Investigation of the polymerization mechanism of ferrocene doped C_{60} under high pressure and high temperature

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In situ high pressure and high temperature (HPHT) study has been carried out on C\textsubscript{60}/ferrocene (Fc) in order to detect the process of polymerization and reveal the polymerization mechanism. Pristine C\textsubscript{60} was also studied under same conditions for comparison. In both cases, similar types of polymers can be observed after pressure and temperature release, but with different fractions, i.e. a larger amount of 2D polymers were formed in pure C\textsubscript{60}, while more branch-like polymers were synthesized in C\textsubscript{60}/Fc, although the most fraction of the polymers is still 1D chain-like polymer in both of the materials. The polymers formed in C\textsubscript{60} can be detected both during the “up” run (pressure and temperature increase) and the “down” run (pressure and temperature decrease), while in C\textsubscript{60}/Fc, the polymers can only be synthesized in the “down” run. The differences between the two cases were attributed to the different initial lattice structures of the two materials and the confinement effect of the dopant. The polymerization mechanism on C\textsubscript{60}/Fc under HPHT was also revealed in this work.

Doping process can greatly improve the electrical and optical features of materials, which are very important for high technical products\textsuperscript{1-3}. Among these, doped fullerene materials have aroused a research fever for creation of new materials, by using molecular confinement or co-intercalation by template molecules before the reaction\textsuperscript{4, 5}. More importantly, doping is effectively used to synthesize controllable pressure induced polymerized fullerene. For example, a reversible orthorhombic polymerization has been observed in Na\textsubscript{2}RbC\textsubscript{60} and Na\textsubscript{2}CsC\textsubscript{60} under pressure at room temperature\textsuperscript{6}. Popov et al. reported that a 3D-polymerized C\textsubscript{60} with high bulk module of 585 GPa was formed in C\textsubscript{60}/CS\textsubscript{2} at pressure 6–7 GPa and room temperature\textsuperscript{7}. The covalent bonds between C\textsubscript{60} molecules were formed in [Cd(dedtc)\textsubscript{2}]*C\textsubscript{60} under pressure\textsuperscript{8}. Moreover, pressure-induced metastable ordered polymers were synthesized from C\textsubscript{60}/AgNO\textsubscript{3} and C\textsubscript{60}/Ni(OEP) under high pressure\textsuperscript{9}. Both the quenched materials contain chain-like polymers and dimers but with different fractions, which can be understood by the different initial lattice structures of these materials and the confinement effects of the dopants. Besides polymerization, doped C\textsubscript{60} materials and some other carbon materials can also transform into many novel phases with various properties under pressure. For example, long range ordered structures with the building block of amorphized C\textsubscript{60} and C\textsubscript{70}\textsuperscript{*} cluster were synthesized from C\textsubscript{60}/m-xylene and C\textsubscript{70}/m-xylene under high pressure, respectively, which phases were superhard and can indent diamond anvils\textsuperscript{10-12}. Wang et al. synthesized several new crystal structures of carbon (e.g., bet-C\textsubscript{44}, H\textsubscript{2}, M\textsubscript{2}, R\textsubscript{2}, S\textsubscript{2}, W\textsubscript{2}, and Z-carbon) from compressed graphite\textsuperscript{13-14}. Therefore, applying pressure is a useful tool to synthesize new materials from doped C\textsubscript{60} and carbon based materials, since pressure can tune the distance between neighboring molecules to form new bonds.

Besides, temperature is another important factor to obtain new C\textsubscript{60} based materials. Combination of the two technical methods can bring us some new phenomena and obtain more new phases, especially unique polymeric structures, with novel properties\textsuperscript{15-19}. For example, Yamanaka et al.\textsuperscript{15} obtained a body-centered orthorhombic 3D C\textsubscript{60} polymer from a 2D polymeric C\textsubscript{60} single crystal at 15 GPa and 600°C. In contrast with the nonconductive behavior of 2D polymers, the obtained 3D C\textsubscript{60} polymer was electronically conductive. In our recent study, metastable 1D or 2D polymers were formed from C\textsubscript{60}/Fc, C\textsubscript{60}/AgNO\textsubscript{3} and C\textsubscript{60}/Ni(OEP) after high pressure and...
We found that due to the spatial and geometrical confinement effects of the dopants, the polymerization degree is always lower than that of pure C$_{60}$ treated at the same conditions. Meanwhile, the polymeric phases formed in the three doped materials were also different, which was attributed to the unique initial lattice structures and the different degrees of spatial confinement provided by the dopants. However, in this HPHT method it is difficult to detect and study the phase transition process of the samples. The polymerization mechanism in doped C$_{60}$ materials under HPHT is still unclear. Thus, searching a new method to track the process of polymerization is a challenge subject.

