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High pressure and high temperature induced polymerization of doped C₆₀ materials

Wen Cui^a, Bertil Sundqvist^{b,d}, Shishuai Sun^c, Mingguang Yao^b, Bingbing Liu^b

^a College of Physics and Materials Science, Tianjin Normal University, Tianjin, 300387, China.

^b State Key Laboratory of Superhard Materials, Jilin University, Changchun, 130012, China.

^c College of Science, Tianjin University of Technology, Tianjin, 300 384, China.

^d Department of Physics, Umeå University, S-901 87 Umeå, Sweden

Abstract

Several metastable doped C₆₀ polymers are synthesized under high pressure and high temperature (1.5GPa, 573K and 2GPa, 700K, respectively), using C₆₀/ferrocene (Fc, Fe(C₅H₅)₂), C₆₀/Ni(OEP) and C₆₀/AgNO₃ as starting materials. Raman and IR spectroscopy are used to study the polymerization of these samples after HPHT treatment. It is found that the polymerization degree is always lower than that of pure C₆₀ treated at same conditions, which is attributed to the space limitation by the dopants. We also find that even at same conditions, the three doped materials form different polymeric phases of the doped materials. This is attributed to the unique initial lattice structures and the different degrees of spatial confinement provided by the dopants.

1. Introduction

Polymerized fullerene C_{60} has aroused a research fever for creation of new materials with dramatically different physical and chemical properties [1–3]. C_{60} can be polymerized by various methods, such as applying high pressure and temperature (HPHT) [4,5], by irradiation [6,7] and by intercalation [8,9], resulting in 1D, 2D or 3D polymers. Recent research interest has focused on controllable polymerization of fullerenes for creation of new materials, by using molecular confinement or co-intercalation by template molecules before the reaction. For example, a recent remarkable report revealed that when C_{60} molecules were separated and confined by *m*-xylene molecules, forming solvated C_{60} , the amorphized C_{60} cluster units formed by molecular collapse at high pressure can still be arranged in a crystalline structure with long range periodicity. This material was superhard and indents diamond anvils [10]. A 3D-polymerized C_{60} is synthesized in C_{60}/CS_2 at pressures 6-7 GPa and room temperature by Popov et al. [11]. The obtained phase can plough diamond and is identical to ultrahard fullerite synthesized from pure C_{60} at 18 GPa pressure, with high bulk modulus of 585 GPa. Moreover, a reversible polymerization of bulk C_{60} and C_{70} was obtained under high pressure with the help of dopant ferrocene (Fc, $Fe(C_5H_5)_2$) [12,13]. In this case, the Fc molecules formed a layered structure in the crystal and acted as spacers that allow polymerization of C_{60} s and C_{70} s only within a 2D layer. However, whether the polymeric phase(s) of such doped C_{60} materials can be preserved after extreme condition treatment is still unknown. Retention of the doped C_{60} polymers under ambient conditions is valuable for studying the structures and properties of this new fullerene-based polymers and for understanding the physical mechanism of polymerization.

Compared to cold compression, compressing C_{60} at elevated temperatures is an effective method to obtain metastable polymers and most such states have unique polymeric structures with novel properties[14-16]. For example, a 3D C_{60} polymer with a body-centered orthorhombic structure was formed in a 2D polymeric C_{60} single crystal at pressure of 15GPa at 600 °C . The 3D C_{60} polymer obtained was electronically conductive, in contrast with the nonconductive behavior of 2D

polymers [14]. Similarly, Yamanaka *et al.*[15] compressed monomeric C₆₀ crystals at 15 GPa and 500-600°C to form a 3D C₆₀ polymer with a high hardness, comparable with that of cubic boron nitride (c-BN). Although much exciting progress has thus recently been made on C₆₀ bulk materials, less effort has been spent on doped C₆₀ materials under HPHT. Motivated by the progress with C₆₀ and doped C₆₀ materials, we focused on the effect of spatial confinement on the behavior of C₆₀ in several typical co-crystals with C₆₀ under HPHT in order to obtain various polymeric phases and create new C₆₀ fullerides with novel properties. Based on these considerations, Fc, Ni(OEP) and AgNO₃ were chosen as dopants for this study. These materials have quite different structures: the Fc molecule has an “hourglass-like” shape, the Ni(OEP) molecule has large planar surfaces and AgNO₃ forms a porous lattice structure. When co-crystallized with C₆₀, each of these compounds forms different frameworks which confine the C₆₀ molecules in geometrically different environments. These differences thus provide us with good models for studying the effect of spatial confinement on the polymerization of doped C₆₀ materials and the resulting potential to create new polymeric structures, as well as to improve our understanding of the polymerization mechanism of confined doped C₆₀.

