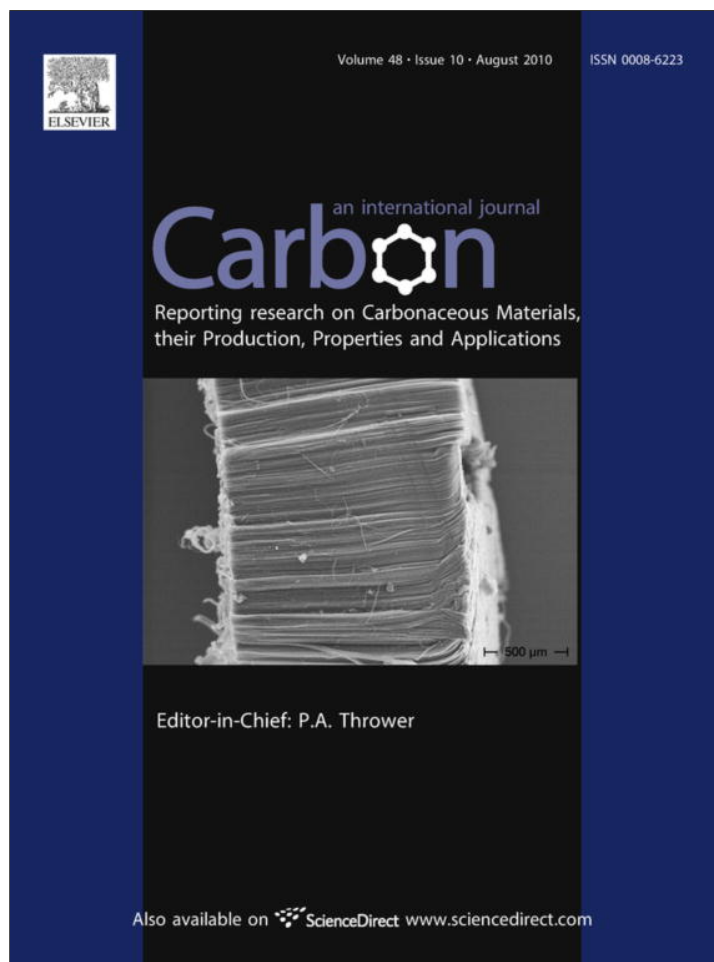


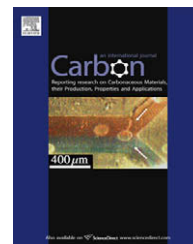


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# Raman study of the temperature-induced decomposition of the two-dimensional rhombohedral polymer of C<sub>60</sub> and the intermediate states formed

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## ARTICLE INFO

### Article history:

Received 6 November 2009

Accepted 22 April 2010

Available online 28 April 2010

## ABSTRACT

Raman spectra of single crystalline two-dimensional rhombohedral (2D-R) polymer of C<sub>60</sub> were measured at ambient conditions after its high temperature treatment (HTT) in order to study the polymer decomposition process. The data obtained indicate that the 2D-R polymer remains stable after 0.5 h treatment up to ~503 K, while at higher temperatures a material transformation takes place. New Raman lines appear in the Raman spectrum after HTT in the range of 513–553 K, related to the A<sub>g</sub>(2) pentagon pinch (PP) mode of 2D tetragonal-like (2D-T-like) and 1D orthorhombic-like (1D-O-like) oligomers as well as to C<sub>60</sub> dimers and monomers, typical for an intermediate state of partially decomposed 2D-R polymer. Above 553 K, the material changes completely and its new composition is dominated by C<sub>60</sub> monomers with some possible inclusion of C<sub>60</sub> dimers. The activation energy of the 2D-R polymer decomposition, obtained from the dependence of the decomposition time on the treatment temperature, is  $E_A = 1.76 \pm 0.07$  eV/molecule.

