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## Bulk structure of phototransformed C<sub>60</sub>

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### Abstract

We have produced phototransformed C<sub>60</sub> in powder form and in bulk quantities. The availability of several milligram batches allowed us to collect good quality X-ray powder diffractograms, infrared transmission spectra and differential scanning thermograms. Based on these data a disordered structural model is proposed which is built up from small closed oligomers. © 1999 Elsevier Science Ltd. All rights reserved.

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### 1. Introduction

Phototransformation of C<sub>60</sub> was the first case when direct intermolecular linkage of fullerene molecules was proposed [1]. Now it is well established that the bonding of neutral C<sub>60</sub> molecules occurs through [2 + 2] cycloaddition reaction [2]. The photoreaction is effective in the 260–450 K temperature range [2–4]. Extensive Raman studies on thin films followed the transformation kinetics as function of time and temperature [2–4]. The reaction temperature is a crucial factor determining the type of the phototransformed product. By comparing the experimental Raman data of C<sub>60</sub> single crystals [4] and the calculated spectra for a number of small oligomers [5,6] it was concluded that phototransformation at high temperature leads to the formation of (C<sub>60</sub>)<sub>2</sub> dimers. In contrast, the material produced at room temperature—and termed as the “photopolymer”—cannot be identified with any of the simple clusters for which ab initio calculations were available. While infrared and Raman spectroscopies are successful to indicate the

drastic change of symmetry caused by intermolecular bonding, the assignment of the photopolymer peaks is still an open question.

Unfortunately, a structural picture which could help is still missing. The X-ray evidence for photopolymerization is weak. In their pioneering work Rao et al. found that the original fcc lattice is preserved in the polymerization process, the only modification is a 0.1 Å contraction of the lattice. This effect is surprisingly small as covalent bonds should decrease interfullerene distances by 0.8 Å. A larger contraction of the lattice is detected by the only other X-ray diffraction work [7] but its value ( $\Delta a = 0.5 \text{ \AA}$ ) is still less than 50% of what is expected for an ordered polymer. These results assume serious disorder in the bonding pattern and therefore the first level of structural description is the average number of [2 + 2] bonds formed by a C<sub>60</sub> molecule. In a series of papers Onoe et al. [8–10] determined this number for surfaces phototransformed at room temperature. X-ray photoelectron spectroscopy shows that the average number of bonds increases with irradiation time and saturates just below the value of 6. This number can only be interpreted by a 2D polymeric surface structure which

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is identical to the bulk rhombohedral phase obtained by high-pressure high-temperature synthesis [11–14].

All the above works were done either on thin films or on single crystal surfaces. The penetration depth of the experimental probes differ considerably, with the extreme of X-ray photoelectron spectroscopy which senses only the upper 18 Å of the surface [10]. Therefore, the motivation of the present work was to determine the bulk structure of phototransformed  $C_{60}$ . We have devised a simple technique to obtain the phototransformed material in larger quantities. The availability of several milligram batches of the material allowed us to collect good quality X-ray powder diffractograms (XRD), infrared transmission spectra (IR) and differential scanning thermograms (DSC). Based on these data, we arrived at a structural picture of the photopolymer which excludes long range ordered polymerized networks and is rather described by a disordered array of small closed oligomers.

## 2. Experimental

Bulk quantities of  $C_{60}$  photopolymer were produced by irradiating the  $C_{60}$  powder by UV–visible light. To provide the inert atmosphere required for photopolymerization, a small cell was constructed which can be loaded in a glove box. At each loading, 5–10 mg of fine  $C_{60}$  powder was spread between the two facing quartz windows of the cell. The  $C_{60}$  powder was irradiated with a 1.5 kW Xe arc lamp providing a power density of 0.2 to 0.4 W/cm<sup>2</sup>. Forced air cooling was applied to keep the temperature of the cell at  $\sim 50^\circ\text{C}$ , which is well below the depolymerization temperature. X-ray powder diffraction data were collected in transmission geometry with a Huber G670 Image Foil Guinier Camera at the Cu  $K\alpha_1$  wavelength of 1.54056 Å. Infrared spectra were taken by a Bruker IFS-28 Fourier transform interferometer equipped with a microscope. DSC measurements were performed on a Perkin–Elmer DSC-2 calorimeter.

