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Photo-induced Coalescence of C_{60} Molecules in a Potassium-doped C_{60} Film: Mass Spectral Evidence

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Photochemical reaction in a potassium-doped C_{60} film was studied using Fourier transform mass spectrometry (FT-MS). The FT-MS results for the film before and after UV–visible irradiation show that no C_{60} monomer was observed in the spectrum of the photoirradiated film. This indicates that all C_{60} molecules were completely photopolymerized. The structure of the present C_{60} polymer is discussed in comparison with the C_{60} dimer formed via a [2 + 2] cycloaddition ring. © 1998 John Wiley & Sons, Ltd.

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INTRODUCTION

Since Rao *et al.*[1] first reported that C_{60} molecules are polymerized by an argon ion laser or UV–visible irradiation of a pristine C_{60} film, there have been many reports on C_{60} dimers or polymers formed by various methods such as photoirradiation, high pressure at high temperature and alkali metal doping.[2] The cross-link between adjacent C_{60} molecules has been found to be a [2 + 2] cycloaddition four-membered ring[3–12] for C_{60} dimers formed by the photoirradiation and high pressure at high temperature and to be a C—C single bond[13–15] for those formed by alkali metal doping.

Strout *et al.*[5] reported several possible structures of C_{60} dimers, using MNDO and tight-binding calculations. They predicted that not only a C_{60} dimer formed via a [2 + 2] cycloaddition four-membered ring but also a C_{120} bucky peanut formed via coalescence of C_{60} molecules is energetically stable, and that the latter isomer is more stable than the former. Osawa and coworkers[16] recently pointed out that C_{120} bucky peanuts can be formed from [2 + 2] cycloadduct C_{60} dimers through iteration of the generalized Stone–Wales rearrangement (GSW). However, since the activation energy of this rearrangement has a very high value of 4–6 eV,[17,18] GSW rarely occurs in solid phases under the experimental conditions of photoirradiation, high pressure at high temperature, and alkali metal doping.[2] Coalescence of fullerenes has so far been observed only in gas phases under severe experimental conditions such as during laser ablation of C_{60} films[19–23] and high-energy collision between C_{60} molecules.[24]

In this paper, we present mass spectra that C_{60} molecules were completely photopolymerized in a potassium-doped C_{60} film after 20 h of UV–visible irradiation, and the Fourier transform mass spectrometric (FT-MS) results suggest that C_{60} dimers formed in the film are more stable than [2 + 2] dumb-bell shaped dimers.

EXPERIMENTAL

About 1000 mg of C_{60} powder (Matsubo, >99.98% pure) was placed in a quartz crucible (15 mm in diameter and 50 mm long), which was then heated at 200 °C *in vacuo* for more than 10 h in order to remove the residual organic solvents from the C_{60} powder. Thin films of C_{60} were formed on CsI substrates (Pureoptics, 20 mm in diameter and 2 mm thick) by sublimation at 400 °C for 90 min in a vacuum chamber (base pressure 2×10^{-8} Torr at a pressure of about 10^{-7} Torr (1 Torr = 133.3 Pa). During the deposition of C_{60}, the substrate was heated to and maintained at 100 °C to achieve good crystallinity (fcc structure) in the C_{60} film. The C_{60} films thus formed were estimated to be 100–150 nm thick.

Potassium was doped into the C_{60} films by means of a K-dispenser (SAES Getter) from which K atoms were desorbed by Joule heating. For efficient diffusion of potassium into the films, the substrate temperature was maintained at 100 °C. The composition of the K_xC_{60} films was determined by X-ray photoelectron spectroscopy (VG Escalab MkII) and x was estimated to be 0.5–2.0. According to the provisional binary phase diagram for K_xC_{60} at 1 atm pressure,[25] the [α + 3]

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phase is well known to be a stable phase in the range $x = 0$–3 at temperatures of 260–425 K. Consequently, C_{60}^{3-} anions are present in the K_xC_{60} films. Furthermore, we measured *in situ* FT-IR spectra of the K_xC_{60} films and found that a new IR peak appeared at 1370 cm^{-1} (we have developed an apparatus for the study of C_{60} films using *in situ* high-resolution FT-IR spectroscopy, the details of which have been described elsewhere[26]). Martin *et al.*[27] reported on the dependence of the four fundamental IR mode frequencies on dopant concentration x for K_xC_{60} films. In comparing our IR results with theirs, we found that the mode at 1370 cm^{-1} corresponds well with the $F_{1u}(\omega_4)$ mode for K_3C_{60}.

