as (111) [14,15], (110) [16,17], and (001) [18], as well as on polycrystalline substrates [19,20]. Although the surface structure of the present C_{60} film was not observed using STM, it can be assumed, based on the previously reported results [14–20], that the present C_{60} film also has the (111) fcc structure.



(a) 2D-Rhombohedral (b) 3D-Octahedral

FIG. 3. Possible configurations of C_{60} polymers with six [2 + 2] cycloadditional four-membered rings formed on a C_{60} molecule: (a) 2D-rhombohedral and (b) 3D-octahedral configurations. The designed atoms are those including intermolecular C—C bonds.

On the basis of the above results, the 2D-rhombohedral arrangement of C_{60} polymers shown in Fig. 3(a) is energetically preferable over the 3D-octahedral arrangement in the photopolymerized C_{60} film. If the C_{60} polymer forms the 3D-octahedral configuration, many C_{60} molecules in bulk must be displaced so as to change from the fcc to the bcc structure. Although the activation energy for the diffusion of C_{60} molecules in its bulk fcc structure is still unknown, it is presumably comparable to that of 1.4 eV [21] for desorption of a C_{60} molecule from its solid. Since the present experiment was performed at room temperature, it is very difficult for the fcc structure to transform to the bcc structure. Consequently, the saturation number obtained in Fig. 2 indicates that the 2D-rhombohedral C_{60} polymer was formed when photopolymerization was saturated. This polymer configuration has recently been observed for pressure-induced C_{60} polymers, using x-ray diffraction [22,23] and ^{13}C NMR [4]. Since the cross-link of the pressure-induced polymer is the same as that of the photopolymerized C_{60} polymer [4], configuration (a) in Fig. 3 is reasonable.

If the present C_{60} film has the perfectly (111) fcc structure, the saturation number would be 6. As shown in Fig. 2, the saturation number was, however, not 6 but was around 5.5. This may be due to the fact that other packing arrangements, such as tetragonal (saturation number $=$ 4), are present in the pristine C_{60} film deposited on the polycrystalline Au-coated substrate [20] and play a role in reducing the saturation number, to some extent.

To summarize, we examined how many [2 + 2] four-membered rings can be formed on a C_{60} molecule when photopolymerization is saturated, using the intensity of the C 1s shake-up satellite obtained by XPS. We have successfully evaluated the saturation number to be 6. Based on both the steric size of C_{60} molecules and the (111) fcc arrangement of a pristine C_{60} film deposited on a Au-coated substrate, the saturation value obtained in the present Letter suggests that a 2D-rhombohedral C_{60} polymer was formed when photopolymerization was saturated.

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