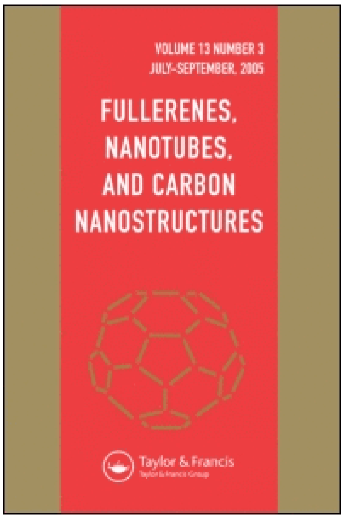

Fullerenes, Nanotubes and Carbon Nanostructures
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597253

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To cite this Article Meletov, K. P. , Arvanitidis, J. , Christofilos, D. , Kourouklis, G. A. , Iwasa, Y. and Yamanaka, S.(2010) 'High Temperature Depolymerization of the 2D-R Polymer of C_{60} Studied by Raman Spectroscopy', Fullerenes, Nanotubes and Carbon Nanostructures, 18: 4, 396 — 400

To link to this Article: DOI: 10.1080/1536383X.2010.487441

URL: http://dx.doi.org/10.1080/1536383X.2010.487441

Fullerenes, Nanotubes, and Carbon Nanostructures, 18: 396–400, 2010
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ISSN: 1536-383X print / 1536-4046 online
DOI: 10.1080/1536383X.2010.487441

High Temperature Depolymerization of the 2D-R Polymer of C_{60} Studied by Raman Spectroscopy

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Raman spectra of the two-dimensional rhombohedral (2D-R) polymer of C_{60} were measured at ambient conditions after 0.5 hour of treatment at various elevated temperatures in order to study the process of polymer degradation. The 2D-R polymer is stable up to ~510 K, while at higher temperatures an intermediate state appears where the initial 2D-R polymer coexists with inclusions of tetragonal-like (T-like) and orthorhombic-like (O-like) oligomers, as well as C_{60} dimers and monomers. The polymeric material changes drastically its composition after treatment at ~560 K resulting in the domination of C_{60} monomers.

Keywords Fullerenes, Polymers, Raman study

The *fcc* fullerene C_{60} transforms under visible light illumination with a power density exceeding 5 W/cm^2 in fullerene oligomers, $(C_{60})_n$ with $n = 2–20$, due to covalent bonding between adjacent C_{60} molecules via [2+2] cycloaddition reactions (1). Contrary to the photo-induced polymerization that takes place in thin films or surfaces of bulk samples because of the small light penetration depth (~1 μm), the treatment of C_{60} at high pressure and high temperature results in bulk crystalline polymeric samples. Their crystal structures can be orthorhombic (1D-O linear polymer), tetragonal (2D-T planar polymer), rhombohedral (2D-R planar polymer), or face-centered cubic (three-dimensional polymer), depending on the number of the sp^3-like coordinated carbon atoms (2–4). The polymerization of C_{60} fullerene results in distinct changes in the Raman and IR spectra related to the lowering of the C_{60} molecular symmetry, which leads to the splitting of the bands as well as to their softening due to the decrease of the mean intramolecular bond strength (5). As was shown by differential scanning calorimetry and X-ray studies, the fullerene polymers are metastable; heating to ~560 K results in the destruction of the intermolecular C-C bonds and the recovery of the initial *fcc* monomeric structure (6,7). In view of this, we have measured the Raman spectra of single crystalline 2D-R polymer of C_{60} at

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ambient conditions after its treatment at various temperatures up to 600 K to study the process of polymer decomposition. Detailed studies of their optical spectra combined with X-ray structural investigations reveal that the Raman spectra of polymeric fullerenes are prominent and differ significantly in the 1D-O, 2D-T, and 2D-R phases (8). Thus, Raman spectroscopy can be reliably used for the identification of the various polymeric phases of C_{60} and for the study of the polymer decomposition process.

