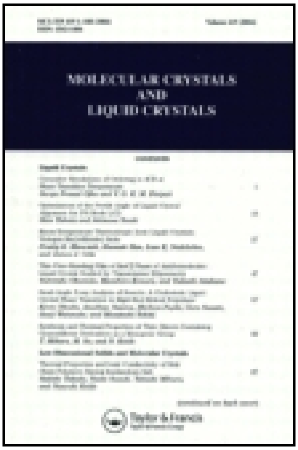

Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl20

Fullerene synthesis by pulse ARC discharge and formation process

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Version of record first published: 18 Oct 2010

To cite this article: Hironobu Matsuo & Hiroyuki Takatsu (2002): Fullerene synthesis by pulse ARC discharge and formation process, Molecular Crystals and Liquid Crystals, 386:1, 121-127

To link to this article: http://dx.doi.org/10.1080/713738823

Mol. Cryst. Liq. Cryst., Vol. 386, pp. 121–127
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1058-725X/02 $12.00 + .00
DOI: 10.1080/10587250290113330

FULLERENE SYNTHESIS BY PULSE ARC DISCHARGE AND FORMATION PROCESS

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Fullerenes were synthesized by pulse arc discharge of 50 Hz–10 kHz, 150 A–500 A with graphite electrode and He ambient (about 80 Torr). Fullerene productivity was evaluated with colorimetry by toluene dissolution and with TOF-MS analysis. As a result, fullerene yield achieved a maximum at 500 Hz, 200 A, and content rate of higher order fullerenes increased with higher frequency. In addition, correlation of each fullerene was evaluated by statistical processing from TOF-MS spectra and the fullerene formation mechanism was examined.

Keywords: fullerene; pulse arc discharge; TOF-MS; productivity; formation process

1. INTRODUCTION

Fullerenes are synthesized widely by the arc discharge method due to its higher productivity. Still, fullerene yields of only about 10–20% have been achieved using this method. For industrial application, fullerenes are still expensive. Also, it is very difficult to get higher order fullerenes. Therefore, the synthesis method needs improvement. It was reported that fullerene yield is increased by use of a pulse arc discharge (up to 500 Hz) [1]. Fullerenes were formed from carbon, which evaporated from anode and cathode spots in a process, which spreads to circumferential areas and cools down on the arc discharge method. We anticipated increased yields of higher order fullerenes if we controlled carbon vapor density by changing arc current, and cooling time by pulse frequency and duty ratio. Various models of the formation process such as the Pentagon Road [2], Ring Stacking [3], the Fullerene Road [4], Folding [5], and Random Cage [6] have been proposed up to now. However, the formation process is not clear yet. In order to improve productivity and understanding of the formation

We wish to thank Prof. Mieno for use of LD-TOF-MS at SVBL Shizuoka University.

process, fullerenes were synthesized by pulse arc discharge and analyzed by laser desorption time of flight mass spectrometer (LD-TOF-MS). Correlations between fullerenes were investigated and the formation process was discussed.

2. FULLERENE SYNTHESIS

The apparatus composed with a graphite electrode was set horizontally into a cylindrical vacuum chamber (height: 200 mm, inner ϕ: 200 mm) as shown in Figure 1. The collection electrode (ϕ: 100 mm) was placed 30 mm away from the electrode axis. Soot including fullerenes was produced by the pulse arc discharge under the following experimental conditions. Graphite electrodes ϕ: 10 mm, gap length: 2 mm, He ambient: about 80 torr (without flow), discharge time: 30 s, amplitude of pulse arc current: 100–500 A, pulse frequency: 50 Hz–10 kHz and duty ratio: 15–85% [7]. The chamber was opened to the atmosphere after sufficient cooling and soot was collected. Soot was investigated by toluene colorimetry and LD-TOF-MS of negative ion mode. Figure 2 shows one of the TOF-MS spectra as an example. It can be seen that not only fullerenes with so-called magic numbers (C_{60}, C_{70}, C_{76}, and so on) but also many other higher order fullerenes are included in each C_2. It is not possible to know the fullerene content ratio by comparing

