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Synthesis of Fullerene Oxides [$C_{70}O_n$] (n=1~3 or n=1) under Microwave Irradiation

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마이크로파 조건에서 풀러렌 산화물 [$C_{70}O_n$] (n=1~3 or n=1)의 합성

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ABSTRACT : Synthesis of fullerene oxides [$C_{70}O_n$] (n=1~3 or n=1) in solid state by fullerene [C_{70}] and several oxidants such as 3-chloroperoxy benzoic acid, chromium(VI) oxide, benzoyl peroxide, and trichloroisocyanuric acid was taken place under microwave irradiation. The reactivity in solid state of fullerene [C_{70}] with various oxidants under same microwave condition increased in the order of 3-chloroperoxy benzoic acid > chromium(VI) oxide > trichloroisocyanuric acid ≅benzoyl peroxide. The MALDI-TOF-MS, UV-visible spectra and HPLC analysis confirmed that the products of fullerene oxidation were [$C_{70}O_n$] (n=1~3 or n=1).

요 약 : 풀레렌[C_{70}]을 3-chloroperoxy benzoic acid, chromium (VI) oxide, benzoyl peroxide, trichloroisocyanuric acid 등의 산화제를 사용하여 마이크로파 조건에서 반응시켜 풀러렌 산화물 [$C_{70}O_n$] (n=1~3 or n=1)을 합성하였다. 동일한 마이크로파 조건에서 여러가지 산화제와 풀러렌 [C_{70}]의 고체상태 반응성은 3-chloroperoxy benzoic acid > chromium(VI) oxide > trichloroisocyanuric acid ≅ benzoyl peroxide 순으로 증가함을 나타냈다. MALDI-TOF MS, UV-visible, 그리고 HPLC를 사용하여 분석한 결과 생성된 풀러렌 산화물은 [$C_{70}O_n$] (n=1~3 or n=1)임을 알 수 있었다.

Keywords : Fullerene Oxides [$C_{70}O_n$] (n=1~3 or n=1), Several Oxidants, Microwave Irradiation, MALDI-TOF-MS

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Ⅰ. Introduction

Microwave irradiated reactions have been extensively studied and proven to be a useful synthetic technique for a variety of chemical reactions.[1] The reactions under microwave irradiation sometimes proceed faster than conventional heating reactions.[2] Also, one of merits of a microwave irradiated reaction is the solvent free condition.[3] Microwave-assisted solvent free reactions have been widely investigated in chemical synthesis.[4] Amorphous carbon and graphite, in their powdered form, irradiated at 2.45 GHz, reach very high temperatures.[5] Many reactions have been accelerated by the use of microwave irradiation.[6] Thus, the microwave assisted process will be of interest to many chemists who work with fullerene chemistry.

The very rapid rise of temperature of the reactants by microwave irradiation favors some reaction pathways over others and thus leads to selectivity and hence cleaner products.[7] This methodology is expected to be applicable to the simple and efficient preparation of fullerene oxides in solid state under microwave irradiation. Since the discovery of fullerene by Kroto et al. in 1985,[8] the research in this area has become one of the most popular topics in pure and applied physics, chemistry, and materials science,[9,10] and fullerene oxides have attracted much attention.[11] A variety of synthetic methods[12-17] are at hand to introduce the epoxide functionality to fullerenes. Also, fullerene oxides show an interesting reaction behavior both with themselves and in reactions with pure fullerenes.

In contrast to C_{60}, few investigations have been conducted on the synthesis of C_{70}.[18] The oxidation of C_{70} is more difficult compared with that of C_{60}.[19]The conceded difficulty is revealed to be the availability of fewer reactive double bond present in C_{70} as compared with C_{60}.[20] Fullerene oxidation has been shown to produce $C_{70}O_1$ and $C_{70}O_2$ which have an epoxide structure, and also higher oxides.[21,22] The first stable C_{70} monoxide, $C_{70}O$ was isolated by Diederich's group.[23] The fullerene oxides $C_{70}O_n$ ($n=1\sim3$) are interesting precursors to the formation of other fullerene-based materials or starting materials for the formation of odd-numbered fullerene derivative species.[24] Van Cleempoel et al.[25] have reported that $C_{70}O$ and higher C_{70} oxides in toluene solution oxidize further upon standing by the addition of one oxygen atom to each oxide.[22] C_{70} can also be oxidized with various oxidants under microwave irradiation.