In this study, we used a self-assembly external heating assembled diamond anvil cell (DAC) to in situ study the polymerization of a typical doped C$_{60}$ material, C$_{60}$/Fc, up to 3.2 GPa and 190 °C. The usage and assembly details of the DAC were similar as that presented in previous works. To reveal the process of polymerization, pristine C$_{60}$ was also treated under same conditions for comparison. Our results showed that both C$_{60}$ and C$_{60}$/Fc can form similar types of polymers under studied conditions but with different fractions. In C$_{60}$ the polymers were formed under all of our studied conditions, while in C$_{60}$/Fc, the polymers can only be synthesized when pressure and temperature release. We found that the different initial lattice structures of these materials and the confinement effect of the dopant were contributed to the differences between the two cases. The polymerization mechanism on C$_{60}$/Fc was also uncovered in this study. This work also opens a new sight on the research method of phase transition in doped C$_{60}$ materials and establishes favorable foundation on the synthesis of new materials with various phases and unique properties.

Results and Discussion

Structure of C$_{60}$/Fc. The packing arrangement of C$_{60}$/Fc was shown in Fig. 1a (calculated by Materials Studio from the data in ref. 23). C$_{60}$/Fc has a unique layered structure which consists of close-packed layers of C$_{60}$ molecules stacked directly one above the other. To study the structure of C$_{60}$/Fc, Raman spectroscopy was employed and the result was shown in Fig. 1b. The spectra of pure C$_{60}$ and the dopants were also presented in Fig. 1b for comparison. The spectrum of pristine C$_{60}$ contains ten peaks, including eight Hg modes and two Ag modes. From this figure, we can see that both C$_{60}$/Fc and the dopants were also presented in Fig. 1b for comparison. The spectrum of pristine C$_{60}$ contains ten peaks, including eight Hg modes and two Ag modes. From this figure, we can see that the spectrum of C$_{60}$/Fc contains Raman signals from both the intercalant molecules and from C$_{60}$, which indicates that the dopants are efficiently intercalated to the lattice of C$_{60}$.

Results of the samples treated after HPHT. We first present the results of pure C$_{60}$ and C$_{60}$/Fc after the treatment of 3.2 GPa and 190 °C. The Raman spectra for the two samples were shown in Fig. 2. We also magnified the Ag(2) mode in the insets, since polymers are usually identified from the shift of the high-intensity Raman Ag(2) mode, which at room temperature falls at 1469 cm$^{-1}$. The formation of intermolecular bonds shifts the electron density away from the remaining double bonds, which became weaker. This causes a shift of about 5 cm$^{-1}$ for dimers, a shift of 10 cm$^{-1}$ for linear chains, and 21 cm$^{-1}$ for tetragonal phase which has been thoroughly studied and generally accepted in the field of fullerene studies. From this figure, we can see that for pure C$_{60}$, the Ag(2) peak splits into five peaks with positions at 1468, 1464, 1459, 1452 and 1447 cm$^{-1}$ (shown in the left inset of Fig. 2), indicating that the quenched sample is a mixture of free molecules, dimers, 1D chain-like polymers, branch-like polymers and 2D polymers, respectively. For C$_{60}$/Fc, the Ag(2) peak splits into four peaks with positions at 1467, 1460, 1453 and 1446 cm$^{-1}$ (shown in the right inset of Fig. 2), indicating that the quenched sample is a mixture of free molecules, 1D chain-like polymers, branch-like polymers and 2D polymers, respectively. Further analyzing, we found that although both of the quenched samples contained similar components of polymers, the fractions are very different, especially the fractions of branch-like polymers and 2D polymers, which can be easily detected by the areas of the peaks at around 1452 cm$^{-1}$, respectively. The areas of the peak at around 1447 cm$^{-1}$ are 12.1% and 5.1% in quenched C$_{60}$ and C$_{60}$/Fc, respectively; and the percentages are 11.9% and 33.6% for the areas of the peak at around 1452 cm$^{-1}$. This result demonstrated that a larger amount of 2D polymer was synthesized from pure C$_{60}$, while more branch-like polymers were obtained.
from C_{60}/Fc. It should be noted, however, that the most fraction of the polymers is still 1D chain-like polymer in both of the two samples, due to the largest area of the peak at around 1460 cm\(^{-1}\).

