Pressure-induced polymerization of fullerenes: A comparative study of C_{60} and C_{70}

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To investigate the polymerization of fullerenes, solid C_{60} and C_{70} have been subjected simultaneously to high pressures and temperatures, with pressures up to 7.5 GPa and temperatures up to 800 °C. X-ray-diffraction measurements indicate that the fcc solid C_{60} transforms to an orthorhombic structure consisting of a polymerized linear chain of C_{60} molecules. The associated changes in the intramolecular vibrational modes have been probed through Raman and infrared measurements. In contrast to solid C_{60}, under similar conditions, polymerization is not observed in the case of solid C_{70}, although there is a structural transition from the initial hcp structure to a rhombohedral structure. This lack of polymerization in C_{70} is discussed in terms of the structure of solid C_{70} under high pressure and temperature conditions, coupled with the topochemical features of the C_{70} molecule.

During the last two years, the formation of yet another structure involving fullerenes, the polymerized C_{60}, has attracted considerable attention.[1] The experiments were carried out by Rao *et al.*,[2] who observed that under laser irradiation, C_{60} films transformed into a toluene insoluble product. Evidence for the polymerization was obtained through infrared (IR) and Raman measurements which indicated the loss of icosahedral symmetry of the molecule, and through laser desorption mass spectrometry which indicated the presence of oligomers as large as $(C_{60})_{20}$. This photopolymerization reaction is associated with the (2+2) cycloaddition reaction[3] involving the photoexcited triplet state of C_{60} wherein the double bonds of the neighboring molecules react to form a polymerized chain, linked through a four-membered ring. The polymerization of C_{60} is also observed[4,5] when pristine solid C_{60} is subjected to high pressure ($\sim$ 5 GPa) and high temperature ($\sim$ 800 °C) treatment. This results in a transformation to rhombohedral, orthorhombic or tetragonal structures which are characterized by a short interfullerene distance of 9.2 Å, compared to 10 Å in the starting fcc solid. Theoretical calculations in support of these polymerized structures have been carried out.[6] The formation of polymeric chains of C_{60} is also seen in the experiments on RbC_{60} and KC_{60}, whose quasi-one-dimensional structure and electronic properties have attracted considerable attention.[7]

Following the above studies, it is pertinent to enquire if C_{70}, the next higher fullerene will undergo a polymeric reaction. The occurrence of photopolymerization in solid C_{70}, with a much lower efficiency compared to C_{60}, has been reported,[8] and it is of interest to see if polymerization can also be induced by high-pressure high-temperature (HPHT) treatments. With this motivation, the present investigations on the C_{70} samples treated at pressures of 5 and 7.5 GPa and various temperatures from ambient up to 800 °C have been carried out. The structural information on the HPHT-treated samples has been obtained through x-ray-diffraction measurements and the intramolecular vibrational modes have

been probed by Raman and IR measurements. We also present our results in solid C_{60} and compare with earlier results.[4,5] It is shown that while solid C_{60} polymerizes, as reported earlier, polymerization is not seen in the case of solid C_{70} under similar HPHT treatments. These results are discussed in terms of the known information[9–15] on the evolution of structure of solid C_{70} with the variation of temperature and pressure, coupled with the topochemical features of the C_{70} molecule.