In this paper, we reported a novel, simple, and efficient method for the preparation of fullerene oxides, with the formation of $[C_{70}O_n]$ ($n=1\sim3$ or $n=1$) by the reaction of fullerene $[C_{70}]$ with several kind of oxidants, such as 3-chloroperoxy benzoic acid, chromium(VI) oxide, benzoyl peroxide, and trichloroisocyanuric acid under microwave irradiation.

Ⅱ. Experimental

Fullerene $[C_{70}]$ used in this work was 99.0% purity of Tokyo Chemical Inc(TCI). The oxidants used were 3-chloroperoxy benzoic acid (Fluka, 99.0%), chromium(VI) oxide (Aldrich, 97.0%), benzoyl peroxide (Fluka, 99.0%), and trichloroisocyanuric acid (Aldrich, 99.0%). The microwave irradiation of all the samples was conducted in multimode with continuous heating at full power by a domestic oven (2450 MHz,700W). All the samples were analyzed by MALDI-TOF-MS (Voyager-DE STR) and the matrix was a cyano-4-hydroxy cinnamic acid. HPLC analysis was performed with a Shiseido nanospace SI-2 model. Column was used a Cosmosil 5 μPBB (250 X 4.6 mm) made by Phenomenex. UV- Detector was used at 330 nm. The flow rate was 1.0 ml/min during the mobile phase for toluene / hexane at the ratio of 6:4(v/v). The injection volumn was 20.00 $\mu\ell$ at a pump pressure of 5.0 MPa. The electronic absorption spectra was obtained by UV-visible spectrophotometer (Shimadzu UV-1601 PC).

1. The reaction of fullerene [C_{70}] with 3-chloroperoxy benzoic acid by microwave irradiation.

The mixture of fullerene [C_{70}] (20 mg, 0.024 mmol) and 3-chloroperoxy benzoic acid (41.4 mg, 0.240 mmol) was prepared by grinding with a mortar and pestle until it was visually homogeneous. The powdered mixture was poured into a 50ml round bottom flask. The flask was placed into the microwave oven and was irradiated microwave for 20 min. The resulting solid was obtained as a mixture of fullerene oxides.

2. The reaction of fullerene [C_{70}] with chromium(VI) oxide by microwave irradiation.

The mixture of fullerene [C_{70}] (20 mg, 0.024 mmol) and chromium(VI) oxide (24.0 mg, 0.240 mmol) was prepared by grinding with a mortar and pestle until it was visually homogeneous. The powdered mixture was poured into a 50ml round bottom flask. The flask was placed into the microwave oven and was irradiated microwave for 20 min. The resulting solid was obtained as a mixture of fullerene oxides.

3. The reaction of fullerene [C_{70}] with benzoyl peroxide by microwave irradiation.

The mixture of fullerene [C_{70}] (20 mg, 0.024 mmol) and benzoyl peroxide (58.0 mg, 0.240 mmol) was prepared by grinding with a mortar and pestle until it was visually homogeneous. The powdered mixture was poured into a 50 ml round bottom flask. The flask was placed into the microwave oven and was irradiated microwave for 20 min. The resulting solid was obtained as a mixture of fullerene oxides.