## 3. Results

Powder diffractograms of phototransformed  $C_{60}$  were measured after different irradiation times and are shown in Fig. 1. All patterns are two phased and

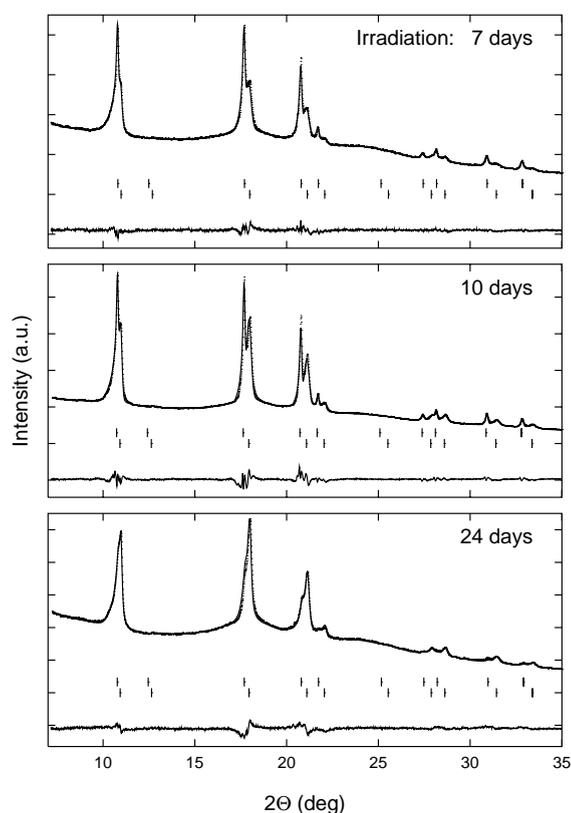


Fig. 1. XRD patterns of  $C_{60}$  powder irradiated for different times. Dots and solid lines correspond to experimental points and Rietveld fits. The top and bottom rows of tick marks above the difference plots show the peak positions of the pristine and phototransformed  $C_{60}$  phases, respectively.

well indexed by face centred cubic lattices. The two phases have lattice parameters near 13.90 Å and 14.15 Å and will be naturally termed as phototransformed and pristine  $C_{60}$ .

Data analysis was done by full profile matching [15] using the axial divergence convoluted pseudo-Voigt peak shape [16] which describes the asymmetry of low- $q$  peaks. We have fitted each diffraction pattern in two slightly different ways. In the first, both phases were treated by the Rietveld technique in which case a structural model is required. This is extremely simple,  $C_{60}$  molecules occupy the lattice sites and the molecular scattering is approximated by that of a spherical shell. In the second method, the phototransformed phase was treated with the Le Bail technique. In this case no structural model is required, intensities of this

Table 1  
Summary of parameters obtained by Rietveld fits of XRD data

Irradiation time	Pristine C <sub>60</sub>		Phototransformed C <sub>60</sub>	
	Relative quantity	Lattice parameter	Relative quantity	Lattice parameter
7 days	51%	14.15 Å	49%	13.93 Å
10 days	42%	14.14 Å	58%	13.90 Å
24 days	23%	14.09 Å	77%	13.89 Å

phase are automatically adapted to values which lead to the best fit for lattice and profile parameters. For this problem the second method did not substantially improve the fits, and thus the Rietveld results will be discussed here.

The relative quantities and lattice parameters of the two phases are shown in Table 1. Clearly, longer irradiation times increase the amount of the phototransformed phase and decrease that of the pristine C<sub>60</sub>. The lattice parameter of the photopolymer is significantly contracted from early stages of irradiation. Its value is only marginally dependent on the radiation dose: after a slight decrease it saturates at 13.90 Å. In contrast, the lattice parameter of pristine C<sub>60</sub> is unchanged and identical to its literature value. A

small contraction can only be observed after the longest irradiation when the photopolymer fraction is already saturated. The phototransformed phase differs from the coexisting pristine C<sub>60</sub> not only in its contracted lattice. Peak broadening vs scattering angle is more pronounced which can either come from large strain or small crystallite size. The limited  $q$ -range in which scattering occurs does not allow to separate the two effects. Unfortunately, this broadening prevents the extraction of reliable isotropic displacement parameters which could express how much the molecules are shifted off the lattice sites.

Infrared spectroscopy could also follow the growth of the phototransformed phase. The change in the vibration spectra is apparent in Fig. 2. Two peaks are very clear markers: increased irradiation diminishes the C<sub>60</sub> peak at 1428 cm<sup>-1</sup> while it increases the photopolymer peak at 1424 cm<sup>-1</sup>. This is a change which corresponds to the relative weight of the two phases. The spectral features of the photopolymer are unchanged at all stages of irradiation. It is nearly identical to literature data obtained for thin films and therefore can be considered as an IR fingerprint. This means that the local symmetry and bonding configuration of the photopolymer are not much affected by the macroscopic form or by the details of sample preparation.

