Microwave synthesis of fullerenes from chloroform

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Fullerenes C_{60} and C_{70} were synthesized continuously via microwave plasma from chloroform at low pressure argon atmosphere, and identified in toluene extracts of soot, using high-performance liquid chromatography coupled with atmospheric pressure chemical ionization mass spectrometry and diode-array spectrophotometric detection. Yield of C_{60} (0.3%–1.3%) and C_{70} (0.1%–0.3%) and their ratio depend on the temperature gradient and the collision probability. Besides fullerenes, a series of perchlorinated carbon clusters were found in the synthesis products. Since frameworks of the products are fragments of fullerenes, the further investigation of this process may lead to a better knowledge of the formation mechanisms of fullerenes. © *1999 American Institute of Physics.* [S0003-6951(99)03944-3]

Since macroscopic quantities of C_{60} and other fullerenes were prepared by Kratschmer and Huffman,[1] various methods have been explored to produce fullerenes, for instance, incomplete combustion of benzene or hydrocarbons,[2] pyrolysis of naphthalene,[3] vaporization of graphite in Odeillo (France) solar furnace,[4] and dissociation of hydrocarbons in thermal plasma,[5–7] but Kratschmer's method, arc discharge between graphite rods under a low-pressure inert-gas atmosphere, remains to be the most efficient one.[8]

Although fullerenes can be accessed via these methods, the methodology is still a kind of ''black box'' operation[1,8] and the formation mechanism of Buckminsterfullerenes is still a puzzle to physicists and chemists.[9] None of the earlier mentioned operations was predictable or understandable and amenable to yield desired intermediates along the way. Thus, there has also been interest in the synthesis of fullerene intermediates based on classical organic reactions[10] and trapping the intermediates in the course of fullerene formation.[11–15] Up to now, however, with the exception of corannulene ($C_{20}H_{10}$), the fullerene intermediates[16,17] are still scarce and not yet available for a detailed scrutiny of their potentially rich chemistry.[10] The microwave plasma synthesis from chloroform, described in this letter, may open a way to large quantity and low cost production, not only for fullerenes but also for various perchlorinated intermediates of fullerenes, the perchlorinated carbon clusters which frameworks are parts of fullerenes.

Fullerenes soot was produced in a quartz column reactor [length=40 cm, inner diameter (i.d.)=30 mm], as shown in Fig. 1. When the reactor chamber was pumped by a water cycled pump to a pressure of 0.005 Mpa and a 250 W microwave was introduced along square wave-conduct pipe, stable plasma could be observed in the reactor under a low-pressure argon atmosphere. Chloroform, fed at 0.15 g/min, was vaporized into a reactor through the central nozzle of a transferred direct current plasma torch, which equipped on the top of the quartz column, while Ar was introduced at a flow rate of 120 ml/min from the side of the plasma torch. At the plasma zone chloroform was dissociated to form a reactive cloud of atoms and small clusters. By controlling the operating parameters, such as cooling temperature and reaction time, the reactive atoms and clusters could self-assemble to fabricate fullerenes, which condensed with intermediates and other by-products onto the reactor chamber wall or cooling trap. For improving the collision efficiency among the reactive intermediates, a glass nozzle was designed direct to the wall of cooling trap, which was quenched by ice water. As indicated at Fig. 1, the temperature gradient for fabricating fullerenes can be typically described as high-, middle-, and low-temperature zone, respectively.

After reaction for several hours, the products were collected for extraction with toluene using an ultrasonic bath and filtration at room temperature. Reddish brown solution
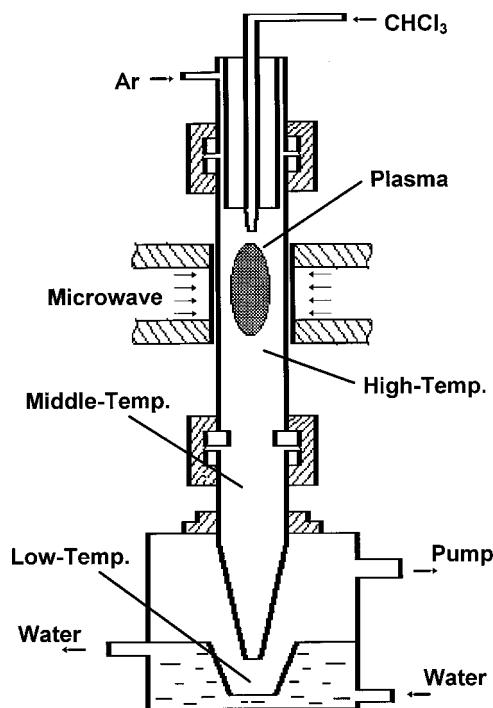

FIG. 1. Schematic of microwave synthesis system.

