

Spectroscopic study of phase transformations between orthorhombic and tetragonal C₆₀ polymers

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Abstract. We present a detailed study of transformations between the orthorhombic and tetragonal polymeric states of C₆₀. The transformations are characterised by Raman spectroscopy and X-ray diffraction. We show that the transformation from the orthorhombic (O) phase to the tetragonal (T) phase is very fast and our results indicate that the transformation goes via an intermediate dimer (D) state in a two-stage process, O → D and, D → T transformations, where the second process is slower than the first. On the other hand, the transformation from the tetragonal to the orthorhombic phase is significantly slower, indicating a high-energy threshold to break the polymer bonds at the temperatures used. The results also support earlier suggestions that the tetragonal phase contains disordered dimers that can be viewed as lattice defects in the formation of higher polymers.

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1 Introduction

One of the most interesting properties of C₆₀ is its ability to form polymeric phases. It is now well known that pressure polymerisation of pure C₆₀ below 8 GPa occurs by a 2 + 2 cycloaddition mechanism which connects the molecules into one-, two-, or even three-dimensional (1D, 2D, or 3D) polymeric structures [1–3]. However, the resulting four carbon ring intermolecular bond is not the only possible type of intermolecular bond in polymeric C₆₀, and some intercalated polymeric phases are based on single C–C intermolecular bonds [4–6].

With the exception of the photopolymerized phase, which consists of linear chains [7,8] that might be branched [9], all pure C₆₀ polymers are produced at high pressure at an elevated temperature. In the past years the 1D orthorhombic phase (O-phase) and the 2D tetragonal phase (T-phase) has been characterised in detail by X-ray diffraction [10,11], inelastic neutron scattering [12,13], Raman spectroscopy [14–17], and measurements of specific heat capacity [18,19] and thermal expansion [20]. The tetragonal phase was the last of the pure C₆₀ polymers that was produced as a single phase [21] and by polymerising a single crystal into the tetragonal phase at $P = 2$ GPa, $T = 700$ K, we were able to characterise its structure in detail [11]. We found that this phase

has a P4₂/mmc space group symmetry, as predicted by Dzyabchenko et al. [22], meaning that successive polymeric layers are rotated 90° about the stacking axis. However, using another path (pressing then heating) in the p - T diagram, Chen et al. [23] produced crystals that could be described within the Immm symmetry, which seems to be a competitive stacking when the tetragonal phase is formed [24]. Although many properties of this phase have now been well studied [25] many questions still exist, and an especially intriguing one is the thermodynamics of the transformation between the different polymeric phases. Davydov et al. reported a transformation from the rhombohedral phase to the tetragonal one [21], and Talyzin et al. discussed the transformation from the tetragonal to the rhombohedral structure at 800 K and 8 GPa [26]. In a very recent study, Moret et al. [27] compared the polymeric structures of single crystals that were polymerised at 1.8 GPa and 700 K, but being brought to these conditions after passing through different paths in the p - T diagram. They concluded that the conditions for the initial polymerisation can have strong influence on the final polymeric structure if the temperature at the later stage is too low to reorganise the crystal into the normally thermodynamically stable phase. We therefore believe that it is the early stages in the polymeric evolution that is of largest interest and we have thus concentrated our study on the transformation from the orthorhombic to the tetragonal

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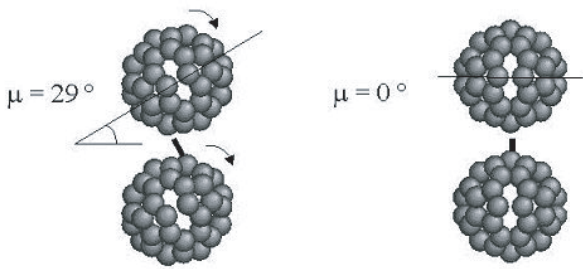


Fig. 1. Polymeric linear chains in a direction perpendicular to the plane of drawing. Left: shows the probable chain orientation in the Pmnn structure and indicates the rotation that has to occur to form an intermolecular bond to a neighbour chain, right: shows the chain orientation in the tetragonal P₄₂/mmc structure. Picture is redrawn with permission from [10].