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## 1. Introduction

Pristine C<sub>60</sub> has a great potential for polymerization due to the existence of 30 double C=C bonds in the fullerene molecular cage. The photo-induced polymerization of C<sub>60</sub> was observed, for the first time, under intense illumination by light and the so-called [2+2] cyclo-addition mechanism was proposed to explain the creation of covalent bonds among adjacent fullerene molecules [1]. Contrary to the photo-induced polymeriza-

tion that takes place in thin films or surfaces of bulk samples owing to the small light penetration depth (~1 μm), the treatment of C<sub>60</sub> under various conditions of high pressure and high temperature results in the formation of bulk crystalline polymeric networks of various dimensionalities based on the C<sub>60</sub> molecular cage [2–5]. The crystal structures of the polymeric phases have been identified as one-dimensional orthorhombic (1D-O), two-dimensional tetragonal (2D-T), two-dimensional rhombohedral (2D-R) and three-dimen-

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doi:10.1016/j.carbon.2010.04.039

sional face centered cubic [2–4]. The infrared (IR) absorption and Raman scattering spectra of these polymeric phases and their crystal structure were studied in detail for samples prepared under carefully controlled conditions of high pressure and high temperature treatment [6]. The polymerization of 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 [7]. In addition, the treatment of  $C_{60}$  under non-hydrostatic high pressure and high temperature results in the production of several disordered polymeric phases, the so-called hard fullerite phases, which have also three-dimensional polymeric character [8–10]. The polymerization of  $C_{60}$  is characterized by the destruction of a number of double C=C bonds and the creation of intermolecular covalent bonds associated with  $sp^3$ -like fourfold coordinated carbon atoms in the fullerene molecular cage. Their number increases from 4 to 8 and to 12 per molecular cage for the 1D-O, 2D-T and 2D-R polymeric phases, respectively, while it is expected to further increase in the three-dimensional polymeric phases.

Differential scanning calorimetry (DSC) and IR spectroscopic measurements have shown that the fullerene polymers are not stable at elevated temperature; heating to  $\sim 560$  K results in the destruction of intermolecular C–C bonds and reversion to the initial monomeric phase [11,12]. The DSC studies performed for various polymers under a heating rate of 10–20 K/min show a strong endothermic peak between 525 and 565 K, but no signal was observed during the cooling scan. The transition temperature depends on the polymeric phase and somewhat on the scanning rate, indicating that the polymer decomposition process is controlled by kinetics. The change of enthalpy related to the complete decomposition of polymers is the highest for the  $C_{60}$  dimers, its value decreases for the linear polymeric chains and becomes minimum for the planar polymeric networks [11]. The differences in the enthalpy change between the various polymeric networks and the kinetics of the polymer decomposition suggest the possible formation of intermediate polymeric/oligomeric states during the process of the temperature-induced decomposition of the polymeric fullerene networks.

In view of this, we have measured the spatially-resolved Raman spectra of the single crystalline 2D-R polymer of  $C_{60}$  after its treatment at various temperatures up to 600 K in order to study the process of the polymer decomposition. The distinct difference between the Raman spectra of the various polymeric/oligomeric phases allows their identification in the intermediate state, appearing upon the temperature-induced polymer decomposition. The Raman data show that the 2D-R polymer is stable after 0.5 h treatment to temperatures up to  $\sim 503$  K, while at higher temperatures a material transformation takes place. In the Raman spectrum, after high temperature treatment (HTT) in the range of 513–553 K, new lines appear related to the  $A_g(2)$  PP-mode of 2D-T-like and 1D-O-like oligomers as well as to  $C_{60}$  dimers and monomers, which characterize the intermediate state of the partially decomposed 2D-R polymer. At higher temperatures, the Raman modes of the 2D-R polymer disappear completely as the material changes drastically its composition resulting in the

domination of  $C_{60}$  monomers with some possible inclusion of  $C_{60}$  dimers. The kinetics of the 2D-R polymer decomposition was studied by Raman measurements of 2D-R polymer single crystals after their HTT in the region 503–533 K for various treatment times. The activation energy  $E_A$  of the 2D-R polymer decomposition, obtained from the dependence of the decomposition time on the treatment temperature, is  $1.76 \pm 0.07$  eV/molecule.