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TABLE I. Typical conditions for analysis of the products.

HPLC	DAD–UV	APCI–MS
Instrument:	Instrument:	Instrument:
TSP P200 HPLC system	TSP UV3000	Finnigan LCQ
Stationary phase:	Wavelength scan range:	Vaporization
temperature:		
SUPELCOSIL LC-18,	210–400 nm	400 °C
5 μm, 25×4.6 mm i.d.	Wavelength for quantity analysis:	Sheath gas:
Mobile phase:	335 nm	N2 70 ml/min
methanol/ethanol/cyclohexane	Software:	Auxiliary gas:
gradient (in 240 min):	PC 1000	N2 20 ml/min
methanol from 85% to 55%		Capillary temperature:
ethanol from 15% to 10%		200 °C
cyclohexane from 0 to 35%		Capillary voltage:
Flow rate:		−28 V
1.0 ml/min		Scan range:
Operation temperature:		200–2000 m/z
room temperature		

of the extract containing dissolved fullerenes and other products was separated and analyzed by high performance liquid chromatography with diode-array spectrophotometric detection (HPLC/DAD). This technology involves the continuous acquisition of ultraviolet (UV) spectra as peaks elute from the HPLC, and the UV adsorption spectrometry is highly sensitive to characterize fullerenes and polycyclic aromatic hydrocarbons having upward of four rings. The products were also analyzed by mass spectrometry, which is coupled with HPLC by atmospheric pressure chemical ionization (APCI) source. From the masses and the isotopic patterns of molecular ion peaks in the recorded mass spectra, chemical formulas of the products separated by HPLC could be determined. Typical parameters and conditions of the analyze are listed in Table I.

Figure 2 displays a typical HPLC—mass spectrometer (MS) spectrum of the products from high-temperature zone in microwave plasma of chloroform. Among the products, eluting times of C_{60} and C_{70}, which were identified by their MS spectrums, are 172 and 219 min, respectively. Their UV spectra (Fig. 3) acquired from HPLC/DAD analysis at their retention times closely match those of the standard C_{60} and C_{70}.[8] Quantitative analysis of HPLC at 335 nm indicated that
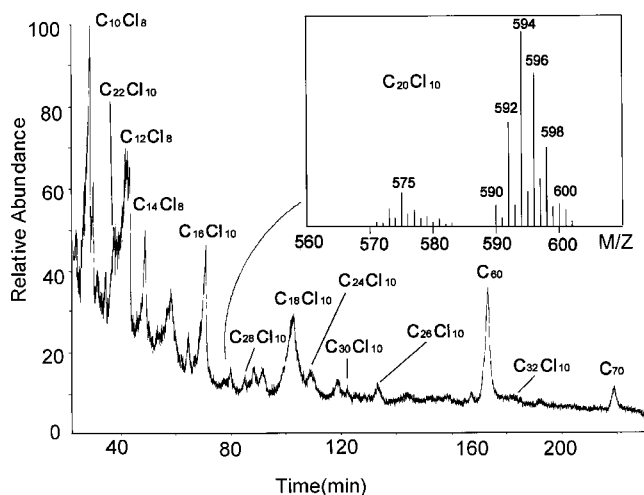
the yields of C_{60} and C_{70} are 0.3%–1.3% and 0.1%–0.3% in the collected soot products, respectively, varying with the operating parameters as follows.

In this preliminary study, various experimental parameters, including vacuum pressure, microwave energy, flow rate of argon gas and feed rate of chloroform, were investigated for the production of fullerenes. It was found in the experiment that relatively high vacuum in the reactor is necessary for the plasma reaction. When the vacuum was worse than 0.01 MPa, the plasma could not be maintained. Increase of the flow rate of the argon gas would help to maintain the plasma, but yield of the products was reduced. As the flow rate was raised to be higher than 350 ml/min, stable glow of
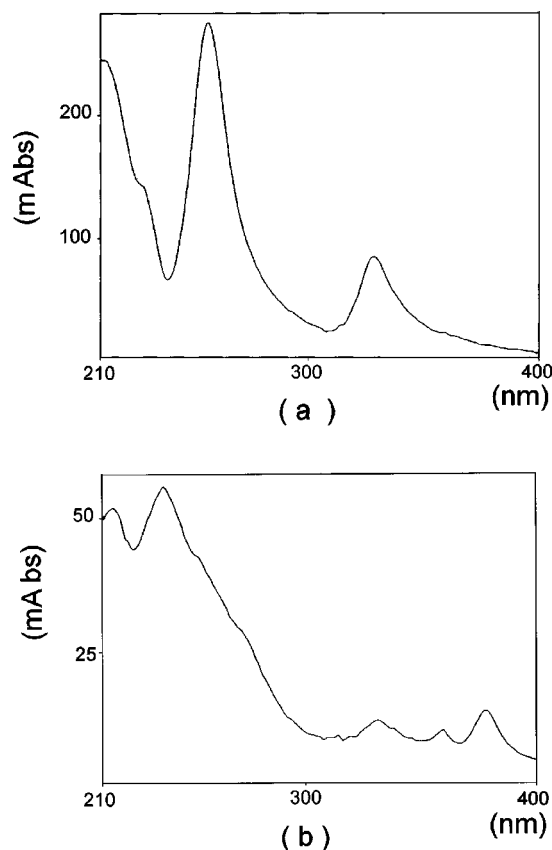