phase. In an X-ray study of the orthorhombic phase obtained at “low” pressures, Moret et al. concluded that the lattice had a Pmnn symmetry, where the plane of the four-member rings in the linear polymeric chains forms an angle of 45° (or 29°) to the *c*-axis (see Fig. 1). To form a tetragonal polymer by directly connecting the chains existing in the orthorhombic phase, the chains must therefore be able to rotate. Such a direct transformation might thus involve a rotational energy barrier with a high threshold, possibly so high that the transformation is not possible at all. Later, this was also discussed by Davydov et al. [28], who observed a very slow transformation from the orthorhombic to the tetragonal phase at 723 K and 1.5 GPa and also concluded that the transformation would not be possible without breaking the polymer bonds. This means that the path from the orthorhombic to the tetragonal phase must go via some intermediate phase, either molecular C₆₀, dimers (D) or small oligomers.

In this paper we report the results of a study in which we have tried to induce phase transformations between the orthorhombic and tetragonal phases. We have started by producing nearly single-phase T and O materials. After characterisation by Raman spectroscopy and X-ray diffraction we have annealed the orthorhombic polymer in the region of the *p*-*T* phase diagram [2,3] where the pure tetragonal phase is stable and the tetragonal polymer in the region where the orthorhombic polymer is obtained. A *p*-*T* phase diagram is shown for pressures up to 5 GPa in Figure 2.

This experiment was repeated for different treatment times to study the kinetics of the transformation and, if possible, to identify any intermediate states. The transformation from the orthorhombic phase to the tetragonal phase was also compared with the transformation directly from pristine C₆₀ to the tetragonal phase.

2 Experimental

As starting material we have used C₆₀ with a purity of 99.95% obtained from Term USA, Berkeley, CA. All sam-

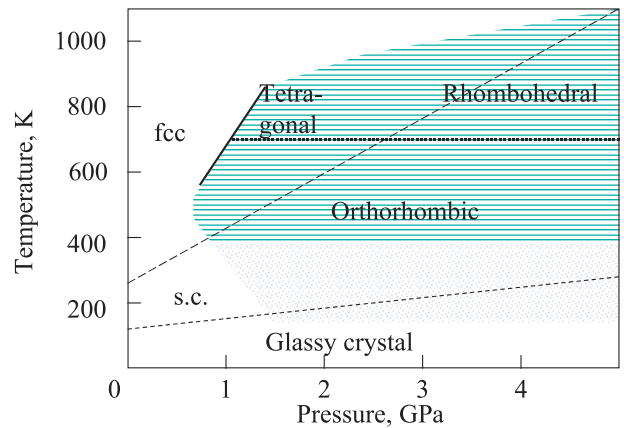


Fig. 2. Pressure-temperature phase diagram of C₆₀.

ples were handled in air but were stored in evacuated containers between the transformations. Our samples were treated in a piston-cylinder device with a Teflon pressure cell containing a helical internal heater. The samples were inserted into thin-walled stainless steel cylinders that were placed in the heater. As pressure medium we used talc, which is known to give a quasi-hydrostatic pressure in the cell. A layer of talc mixed with glass beads was used as thermal insulation at the walls of the Teflon cell [29]. We found that the best parameters for producing single-phase tetragonal C₆₀ were a pressure of 2.5 GPa and a temperature of 830 K. To avoid passing through the orthorhombic region in the phase diagram these conditions were reached by first raising the pressure to 0.5 GPa and then the temperature to 830 K before the pressure was raised to its final value. For the production of single-phase orthorhombic material we used the same parameters as in our earlier studies of this phase, 1.0 GPa and 570 K [14]. After the high-pressure, high-temperature treatment the samples were quenched to room temperature, at an initial rate of ≈200 K/min, before the pressure was released. For both phases the treatment time used to produce single-phase starting material was 5 h. These starting materials were then characterised with X-ray diffraction and Raman spectroscopy before being divided into several smaller samples. The latter were then treated under high-temperature high-pressure conditions in such a way as to transform the O-samples into the T-phase and vice versa. To avoid depolymerisation, the orthorhombic samples treated in the “T-phase region” had to pass briefly through the “O-phase region” of the *p*-*T* phase diagram but this should not lead to any complications.

We can divide our study into three parts.

- 1) The single-phase orthorhombic C₆₀ polymer was divided into four identical samples that were treated at 873 K and 2.5 GPa for 15, 60, 120 and 360 min, respectively.
- 2) Pristine C₆₀ was also treated at 873 K and 2.5 GPa for 15, 60, 360 and 960 min, respectively, and the results were compared with the results of the previous experiments.