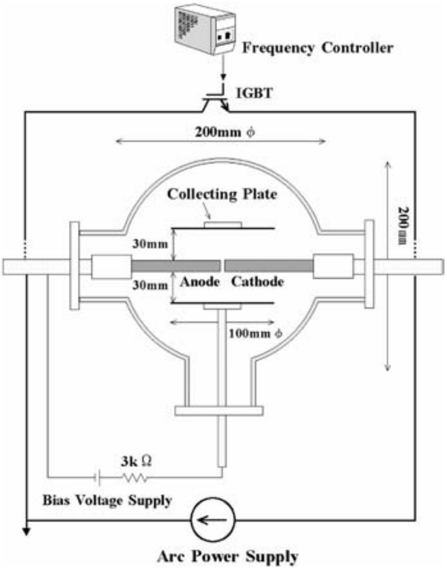


FIGURE 1 Experimental apparatus.

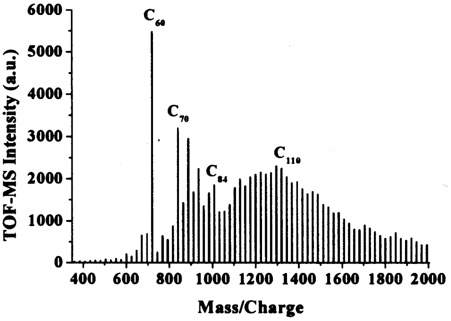


FIGURE 2 TOF-MS spectrum [arc current: 200 A, frequency: 500 Hz, and duty ratio: 50%].

their intensities directly, because their ionization rates, secondary electron emission rates, and other characteristics are different. Therefore, we used fullerene intensity ratios to get an idea of the relative content ratio. Frequency dependence was shown as an example of results. Figure 3 shows dependence of electrode weight changes on pulse frequency. Anode evaporation and cathode deposition apparently increase with increasing arc current; then, above some critical level of the pulse frequency, they decrease and become saturated. This condition arises from delay of positive feed back of C_2 radiation formed in front of the anode surface [1]. Figure 4 shows dependence of the TOF-MS intensity ratio. Clearly, the content ratio of higher order fullerenes increases with increasing frequency; and influence of frequency on the content ratio becomes weaker with increasing order of fullerenes. On the other hand, toluene colorimetry indicates that the fullerene yield becomes highest at arc current of 200 A and frequency of 500 Hz. On the other hand, dependence of arc current at a

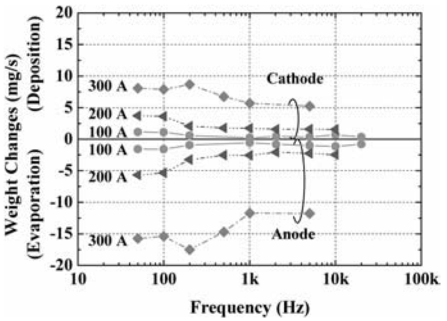


FIGURE 3 Dependence of weight change of electrodes.

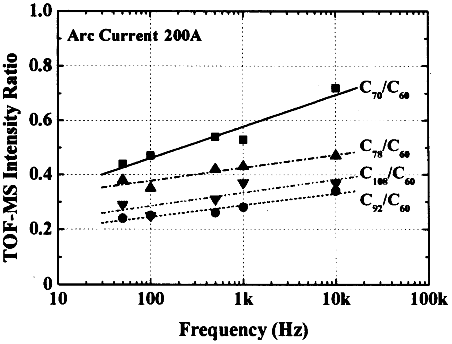
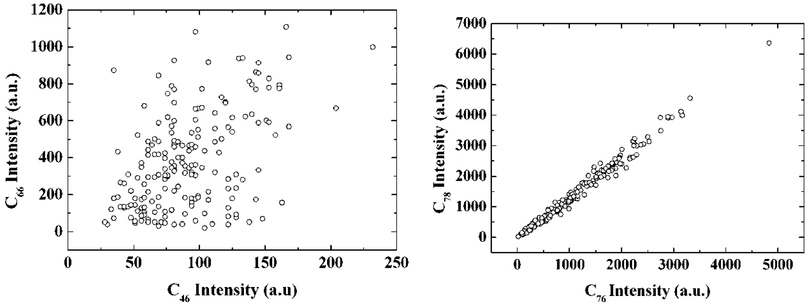