A 500 W mercury lamp (Ushio Electric, Model HB-50110AA) was used as a light source for photopolymerization in the K_xC_{60} films. Since infrared radiation from the lamp causes an undesirable rise in substrate temperature, the IR radiation was cut off by a colored glass filter (Toshiba, IR-25S). Thus only UV–visible radiation (emission lines in the range 2–4 eV) from the Hg lamp was used for photopolymerization. The intensity of this UV–visible radiation over a 50 mm diameter area was 3–4 W. The K_xC_{60} films were irradiated with the focused UV–visible radiation for 20 h through a CaF_2 optical window (40 mm in diameter and 4 mm thick). A quartz lens (50 mm in diameter with a 500 mm focal length) was used to focus the radiation on the K_xC_{60} films for photopolymerization.

When FT-MS measurement was performed on K_xC_{60} films before and after irradiation, the films were taken out of the vacuum chamber and subsequently mechanically removed from the CsI substrates. Then the films were deposited on an electroconducting carbon sheet glued to a stainless-steel sample holder. The sample holder was introduced into the vacuum chamber of an FT-MS system (Extrel, FT-MS 2001). The sample was measured by laser desorption FT-MS (N_2 lase, Laser Science, Model VSL337ND; wavelength, 337 nm; intensity <10 mJ cm^{-2}). When a pristine C_{60} film was examined as a blank, Fig. 1 shows that only a mass peak due to C_{60} monomers was observed, that is, no peak corresponding to C_2 fragments or polymers of C_{60} was detected under the FT-MS measurement conditions used.

RESULTS AND DISCUSSION

Figures 2 and 3 show the negative ion FT mass spectra of the K_xC_{60} films before and after UV–visible irradiation, respectively. Figure 2(a) shows that not only C_{60} monomers but also C_{60} dimers were present in the pristine film and that fragmentation from the monomers and dimers occurred in this film with increasing C_2 loss. While no fragments of C_{60} by C_2 loss was observed in the pristine C_{60} film, as shown in Fig. 1, C_{60} fragments such as C_{54}, C_{56} and C_{58} were observed in K_3C_{60} film. This may be due to the difference in stability between neutral C_{60} and C_{60}^{3-} anion. Since the anion is more unstable than the neutral species, fragmentation can easily take place in the laser desorption process for the K doped film. Although the sample was exposed to air for a few minutes before FT-MS measurement, the K_3C_{60} phase was reported to be air stable for several