- 3) The single-phase tetragonal C₆₀ polymer was divided into six identical parts. Four of these were treated at 570 ± 10 K and 1.0 GPa for 90, 150, 330 and 1440 min, respectively. The other two samples were treated at the same pressure but at 595 K and 620 K, respectively, for 240 min, to study the effect of temperature on this transformation.

After the pressure treatment all samples were characterised with micro-Raman spectroscopy and X-ray diffraction analysis. The Raman studies were performed using a Renishaw 1000 grating spectrometer with a CCD-detector. A notch filter was used to remove the Rayleigh line. We used an argon ion excitation laser (514.5 nm) with a power density of approximately 10 W/cm^2 . The low power density ensured that no additional photo-induced polymerisation occurred in the samples and minimised sample heating. The resolution of the Raman spectra was about 2 cm^{-1} . All samples were characterised at four or more different spots to get an overall characterisation of the samples. For all the measured samples the spectra indicated homogeneous samples and the ratios $I_{1447/1459}$ and $I_{1447/1464}$, which are used later for the analysis, differed at most ± 0.2 from the mean value.

The X-ray data were collected at ambient conditions on a Philips powder diffraction system with a PW1820 goniometer using the CuK_α radiation.

3 Results and discussion

In the Raman spectrum of pristine C₆₀ ten modes can be easily detected, eight five-fold degenerate H_g modes and two singlets A_g modes. After polymerisation most of the H_g modes split into several components and new modes, which were optically silent earlier, appear. It has been shown [9,33,34] that the most useful method to identify the polymeric structure of C₆₀ by Raman spectroscopy is to follow the evolution of the pentagonal pinch mode, A_g(2), which for pristine material falls at 1469 cm^{-1} . This mode corresponds to the vibration of the double bonds forming borders between hexagons and thus also the bonds that break up to form the intermolecular bonds. Because of electron transfer to the intermolecular bonds, this mode shifts in a predictable way upon polymerisation. Porezag et al. [30] calculated that the shift should be proportional to the number of intermolecular bonds per molecule, and it has been shown experimentally that the dimers, linear chains and tetragonal polymer planes are each characterised by their own well-defined shifts. Thus the pentagonal pinch mode shifts to 1464 cm^{-1} for dimers [8,31,32], to 1459 cm^{-1} for linear chains [7,8], and to 1447 cm^{-1} for tetragonal polymers [11,21,33,34].

The primary aim of this study was to detect changes in the relative amount of different polymeric structures. To do this we have used a peak-fitting program to fit Voigt shape peaks to the data in the pentagonal pinch mode area to detect the presence of, and integrated intensities of, the characteristic modes of the different polymeric structures. It should be pointed out that this method does not give

a fully quantitative description of the amounts of different polymers in the sample. However, when studying the evolution of the transformation it has proved to be very powerful.

3.1 Orthorhombic-tetragonal transformation

We start our analysis with the first group of samples in our study and with transformations from the orthorhombic phase to the tetragonal phase. In Figure 3 we show Raman spectra for the initially orthorhombic sample, treated at high pressure for the times specified above and in the figure. As expected, the dominating peak in the spectrum of the orthorhombic sample (a) is the pentagonal pinch mode at 1459 cm^{-1} , characteristic for linear chains. Other modes that can be seen for this phase but not for the tetragonal phase are located at 344 cm^{-1} and 710 cm^{-1} . However, the mode at 344 cm^{-1} has also been reported for dimers as well as for the rhombohedral phase [34]. From spectrum (b) in the figure we see that already after 15 min of high-pressure treatment the mode pattern has changed drastically. The pentagonal pinch mode now contains three components, positioned at 1447 cm^{-1} , 1459 cm^{-1} and 1464 cm^{-1} , where the 1447 cm^{-1} mode is the strongest. A large number of new, sharp peaks has also appeared, e.g. a very strong mode at 430 cm^{-1} , two components of the split H_g(3) mode at 668 cm^{-1} and 685 cm^{-1} , and a new component of the former H_g(4) mode at 748 cm^{-1} . All these modes are characteristic for the tetragonal phase [11,21,34]. Looking in more detail at the evolution of the spectra we can see, even without using the peak-fitting program, that the 430 cm^{-1} mode becomes more and more dominating as the treatment time in the “tetragonal phase” p - T region increases. The large intensity of this mode for the tetragonal phase if probed by an argon ion laser is in agreement with earlier results [21]. Other modes that increase strongly in relative intensity are, for example, those at about 580 cm^{-1} and 950 cm^{-1} . The latter is usually attributed to vibrations of the atoms that participate in the intermolecular bonds [17,35]. It therefore seems reasonable that the relative intensity of this mode should increase as the number of intermolecular bonds per molecule increases. As for the A_g(2) mode, the frequency of the mode near 950 cm^{-1} seems to depend on the average number of intermolecular bonds per molecule. For the almost pure orthorhombic sample (curve a) the dominating component can be found at 968 cm^{-1} with a smaller peak at 952 cm^{-1} . When the sample transforms to the tetragonal phase the component at 952 cm^{-1} grows significantly but a small shoulder remains at 968 cm^{-1} . Thus the component at 952 cm^{-1} seems to be characteristic for the tetragonal phase while that at 968 cm^{-1} probably represents linear chains or dimers in the orthorhombic phase. For rhombohedral C₆₀ this mode is also reported near 968 cm^{-1} [34].