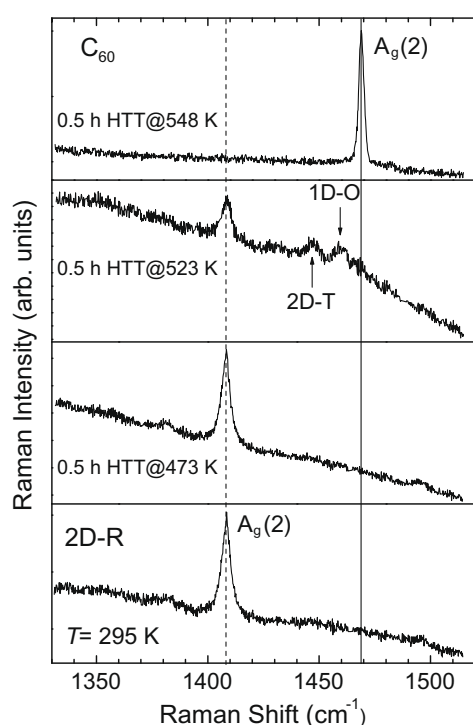
## 2. Experimental

High quality 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. The X-ray diffraction analysis revealed that the sample adopts the rhombohedral structure (space group:  $R\bar{3}m$ ) [13]. The preliminary micro-Raman tests of the synthesized species showed spatially uniform Raman spectra typical for 2D-R polymer of  $C_{60}$  without any detectable inclusions of other polymeric forms of  $C_{60}$ . High purity of the initial 2D-R polymer is of great importance in the study of the intermediate states that may appear during the temperature-induced decomposition of the starting polymer. The HTT of the 2D-R polymer was performed for 0.5–6 h at various temperatures up to  $\sim 600$  K using a high temperature cell with a quartz window. The cell was equipped with a temperature controller unit that maintains temperatures up to 700 K with an accuracy of  $\pm 2$  K. The heating and cooling rates in the temperature range of interest in our experiments are  $\sim 15$  and  $\sim 10$  K/min, respectively.

Raman spectra were recorded from samples with typical dimensions  $\sim 100 \mu m$  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 20 $\times$  objective in a spot of  $\sim 3 \mu m$  diameter, while the laser power on the sample was kept below 0.3 mW in order to prevent sample overheating, laser induced polymer decomposition and/or damage.

## 3. Results and discussion

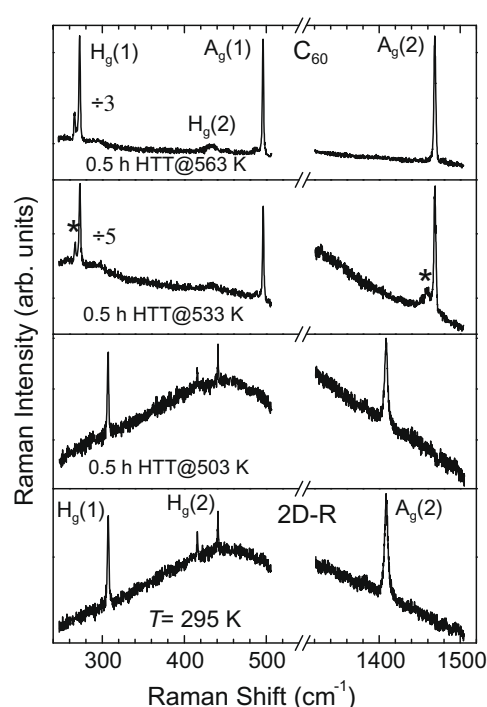
Raman spectra of the 2D-R polymer measured in the region of the  $A_g(2)$  pentagon pinch (PP) mode, after sample treatment for 0.5 h at various temperatures, are presented in Fig. 1. The spectra were measured at room temperature to avoid the sample damage that was observed within the laser spot for  $T \geq 430$  K even at laser intensity as low as 0.005 mW. The  $A_g(2)$  PP-mode of the 2D-R polymer is downshifted to 1408–1410  $cm^{-1}$  from  $\sim 1469$   $cm^{-1}$  for pristine fcc fullerene  $C_{60}$  due to the reduction of the mean intramolecular bond stiffness related to the 12  $sp^3$ -like coordinated carbon atoms in the fullerene molecular cage [7]. The softening of the PP-mode depends on the number of  $sp^3$ -like coordinated carbon atoms and is smaller for the 2D-T and the 1D-O polymeric phases. The Raman spectra measured after the sample treatment for 0.5 h at various temperatures show that the 2D-R polymer is stable up to  $\sim 510$  K, while at higher temperature a material transformation takes place as it can be inferred



**Fig. 1** – Raman spectra of the 2D-R polymer measured at room temperature in the frequency region of the  $A_g(2)$  mode before (dotted vertical line) and after HTT for 0.5 h at various temperatures. The arrows mark peaks related to oligomers resulting from the partial decomposition of the 2D-R polymer. The heat treatment at 548 K leads to complete decomposition of the 2D-R polymer and only the peak attributed to the  $A_g(2)$  mode of monomeric  $C_{60}$  appears in the spectrum (solid vertical line).

