Thermal Study of a Silylmethylated Fullerene Leading to Preparation of Its Vacuum Deposited Thin Films

Hideo Nagashima,* Yoshiyuki Kato, Hirohisa Satoh, Naoki Kamegashima, Kenji Itoh,[#] Kazuhiro Oi,[†] and Yahachi Saito*[†]
Department of Materials Science, Toyohashi University of Technology, Toyohashi, Aichi 441
[†]*Department of Electrical Engineering, Mie University, Tsu, Mie 514*

(Received March 11, 1996)

Thermal study of a C_{60} derivative containing a siloxane structure revealed that it was unstable above 350 °C. A major decomposition pathway was formation of C_{60} and $(Me_3Si)_2O$ presumably *via* homolysis of bonds between the α-carbon of the silyl group and the cage carbon. By careful control of the crucible temperature below 350 °C, amorphous vapor-deposited thin films on NaCl or mica were successfully prepared.

High chemical reactivity of fullerenes has resulted in their organic or organometallic derivatization, producing a number of new compounds bearing a variety of functional groups on the carbon cage.[1,2] One promising approach to discover new physical properties of the fullerene derivatives is synthesis of vapor-deposited thin-films, since it is well known that successful preparation of vapor-deposited thin films of C_{60} on a variety of substrates has made it possible to measure various such properties; this includes the famous discovery of superconductivity in alkali-metal doped C_{60} films.[3,4] Little exploration has been done, however, on preparation of the films of fullerene derivatives by vapor-deposition, presumably because the derivatives of C_{60} are generally unstable at crucible temperatures used to vaporize C_{60} in vacuum. In our studies to synthesize derivatives of C_{60} containing organosilylmethyl groups,[5] we were aware that many of them decomposed around 200 °C, but the compound having a cyclic siloxane structure, $C_{60}(CH_2SiMe_2)_2O$(**1**) illustrated in Figure 1 did not have a critical melting or decomposition point below 300 °C. This prompted us to make a thermal study of **1**, which may lead to successful preparation of its vapor deposited films.

We first carried out thermogravimetry (TG) analysis of the solid sample of **1** in flowing argon. There were two stages of weight loss: 1.1 wt% was lost in the temperature region of 112 to 337 °C and 12.0 wt% of weight loss was observed at 350 °C~550 °C (Figure 2). This first (1.1%) was presumably due to tenaciously held water; ^1H NMR and HPLC analysis of the samples of **1** heated in a TG cell up to 250 °C, which brought about 1% weight loss, revealed no substantial change of the spectrum or the chromatogram.

The second weight loss of **1** reflected chemical reactions. After TG analysis of **1** (8.56 mg) in the temperature range including the second weight loss (~550 °C; 12~13 wt%), 7.45 mg of the compounds was recovered. A major part of this recovered sample was soluble in toluene and CS_2 (6.4 mg in total, 86 wt% of the recovered sample); IR and HPLC analysis of this soluble compound showed that the product was exclusively C_{60}. The residual part of the recovered sample was insoluble in any organic solvent; carbon and hydrogen contents observed by elemental analysis were similar to those of **1**, and its FT-IR spectrum showed a broad absorption around 1035 cm^{-1} assignable to a Si-O-Si stretching vibration. This suggests that the side reaction may be formation of siloxane polymers containing C_{60} as the partial structure.

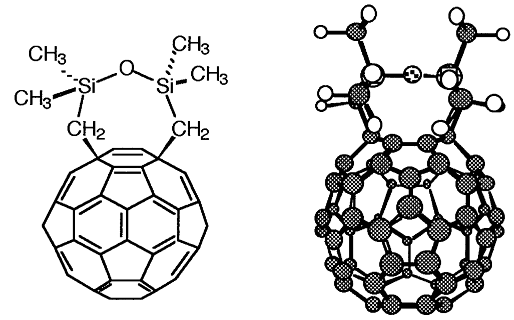


Figure 1. PM3 optimized structure of **1**.

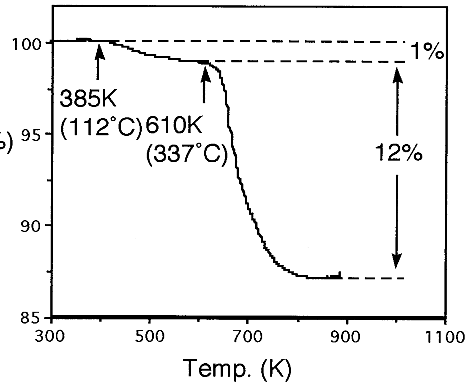


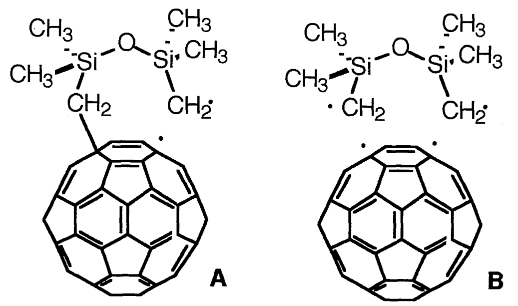
Figure 2. TG curve of **1**. [5 °C/min in flowing argon (150ml/min)] .