The different fractions of the obtained polymers formed in quenched C\(_{60}\) and C\(_{60}/Fc\) can be understood by the different initial lattice structures of the samples. Because pure C\(_{60}\) is free from steric effects, the polymerization is random, a large number of randomly oriented dimers can be obtained first and these can grow in any direction to form straight chains, branched chains, 2D polymers and possibly large amorphous structures. Meanwhile, the initial fcc structure makes it easily to form 1D chain-like polymers first and then 2D T-phase polymers (the basic polymeric structures were shown on the right of Fig. 2) in our studied conditions. For C\(_{60}/Fc\), the geometrical separation of the C\(_{60}\) layers prevents the formation of intercage polymer bonds in the c direction (see Fig. 1a). Thus, the polymerization in C\(_{60}/Fc\) can be more likely to proceed within each fullerene layer. The special plane distribution of C\(_{60}\)s makes it more possible to form 1D chain-like polymers first and then branch-like polymers under high temperature and high pressure, while only a few fraction of inter-layered C\(_{60}\)s can form 2D square-like polymers (similar to the 2D T-phase polymers formed in pure C\(_{60}\)). The most possible polymeric structures were also drawn in Fig. 2.

**In situ HPHT study on C\(_{60}\) and C\(_{60}/Fc\).** To further study the formation process of the polymers and reveal the polymerization mechanism on C\(_{60}/Fc\), *in situ* HPHT Raman study was carried out on C\(_{60}\) and C\(_{60}/Fc\). Figure 3a,b show the Raman spectra of C\(_{60}\) recorded at different pressures and temperatures in the “up” run and “down” run, respectively. From Fig. 3a, we can see that as the pressure and temperature increasing, the Ag(2) modes become broad and a wide shoulder centered around 1455 cm\(^{-1}\) at the lower frequency of Ag(2).
was appeared from 0.29 GPa and 60 °C. The shoulder can still be observed up to 3.2 GPa and 190 °C. This indicated that C60 can form polymers from very low pressure and temperature and the polymers can always exist under the studied conditions. When the pressure and temperature gradually released to atmosphere condition, a broad shoulder at the lower frequency of Ag(2) was appeared from 2.45 GPa and 140 °C and the shoulder can be observed in all of the studied conditions. Until the pressure and temperature released to atmosphere, the Ag(2) mode obviously split to five peaks as we have mentioned above. These results indicated that the polymeric phases can be synthesized both in the “up” run and “down” run.

The Raman spectra of C60/Fc under different pressures and temperatures were shown in Fig. 4. As the pressure and temperature increasing, it was found that the Ag(2) modes did not change a lot and the positions were always located at around 1467 cm\(^{-1}\) (shown in Fig. 4a), which was very different from the phenomenon observed in pure C60 under the same conditions. However, as the pressure and temperature decreasing, a broad shoulder at the lower frequency of Ag(2) was appeared from 2.45 GPa and 140 °C which is similar as the phenomenon observed in pure C60 and the shoulder can also be observed in most of the studied conditions. Until the pressure and temperature released to atmosphere, we found that the Ag(2) mode obviously split to four peaks as we have mentioned above. These results demonstrated that the polymers cannot be formed in the “up” run, but in the “down” run the polymers were gradually synthesized.