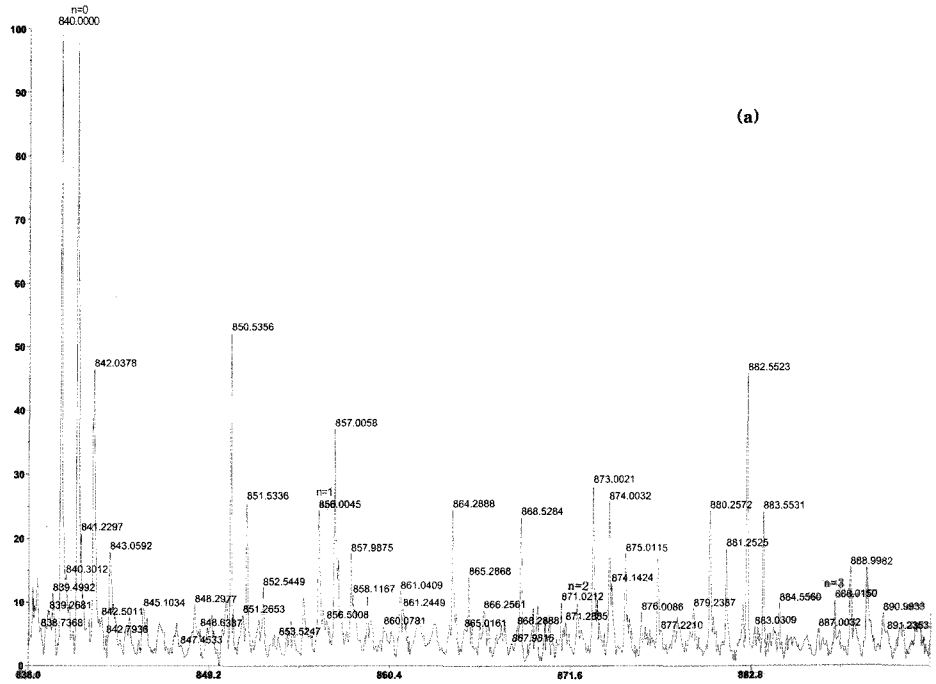
4. The reaction of fullerene [C_{70}] with trichloroisocyanuric acid by microwave irradiation.

The mixture of fullerene [C_{70}] (20 mg, 0.024 mmol) and trichloroisocyanuric acid (56.0 mg, 0.240 mmol) was prepared by grinding with a mortar and pestle until it was visually homogeneous. The powdered mixture was poured into a 50 ml round bottom flask. The flask was placed into the microwave oven and was irradiated microwave for 20 min. The resulting solid was obtained as a mixture of fullerene oxides.