In this work, C₆₀/Fc, C₆₀/Ni(OEP) and C₆₀/AgNO₃ were each treated under two well tried pressure-temperature conditions, at 1.5GPa and 573K and at 2GPa and 700K, respectively. Raman and IR studies revealed that doped C₆₀ polymers were obtained under suitable conditions, but with a lower degree of polymerization compared to pristine C₆₀. We also found that the degree of polymerization was different among these three materials even under identical conditions. The results indicated that the spatial confinement of the C₆₀ molecules prevented the formation of the well-known long-range ordered polymers observed in pure bulk C₆₀ and that the different degrees of confinement caused the formation of various other polymeric phases in these samples.

2. Experimental

The methods and procedures for synthesis of the three materials have been described in previous studies [12, 17-19].

The C₆₀/Fc nanosheets were prepared by introducing 200mg Fc into 3 ml of saturated C₆₀/toluene solution. After ultrasonication we then added 3ml isopropyl alcohol (IPA) and the mixture was maintained at 10° C for 24h for the growth of single crystalline C₆₀/Fc nanosheets.

The C₆₀/Ni(OEP) blocks were synthesized by dissolving 0.020g C₆₀ in 50 ml of chlorobenzene. The solution was filtered and then mixed with a filtered solution of 0.017g of Ni(OEP) dissolved in 50 ml of benzene. The resultant mixture was maintained for 1 month, during which dark crystals were formed.

Cubic crystals of C₆₀/AgNO₃ were obtained by carefully placing a saturated solution of silver nitrate in absolute ethanol over a saturated solution of C₆₀ in benzene. The mixture was allowed to stand for one week, during which the mixture solution was undisturbed and protected from light.

The morphologies of the obtained as-grown samples were characterized with scanning electron microscopy (SEM, JEOL JSM-6700F) and the composition of the samples were characterized using a Bruker Vertex80V FTIR spectrometer and using a Raman spectrometer (Renishaw inVia) with a 514 nm Ar⁺ laser line as excitation.

A piston-cylinder device was used to carry out the HPHT experiments and silicone oil was chosen as hydrostatic pressure medium to keep the initial morphologies of C₆₀-based crystals. Experiments were performed at two different conditions, at 1.5 GPa and 573 K and at 2.0 GPa and 700 K. These conditions were chosen because pure C₆₀ is known to transform into preferentially 1D (orthorhombic, “linear chain”) and 2D (tetragonal) polymers, respectively, under these conditions. The structures of the HTHP-treated samples were analyzed at ambient conditions using the same Raman spectrometer as discussed above.

Figure 1. SEM images of the as-grown C_{60} -based crystals: (a-b) C_{60}/Fc , (c-d) $C_{60}/AgNO_3$, (e) $C_{60}/Ni(OEP)$.

3. Results and discussion

3.1 Sample characterization

Representative SEM images of the as-grown C_{60} -based crystals are shown in Fig. 1. From this figure we can see that the C_{60}/Fc nanosheets have a hexagonal morphology. The size of the nanosheets is from 3 to 6 μm (see Fig. 1 (a)) and the thickness is in the range of 250-500nm (Fig. 1 (b)). $C_{60}/AgNO_3$ crystals possess a uniform cubic morphology and the length of a side is about 7.5 μm (see Fig.1(c-d)). In contrast to these ordered shapes, $C_{60}/Ni(OEP)$ crystals have an irregular block shape (see Fig. 1 (e)). In order to confirm the composition of these samples, Raman and IR spectra were employed for this study.

Figure 2. The packing arrangements of (a) C_{60}/Fc , (b) $C_{60}/Ni(OEP)$ and (c) $C_{60}/AgNO_3$ and the structures of the three materials are shown on the right of each figure. (A color version of this figure can be viewed online.)