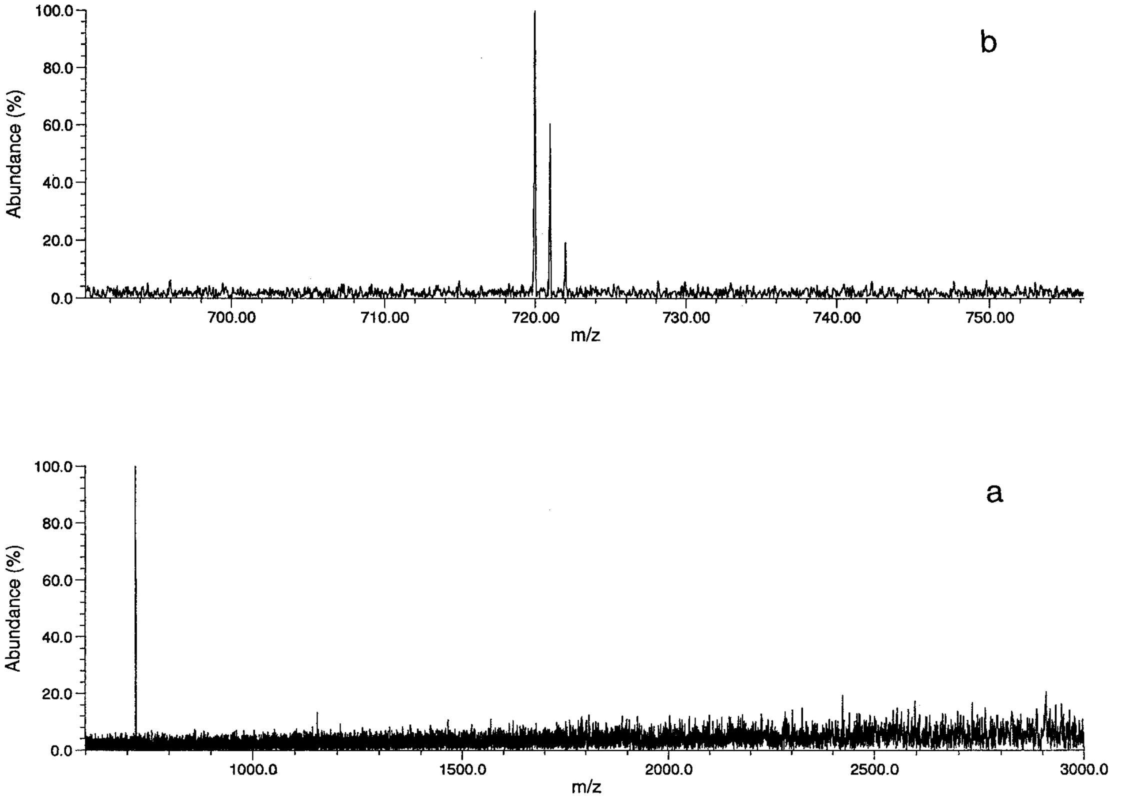

Figure 1. FT mass spectra of a pristine C_{60} film in the ranges (a) m/z 0–3000 and (b) m/z 690–750.