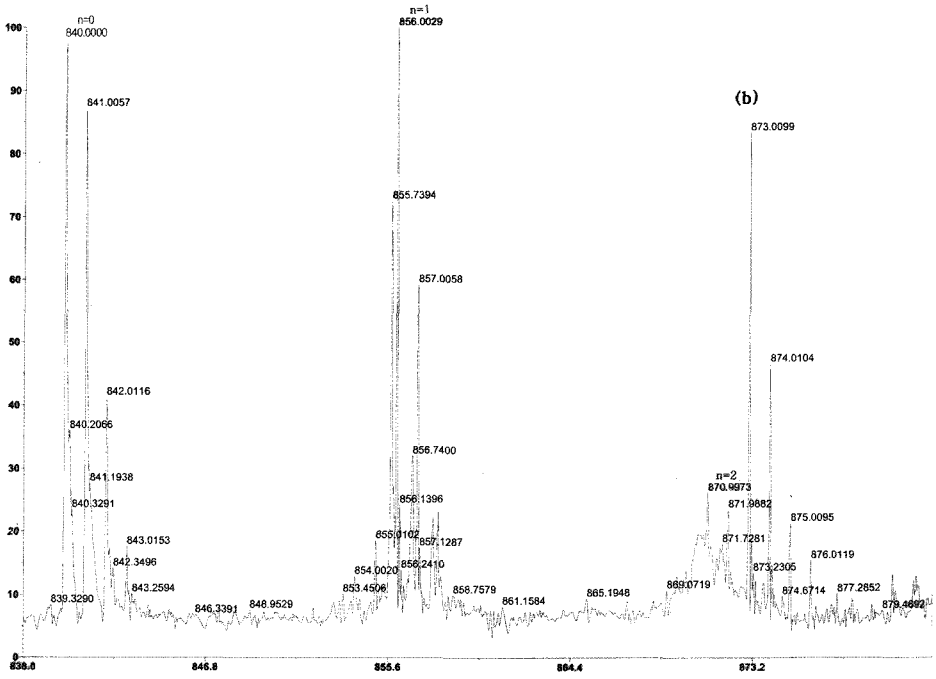
Ⅲ. Results and discussion

The microwave irradiating process is applied to the synthesis of fullerene oxides in solid state by the reaction of fullerene [C_{70}] with several oxidants such as 3-chloroperoxy benzoic acid, chromium(VI) oxide, benzoyl peroxide, and trichloroisocyanuric acid, which give rise to the oxidation of fullerene [C_{70}] with the formation of [$C_{70}O_n$] (n=1~3 or n=1). For many chemical syntheses, the development of microwave-assisted solvent-free procedures has led to enhanced reaction rates, compared to conventional heating. The MALDI-TOF-MS spectra and HPLC profile revealed the oxidation of fullerene [C_{70}] by microwave irradiation in the presence of oxidants. These reaction are of the microwave induced chemical oxidation type in solid state. The reactivity in solid state of fullerene [C_{70}] with the oxidants under microwave condition increased in the order of 3-chloroperoxy benzoic acid > chromium (VI) oxide > trichloroisocyanuric acid ≅ benzoyl peroxide.

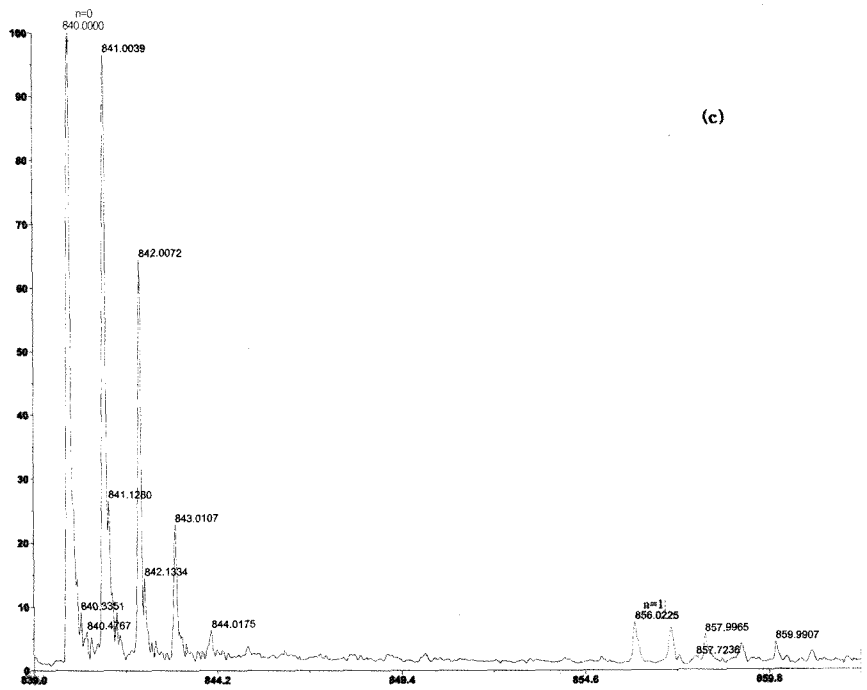
The difference between various oxidation reactions with and without microwave irradiation is as follow; the reaction time is shortened due to high pressure and temperature under microwave condition. Epoxidation mediated by microwave irradiation with various oxidants is efficient for both electron-rich olefins and fullerenes. MALDI-TOF-MS and HPLC analysis data in Table 1 show the formation of [$C_{70}O_n$] (n = 1~3 or n = 1). The MALDI-TOF-MS analysis in Figure 1 shows the formation of [$C_{70}O_n$] (n = 1~3 or n = 1) observed at m/z 840(C_{70}), 856($C_{70}O_1$), 872($C_{70}O_2$), 888($C_{70}O_3$) in the MALDI-TOF-MS spectrum. The most intense peak