Chromatographically separated C_{60} and C_{70} powders were synthesized using the procedure described in Ref. 16. These were heat treated in vacuum at 250 °C for over 24 h to get rid of the trapped organic solvents and their purity were characterized by UV-Vis and IR measurements. Pellet of 3 mm diameter and 2 mm thickness, wrapped in a 7.5 μm stainless-steel foil, was mounted along with steatite disks inside a pyrophyllite gasket containing a small annular graphite ring heater, and this assembly was loaded into an opposed anvil high-pressure apparatus.[17] This whole procedure, which was carried out under ambient conditions, entailed an exposure of the samples to atmospheric oxygen for a period of $\sim$ 30 min, before being sealed between the gaskets. After raising the pressure up to 7.5 GPa maximum, over a period of 10 min, the temperature was increased up to a maximum of 800 °C. The sample was allowed to cook under high pressure and temperature for $\sim$ 6 h, following which the temperature was lowered initially and the pressure was subsequently released slowly. X-ray-diffraction measurements on finely chopped pellets were carried out using Siemens D-500 diffractometer operating in the Bragg-Brentano arrangement. Raman measurements were carried out, under ambient conditions, using DILOR X-Y spectrometer with liquid-nitrogen-cooled CCD detector. IR-absorption measurements on a sample pelletized with KBr were carried out using a NICOLET, Model IMPACT 400, FTIR spectrometer.
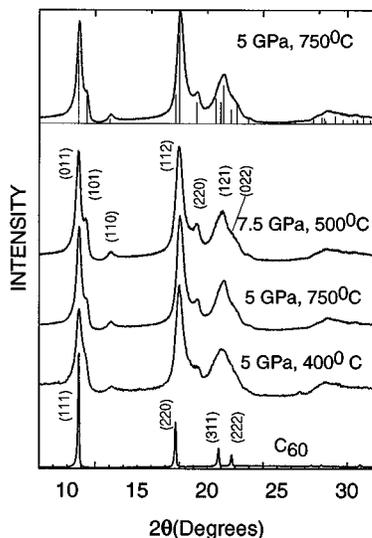
FIG. 1. X-ray diffractograms of the starting C_{60} powder, indexed to fcc structure, and those treated at various pressures and temperatures. These are indexable to orthorhombic structure and comparison with the calculated diffraction intensities is shown in the top panel.

Figure 1 shows the x-ray diffractograms of the starting C_{60} and those of samples treated at high pressures and temperatures. Following the earlier investigations,[4,5] which reported the formation of rhombohedral, orthorhombic, and tetragonal structures under various conditions of pressure and temperatures, we have analyzed our diffractograms in terms of these structures. All our diffractograms of the various HPHT samples were indexable to an orthorhombic structure (space group $Im3$) with $a = 9.23$ Å, $b = 10.00$ Å, and $c = 14.32$ Å, and these lattice parameters are consistent with those reported earlier.[5] The intensity of the diffraction pattern calculated for the orthorhombic structure, using the form factor of a spherical molecule ($R = 3.54$ Å), is seen to be in very good agreement with the experimental results as shown in the top panel of Fig. 1. While the exact reason for the observation of only the orthorhombic structure amongst the various possible metastable structures is not clear, it may be remarked that theoretical calculations indicate[6] that this structure consisting of linearly polymerized C_{60} chains is characterized by the smallest increase in energy compared to the fcc structure with freely rotating C_{60} molecules.