The reaction produces a volatile organosilicon compound, structure of which was determined by the following experiments: thermolysis of **1** (69.7 mg) was carried out at 500 °C under reduced pressure (0.1 mmHg). A volatile compound (8.2 mg, 12 wt% of the charged **1**) was condensed in a cold trap. Spectroscopic data (^1H, ^{13}C, and ^{29}Si NMR) of the product are coincident with those of $(Me_3Si)_2O$. From the non-volatile residue (56.4 mg), C_{60} (48.0 mg) and the insoluble materials (the siloxane polymer described above; 7.3 mg) were also obtained.

These results indicate that the overall chemical equation in thermolysis of **1** can be drawn as shown in Scheme 1. C_{60} is known to be regenerated from its Diels-Alder adducts by cleavage of carbon-carbon bonds.[6] However, the simple dialkyl adducts of C_{60}, of which decomposition through the retro Diels-Alder pathway is difficult or not allowed, are thermally stable.[7,8] One possible scheme to generate C_{60} from **1** is homolytic cleavage of bonds between the C_{60} cage and the organosilicon moiety in **1** involving radical species **B** as an intermediate. The formed radicals afford C_{60} and $(Me_3Si)_2O$. Species **B** may be formed through **A** from **1**.

The above results indicate that if the vaporization takes place below 337 °C, the vapor-deposition method is useful for

$$1 \xrightarrow{\Delta} C_{60} + (CH_3)_3SiOSi(CH_3)_3 + \text{insoluble compounds (siloxane polymer?)}$$



Scheme 1. Thermal decomposition of **1**.

preparation of thin-films of **1**. Vacuum deposition of thin films of **1** on NaCl or mica as the substrate was done at the crucible temperature of 350 °C in vacuum (6 x 10^{-6} Torr). Although films of C_{60} could not be synthesized under the same conditions, those of **1** were available as golden thin-films (40 nm thick) at two substrate temperatures (Ts; 160 and 200 °C). A typical TEM image of the films together with the corresponding electron diffraction patterns (inset) is shown in Figure 3 (on NaCl). Flat and continuous films were obtained on both substrates at both substrate temperatures. Diffraction patterns from these films show only halos, indicating that the films consist of minute grains or have a highly disordered structure. FT IR and UV spectra of the film on the NaCl were analogous to **1**. The purity of the films were finally determined by dissolving them in toluene and CS_2. HPLC analysis of the obtained solutions revealed that the films contained **1** almost exclusively, and only a tiny peak of C_{60} was visible.

As indicated from the TG analysis, preparation of the thin films at higher crucible temperatures resulted in the thermal decomposition of **1** to form films consisting of C_{60} and **1**. At crucible temperatures (380~660 °C) which are usually used to make vapor deposited films of C_{60}, polycrystalline films were obtained both on NaCl and mica (Ts = 160 and 200 °C). The films were discontinuous and made up of small particles; particle size in those prepared with Ts = 160 °C (ca. 100 nm) was smaller than that with Ts = 200 °C (300~400 nm). The diffraction patterns from these films were composed of spotty rings, and the Debye-Scherrer rings can be indexed by the fcc (face-centered cubic) lattice with a lattice parameter $a = 1.44 \pm 0.02$ nm. Absence of reflections, (200), (400), and so on, was similar to that seen in the diffraction pattern of C_{60}. EDX spectra obviously showed the presence of silicon, and IR spectra of the films on NaCl were analogous to those of **1**. However, their HPLC analysis revealed that **1** was only a minor component (~ 40%), and the major product (~60%) was C_{60}. Since the lattice parameter is slightly larger than that for pure C_{60} ($a = 1.417$ nm), the polycrystalline structure in the films would be derived from a mixture of crystals of C_{60} and compound **1**. The organosilicon moiety would be located at the interstitial sites of the fcc lattice.

In summary, the siloxane **1** was thermally stable below approximately 350 °C, and fission of carbon-carbon bonds between the α-carbons of the silyl group and the cage carbons took place above this temperature to form C_{60} and hexamethyldisiloxane as the major reaction. The thermal study led to the successful preparation of vapor-deposited thin films of organofullerenes by controlling the crucible temperatures below 350 °C. Further studies on physical properties of the thin films are in progress.