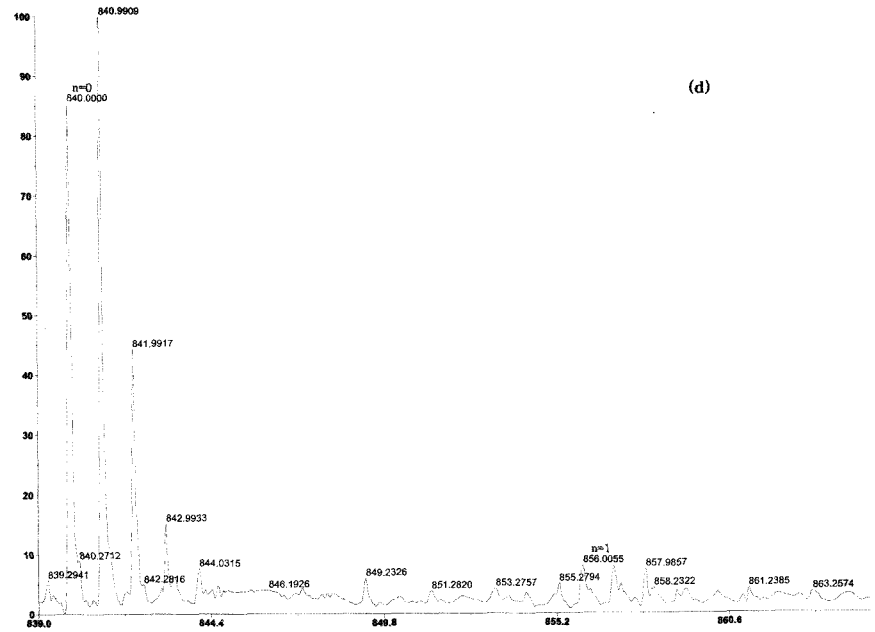
(a) The reaction products of fullerene [C_{70}] with 3-chloroperoxy benzoic acid, n = 0, 1, 2, 3 by microwave irradiation shows the presence of C_{70}, $C_{70}O_1$, $C_{70}O_2$, $C_{70}O_3$.



(b) The reaction products of fullerene [C_{70}] with chromium(VI) oxide, n = 0, 1, 2 by microwave irradiation shows the presence of C_{70}, $C_{70}O_1$, $C_{70}O_2$.



(c) The reaction products of fullerene [C_{70}] with trichloroisocyanuric acid, n = 0, 1 by microwave irradiation shows the presence of C_{70}, $C_{70}O_1$.



(d) The reaction products of fullerene [C_{70}] with benzoyl peroxide, n = 0, 1 by microwave irradiation shows the presence of C_{70}, $C_{70}O_1$.

Figure 1. MALDI - TOF MS spectra of [$C_{70}O_n$] (n = 1~3 or n = 1).

Table 1. The MALDI-TOF-MS and HPLC analysis of [$C_{70}O_n$] (n=1～3 or n=1) produced by microwave irradiation for 20min

Various oxidant	Fullerene	Formation of $C_{70}(O)_n$ (n=1～3 or n=1)	Mass unit (m/z)	Retention time and intensity in HPLC, (min and %)
3-chloroperoxy benzoic acid	C_{70}	$C_{70}O_3$ $C_{70}O_2$ $C_{70}O_1$ C_{70}	888 872 856 840	20.02 (6.49) 21.27 (19.48) 21.70 (18.18) 22.62 (100.0)
Chromium(VI) oxide	C_{70}	$C_{70}O_2$ $C_{70}O_1$ C_{70}	872 856 840	21.44 (14.74) 21.75 (15.79) 22.65 (100.0)
Trichloroisocyanuirc acid	C_{70}	$C_{70}O_1$ C_{70}	856 840	21.72 (7.59) 22.63 (100.0)
Benzoyl peroxide	C_{70}	$C_{70}O_1$ C_{70}	856 840	21.71 (6.49) 22.61 (100.0)