The crystal structures and packing arrangements for C_{60}/Fc , $C_{60}/Ni(OEP)$ and $C_{60}/AgNO_3$ calculated by Materials Studio (from data in Refs. 17-19) are shown in Fig. 2. It is found that the C_{60}/Fc we have studied consists of close-packed layers of C_{60} molecules stacked directly one above the other, parallel to [001] (Fig. 2(a)). From Fig. 2 (b), we can see that the $Ni(OEP)$ molecules have large planar surfaces and can co-crystallize with C_{60} to form solids with remarkably close contact, that is, an interaction takes place between the curved pi surface of a fullerene with the planar pi surface of a porphyrin, without the need for matching convex with concave surfaces [20,21]. In the case of $C_{60}/AgNO_3$, the solid has a complex structure (shown in Fig. 2 (c)) in which the silver nitrate forms a zeolite-like network [19]. Analyzing the structure of $C_{60}/AgNO_3$, we find that the cavities that are occupied by the fullerenes form apparent channels within the silver nitrate network and the C_{60} s are surrounded by four “straps” in two perpendicular planes.

Raman and IR spectroscopy are powerful tools to characterize C_{60} and C_{60} -based materials. The Raman and IR spectra of C_{60}/Fc , $C_{60}/Ni(OEP)$ and $C_{60}/AgNO_3$ are shown in figures 3-5, respectively. For comparison, the spectra of pure C_{60} and the dopants are also presented in these figures. For pristine C_{60} , the spectrum contains ten peaks, including eight Hg modes and two Ag modes. Among these peaks, the pentagonal pinch mode Ag (2) is very sensitive to the bonding configuration and its frequency depends on the number of intermolecular bonds to the molecule[22]. The IR spectrum of C_{60} shows four sharp absorption peaks at the positions 527, 576, 1182 and 1429 cm^{-1} . From figures 3 and 4, we can see that the spectra of C_{60}/Fc and $C_{60}/Ni(OEP)$ contain Raman and IR signals from both the intercalant molecules and from C_{60} . Although the Raman spectrum of $C_{60}/AgNO_3$ (shown in figure 5(a)) mainly contains the vibration modes of C_{60} , the IR spectrum (shown in figure 5(b)) is still composed by the characteristic peaks of C_{60} and $AgNO_3$. These results indicate that the dopants are efficiently intercalated to the lattice of C_{60} , which is in accord with previous reports[12].

Figure 3. The Raman spectra of C_{60} , Fc and C_{60}/Fc , respectively.

Figure 4. The Raman (a) and IR (b) spectra of C_{60} , Ni(OEP) and $C_{60}/Ni(OEP)$, respectively.

Figure 5. The Raman (a) and IR (b) spectra of C_{60} , $AgNO_3$ and $C_{60}/AgNO_3$, respectively.

3.2 Results for HTHP treated samples

To study the polymeric phases of these C₆₀-based materials after different HPHT treatments, Raman spectra of the relevant confined samples and of C₆₀ bulk material, included for comparison, are shown in figure 6. The P/T conditions (1.5 GPa, 573 K and 2 GPa, 700 K) we choose here are well known to give certain types of polymers for pure fullerenes [22], and thus using these conditions is a good way to demonstrate similarities and differences between pure fullerenes and the topochemically constrained samples we studied.

We first present the results for the three materials after treatment at 1.5 GPa, 573 K. The Raman spectra for our samples are shown in Figure 6 (a). For pure C₆₀, the Ag(2) peak is observed at 1459 cm⁻¹, which is consistent with earlier reports and indicates that a 1D linear polymer was formed[2,22]. Similarly, the Ag(2) mode of C₆₀ in the Raman spectrum for C₆₀/Fc is also observed at 1459 cm⁻¹ and a peak at around 960 cm⁻¹, characteristic for the intermolecular polymer bonds, is observed. The Raman spectrum of C₆₀/Fc thus has features very similar to those of the one-dimensional chainlike polymeric structure of C₆₀, which indicates the formation of 1D polymeric phase in this sample. However, we also find that polymerized and unpolymerized C₆₀ (not shown in the picture) coexisted in this material. This is consistent with our previous in-situ high pressure study on C₆₀/Fc[12], in which case partial polymerization was observed at about 5 GPa. We then discussed possible reasons for the incomplete polymerization which included the layered packing arrangement, insufficient reduction of the volume at the polymerization pressures used and the competing orientational ordering of C₆₀. These factors may also contribute to the incomplete polymerization in the present case. For C₆₀/AgNO₃, the A_g(2) mode also shifts from the initial value 1469 cm⁻¹ to 1460cm⁻¹, again implying the formation of a chainlike polymer in the same way as for bulk C₆₀ and C₆₀/Fc treated at the same conditions.