The different formation process of the polymers synthesized from C60 and C60/Fc can also be reasonably explained by their different initial lattice structures. Due to the existence of Fc molecules in C60/Fc, which can interact with the C60 molecules to affect the rotation and the available volume for the C60 molecules under HPHT, the formation of polymers is more difficult than that in pure C60 under the same conditions. Thus only at suitable pressures and temperatures can the polymers be formed in C60/Fc, while for pure C60, the free steric effects made it easily to form different polymers under various pressures and temperatures.

Further analyzing, we found that the peak positioned at around 317 cm\(^{-1}\) which represented the vibrational modes from the inserted Fc molecules (marked by rectangles in Fig. 4) could be always obviously observed up to the highest pressure and temperature in the “up” run. However, only very weak signals can be detected in the “down” run. We thus try to describe the polymerization mechanism as follows and draw the schematic image of this mechanism in Fig. 5 for clear understanding. In the “up” run (see process 1 in Fig. 5), although the Fc molecules can be gasified above 100 °C, the gaseous Fc molecules cannot leave the initial lattice but become more closed to neighboring molecules with the presence of pressure, which caused the effect of spatial confinement to hinder the bonding between C60s. Meanwhile, the temperature can affect the rotation of C60 molecules which

![Figure 4](image_url)

**Figure 4.** The Raman spectra of C60/Fc recorded at different pressures and temperatures in the “up” run (a) and “down” run (b), respectively. The modes from Fc were marked by rectangles.

![Figure 5](image_url)

**Figure 5.** The schematic image of the polymerization mechanism. The blue solid circle represents C60 molecule and the red hourglass-like shape represents Fc molecule.
makes the neighboring C_{60}s may not face to each other in a favorable position for polymerization. That was the reason why no polymeric phases were obtained in the “up” run. However, in the “down” run (see process 2 in Fig. 5), as pressure decreasing the crystal lattice will slightly expand and the gaseous Fc molecules may move and depart from their original positions in a certain degree which induced some parts of C_{60}s molecules can bond to each others to form polymers (the possible polymerized directions were drawn with imaginary line shown in Fig. 5), but some other parts of C_{60}s are still separated by Fc molecules. That was the reason why only weak Raman signals of Fc can be observed in the polymeric phases shown in Fig. 4b and for some parts of quenched C_{60s}/Fc which cannot form polymers, the obvious peak of Fc molecules was still be observed (not shown in Fig. 4b).

The polymerization process of C_{60s}/Fc under HPHT is different from that of our previous study on C_{60s}/Fc under cold compression^{38}, in which case that the 1D chain-like polymers were obtained when pressure increased to 5 GPa. However, higher dimensional polymers, such as 2D polymers, cannot be observed in that case. The differences verified that temperature plays an important role in the process of higher dimensional polymerization between neighboring C_{60}s molecules. First, although the polymeric bonds can be most likely formed within each fullerene layer due to the special arrangement of C_{60}s under pressure, the suitable temperature must be chosen because the temperature will affect the rotation of C_{60}s and eventually influence the bonding between C_{60}s. That may be the reason why 1D polymers can be formed under cold compression in our previous work but not in the “up” run of this work. Second, due to the gasification or movement of Fc molecules with the help of temperature and accompanying by the effect of pressure, it is possible for inter-layered C_{60}s to get close enough to form bonds. Thus, we can not only obtain 1D chain-like polymers and branch-like polymers within each fullerene layer, but also the 2D polymers formed between layered fullerenes. However, under room temperature only 1D polymers can be synthesized but not higher dimensional polymers. These differences thus provide us with good models for studying the effect of spatial confinement on the polymerization of doped C_{60}s materials and the resulting potential to create new polymeric structures, as well as to improve our understanding of the polymerization mechanism of confined doped fullerene.