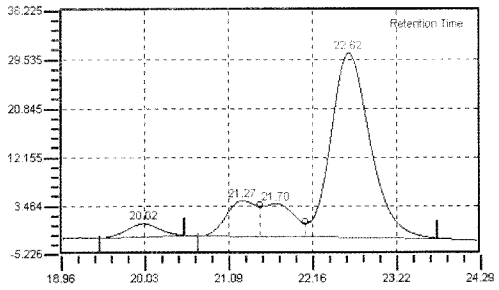


Figure 2. HPLC Chromatogram of Fullerene Oxides [$C_{70}O_n$] (n = 1～3).

was at m/z 840 in the MALDI-TOF-MS spectra Figures 1(a)-1(d) which are due to the unreacted fullerene [C_{70}] and the fragmentation[12,23] of fullerene oxide [$C_{70}O_n$] (n = 1～3 or n = 1). HPLC analysis in Table 1 shows the formation of [$C_{70}O_n$] (n = 1～3 or n = 1). The HPLC chromatogram(Figure 2) is for the most oxidated fullerene oxides of fullerene [C_{70}], among various oxidants under microwave irradiated condition was 3-chloroperoxy benzoic acid, which showed C_{70}, $C_{70}O_1$, $C_{70}O_2$, $C_{70}O_3$ at different retention times respectively.

Electronic absorption bands (λ_{max}) of [$C_{70}O_n$] (n = 1～3 or n = 1) in benzene were observed at 277, 306, 330, 358, 383, and 453 nm in the mixture of [$C_{70}O_n$] (n = 1～3) and at 278, 311, 334, 364, 383, and 471 nm in the mixture of [$C_{70}O_n$] (n = 1)(in Figure 3). Due to the breaking of the conjugated 6-6 ring junction by addition of oxygen in the fullerene [C_{70}], the bands of electronic absorption moved into blue shift. By the additional breaking of the carbon-carbon double bond in fullerene [C_{70}], the wave length of absorption bands changed and became lower in the UV-visible spectrum. This electronic absorption spectrum of the oxidation of fullerene [C_{70}] by microwave irradiation with various oxidants is not similar to that of pure C_{70} as the number of oxygen atom increases. This indicates that the multiepoxide of fullerene [C_{70}] perturbs the molecular orbital in pure C_{70}, while the monoepoxide of fullerene [C_{70}] does not seriously perturb the molecular orbital in pure C_{70}. The reaction of fullerene [C_{70}] by microwave irradiation with various oxidants may proceed by nucleophilic attack of various oxidants on the 6-6 bond (6-6 ring junction) in the fullerene [C_{70}], followed by the heterolytic cleavage of the O-O bond. The consensus mechanism for fullerene oxidation by microwave irradiation with various oxidants involves oxygen atom transfer to the fullerene [C_{70}]. It is suggested that the fullerene epoxides in the mixture of [$C_{70}O_n$] (n= 1～3 or n=1) may be used as oxygen transfer materials. Also, the fullerene oxides, in the mixture of [$C_{70}O_n$] (n= 1～3 or n=1) are interesting starting