FIG. 2. HPLC–MS chromatogram of a typical soot extract from high-temperature zone in microwave plasma of chloroform.

FIG. 3. UV/visible spectrum of HPLC fullerene peak: (a) C_{60} and (b) C_{70}.

TABLE II. Yields of C_{60} and C_{70} in products A, B, and C.

	C_{60} (%)	C_{70} (%)	C_{70}/C_{60} (%)	Temperature	Reaction atmosphere	
					Temperature gradient	Collision probability
Product A	1.1	0.3	28.6	High	Small	Intensive
Product B	0.3	0.1	39.2	Middle	Middle	Middle
Product C	1.3	0.2	19.9	Low	Small	Middle

the plasma discharge became an unstable arc. Raise of the feed rate of the chloroform was also found to improve the reaction efficiency, but with the costs of disturbing the plasma and depositing soot on the wall of plasma zone. The latter problem can be partly overcame by introducing argon gas on the side of the plasma torch to sweep the soot out of the plasma zone more efficiently and to isolate the plasma from the wall. The yields of fullerenes were found to depend on the microwave energy as well, and any increase in microwave energy will entail an increase of fullerenes yield. In addition to $CHCl_3$, CCl_4 was also investigated as the start material, resulting in a similar fullerene yield as $CHCl_3$.

Further study focused on evaluating dependence of the fullerene formation with temperature and collision probability. According to the temperature difference in the reactor chamber, we distinguish the products collected at high-, middle-, and low-temperature zone as products A, B, and C, respectively. Yield of C_{60} and C_{70} collected from these three zones are summarized in Table II. The table also compares the differences of the reaction atmosphere among the high-, middle-, and low-temperature zone. The data shows that yields of both C_{60} and C_{70} are lowest in product B, while those in products A and C are approximately similar. The result suggests that the fullerene formation does not simply depend on the temperature but relies more on the temperature gradient and collision probability. The small temperature gradient and intensive collision probability seem to be favorable for the production of fullerenes. Additionally, the significant variation of the C_{70}/C_{60} ratio in the three samples implies that it is possible to improve the yields of C_{70} and high fullerenes by adjusting the temperature gradient and collision probability.

Yield of fullerenes on this process is relatively small comparing to what achieved by arc discharge methods,[8] but the proposed method is a preliminary study and the limited number of sets of conditions studied does not provide the parameters space to reveal the optimum conditions for fullerenes production. There is still much room to improve the yields of C_{60} and C_{70}, and a more detailed systematic exploration of the parameter space is now underway. In fact, compare to the previous experiment performed in plasma synthesis,[5,6,18,19] slight higher conversion (about 2.3%) of the carbon in $CHCl_3$ to fullerenes were obtained in microwave plasma reaction under proposed condition. In addition, this process can be operated continuously and the reaction device can be easily scaled up, so the microwave synthesis reaction from chloroform might be applied to the economical production of fullerenes in the future, by solving the problems such as disposal of the annoying gaseous products in a mass production.

Meunier and his co-workers had developed PyroGenesis Process, a high thermal plasma, for the synthesis of fullerenes,[5,6] and revealed that the collection temperature of the fullerene soot in the process plays a critical role in the collection rate of fullerenes. The occurrence of perchlorinated carbon cluster was not mentioned by the authors. In addition to fullerene products, however, microwave plasma synthesis from chloroform produced a series of perchlorinated carbon clusters, which have been identified by HPLC/DVD and HPLC–MS under the analysis conditions listed in Table I. Some of these perchlorinated carbon clusters, labeled in Fig. 2, can be identified from its mass and the isotopic pattern from mass spectrum. As an example, a typical mass spectrum of $C_{20}Cl_{10}$ was inserted in the figure. In the proposed microwave plasma reaction, all the products, fullerenes, and the perchlorinated carbon clusters, were produced from chloroform, a compound containing a single carbon atom only. Therefore, it is reasonable to considerate these perchlorinated carbon clusters as the perchlorinated intermediates of fullerenes, and further investigation of their structures will shed light to the formation mechanism of fullerenes.

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