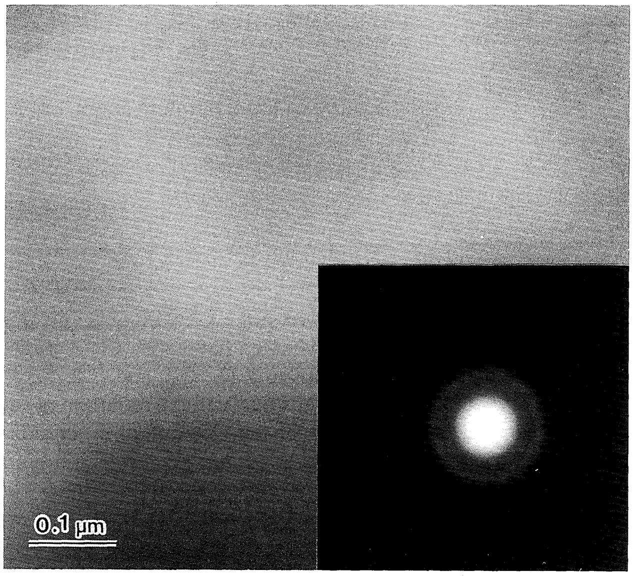


Figure 3. TEM image and diffraction pattern (inset) of **1** on NaCl at Ts=160 °C.

This work was supported by a Grant-in-Aid for Scientific Research from the Ministry of Education, Science, Sports, and Culture (05233105) and Tatematsu Foundation.

References and Notes

\# Present address: Department of Applied Chemistry, Nagoya University, Chikusa, Nagoya, Aichi 441.

1 For general reviews on fullerene research, a) H. W. Kroto, A. W. Allaf, and S. P. Balm, *Chem. Rev.*, **91**, 1213 (1991); b) "Special Issue on Buckminsterfullerene" *Acc. Chem. Res.*, **25**, 98 (1992); c) "Fullerenes: Synthesis, Properties, and Chemistry of Large Carbon Clusters", ed. G. S. Hammond and V. J. Kuck, ACS Symposium Series 481, American Chemical Society, Washington DC (1992).

2 For reviews on fullerene derivatives, A. Hirsch, *Synthesis*, **1995**, 895; M. Iyoda and M. Yoshida, *J. Syn. Org. Chem. Jpn.*, **53**, 756 (1995).

3 A recent review article of C_{60} thin films; C. A. Mirkin and W. B. Caldwell, *Tetrahedron*, **52**, 5113 (1996) and references cited therein.

4 For example, A. F. Hebard, M. J. Rosseinsky, R. C. Haddon, D. W. Murphy, S. H. Glarum, T. T. M. Palstra, A. P. Ramirez, and A. R. Kortan, *Nature*, **350**, 600 (1991); K. Tanigaki, T. W. Ebbesen, S. Saito, J. Mizuki, J. S. Tsai, Y. Kubo, and S. Kuroshima, *Nature*, **352**, 222 (1991)

5 a) H. Nagashima, H. Terasaki, E. Kimura, K. Nakajima, and K. Itoh, *J. Org. Chem.*, **59**, 1246 (1994); b) H. Nagashima, H. Terasaki, Y. Saito, K. Jinno, and K. Itoh, *J. Org. Chem.*, **60**, 4966 (1995); c) H. Nagashima, M. Saito, Y. Kato, H. Goto, E. Osawa, M. Haga, and K. Itoh, *Tetrahedron*, **52**, 5053 (1996).

6 For example, F. Wudl, A. Hirsch, K. C. Khamani, T. Suzuki, P.-M. Allemand, A. Koch, H. Eckert, G. Srdanov, and H. M. Webb, in ref. 1c, p. 161; K. Komatsu, Y. Murata, N. Sugita, K. Takeuchi, T. S. M. Wan, *Tetrahedron Lett.*, **34**, 8473 (1993); M. Tsuda, T. Ishida, T. Nogami, S. Kurono, and M. Ohashi, *J. Chem. Soc., Chem. Commun.*, **1993**, 1296; Y. Rubin, S. Khan, D. I. Freedberg, and C. Yeretzian, *J. Am. Chem. Soc.*, **115**, 344 (1993); K. I. Guhr, M. D. Greaves, and V. M. Rotello, *J. Am. Chem. Soc.*, **116**, 5997 (1994) and references cited therein.

7 H. Takeshita, J.-F. Liu, N. Kato, A. Mori, and R. Isobe, *Chem. Lett.*, **1995**, 377; P. Belik, A. Gügel, J. Spickerman, and K. Müllen, *Angew. Chem., Int. Ed. Engl.*, **32**, 78 (1994); X. Zhang and C. S. Foote, *J. Org. Chem.*, **59**, 5235 (1994); T. Tago, T. Minowa, Y. Okada, and J. Nishimura, *Tetrahedron Lett.*, **34**, 8461 (1993).

8 Hydrolytic cleavage of a carbon-carbon bond connected to C_{60} was reported; H. Tomioka, M. Ichibashi, and K. Yamamoto, *Tetrahedron Lett.*, **36**, 5371 (1995) and references cited therein.