Single crystals of the 2D-R polymer of C_{60} were prepared by the polymerization of C_{60} single crystals under a high pressure of 5 GPa at 773 K. X-ray diffraction analysis revealed that the sample adopts the rhombohedral structure (space group:$R\bar{3}m$) (9). High temperature treatment (HTT) of the 2D-R polymer was performed for 0.5 hour at various temperatures up to 600 K using a high temperature cell with a quartz window. The cell was equipped with a temperature controller unit that maintained temperatures up to 700 K with an accuracy of ±2 K. Raman spectra were recorded in the back-scattering geometry using a micro-Raman triple grating system (DILOR XY), equipped with a cryogenic CCD detector. The laser beam of a Ti:sapphire tunable laser operating at 780 nm was focused on the sample by means of a long working distance 20x objective in a spot of ~3 μm diameter, while the beam intensity on the sample was less than 0.3 mW in order to prevent sample overheating, laser induced depolymerisation, or damage.

Raman spectra of the 2D-R polymer measured at ambient conditions after its treatment for 0.5 hour at various temperatures up to ~550 K are illustrated in Figure 1. The spectra

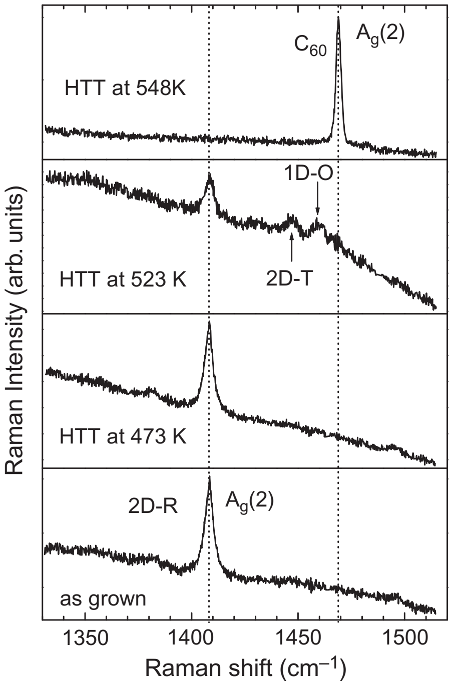

Figure 1. Room temperature Raman spectra of the 2D-R polymeric C_{60} in the frequency region of the $A_g(2)$ mode before and after treatment for 0.5 hour at various temperatures. The arrows mark peaks associated with the presence of other polymeric forms resulting from partial 2D-R depolymerization. The heat treatment at 560 K leads to complete depolymerization of the material and a single peak attributed to the $A_g(2)$ mode of monomeric C_{60} appears in the spectrum.

were measured at room temperature to avoid the sample damage that was observed within the laser spot for T $\geq$ 430 K even at laser intensity as low as 0.005 mW. The polymerization of C_{60} is characterized by the destruction of a number of double C=C intramolecular bonds and the creation of intermolecular covalent bonds associated with *sp*^{3}-like coordinated carbon atoms in the fullerene molecular cage. Their number increases from 4 to 8 and to 12 per cage for 1D-O, 2D-T, and 2D-R, respectively. Breaking of double C=C intramolecular bonds results in the softening of the $A_g(2)$ pentagon pinch (PP) mode from ~1469 cm^{-1} in the pristine *fcc* fullerene C_{60} to ~1409 cm^{-1} for the 2D-R polymer due to the reduction of the mean intramolecular bond stiffness (8). Our Raman measurements show that the 2D-R polymer is stable to temperatures up to ~510 K where a material transformation is initiated. The sample treated at 523 K shows new Raman peaks typical of the $A_g(2)$ mode in the 2D-T and 1D-O polymer, as well as to the C_{60} dimers and monomers (8), which coexist with the PP-mode of the initial 2D-R polymer (Figure 1). The appearance of the Raman peak at ~1447 cm^{-1} is related to the breaking of 4 intermolecular C-C bonds of the initial 2D-R polymer and the formation of T-like oligomers having 8 intermolecular C-C bonds per C_{60} molecule. Another peak at ~1459 cm^{-1} is indicative of the destruction of 8 intermolecular C-C bonds of the initial 2D-R polymer and the formation of O-like oligomers having 4 intermolecular C-C bonds per C_{60} molecule. In addition, the appearance of a relatively weak peak at ~1453 cm^{-1} in some spectra (not shown) typical of conjugated linear polymeric chains (6 intermolecular bonds per C_{60} molecule) possibly reflects the presence of conjugated O-like oligomers. Finally, the appearance of a weak peak at ~1465 cm^{-1} can be related to the $A_g(2)$ PP-mode of the dimeric C_{60} with 2 intermolecular C-C bonds per C_{60} molecule.