**Conclusion**

In summary, in situ HPHT study has been carried out on C_{60}s and C_{60s}/Fc up to 3.2 GPa and 190 °C. Our results showed that both materials can form similar types of polymers under HPHT but with different fractions, i.e. besides the most fraction of the polymers is still 1D chain-like polymer in both cases, a larger amount of 2D polymers were synthesized from pure C_{60}s while more branch-like polymers were obtained from C_{60s}/Fc. The polymers formed in C_{60}s can be detected both during the “up” run and “down” run, while in C_{60s}/Fc, the polymers can only be synthesized in the “down” run. The polymerization mechanism on C_{60s}/Fc under HPHT was also revealed in this study. We found that the different initial lattice structures of the two materials and the confinement effect of the dopant were contributed to the differences between the two cases.

**Methods**

C_{60s}/Fc crystals were synthesized by introducing sufficient Fc (200 mg) into a certain amount of saturated C_{60}/toluene solution (3 ml). After ultrasonication we then gently added 3 ml isopropyl alcohol (IPA) into the mixture. Finally, the mixture was maintained at 10 °C for 24 h for the growth of single crystalline C_{60s}/Fc. The detailed method has also been described in previous studies^{33,38}.

We used a special three columned diamond anvil cell (the culet is 500 micrometer) to carry out the in situ HPHT experiment. For comparison, pristine C_{60}s and C_{60s}/Fc were both loaded in one gasket. In the “up” run, the samples were firstly applied to a certain pressure and then heated to target temperatures, while in the “down” run, the samples were firstly cooled down to target temperatures and then released to the given pressures. The samples were heated by the local electric resistance wires wrapped around the tungsten carbide seats which support the diamond anvils and the temperatures were recorded by a digital thermometer. In this study, no pressure medium was used and the highest pressure and temperature was 3.2 GPa and 190 °C. HPHT Raman measurements have been carried out using a Raman spectrometer (Renishaw in Via) with a 633 nm He-Ne laser line as excitation. The light spot diameter is about 1.7 micrometer and the exposure time is 50 s. The laser power is altered between 0.04–0.05 mW (for the measurement on the recovered samples to avoid the formation of photo-polymerization) and 4–5 mW (for the measurement during the experiment).

**Data Availability.** The datasets generated during and/or analysed during the current study are available from the corresponding author on reasonable request.

**References**

1. Wang, Y. et al. Anomalous Surface Doping Effect in Semiconductor Nanowires. *J. Phys. Chem. C* 121, 11824–11830 (2017).
2. Wu, J., Cofer, J. L., Wang, Y. & Schulze, R. Oxidized Germanium as a Broad-Band Sensitizer for Er-Doped SnO_{2} Nanofibers. *J. Phys. Chem. C* 113, 12–16 (2009).
3. Senter, R. A. et al. Structural Influence of Erbium Centers on Silicon Nanocrystal Phase Transitions. *Phys. Rev. Lett.* 93, 175502 (2004).
4. Wagberg, T. & Sundqvist, B. Raman study of the two-dimensional polymers Na_{3}C_{60} and tetragonal C_{60}. *Phys. Rev. B* 65, 155421–155427 (2002).
5. Pekker, S. et al. Single-crystalline (KCl)_{2}m: a conducting linear alkali fulleride polymer. *Science* 265, 1077–1078 (1994).
6. Zhu, Q. Pressure-induced polymerization of ternary fulleride superconductors. *Phys. Rev. B* 52, R723–R726 (1995).
7. Popov, M. et al. Synthesis of ultrahard fullerite with a catalytic 3D polymerization reaction of C_{60}. *Carbon* 76, 250–256 (2014).
8. Meletov, K. P., Konarev, D. V. & Tofstikova, A. O. Phase transitions and photoinduced transformations at high pressure in the molecular donor-acceptor fullerene complex{Cd(dedtc)_{2}}^{*}C_{60}. *J. Exp. Theor. Phys.* 120, 989–997 (2015).
9. Cui, W., Sun, S. S., Sundqvist, B., Wang, S. M. & Liu, B. B. Pressure induced metastable polymerization in doped C_{60}s materials. *Carbon* 115, 740–745 (2017).
10. Wang, L. et al. Long-Range Ordered Carbon Clusters: A Crystalline Material with Amorphous Building Blocks. *Science* 337, 825–828 (2012).
11. Cui, W. et al. A New Carbon Phase Constructed by Long-Range Ordered Carbon Clusters from Compressing C_{70} Solvates. *Adv. Mater.* 26, 7257–7263 (2014).