The data in the pentagonal pinch mode area were analysed using a peak-fitting program as described above. For all samples a very good fit was obtained by fitting three modes at 1464 cm^{-1} , 1459 cm^{-1} and 1447 cm^{-1} . In

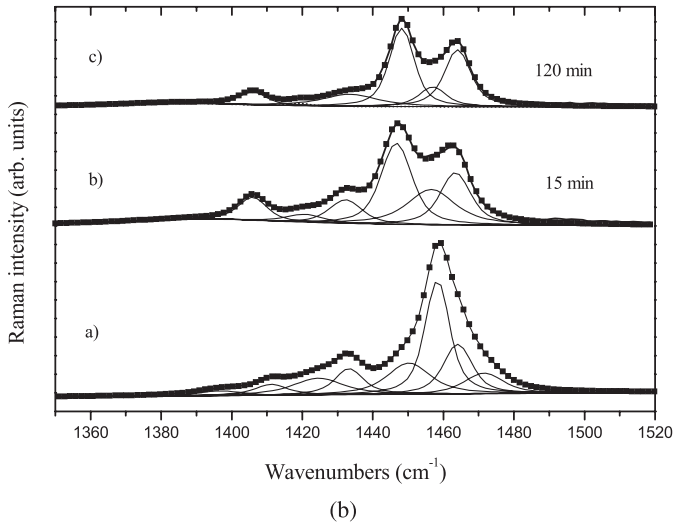
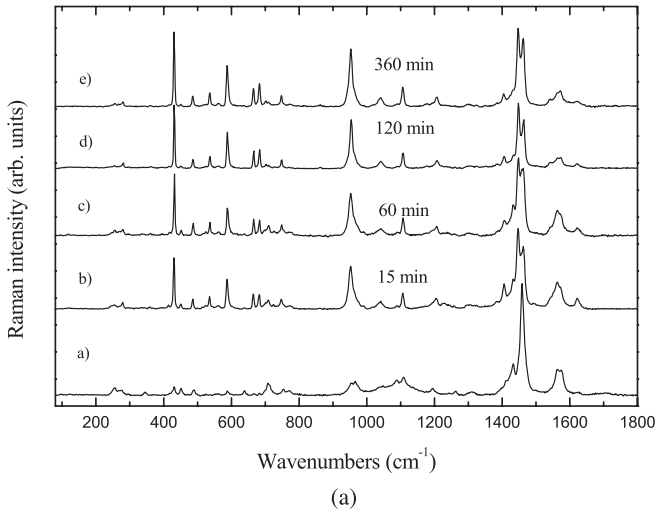


Fig. 3. Panel (a) Raman spectra for (a) an initially orthorhombic polymeric sample, treated at 830 K and 2.5 GPa for: (b) 15 min, (c) 60 min, (d) 120 min and (e) 360 min. Panel (b) Fits of Voigt lineshapes to the $A_g(2)$ -mode for: (a) orthorhombic polymeric sample, (b) sample treated at 15 min, and (c) sample treated at 120 min.