FIGURE 4 Dependence of TOF-MS intensity ratio on pulse frequency [arc current: 200 A and duty ratio: 50%].

duty ratio of 50% indicates that fullerene yield had a peak at arc current of 200 A and the higher fullerene content ratio decreased with increasing arc current beyond 250 A. Dependence of the duty ratio at arc current of 300 A showed that fullerene yield and higher fullerene content ratio had a peak at duty ratios of 40–50%.

3. CORRELATION BETWEEN FULLERENES

In order to avoid influences introduced by analytical conditions, correlation was obtained by using a statistical technique. Correlation coefficients were estimated using 206 spectra ranging from C_{30}–C_{166} as shown in Figure 2. One set of clusters was chosen from the TOF-MS spectra as shown in Figure 5. It can be seen that there was no correlation between



(a) C_{66} and C_{46} (b) C_{78} and C_{76}

FIGURE 5 Correlation between fullerenes.

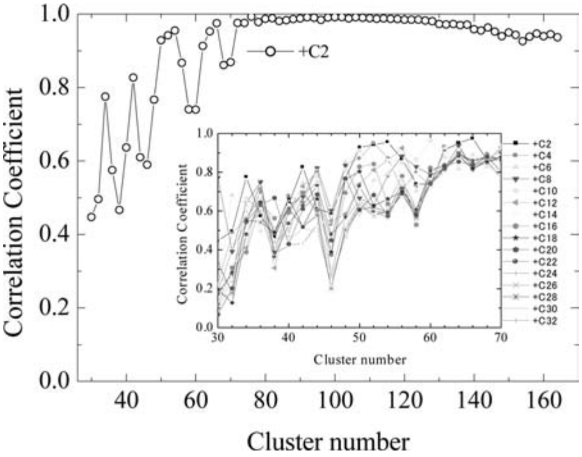


FIGURE 6 Correlation coefficient of $+C_2$ and others.

C_{66} and C_{46} and very good correlation between C_{78} and C_{76}. For numerical estimation, Pearson's product rate correlation coefficient was introduced. Correlation coefficients with clusters are shown in tFigure 6 for consecutive clusters, e.g., $C_x + C_{x+2}$ where $x = 30$–158 and inset figure for clusters $C_y + C_{y+z}$, where $y = 30$–70 and $z = 2$–32. It is apparent that the correlation coefficient is excellent above C_{72}, but below C_{72} it is comparatively good for C_{34}, C_{42} and certain other clusters. Similarly, comparatively good correlation is seen with certain clusters such as C_{52} in $+C_4$, C_{36} in $+C_6$, and C_{30} in $+C_8$. Also, one can see from the inset that correlation of $+C_2$–$+C_{32}$ becomes weak with decreasing cluster number, but correlation is usually better for C_{36}, C_{44}, C_{50}, and C_{56}, though worse for C_{38}, C_{46}, and C_{58}. These better and worse correlation clusters conformed well with cluster stability [8].