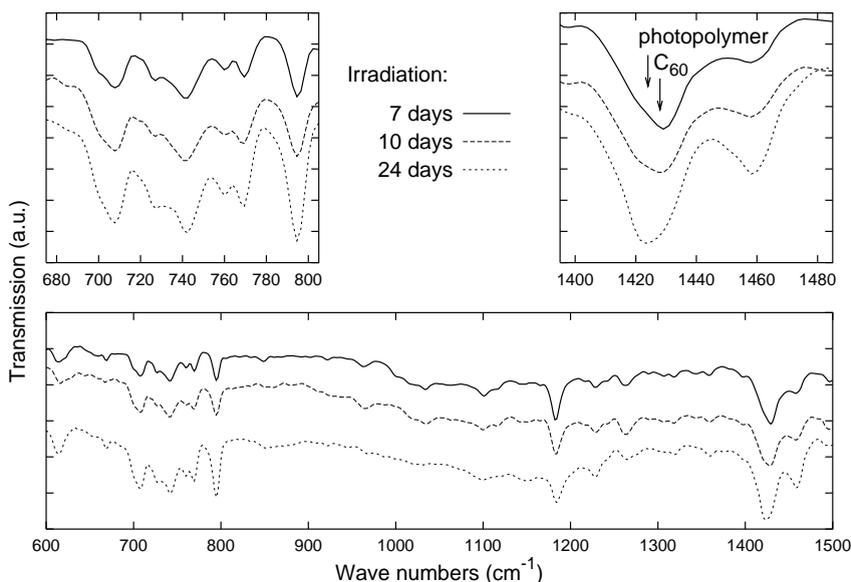


Fig. 2. IR transmission spectra of C<sub>60</sub> powder irradiated for different times. The top two panels show enlarged views of two characteristic regions.

The thermal stability of the photopolymer gives information on the average number of [2 + 2] cycloadduct bonds formed by a  $C_{60}$  molecule. Therefore, thermal properties of the irradiated samples were determined by differential scanning calorimetry. At a heating rate of 20 K/min, the onset and peak temperatures of depolymerization are  $\sim 420$  K and  $\sim 520$  K, respectively. After taking into account the phototransformed and pristine  $C_{60}$  phase ratio, we obtained a 23 J/g transformation enthalpy for the phototransformed phase. Then this value was compared with experimental data for a range of well ordered polymeric structures of  $C_{60}$  published by Iwasa et al. [17]. We found that the formation enthalpies of the phototransformed phase and the high pressure linear polymer are very close. With the assumption that non-bonding interactions and molecular distortions are comparable in the two phases, it is likely that the average number of bonds formed by a  $C_{60}$  molecule of the photopolymer is similar and is near 2. The value of the lattice parameter is also consistent with the formation of bonds towards 2 of the possible 12 nearest neighbours.

#### 4. Conclusion

Up to now photopolymerization of  $C_{60}$  implicitly meant the study of thin films or single crystal surfaces. Here with a simple sample preparation technique we were able to extend this field towards powders. Bulk quantities of the phototransformed product allowed us to apply X-ray diffraction, infrared spectroscopy and differential scanning calorimetry on the same batch of materials. Apart from being able to follow the evolution of the photoreaction, three weeks of intense irradiation lead to a saturated product for which our main experimental findings are summarized here: I. There is no sign of a rhombohedral distortion, the structure remains face centred cubic with a 0.25 Å contraction of the lattice. II. The infrared vibration spectrum is identical to that of thin films and can be used as a fingerprint of this phase. III. The formation enthalpy of the phototransformed phase suggests that the average number of [2 + 2] bonds formed by a  $C_{60}$  molecule is near 2.

Unfortunately proper structure solution on the atomic or molecular scale cannot be attempted. This

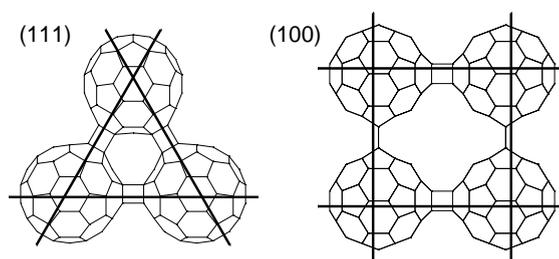


Fig. 3. Closed  $C_{60}$  trimer and tetramer. Bold lines mark the (111) and (100) fcc planes. Note the [2 + 2] bonded regions which show well the shift of molecules off the lattice sites.

is mainly due to the inherent disorder in the bonding pattern and partly to the serious broadening of high- $q$  reflections. However, a structural picture of the photopolymer emerges which is consistent with experiments. This model was already envisaged by Refs. [4–6] without X-ray and DSC results. There are a number of factors which impose limitations on conceivable models: the metrics of the fcc lattice, the magnitude of the contraction, the absence of superreflections, the possible bond directions compatible with the  $C_{60}$  geometry and that every  $C_{60}$  molecule is bonded to two of its 12 first neighbours. While the 2D polymeric rhombohedral phase can develop at very thin surface layers [10], in the bulk we can exclude long range ordered polymerized networks such as extended sheets or long linear chains. If one assumes a model in which long linear or zig-zag polymers are formed, the mismatch between molecular and lattice positions soon accumulates and destroys the constructive interference of X-rays. Therefore the mismatch must be localized around lattice sites and the structure is constructed by a disordered array of small closed oligomers such as trimers and tetramers, as shown in Fig. 3. The magnitude of the lattice contraction requires the molecules to shift off the lattice sites so that both bonding and non-bonding distances take physically meaningful values (9.2 Å and 10 Å). This model is also realistic considering how the strain is minimized during the formation of the phototransformed phase. When randomly oriented bonds form and break dynamically, small closed oligomers can minimize the strain locally without cooperative long range interactions.

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