Figure 2 shows the results of Raman spectroscopy measurements, which have been carried out at a laser power density of about 10 W/cm^2 to eliminate the well-known[2] effects of photopolymerization. A comparison with the Raman spectrum of starting C_{60}, shows that on HPHT treatment, all the discernable Raman modes soften. In particular, A_g Raman mode at 1469 cm^{-1} (Refs. 15 and 18) is seen to shift to 1460 cm^{-1} and develop a shoulder. This feature is similar to that seen[4] in the case of C_{60} treated at 5 GPa, 300 °C. However, the large Raman shift of 39 cm^{-1} as reported by Iwasa et al.[4] for the case of the C_{60} sample treated at 5 GPa, 800 °C, is not observed in the present experiments and needs to be investigated further. The characteristic shift and the splitting of the 1469 cm^{-1} Raman mode, which is also seen in the experiments on photopolymerized C_{60},[2] can be qualitatively understood in terms of the stretching of the
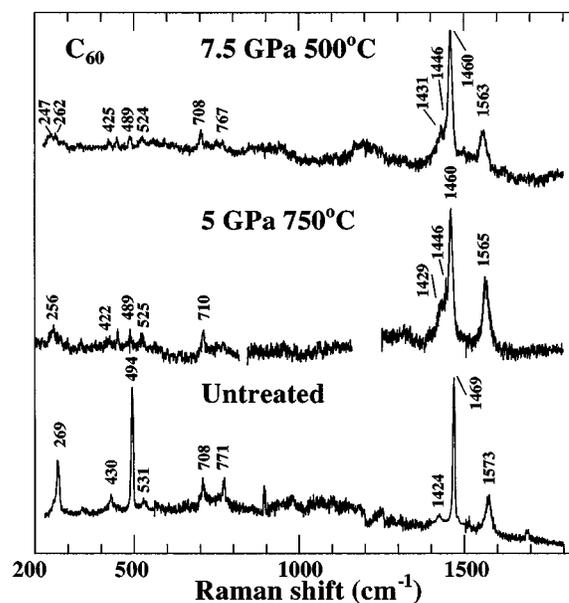
FIG. 2. Raman spectra of C_{60} treated at various high pressures and temperatures. Note the shift and broadening of the 1469 cm^{-1} mode of pristine C_{60}.

carbon bonds[6] associated with the formation of polymerized C_{60} structure. The lowering of icosahedral symmetry associated with the formation of polymerized structure is also evinced from the results of IR measurements shown in Fig. 3(a) for the C_{60} sample treated at 7.5 GPa and 500 °C. The four distinctive IR modes[18] of the C_{60} molecule are seen to give way to a complex pattern which are seen to match within ±4 cm^{-1} the spectrum[2] of photopolymerized C_{60}.

Experiments similar to those in C_{60} have been carried out in C_{70} to look for polymerization in the next higher fullerene. Figure 4 shows the results of x-ray diffraction (XRD) studies. The XRD pattern of the starting C_{70} powder can be indexed to hcp structure with lattice parameter
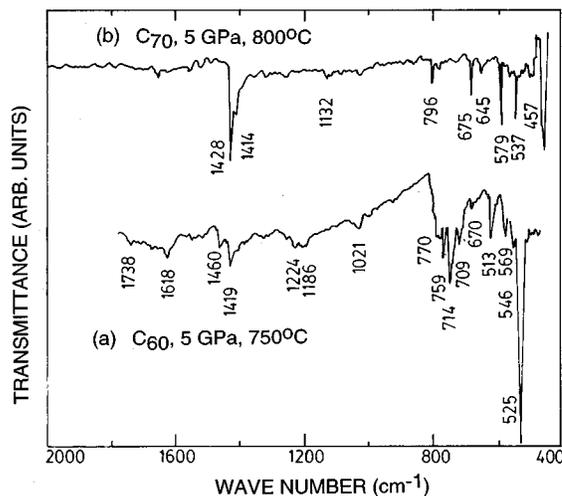
FIG. 3. (a) Infrared spectra of C_{60} sample treated at 5 GPa, 750 °C, dramatically different from that of starting C_{60}, indicating the loss of icosahedral symmetry. (b) Infrared spectrum of C_{70} sample treated at 5 GPa, 800 °C, retains the characacteristic vibrational modes of C_{70} molecule.
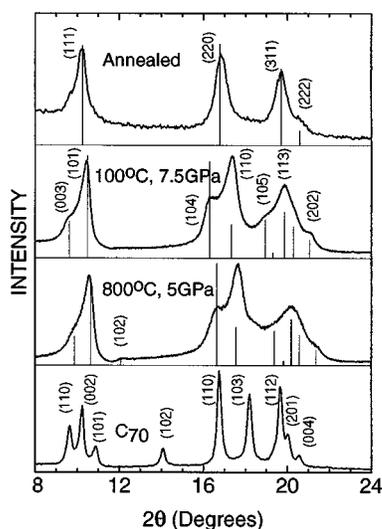
FIG. 4. X-ray diffractograms of the starting C_{70} powder, indexed to hcp structure, and those of samples treated at 5 GPa, 800 °C and at 7.5 GPa, 100 °C, which are indexable to rhombohedral structure. The sample treated at 5 GPa, 400 °C and subsequently annealed in vacuum at 250 °C is indexed to fcc structure. The calculated diffraction intensities are indicated by the stick diagram.