addition to these, two other modes, at 1432 cm^{-1} and 1408 cm^{-1} , were needed to obtain a good fit as shown in Figure 3b. The latter is a mode known to be significant for the rhombohedral polymer phase [33,34], while the representation of the former is unclear. We have previously observed that a single crystal treated at 2.0 GPa and 700 K contained a fraction (≈ 0.25) of the rhombohedral phase [11], and Moret et al. found that this phase could even be the dominant structure when samples were polymerised at the same conditions and by increasing the pressure before the temperature [27]. This effect could probably be explained by the initial orientation of small polymeric units in a fashion that favours continuous growth in the 111 planes. For none of these samples, except for the orthorhombic sample used as starting mate-

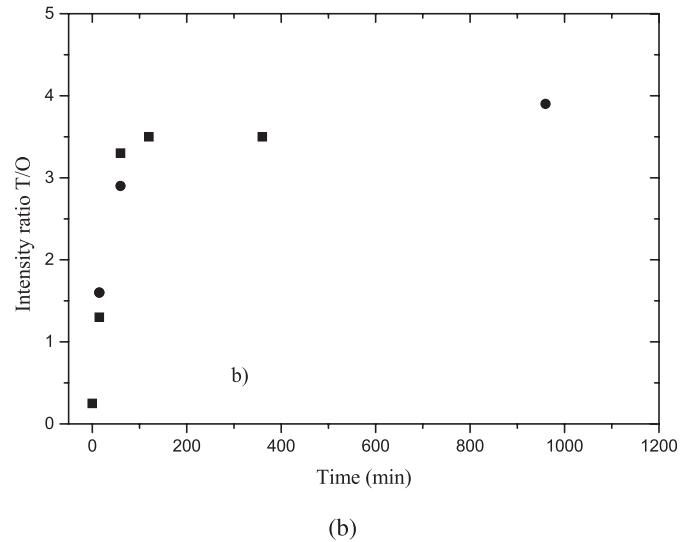
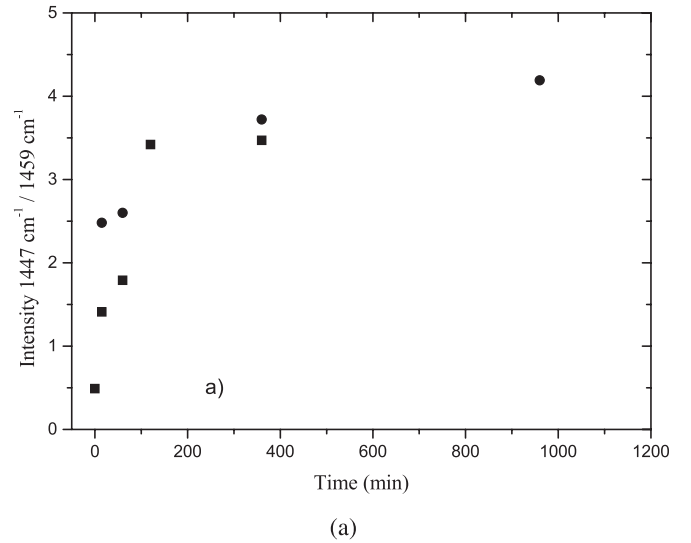


Fig. 4. (a) Raman data: ratio between the fitted integrated areas of the 1447 cm^{-1} and the 1459 cm^{-1} modes, (b) X-ray diffraction results showing the ratio between the fitted intensity of the (101) “T-peak” at $2\theta = 11.3$ and the (011) “O-peak” at $2\theta = 10.8$. In both plots, squares show transformations O-T and dots show transformations P-T.

rial, did adding a mode at 1469 cm^{-1} improve the fit. Typical values for the FWHM of the fitted peaks were about 10 cm^{-1} for the three main peaks and the 1408 cm^{-1} mode, while the 1432 cm^{-1} mode usually had a FWHM of about 14 cm^{-1} .

A very direct way of studying the transformation between two phases is to study the ratio between the areas of significant modes for these phases as a function of treatment time. For the samples transformed from the orthorhombic phase to the tetragonal one the obvious choice is to use the ratio I_{1447}/I_{1459} , which we plot as squares in Figure 4 as a function of treatment time. The ratio changes very rapidly from 0.48 for the almost pure

orthorhombic sample to 1.41 after only 15 min, and then continues to increase to about 3.5 after 360 min. As mentioned above, at no stage of the transformation could any sign of monomeric C₆₀ be seen, indicating either that the transformation does not go via an intermediate monomer state or that this intermediate molecular state is so short-lived that it is impossible to observe in a non-in-situ experiment.