For C₆₀/Ni(OEP), the Ag(2) mode instead shows a shift to 1463 cm⁻¹. This suggests that the C₆₀/Ni(OEP) has been transformed to a dimer-rich phase[2,22] and that a linear polymer could not be formed.

Figure 6. Raman spectra of the samples after treatment of (a) 1.5 GPa, 573 K and (b) 2.0 GPa, 700 K.

Figure 6 (b) shows Raman spectra for bulk C_{60} material and for doped C_{60} materials treated at 2.0 GPa and 700 K. The $A_g(2)$ mode in pure C_{60} shifts from its initial value 1469 cm^{-1} to 1448 cm^{-1} for the bulk single crystals, indicating the formation of the 2D tetragonal polymeric phase[22]. Besides the strong peak at 1448 cm^{-1} , a small shoulder at 1458 cm^{-1} is also present which suggests that a small amount of the 1D polymer co-existed in this bulk crystal. For comparison, after treatment at the same condition the $A_g(2)$ Raman mode of C_{60}/Fc shows a small shoulder at 1446 cm^{-1} , while the strong peak is still at 1460 cm^{-1} . Again a “polymer bond” peak is observed near 950 cm^{-1} , although the relative intensity of this peak is weaker than the corresponding peak in the C_{60} bulk crystals after HPHT. These results imply that 1D and 2D polymers co-exist in this sample, but the main product is still 1D chainlike polymers. This is clearly different from what occurred in pure C_{60} .

For $C_{60}/\text{Ni(OEP)}$, the $A_g(2)$ mode now shifts to 1460 cm^{-1} , implying the formation of 1D chainlike polymers instead of the dimers observed at lower pressure. The formation of a linear chain phase is different from what is observed in pure C_{60} , for which such a 1D linear polymeric chain phase is normally observed at lower pressures and temperatures.

Finally, the $A_g(2)$ mode of C_{60}/AgNO_3 hardly shifts when the temperature-pressure conditions are changed and the peak remains at 1460 cm^{-1} , suggesting the preservation of the same 1D chainlike polymeric phase as was

observed at milder conditions.

All these results indicate that the doped C_{60} materials can be transformed to polymeric phases under suitable HPHT conditions and the polymers formed can be preserved at ambient conditions after the reaction at extreme conditions, which is similar to the phenomena observed in the case of C_{60} bulk crystals. The degree of polymerization also increases with increasing pressure and temperature, except in the case of $C_{60}/AgNO_3$. However, the formation of polymers seems to be more difficult in the materials studied here than in bulk C_{60} crystals under the same conditions. We note this especially at 2 GPa and 700 K, where a small amount of the 2D polymeric phase was formed in C_{60}/Fc only while no such polymer formed in any of the other two materials. The results also suggest that higher pressure and higher temperature are needed to polymerize doped C_{60} materials than is needed for pure C_{60} , which is consistent to the results found for the C_{60} nanorods and nanotubes investigated earlier.[23-25]

The different degrees of polymerization of these doped C_{60} materials under same conditions can be understood by the different initial lattice structures of these samples and the confinement effects of the dopants (Fig. 2 (a-c)). For C_{60}/Fc , the layered structure may cause the C_{60} molecules to restrict the vibration of the Fc molecules under HPHT, and the geometrical separation of the C_{60} layers prevents the formation of intercage polymer bonds in the c direction. Thus, the polymerization in C_{60}/Fc can only proceed within each fullerene layer. However, due to the existence of Fc molecules in the crystal, which can interact with the C_{60} molecules to affect the rotation and the available volume for the C_{60} molecules under pressure, the formation of polymers is more difficult than in bulk C_{60} under same conditions. The unique lattice structure is also probably the reason why polymerized and unpolymerized C_{60} are observed to coexist in our study.