from the decrease of the PP-mode intensity, the increase of the background and the appearance of new Raman peaks. The transformation takes place through an intermediate state; the Raman spectrum of the material treated at 523 K has a relatively large background and new peaks typical for the PP-mode of the 2D-T and the 1D-O polymer as well as of the  $C_{60}$  dimers and monomers, which coexist with the PP-mode of the initial 2D-R polymer. Inclusion of 2D-T-like oligomers in the intermediate state can be deduced from the Raman line at  $\sim 1447\text{ cm}^{-1}$ , characteristic of the PP-mode in the 2D-T polymer. Their presence is related to the dissociation of four intermolecular C–C bonds of the initial 2D-R polymer, resulting in the creation of 2D-T-like oligomers having eight intermolecular C–C bonds per  $C_{60}$  molecule. The Raman peak at  $\sim 1459\text{ cm}^{-1}$ , typical for linear polymeric chains, suggests the presence of inclusions related to the dissociation of eight intermolecular C–C bonds of the initial 2D-R polymer and the formation of 1D-O-like oligomers having four intermolecular C–C bonds per  $C_{60}$  molecule.

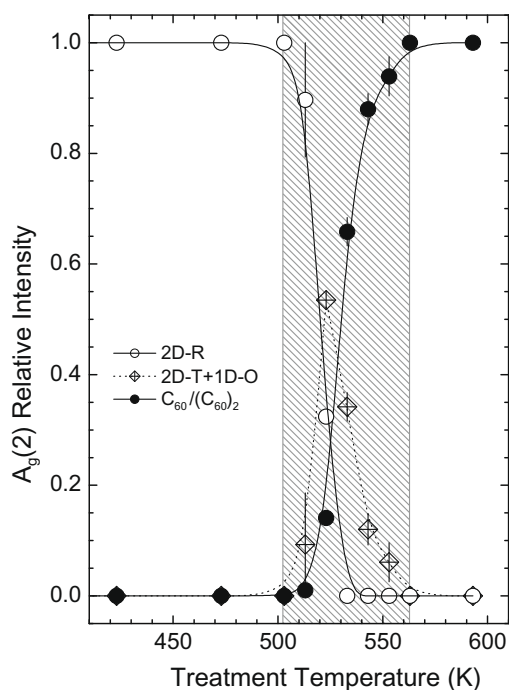
The room temperature Raman spectra of the 2D-R polymer of  $C_{60}$  after 0.5 h HTT at various temperatures are illustrated in Fig. 2. The spectra include the low frequency region suitably scaled and shifted in order to improve readability. The asterisks mark peaks associated with the presence of various oligomers resulting from the 2D-R polymer decomposition.



**Fig. 2** – Raman spectra of the 2D-R polymer at room temperature measured after 0.5 h HTT at various temperatures. The low frequency region has been suitably scaled (numbers on the left) and vertically shifted in order to improve readability. The asterisks mark peaks associated with the presence of various oligomers resulting from the decomposition of the 2D-R polymer.

Namely, the appearance, in some spectra, of a relatively weak peak at  $1452\text{--}1453\text{ cm}^{-1}$  that could be associated with conjugated linear polymeric chains, reflects possibly the appearance of oligomers having six intermolecular bonds per  $C_{60}$  molecule. The appearance of a peak at  $1464\text{--}1466\text{ cm}^{-1}$ , which is related to the  $A_g(2)$  PP-mode of dimeric  $C_{60}$  with two intermolecular C–C bonds per  $C_{60}$  molecule, indicates the presence in the intermediate state of  $C_{60}$  dimers. In addition, the splitting of the low energy  $H_g(1)$  Raman mode of  $C_{60}$  could be also related with the presence of  $C_{60}$  dimers. The treatment at  $\sim 560\text{ K}$  leads to the almost complete decomposition of the polymer and only peaks attributed to the monomeric and dimeric  $C_{60}$  remain in the spectrum. The peak assignment given above refers to the irreducible representations of the parent  $C_{60}$  molecule in accordance to that of Davydov et al. [6].