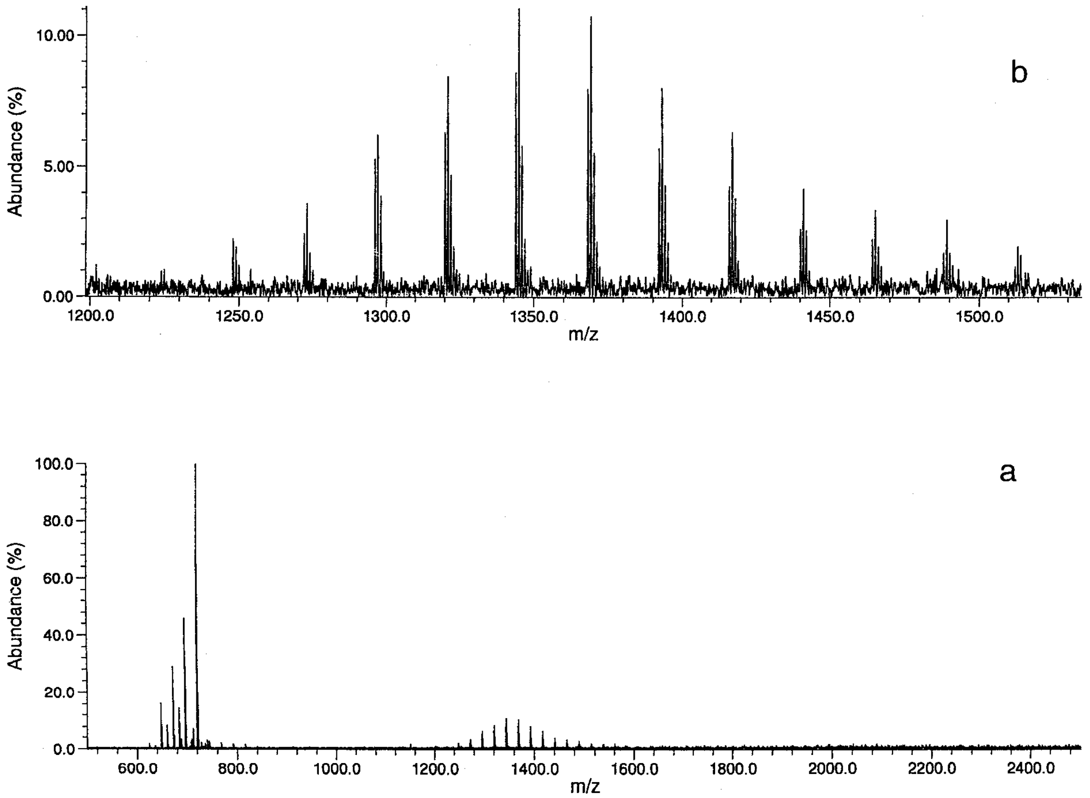

Figure 2. FT mass spectra of the K_xC_{60} film before UV–visible irradiation in the ranges (a) m/z 520–2480 and (b) m/z 1200–1530.

hours.[28] In Fig. 2(a), in addition to signals corresponding to C_{60} and its fragments, some intense mass peaks were observed in the range m/z 600–800. These peaks were due to fragments ($C_{58}O$, $C_{56}O$ and $C_{54}O$) resulting from $C_{60}O$ by C_2 loss, although the parent peak was slightly observed. We next focused our attention on C_{60} dimers and trimers.

The mass spectrum in Fig. 2(a) is magnified in Fig. 2(b), in which mass peaks with higher mass than that of C_{60} dimers (m/z 1440) are observed at m/z 1464 (C_{122}), 1488 (C_{124}) and 1512 (C_{126}). This indicates that collision between C_{60} dimers and C_2 fragment species occurred in the gas phase upon laser desorption. From the abundance of each peak observed in Fig. 2(b), we can identify the kind of elements constituting each mass peak. Table 1 summarizes the calculated natural abundances of C_{60}, C_{120} and C_{180} with 1.11% ^{13}C isotope. Comparison of the calculated natural abundance of C_{120} (with 1.11% ^{13}C isotope) with the experimental results indicates that the mass peaks in Fig. 2(b) contain only carbon.

On the other hand, for the photoirradiated K_xC_{60} film, Fig. 3 shows that mass peaks of $(C_{60})_2$ and its fragments become intense and those corresponding to C_{60} trimers are also observed in comparison with the results in Fig. 2. Since the results in Figs 2 and 3 were obtained under identical FT-MS measurement conditions, the difference in these results is not due to collision between C_{60} and its fragments in the gas phase upon laser desorption and is attributed to UV–visible irradiation of the K_xC_{60} film. If laser desorption had affected the results in Fig. 3, mass peaks larger than the parent peak of $(C_{60})_2$ at m/z 1440 should have been observed, as with the results in Fig. 2(b). However, Fig. 3(b) shows no mass peak due to carbon clusters with mass higher than m/z 1440. Consequently, the effect of laser desorption on the FT mass spectra of the photoirradiated K_xC_{60} film was negligible. This indicates that FT-MS peaks with mass lower than m/z 1440 originated from fragmentation of the $(C_{60})_2$ with increasing C_2 loss. In addition, since the abundance of each mass peak observed in Fig. 3(c) corresponds well with the calculated natural abundance of C_{180} (1.11% ^{13}C isotope),

Table 1. Calculated natural abundances of C_{60}, C_{120} and C_{180} with 1.11% ^{13}C

C_n	m/z	Abundance	Formula
C_{60}	720	100	$^{12}C_{60}$
	721	67	$^{12}C_{59}{}^{13}C$
	722	22	$^{12}C_{58}{}^{13}C_2$
	723	5	$^{12}C_{57}{}^{13}C_3$
	724	1	$^{12}C_{56}{}^{13}C_4$
C_{120}	1440	75	$^{12}C_{120}$
	1441	100	$^{12}C_{119}{}^{13}C$
	1442	66	$^{12}C_{118}{}^{13}C_2$
	1443	29	$^{12}C_{117}{}^{13}C_3$
	1444	9	$^{12}C_{116}{}^{13}C_4$
	1445	2	$^{12}C_{115}{}^{13}C_5$
	1446	1	$^{12}C_{114}{}^{13}C_6$
C_{180}	2160	50	$^{12}C_{180}$
	2161	100	$^{12}C_{179}{}^{13}C$
	2162	100	$^{12}C_{178}{}^{13}C_2$
	2163	66	$^{12}C_{177}{}^{13}C_3$
	2164	32	$^{12}C_{176}{}^{13}C_4$
	2165	13	$^{12}C_{175}{}^{13}C_5$
	2166	4	$^{12}C_{174}{}^{13}C_6$
	2167	1	$^{12}C_{173}{}^{13}C_7$