3.2 Pristine-tetragonal transformation

We can compare these results with corresponding data for the second group of samples, i.e. for the transformation from pristine C₆₀ to the tetragonal phase. These data are shown as dots in Figure 4. Already after 15 min this reaction had proceeded to the point where all traces of pristine C₆₀ had disappeared. Our results show that, even if we start from pristine C₆₀, a certain fraction of the samples first transforms into linear chains and dimers. Since the polymerisation always has to start with a formation of dimers it is reasonable to believe that a fraction of these dimers will continue to grow to longer chains before they evolve to fit into the tetragonal lattice in a process that is discussed below. However, as might be expected, the ratio of linear chains to polymeric planes is always smaller when we start from pristine C₆₀ instead of from the orthorhombic phase. Both transformations seem to saturate at a ratio $I_{1447}/I_{1459} \approx 4$. The time evolutions of both transformations are very rapid and to study the kinetics in detail it would be necessary to extend the study to times shorter than 15 min. However, this is not possible with the equipment used in this study.

X-ray powder diffraction spectra of C₆₀ polymerised at quasi-hydrostatic pressure usually suffer from low quality due to significant peak broadening. This is a result of non-uniform pressure distribution possibly leading to stresses and micro deformations in the samples. This together with the similarity of the diffraction data for different polymeric phases make a detailed quantitative analysis of X-ray diffraction data and structural modelling, using for example the Rietveld method not feasible. We have therefore used another approach to analyse our X-ray diffraction data and to make it easy to compare these with our Raman spectroscopy data. In the X-ray pattern shown in Figure 5 the two most characteristic peaks are the (101) and (011) at $2\theta = 11.3$ and $2\theta = 10.8$, for tetragonal and orthorhombic phases, respectively. For all our samples but the one (p - T , 15 min) we have measured the X-ray diffraction data after grinding. In Figure 4b we have plotted the ratio between the intensity of these peaks (the “T-peak” and the “O-peak”) against the treatment time in the “tetragonal region” of the p - T diagram. The data shows that our interpretation from the Raman data is strongly supported, with a very fast development of the tetragonal phase during the first 60 min, and thereafter a significant change in the reaction rate. Our X-ray data also support our observation that the samples transformed from pristine to tetragonal C₆₀ had a higher ratio of poly-

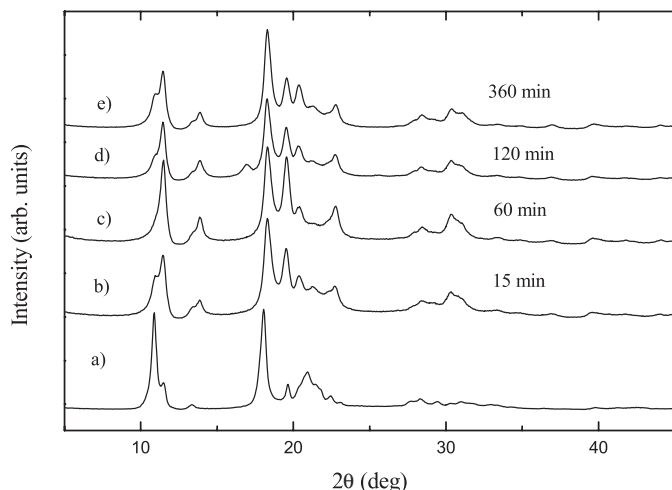


Fig. 5. X-ray diffraction spectra for (a) an initially orthorhombic polymeric sample, treated at 830 K and 2.5 GPa for: (b) 15 min, (c) 60 min, (d) 120 min and (e) 360 min.

meric planes to linear chains than samples transformed from orthorhombic to tetragonal C₆₀.