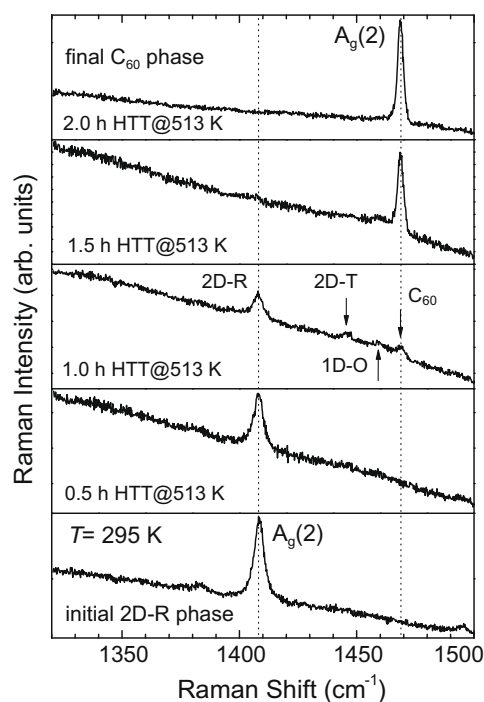
The intermediate state of the partially decomposed 2D-R polymer was observed up to 560 K where the material changes drastically its composition resulting in the domination of  $C_{60}$  monomers with some inclusion of  $C_{60}$  dimers. Fig. 3 shows the relative intensities of the  $A_g(2)$  PP-mode as a function of the treatment temperature of the initial state of the 2D-R polymer (open circles), the final state of the material after HTT comprising of  $C_{60}$  monomers and dimers (closed circles) as well as the intermediate state comprising of 2D-T- and 1D-O-like oligomers (diamonds). The Raman spectra were measured after a number of 0.5 h heat treatments at various temperatures on pieces of fresh sample. For most of the treatments, two or more spectra were aver-



**Fig. 3** – Intensity of the  $A_g(2)$  peak attributed to the initial 2D-R polymer (open circles), the intermediate 2D-T- and 1D-O-oligomers (diamonds) and the  $C_{60}$  monomers/dimers (solid circles) normalized to their sum as a function of the heat treatment temperature. Each HTT lasted for 0.5 h on pieces of fresh sample, the spectra were averaged from different sample sites and/or sample pieces, while the error bars refer to the standard error of the mean. The shaded area denotes the temperature region of the polymer decomposition; the lines through the data are guides to the eye.

aged from different sample sites and/or sample pieces. The relative intensities of the various components, defined as the intensity of the  $A_g(2)$  peak of each component normalized to their sum, reflect their relative concentration in the intermediate state. Thus, the concentration of the 2D-T- and 1D-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 treatment temperature it gradually decreases to zero at ~560 K.

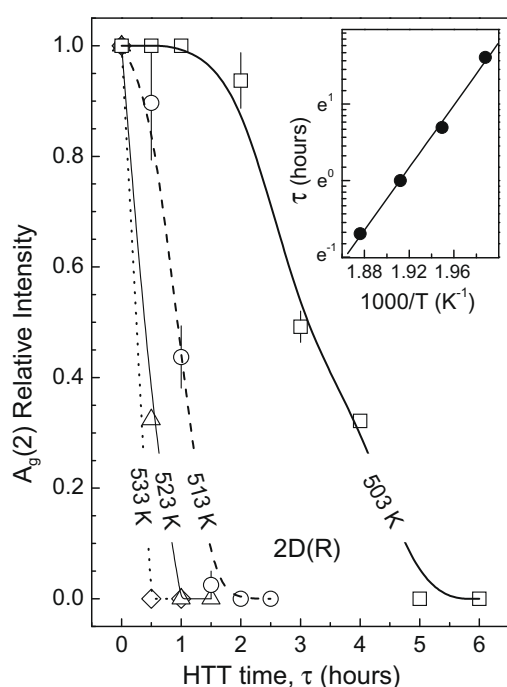
The existence of 2D-T- and 1D-O-like oligomers in the intermediate state underlines the fact that the 12 intermolecular C–C bonds of the 2D-R polymer do not break simultaneously, in spite of their equivalence related to the hexagonal symmetry of the planar rhombohedral polymeric sheets. The broad lineshape of the Raman peaks related to the  $A_g(2)$  mode of the 2D-T- and the 1D-O-like oligomers indicate either the structural disorder or the small size of the oligomer inclusions. It should be also noted, that the formation of oligomeric inclusions was observed earlier in the IR spectra of the partially decomposed 2D-R polymer, while the two-step decomposition of the 2D-R polymer through the formation of an intermediate triangular cyclic trimer state was proposed to account for the observations [14]. According to our Raman data, the situation is more complicated; the polymer decom-