FIG. 5. Raman spectra of C_{70} treated at various high pressures and temperatures.

$a = 10.60$ Å and $c = 17.26$ Å, consistent with earlier studies.[11] On subjecting to HPHT treatment, broad diffraction lines corresponding to a new crystallline phase is observed. From the knowledge of the structural transformations in solid C_{70}, induced by the variations of pressure and temperature,[9–15] it can be expected that this diffraction pattern could correspond to hexagonal, rhombohedral or monoclinic structures, which correspond to various degrees of orientational correlations between the C_{70} molecules, and attempts were made to analyze in terms of these structures. Good fits were obtained for rhombohedral structure (space group $R3m$) with the hexagonal lattice parameters, $a = 10.10$ Å and $c = 26.88$ Å, for the sample treated at 5 GPa, 800 °C. In the case of the sample treated at a pressure of 7.5 GPa and low temperature of 100 °C, the diffraction pattern could again be indexed to rhombohedral structure with lattice parameters $a = 10.23$ Å, and $c = 27.56$ Å. The diffraction intensities have been calculated, using an axially averaged form factor for the C_{70} molecule,[9] and the results are indicated by the stick diagram. While there are some discrepancies, the overall features of the calculated intensities are in conformity with the experimental results giving support to the assigned rhombohedral structure.

The results of Raman spectroscopy measurements on C_{70} samples are shown in Fig. 5. It is seen that the Raman spectra of starting C_{70} is unaltered in the various HPHT-treated samples. The IR spectrum [cf. Fig. 3(b)] of the sample treated at 5 GPa, 800 °C is seen to be similar to that of the pristine sample.[18] Thus, both Raman and IR measurements indicate that the intramolecular vibrational modes of C_{70} are preserved and hence point to the absence of polymerization in the case of C_{70}. Further, in support of the absence of polymerization in the case of C_{70}, we also observe that the HPHT-treated samples are soluble in toluene. Photoluminescence experiments carried out on the HPHT samples are also seen to be no different from the starting C_{70}, in contrast to the behavior in C_{60}.[19]
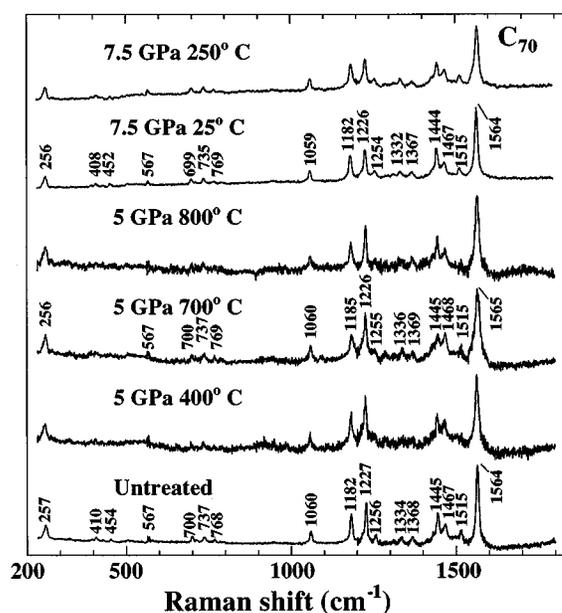
Thus based on the above experiments, it is inferred that in the case of C_{70}, under HPHT conditions, similar to those employed for C_{60}, polymerization is not observed. However, there is a structural transition from the starting hcp to a rhombohedral structure. The rhombohedral structure obtained in the present experiments is similar to that obtained by Kawamura et al.[12] in their experiments on C_{70} subjected to pressure at ambient temperature. However, it may be noted that while in the experiments of Kawamura et al.,[12] the rhombohedral structure was obtained from the initial fcc structure, in the present experiments, the initial hcp phase with "AB"-type stacking has transformed to a rhombohedral structure with "ABC"-type stacking. This rhombohedral structure is seen to transform to fcc structure ($Fm3m$) with $a = 14.94$ Å, on annealing at 250 °C for 24 h, as shown in the top panel of Fig. 4.