The Raman mode at 1464 cm^{-1} is usually attributed to dimers, because experiments on pure dimer samples [31] show a characteristic shift of the pentagonal pinch mode to this value. A strong mode is always observed at this wavenumber in tetragonal samples, and it is an interesting question whether this peak is really due to the presence of dimers or whether it is a characteristic vibration originating in the tetragonal sheets. If this mode is characteristic for the tetragonal phase and the samples do not contain any dimers, the ratio between the peaks at 1464 cm^{-1} and 1447 cm^{-1} should be constant for all pure tetragonal samples. However, looking, for example, at curves d) and e) in Figure 3, we see that this is not the case. This agrees with earlier results, which also indicated the presence of dimers in the tetragonal phase [11]. How these dimers are formed or otherwise play a role in the polymerisation process is not fully clear from our results. We cannot rule out a mixed model, in which there is both a certain variable concentration of dimers, formed as “defects” in the tetragonal phase and giving a signal at 1464 cm^{-1} , and also an intrinsic line at the same frequency coming from the tetragonal phase. Davydov et al. [21] have suggested the C₆₀ F_{1g}(3) mode as a likely candidate for this, but it would then be shifted by more than 100 cm^{-1} from the position reported for pristine C₆₀ [36]. The same type of analysis as for the 1459 cm^{-1} mode shows the evolution of the intensity ratio I_{1447}/I_{1464} for the samples transformed from the orthorhombic to the tetragonal phase. This ratio decreases monotonically from 1.53 for the sample treated only 15 min in the tetragonal region to 0.98 for the sample treated 360 min as we show in Figure 6 below. One way of interpreting this is that the orthorhombic phase transforms to the tetragonal phase in two steps. The first stage is a conversion $O \rightarrow D$, i.e. a breakdown of the molecular chains into dimers, and the second stage a transformation $D \rightarrow T$. If the second process is *slower* than the first

there would be a gradual increase in the relative fraction of dimers and the I_{1447}/I_{1464} intensity ratio would decrease. This process would give a reasonable explanation for how the orthorhombic phase can be transformed to the tetragonal one without having to cross the expected high-energy threshold connected with the rotation of the linear chains in the direct transformation path. It is also reasonable to believe that high pressure would favour dimers instead of monomers as an intermediate state between the two phases, because of the smaller volume of the former. It has also been shown theoretically that some dimer structures are very favourable as building blocks for higher order polymers [37]. In the same study it is reported that a dimer molecule that has to rotate 30° to fit into the tetragonal structure would still gain energy due to the formation of intermolecular bonds [37]. If we further compare the averaged intensity ratio I_{1447}/I_{1464} for the samples in group 1, transformed from orthorhombic to tetragonal, with the group 2 samples, transformed from pristine C_{60} to tetragonal, we get for group 1, $I_{1447}/I_{1464} = 1.3$ and for group 2, $I_{1447}/I_{1464} = 1.6$. Although the difference is small it seems reasonable that a sample transforming via an intermediate dimer state should contain more dimers than a sample transforming directly from the monomer state. We note, however, that some fraction of the pristine C_{60} transforms first into linear chains, which would then have to follow the same path as described for group 1. Furthermore, we should compare the above ratios with the ratio $I_{1447}/I_{1464} = 2.7$ obtained for a C_{60} single crystal polymerised into the tetragonal phase in an earlier study [11]. This indicates that the volume fraction of dimers is much higher in polycrystalline samples of the tetragonal phase than in single crystal C_{60} containing very large domains (variants) of the same phase and that the dimers are not segregated into a single phase, i.e. distributed randomly in the sample, otherwise we believe we would be able to detect this phase in our X-ray experiments. This observation supports our earlier idea that most of the dimers found in the tetragonal structure are located at grain boundaries or at lattice defects. Together with the relatively low concentration of dimers in the well ordered single crystal, this also explains why dimers are so hard to observe in X-ray diffraction studies [11].

3.3 Tetragonal-orthorhombic transformation

Turning finally to the third group of samples, we show in Figure 7 the Raman spectra of initially tetragonal samples treated for different times under conditions where pristine C_{60} is transformed into the orthorhombic phase. Both our Raman spectroscopy results and our X-ray diffraction data show that almost no phase transformations occur in these samples. Following the same mode intensity ratio (not shown) as studied for the orthorhombic to tetragonal transformation in Figure 4 we found that for all samples the ratio $I_{1447}/I_{1459} = 3.9 \pm 0.5$, with a weak tendency to decrease with increasing treatment time. However, the samples treated at the same pressure but at higher temperatures indicate some signs of a partial transformation