**Fig. 4** – Raman spectra of the 2D-R polymer measured at room temperature in the high frequency region after HTT at 513 K for 0.5–2.0 h. HTT for 1 h results in appearance of the intermediate 2D-T- and 1D-O-like oligomers as well as of the monomeric  $C_{60}$ , while HTT for 2 h leads to complete decomposition of the 2D-R polymer.

position takes place through the formation of an intermediate state that is in fact a mixture of the initial 2D-R polymer, 2D-T- and 1D-O-like oligomers of  $C_{60}$  as well as monomeric and dimeric  $C_{60}$ . Nevertheless, the long time HTT results to the complete decomposition of the material and the final state of the decomposed 2D-R polymer is pure monomeric  $C_{60}$ , possibly with small inclusions of  $C_{60}$  dimers. It is important to note, that the final state of the monomeric  $C_{60}$  is structurally ordered and its Raman spectra are characterized by relatively low background and sharp peaks. Moreover, no sign of amorphous carbon formation was evident in the Raman spectra for the temperature and treatment time used in our study.

To study the kinetics of the 2D-R polymer decomposition we have measured the room temperature Raman spectra of samples treated at four different temperatures as a function of the heat treatment time. The Raman spectra of the 2D-R polymer in the frequency region of the  $A_g(2)$  PP-mode after treatment at 513 K for 0.5–2.0 h are illustrated in Fig. 4. The treatment for 0.5 h results in the decrease of the  $A_g(2)$  mode intensity of the 2D-R polymer. The HTT for 1 h results in further decrease of the  $A_g(2)$  peak intensity and the appearance of  $A_g(2)$  mode peaks associated with the presence of the 2D-T- and the 1D-O-like oligomers as well as with the monomeric  $C_{60}$ . Finally, the heat treatment for 2 h leads to the practically complete decomposition of the 2D-R polymer and the  $A_g(2)$  mode peak attributed to monomeric  $C_{60}$  dominates the Raman spectrum. Note that, the effect of heating has an additive character as there is no significant difference between the



**Fig. 5 – Intensity of the  $A_g(2)$  mode peak of the initial 2D-R polymer normalized to the sum of the  $A_g(2)$  peaks associated with the 2D-R polymer, 2D-T- and 1D-O-like oligomers as well as with the monomeric and the dimeric  $C_{60}$ , as a function of the heat treatment time at 503 (squares), 513 (circles), 523 (triangles) and 533 K (diamonds). The data were averaged from different sample sites and/or sample pieces, while the error bars refer to the standard error of the mean. The lines through the data are guides to the eye. Inset: Arrhenius plot of the polymer's complete decomposition time ( $\tau$ ) versus the inverse treatment temperature ( $T$ ).**

spectra recorded from a sample after continuous HTT at 513 K for a certain treatment time from those of a sample treated at the same temperature for the same total time but with intermediate cooling(s) to room temperature.

Fig. 5 shows the intensity of the  $A_g(2)$  mode of the 2D-R polymer normalized to the sum of the corresponding peaks associated with the 2D-R polymer, 2D-T- and 1D-O-like oligomers as well as with the monomeric and the dimeric  $C_{60}$  as a function of the HTT time for different temperatures; diamonds, triangles, circles and squares correspond to treatment temperatures of 533, 523, 513 and 503 K, respectively. The time required for the complete decomposition of the 2D-R polymer at 533 K is  $\sim 0.5$  h, while it increases at lower temperatures. The occurrence of polymer decomposition at temperatures lower than 533 K, as well as the increase of the time needed for complete decomposition with decreasing treatment temperature, indicate the activation-type behavior of the polymer decomposition transition that is typical for chemical reactions.