In order to understand as to why no polymerization is seen in C_{70}, it is required to have information on the state of the system under HPHT conditions. First, we note that for the polymerization reaction to occur in C_{70}, as in the case of C_{60}, it is necessary that the parallel configurations of C=C double bonds of the neighboring molecules be brought close together under compression. In addition, it has been argued[8] that there are topochemical constraints in the polymerization of C_{70}, in that only the double bonds on the polar caps of the molecule are reactive, whereas the cyclic double bonds on the equatorial belt are ineffective in undergoing (2+2) cycloaddition reaction. In the case of solid C_{70}, it is known[9–15] that there are two orientaional ordering transition temperatures, one corresponding to the free rotor phase going to a long-axis-oriented phase and the second corresponding to this going to a completely oriented monoclinic phase. The pressure variation of these transition temperatures have been studied, upto 1 GPa, by Kawamura et al.[13] and Lundin et al.[14] which indicate that the rhombohedral to fcc transition

temperature increases at the rate of 300 K /GPa, whereas the monoclinic to rhombohedral transition temperature increases at a much slower rate of 50 K/GPa. An extrapolation of these trends would suggest that in the range of temperatures investigated in the present study, viz., room temperature to 800 °C at 5 and 7.5 GPa, respectively, solid C_{70} is in the orientationally ordered state which could be either rhombohedral or monoclinic structure depending on the particular pressure and temperature conditions. For example for the sample at 7.5 GPa, 100 °C, the sample is expected to be in the monoclinic structure and such an orientationallly ordered state, in which the electron-rich double-bond regions face the electron-deficient regions of the pentagon and hexagon centers[11] is inimical to the formation of polymerized structure, which involves the reaction betweeen parallel double bonds of neighboring molecules. For the situation corresponding to say, 5 GPa, 800 °C, the sample is expected to be in the rhombohedral structure with long-axis-oriented molecules, and it is possible to conceive of the polymerization reaction involving the double bonds on the polar caps. With the known molecular dimensions[9] of C_{70}, the distance between these double bonds of the C_{70} molecules at (0 0 0) and (2/3, 1/3, 1/3), can be estimated[20] to be 2.23 Å at 5 GPa. This distance is seen to be comparable to a distance of 2.2 Å for the polymerized structure in C_{60}. Thus based on the analysis in terms of geometric factors alone, we are unable to reconcile with the nonobservance of pressure-induced polymerization in the case of C_{70}. This calls for detailed theoretical analysis, incorporating the changes in electronic structure with the application of pressure to explore the formation of polymerized structures and to investigate their stabilty, as has been carried out earlier for C_{60}.[6] In addition, experiments on alkali-doped C_{70} to look for polymerization, and a comparison with the present results and those on photopolymerization in C_{70},[8] would also be instructive.

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[20] For the C_{70} molecules having an equatorial diameter of 7.09 Å and long axis of 7.92 Å, and arranged in the rhombohedral lattice with $a = 10.10$ Å and $c = 26.88$ Å, the smallest distance between the near-neighbor double bonds on the polar caps and on the equatorial belt are 2.61 and 3.01 Å, respectively. At an elevated pressure of 5 GPa, with the lattice parameters derived using the Murnaghan equation of state (Ref. 15), these distances shrink to 2.23 and 2.65 Å, respectively.