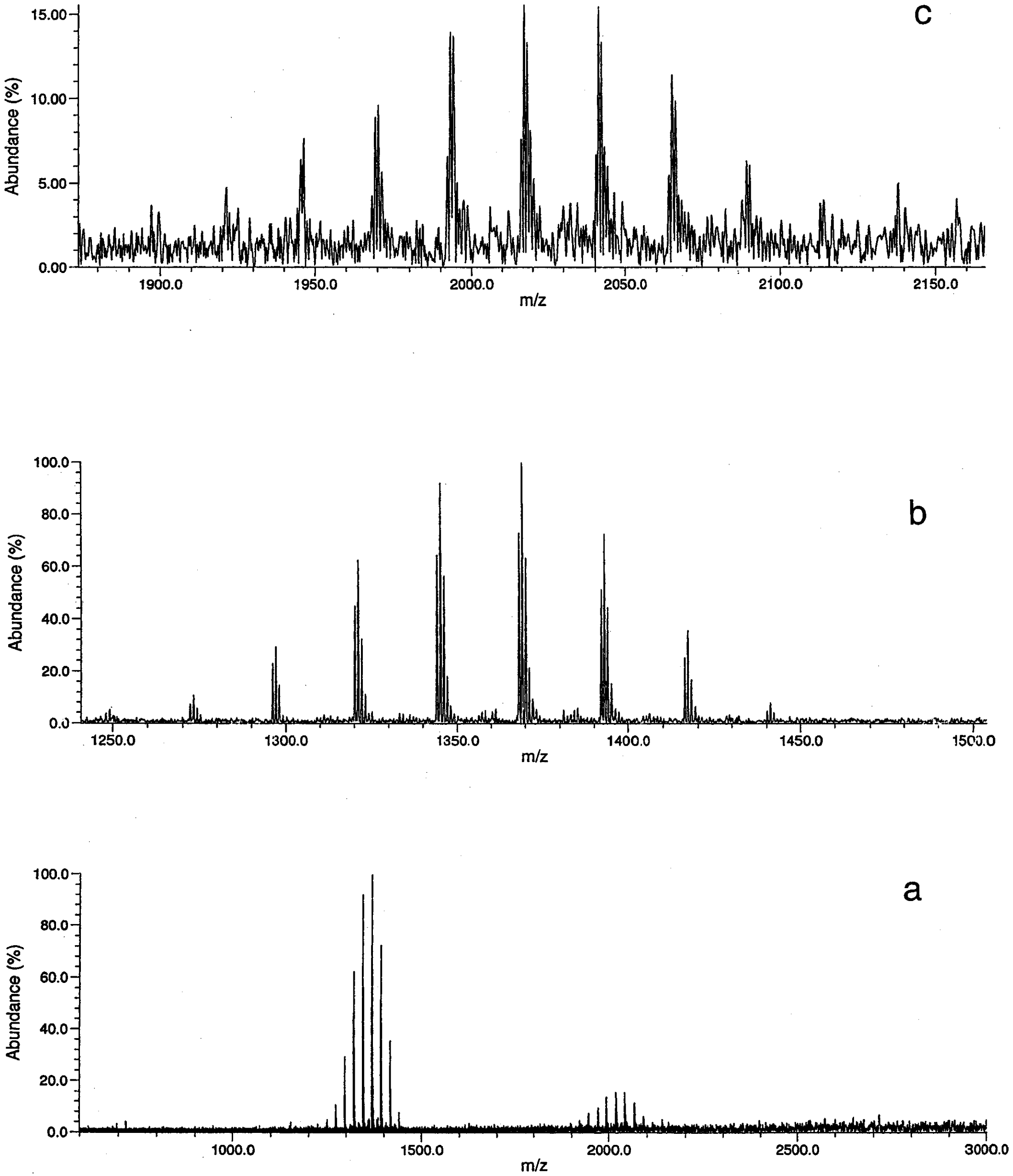

Figure 3. FT mass spectra of the K_xC_{60} film after 20 h of irradiation with UV–visible radiation in the ranges (a) *m/z* 600–3000, (b) *m/z* 1240–1500 and (c) *m/z* 1880–2160.

the mass peaks in Fig. 3(c) were due to the fragmentation of C_{60} trimers (C_{180}), although the parent peak at *m/z* 2160 was not observed.