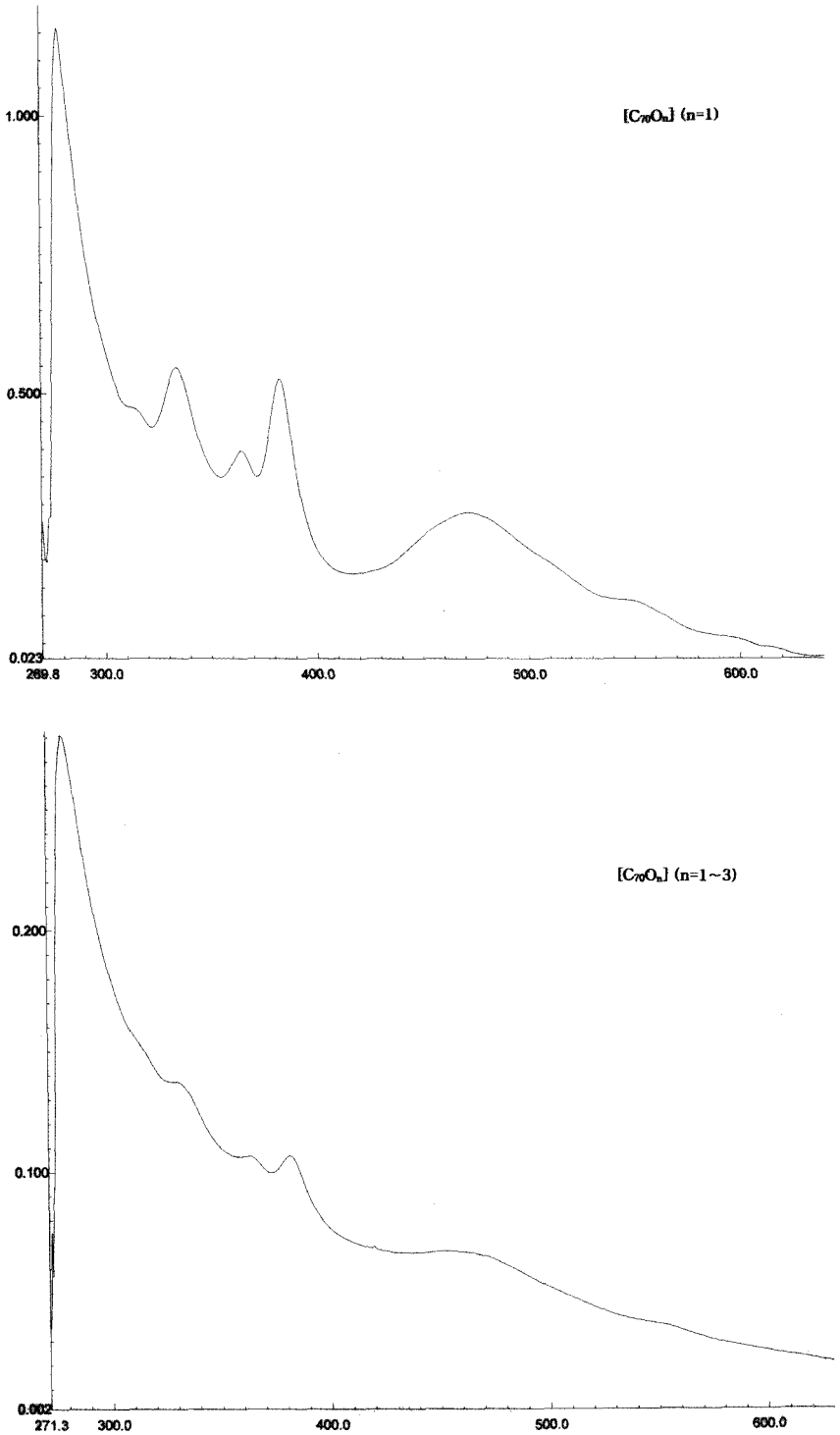


Figure 3. UV-visible Spectrum of Fullerene Oxides [$C_{70}O_n$] (n = 1 ~ 3 or n = 1).

materials for the formation of other fullerene-based entities.

Ⅳ. Conclusions

We have confirmed that the mixture of [$C_{70}O_n$] (n= 1~3 or n=1) was formed in the reaction of C_{70} by microwave irradiation with 3-chloroperoxy benzoic acid, chromium(VI) oxide, benzoyl peroxide, trichloroisocyanuric acid in solid state by the MALDI-TOF-MS, UV-visible spectra and HPLC analysis. These reaction are of the microwave induced chemical oxidation type in solid state. The reactivity of fullerene [C_{70}] with various oxidants under microwave condition increased in the order of 3-chloroperoxy benzoic acid > chromium(VI) oxide > trichloroisocyanuric acid ≅ benzoyl peroxide. The epoxidation of olefin by the multiepoxides of fullerene, in the mixture of [$C_{70}O_n$] (n= 1~3 or n=1) is presently under investigation.

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