According to DSC measurements, the minimum of the total energy related to the fcc monomeric state of  $C_{60}$  is higher by  $\sim 0.13$  eV/molecule than the total energy minimum related to the 2D-R polymer of  $C_{60}$  [11]. The stability of the  $C_{60}$  monomer at ambient conditions is due to the energy barrier that

separates the polymeric from the monomeric state. In the case of the 2D-R polymer, the theoretically predicted energy barrier that separates the total energy minimum of the 2D-R polymer from that of the monomeric state of  $C_{60}$  is 1.6 eV/molecule [15]. Another theoretical calculation of the energy barrier yields a value of 1.7 eV/molecule [16]. We can estimate the barrier value from our Raman data taking into account that the polymer decomposition time versus heat treatment temperature can be described by an Arrhenius equation:

$$\tau(T) = A \times \exp(E_A/k_B T) \quad (1)$$

where  $E_A$  is the activation energy (energy barrier between the polymeric and the monomeric state),  $k_B$  is the Boltzmann constant,  $T$  is the treatment temperature and  $\tau$  the polymer decomposition characteristic time. The constant  $A$  is related to the characteristic phonon frequency and is measured in time units [17]. The Arrhenius plot of the polymer decomposition time versus the treatment temperature, as obtained from the experimental Raman data at the four temperatures mentioned above, is shown in the inset of Fig. 5. The experimental points exhibit a remarkably good linear dependence in logarithmic scale, yielding an activation energy of  $E_A = 1.76 \pm 0.07$  eV/molecule. This value is smaller than the value of  $1.9 \pm 0.2$  eV/molecule obtained in Ref. [17] from thermal expansion measurements on 2D-R polymeric powders. The activation energy obtained from the Raman experiments presented here is in good agreement with the calculated barrier energy; it is  $\sim 10\%$  larger than the data reported in Ref. [15] and coincides within experimental accuracy with the data reported in Ref. [16]. It is important to note, that the enthalpy of the polymer decomposition extracted from DSC measurements, is not related directly to the energy barrier between the polymeric and the monomeric  $C_{60}$  state, but to the difference between the total energy minima. For example, the transition enthalpy for the 2D-R polymer obtained in Refs. [11,12] is equivalent to an energy difference between the two minima of  $\sim 0.13$  and  $\sim 0.11$  eV/molecule, respectively. Another interesting point is that the values for the activation energy of the 2D-R polymer decomposition are almost half of those for the transformation of  $sp^3$  to  $sp^2$  bonding in amorphous tetrahedral carbon (3.3–3.5 eV [18,19]), in line with the intermolecular nature of the bonds in the case of the  $C_{60}$  polymer.

Finally, using the coefficients obtained from the Arrhenius equation we can estimate the complete decomposition time of the 2D-R polymer; at 300 K it is equal to  $\sim 4.49 \times 10^8$  years, but it collapses to  $\sim 62$  h at  $T = 473$  K. These estimations show that the fullerene polymers demonstrate rather large fragility at elevated temperatures that may be a reason preventing their practical use.

#### 4. Conclusion

Summarizing, the room temperature Raman spectra of the 2D-R polymer of  $C_{60}$  after its 0.5 h treatment at high temperature show a gradual decomposition starting at  $\sim 510$  K. The polymer composition changes drastically after treatment at  $\sim 560$  K, resulting in the domination of  $C_{60}$  monomers with some inclusion of  $C_{60}$  dimers. The decomposition of the 2D-R polymer takes place through an intermediate state that, in fact, is a mixture of the initial 2D-R polymer, 2D-T- and

1D-O-like oligomers of  $C_{60}$  as well as monomeric and dimeric  $C_{60}$ . The final state of the decomposed 2D-R polymer is pure monomeric  $C_{60}$  with, possibly, small inclusions of  $C_{60}$  dimers. This state is characterized by Raman spectra with small background and sharp Raman peaks, indicating its high structural order.

The decomposition of the 2D-R polymer may occur at relatively low temperatures. At temperatures lower than 533 K, the decomposition of the 2D-R polymer is characterized by the increase of the decomposition time, indicating the activation-type behavior of the polymer decomposition transition that is typical for chemical reactions. The polymer decomposition time dependence on the treatment temperature is described remarkably well by the Arrhenius law that gives an energy barrier between 2D-R polymer and  $C_{60}$  monomer total energy minima of  $E_A = 1.76 \pm 0.07$  eV/molecule.

## Acknowledgements

K.P.M. acknowledges the support by the Russian Foundation for Fundamental Research, grant #08-02-00890, and the hospitality of the Aristotle University of Thessaloniki, Greece.

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