For $C_{60}/Ni(OEP)$, the large size of the dopant $Ni(OEP)$ molecules may prevent the intermolecular bonding of neighboring C_{60} molecules due to spatial separation, and thus fewer covalent bonds are formed, as compared to C_{60}/Fc treated under same conditions. From figure 2 (b) we can see that the intercage polymer bonds can only be

formed in the b direction because the Ni(OEP) molecules prevent bonding between C₆₀ molecules in the a and c directions. Again, the confinement effect of Ni(OEP) leads to a lower degree of polymerization in C₆₀/Ni(OEP) compared to that of pure C₆₀. Nevertheless, the polymerization degrees in the two materials are enhanced with increasing pressure and temperature, which is consistent with the trend observed in C₆₀ under HPHT.

Finally, in the case of C₆₀/AgNO₃ with its special channel-like structure, it is highly likely that the polymeric bonds may only be formed in the channels running in the c direction. This is the probable reason why we obtained only 1D chainlike polymers even at 2 GPa and 700 K. The unique network structure of C₆₀/AgNO₃ may only allow 1D polymerization between C₆₀ molecules, but not polymerization in 2D or higher dimensions.

In our previous study, C₆₀/Fc was shown to form 1D chain-like polymers at 5 GPa near room temperature but the polymerization is reversible on pressure release. The reversible polymerization was induced by the strengthened charge interaction in C₆₀(Fc)₂ with increasing pressure, which may affect the distribution of the electron cloud between the C₆₀ and Fc molecules and thus induce polymerization of the C₆₀ molecules. However, the stability of the polymer is controlled by the steric repulsion of counterions which can be overridden at high pressure and with decreasing pressure eventually returns to the initial state [12]. In this study, in contrast, the pressure is not high enough to activate the reversible bonding mechanism sketched above. Instead, the high temperature induces a very high molecular rotation rate and thus a high probability to bring adjacent C₆₀ molecules to face each other in the optimum configuration for bond interaction. When a sufficiently high pressure is subsequently applied, molecules are brought close enough together to break the original double bonds on the C₆₀ and trigger the “normal” (2+2) cycloaddition reaction to form polymers with stable intermolecular sp³ bonds. Therefore, the obtained polymers can be retained as metastable structures after decompression, in contrast to the reversible polymerization of C₆₀(Fc)₂ under cold compression mentioned above. Until now, no polymerization was observed in C₆₀/Ni(OEP) and C₆₀/AgNO₃ under cold compression,

but different polymeric phases of these two materials were formed during HPHT treatment. Therefore, we suggest that HPHT is an efficient method to obtain not only metastable polymers of pure C_{60} but also various metastable doped C_{60} polymers. It should be noted, however, that such polymers may be converted back to the monomers by thermal annealing at about 200°C [26]. This knowledge is useful for us in our further studies of polymeric phases and their properties, which may have wide applications in many fields.

4. Conclusions

HPHT experiments have been carried out on several types of doped C_{60} co-crystals, i.e. C_{60}/Fc , $C_{60}/Ni(OEP)$ and $C_{60}/AgNO_3$. These materials have been treated at 1.5 GPa and 573 K and at 2 GPa and 700 K, respectively. Raman and IR spectroscopy have been employed to study the polymerization of these samples after HPHT treatment. Our results show that these doped C_{60} materials can be transformed into different polymeric phases under suitable HPHT conditions. With increasing pressure and temperature the polymerization degree of C_{60}/Fc and $C_{60}/Ni(OEP)$ is enhanced, from a 1D chainlike polymer to a 2D polymeric phase (but only in a small amount) in C_{60}/Fc and from a dimer-rich material to 1D chain-like polymer in $C_{60}/Ni(OEP)$, respectively. However, for $C_{60}/AgNO_3$, the 1D chain-like polymeric phase is observed at both experimental conditions. The unique initial lattice structures of these materials and the confinement effects of the dopants determine the the formation of different polymeric phases. In addition, due to the space restrictions imposed by the dopants the formation of polymers is more difficult in the studied materials than in pure bulk C_{60} crystals under the same conditions.

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