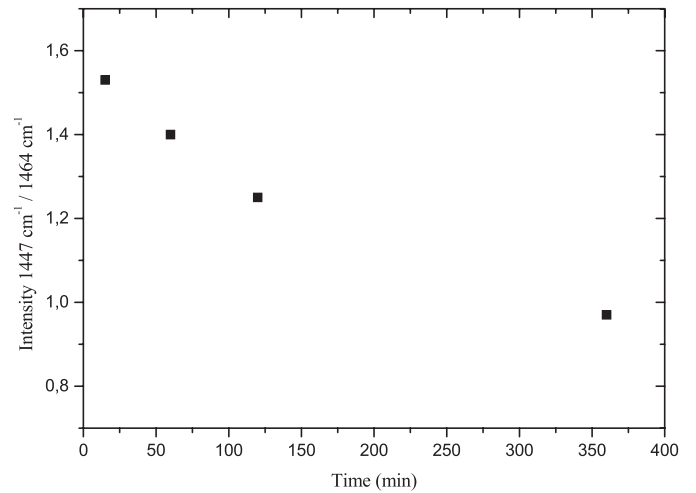


Fig. 6. Ratio between the fitted integrated areas of the 1447 cm^{-1} and the 1464 cm^{-1} modes for samples transformed from the orthorhombic to the tetragonal phase.

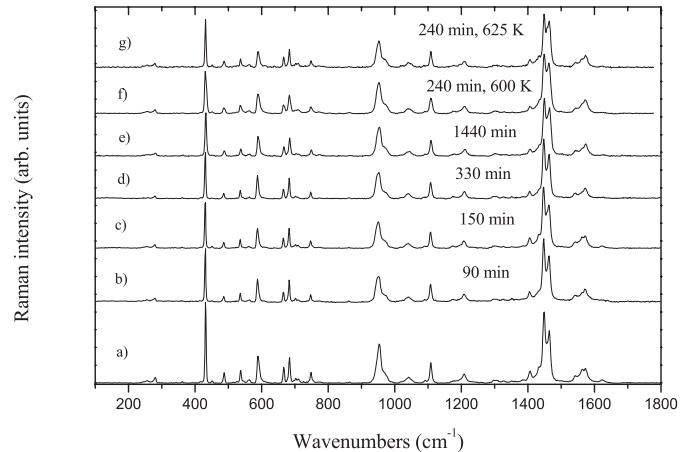


Fig. 7. Raman spectra for (a) an initially tetragonal sample, treated at 570 K and 1.0 GPa for: (b) 90 min, (c) 150 min, (d) 330 min and (e) 1440 min. Top two curves show the spectra for an identical sample treated for 240 min at 1.0 GPa and: 595 K (f) and 620 K (g).

into the orthorhombic phase. The I_{1447}/I_{1459} were 2.9 and 2.8 for the samples treated at 595 K and 620 K respectively, and a similar change can be observed in the components of the mode near 950 cm^{-1} . These results clearly indicate that the transformation from the tetragonal phase to the orthorhombic one is very slow, except possibly at temperatures close to the stability region of the tetragonal phase. This observation shows that transformations from one polymeric phase to another are strongly dependent on the temperature and explains why Davydov et al. [28] see only a very slow transformation from the orthorhombic phase to the tetragonal at a temperature of 723 K and a pressure of 1.5 GPa, while the same transformation proceeds very rapidly at 873 K and 2.5 GPa.

To summarise, we have shown that the transformation from the orthorhombic phase to the tetragonal phase is

very fast and appears to go via an intermediate dimer state in a two-stage process, first a conversion $O \rightarrow D$ followed by a conversion $D \rightarrow T$, where the second process is slower than the first. The transformation of pristine C₆₀ into the tetragonal phase seems to proceed by a very similar process, also involving the initial creation of a large number of chains which would have to follow the same path as the transformation described above. These results are strongly supported by our X-ray diffraction data. The Raman results always seem to indicate the presence of dimers in the tetragonal phase. The complete role of these dimers in the formation process and the final structure is still not totally clear but comparing experiments on polycrystalline and single crystal materials indicate that the dimers could be located at crystal boundaries and at lattice defects. In some way both the dimers and the linear chains can be viewed as defects in tetragonal polymeric C₆₀, where the further growth $D \rightarrow T$ is hindered because of steric constraints. We have also verified that the pentagonal pinch mode together with a number of other modes, for example the 430 cm⁻¹ mode and the region around 950 cm⁻¹, are very useful for studying evolution of polymeric C₆₀ structures.

The transformation from the tetragonal structure to the orthorhombic one is much slower than the orthorhombic-to-tetragonal transformation, and it is even hard to find any signs of transformation in the samples treated. We interpret these results as a high stability of the polymeric bonds under these pressure and temperature conditions, making it almost impossible to reconfigure the lattice into the orthorhombic structure.

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