4. DISCUSSION OF FULLERENE FORMATION PROCESS

From results mentioned above, the fullerene formation process could be explained as follows. The carbon rod is evaporated by heat flux of the arc and forms C_2 as the most fundamental particles [9]. Thereupon, C_4, C_6, C_8, etc. are formed from C_2. They combine with each other and then take a gradual cage structure. Their combinations depend on differential energy states, structures, and cooling rates (e.g., C_{30} combines easily with C_8, C_{52}, with C_4). There may be formed especially many clusters passing through C_{36}, C_{44}, and C_{50}. These combination processes occur continuously with reduced temperature and when the cage approaches C_{60}; then it attempts formation of C_{60} because of its highest stability. If the cooling process is delayed slightly, it forms C_{70} instead of C_{60} because C_{70} exhibits highest stability next to C_{60}. Fullerenes above C_{72} take the closed cage structure and grow with higher clusters with C_2 addition [4,9] to C_{74}, C_{76}, C_{78}–C_{160}–C_{xyz} until it cools and finally stop growing. Then, IPR (Isolated Pentagon Role) has priority because of its higher energy stabilities. Thus, combination of small clusters with particular energies and structures occurs selectively among clusters in the comparatively high temperature region. The higher fullerenes are formed by combination of C_2 in the comparatively low temperature region; after which it achieves stability by Stone-Wales transfer [10]. This model implies the Random Cage model [6] with specified selectivity below C_{70}, and the fullerene road (C_2 addition) model [4,9] above C_{72}. Comparing the Ring Stacking model [3], it was reported that the combinations, which eventually form C_{60}, are either $C_{32} + C_{28}$, $C_{46} + C_{14}$, $C_{50} + C_{10}$, and $C_{58} + C_2$. Still, these combinations have weaker correlation as shown in Figure 5. Comparing it with the Pentagon Road [2], Folding [5] and other models, it is difficult to understand the results mentioned above.

5. CONCLUSION

Fullerenes were synthesized by a pulse arc discharge of 50 Hz–10 kHz, 150 A–500 A with graphite electrode and He ambient (about 80 Torr). Fullerene productivity was evaluated with colorimetry by toluene dissolution and with TOF-MS analysis. As a result, fullerene yields reach a maximum at 500 Hz, 200 A; and the content rate of higher order fullerenes increases with higher frequency. In addition, correlation of each fullerene was evaluated by statistical processing from TOF-MS spectra of 206 data mentioned above. The correlation coefficient of $C_x + C_2$ is excellent above C_{72}. There are some comparatively good correlations such as C_{34}, C_{42} in $+C_2$, C_{52} in $+C_4$, C_{36} in $+C_6$, and C_{30} in $+C_8$. It is apparent that correlation of $+C_2 - +C_{32}$ becomes weak with decreasing cluster number, but correlation is usually good for C_{36}, C_{44}, C_{50}, and C_{56} and weaker for C_{38}, C_{46}, and C_{58}. The fullerene formation process was considered as follows from these results. There may be many clusters formed especially passing through C_{36}, C_{44}, and C_{50} from carbon vapor evaporated from the anode. These combination processes occur continuously with reduced temperature and depend on different energy states, structures, and cooling rates. Fullerenes above C_{72} take the closed cage structure and grow having higher clusters with C_2 addition until they cool and subsequently stop growing.

REFERENCES

[1] Takikawa, H. *et al.* (1996). *Applied Plasma Science*, *4*, 23.
[2] Haufler, R. E. *et al.* (1991). *Mat. Res. Soc. Symp. Proc.*, *206*, 627.
[3] Wakabayashi, T. & Achiba, Y. (1992). *Chem. Phys. Lett.*, *190*, 465.
[4] Heath, J. R. (1992). *Fullerenes*, American Chemical Society.
[5] Lagow, R. J. *et al.* (1995). *Science*, *267*, 362.
[6] Maruyama, S. (1997). *Chemistry*, *52*, 20.
[7] Matsuo, H. *et al.* (1999). *Abstracts of the 17th Fullerene General Symp.*, *50*.
[8] Kietzmann, *et al.* (1998). *Phys. Rev. Lett.*, *81*, 5378.
[9] Matsuo, H. *et al.* (1996). *Trans. of MRS-J*, *20*, 412.
[10] Stone, A. J. *et al.* (1986). *Chem. Phys. Lett.*, *128*, 501.