12. Yao, M. G. et al. Pressure-induced transformation and superhard phase in fullerenes: The effect of solvent intercalation. *Appl. Phys. Lett.* 103, 071913 (2013).

13. Wang, Y., Panzik, J. E., Kiefer, B. & Lee, K. K. M. Crystal structure of graphite under room-temperature compression and decompression. *Sci. Rep.* 2, 520 (2012).

14. Wang, Y. & Lee, K. K. M. From soft to superhard: Fifty years of experiments on cold compressed graphite. *J. Superhard Mater.* 34, 360–370 (2012).

15. Yamanaka, S. et al. Electron Conductive Three-Dimensional Polymer of Cuboidal C_{60}. *Phys. Rev. Lett.* 96, 076602 (2006).

16. Yamanaka, S., Kini, N. S., Kubo, A., Jida, S. & Kuramoto, H. Topochemical 3D Polymerization of C_{60} under High Pressure at Elevated Temperatures. *J. Am. Chem. Soc.* 130, 4303–4309 (2008).

17. Ivanovskaya, V. V. & Ivanovskii, A. L. Simulation of novel superhard carbon materials based on fullerenes and nanotubes. *Journal of Superhard Materials* 32, 67–87 (2010).

18. Sundqvist, B. Mapping intermolecular bonding in C_{60}. *Sci. Rep.* 4, 6171 (2014).

19. Alvarez-Murga, M. & Hodeau, J. L. Structural phase transitions of C_{60} under high-pressure and high-temperature. *Carbon* 82, 38–407 (2015).

20. Cui, W., Sun, S. S., Yao, M. G. & Liu, B. B. High pressure and high temperature induced polymerization of doped C_{60} materials. *Carbon* 109, 269–275 (2016).

21. Bassett, W. A., Shen, A. H., Bucknum, M. & Chou, I. M. A new diamond anvil cell for hydrothermal studies to 2.5 GPa and from 190 to 1200 °C. *Rev. Sci. Instrum.* 64, 2340–2345 (1993).

22. Bassett, W. A. High pressure-temperature aqueous systems in the hydrothermal diamond anvil cell (HDAC). *Eur. J. Mineral.* 15, 773–780 (2003).

23. Crane, J. D., Hitchcock, P. B., Kroto, H. W., Taylor, R. & Walton, D. R. Preparation and characterisation of C_{60}(ferrocene)_2. *J. Chem. Soc., Chem Commun* 1764–1765 (1992).

24. Sundqvist, B. Fullerences under high pressures. *Adv. Phys.* 48, 1–134 (1999).

25. Sundqvist, B. Polymeric Fullerene Phases Formed Under Pressure. *Struct. Bond* 109, 85–126 (2004).

26. Wågberg, T., Jacobsson, P. & Sundqvist, B. Comparative Raman study of photopolymerized and pressure-polymerized C_{60} films. *Phys. Rev. B* 60, 4535–4538 (1999).

27. Arvanitidis, I. et al. Raman modes of the two-dimensional tetragonal polymeric phase of C_{60} under high pressure. *J. Chem. Phys.* 114, 9099–9104 (2001).

28. Talyzin, A. V., Dubrovinsky, L. S., Le Bihan, T. & Jansson, U. Pressure-induced polymerization of C_{60} at high temperatures: An in situ Raman study. *Phys. Rev. B* 65, 245413 (2002).

29. Cui, W. et al. Reversible polymerization in doped fullerides under pressure: the case of C_{60}(Fe(C_{5}H_{5})_2)_2. *J. Phys. Chem. B* 116, 2643–50 (2012).

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**Author Contributions**

Sun, S.S. conducted the experiments and analysed the results, Cui, W. conceived the experiments, conducted the experiments and analysed the results, Wang, S.M. conducted the experiments, Liu, B.B. analysed the results. All authors reviewed the manuscript.

**Additional Information**

**Competing Interests:** The authors declare that they have no competing interests.

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