The coexistence of several polymeric phases, resulting from the partial depolymerization of the 2D-R polymer, was observed up to ~550 K where the material transforms completely to monomeric C_{60}. Figure 2 shows the relative intensities of the $A_g(2)$ PP-mode of the initial state of the 2D-R polymer (open circles), the C_{60} monomers and dimers (closed circles), as well as the intermediate T-like and O-like oligomers (diamonds), as a function of the treatment temperature. The data were obtained from Raman spectra measured after 0.5 hour of heat treatment of a fresh sample for each temperature. For most of the treatment cycles, two or more spectra were averaged from different sample sites or sample pieces, while the error bars refer to the standard error of the mean. The relative intensities of the $A_g(2)$ peaks of the various constituent species, defined as the intensity of the corresponding $A_g(2)$ component normalized to their sum, is indicative of the species concentration in the intermediate state. According to Figure 2, the concentration of the T-like and O-like oligomers in the intermediate state increases with the increase of the treatment temperature up to its maximum at ~525 K, while at higher temperature it gradually decreases and becomes zero at ~560 K. Thus, the 2D-R depolymerization could be considered as a consecutive process evolving through intermediate products, the reaction rate of which increases with temperature. This is in agreement with the infrared spectroscopic studies of polycrystalline 2D-R samples revealing that, unlike the 2D-T and the 1D-O polymeric phases that follow a one-step decomposition route, the 2D-R depolymerization was found to be at least a two-step process (10).

Summarizing, the room temperature Raman spectra of the 2D-R polymer of C_{60} after treatment at high temperature show gradual depolymerization of the material starting from ~510 K. The polymer changes drastically its composition after treatment at ~560 K resulting in monomeric C_{60}. In the intermediate temperature region, the Raman spectra show peaks typical for $A_g(2)$ PP-modes of the 2D-T and 1D-O polymer, as well as of the C_{60} dimers and monomers, which coexist with the initial 2D-R polymer.

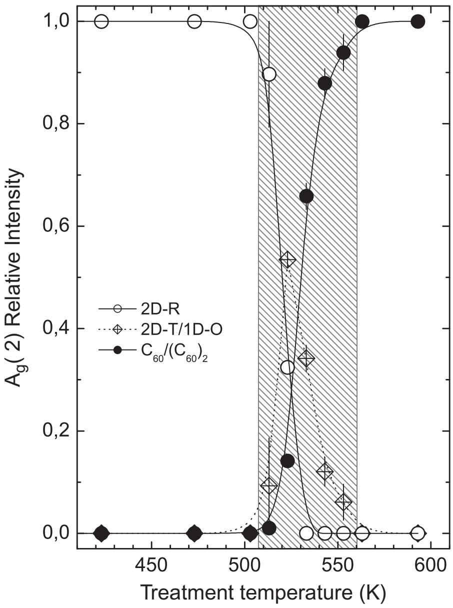

Figure 2. Intensity of the $A_g(2)$ PP-mode attributed to the initial 2D-R polymer (open circles), the intermediate T-like and O-like oligomers (diamonds) and the C_{60} monomers/dimers (solid circles), normalized to their sum as a function of the treatment temperature. The shaded area denotes the temperature region where the gradual depolymerization of the polymeric material takes place and the lines through the data are guides to the eye.

Acknowledgments

The support by the Russian Foundation for Fundamental Research, grant # 08-02-00890 and the hospitality of the Aristotle University of Thessaloniki, Greece are greatly acknowledged.

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