As shown in Fig. 3(b), it is interesting that no mass peak due to the C_{60} monomer and its fragments was observed. This indicates that all C_{60} molecules in the K_xC_{60} film were completely photopolymerized. In the present case, C_{60}^{3-} anions were present in the K_xC_{60} film as described in the previous section. The electron transfer from K atoms to the LUMO π^* molecular orbital (t_{1u}) of C_{60} reduces the molecular symmetry of the neutral C_{60}. The C_{60}^{3-} anion was proposed to have a C_{2v} distortion symmetry which completely removes the degeneracy of the t_{1u} (LUMO) and t_{1g} (LUMO + 1) levels, that is, $t_{1u} \rightarrow a_1 + b_2 + b_1$, and $t_{1g} \rightarrow b_2 + b_1 + a_2$.[29] This leads to an increase in optically allowed transitions compared with those for the neutral species, and the photoabsorption efficiency of the anion is larger than that of the neutral species. In addition, the reactivity of the C_{60}^{3-} anion with the distorted structure is assumed to be greater than that of the neutral species. Consequently, the effect of potassium on C_{60} photopolymerization enhances both photoabsorption efficiency and reactivity of C_{60} molecules.

We next consider the structure of the C_{60} dimer observed in Fig. 3. In C_{60} photopolymerization, the cross-link of C_{60} dimers is well known to be a [2 + 2] cycloaddition four-membered ring.[3–12] Recently, Wang *et al.*[30] synthesized [2 + 2] cycloadduct C_{60} dimers and the FT-MS results showed that C_{60} monomers were observed as a main peak along with C_2 loss from the dimer. Although they presented a positive ion FT mass spectrum of the dumb-bell structure in their paper, they also measured a negative ion FT mass spectrum of the dimer and obtained a similar mass pattern to that for the positive ion.[31] The reason why the monomer was observed as the main ion species for the dumb-bell structure is that the activation energy (E_a) for thermal decomposition of the [2 + 2] cycloadduct dimer was experimentally determined to be 1.25 eV,[32] whereas E_a for C_2 fragmentation from the C_{60} cage is 5–7 eV.[33] On the other hand, Fig. 3(a) shows a mass spectrum different from that of the dumb-bell C_{60} dimer reported by Wang *et al.*: C_2 loss fragmentation took place for $(C_{60})_2$ and $(C_{60})_3$, whereas no peak of C_{60} monomers resulting from decomposition of the dimers and trimers was detected. The present results cannot be explained by the assumption that the product in photoirradiated K_xC_{60} film is the dumb-bell C_{60} dimer. What is an appropriate structure of the $(C_{60})_2$ dimer to explain our present results? In spite of the fact that much C_2 loss from the dimers occurred, the dimers were not decomposed to C_{60} monomers. Based on these experimental facts, it can be speculated that the dimers formed in the K-doped C_{60} film have a more coalesced structure like a C_{120} bucky peanut as described in Fig. 3 in Ref. 5. The cage of the peanut structure can be maintained upon C_2 loss fragmentation.

In order to determine the molecular structure of the present dimer accurately, we are now applying *in situ* high-resolution FT-IR spectroscopy[26] in combination with tight-binding calculations.[34]

CONCLUSION

We have demonstrated by FT-MS that photocoalescence of C_{60} molecules took place in a potassium-doped C_{60} film. Based on the FT-MS results, the structure of the C_{60} dimer observed in this work is speculated to be a C_{120} bucky peanut more stable than the [2 + 2] dumb-bell structure.

Since this C_{60} coalesced dimer is expected to be thermally more stable than the previously reported C_{60} dimers formed via a [2 + 2] cycloaddition ring, the present reaction may open a new way to the synthesis of fullerene-based materials.

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