

Polymerized KC_{60} investigated by scanning tunnelling microscopy (STM)

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Abstract

Polymerized KC_{60} was investigated by scanning tunnelling microscopy (STM) in ambient atmosphere. Linear polymer fibres were found in both as-grown and toluene-etched samples with an intermolecular distance around 9.3 Å. In bundles of polymer fibres the interfibre distance was found to be 14.7 Å. STM images showing intrafibre and intramolecular contrasts were taken.

Keywords: Fullerene; Microscopy; Polymerization

1. Introduction

The discovery of fullerenes a decade ago [1] marked a new era in the physics and chemistry of carbon. New structures have been produced in the last years: carbon nanotubes [2], bucky-onions [3], linearly polymerized KC_{60} [4], pressure-polymerized C_{60} [5], etc.

Scanning tunnelling microscopy (STM) has been used to investigate C_{60} under various conditions [6–9]. Attempts have been made to associate the tunnelling current maxima with the atomic arrangement within C_{60} . However, calculations [8,9] support the idea that the observed intramolecular contrast (IMC) is associated with the convolution of the electronic structure of the fullerene molecule and that of the underlying surface. The stick and ball model, and field ion microscopy [10] yield a diameter around 7 Å for the fullerene cage; STM topography of C_{60} indicates a diameter around 11 Å, and a height of 4–8 Å [6–8]. The height values seem to have a strong dependence on experimental conditions [7]; values in the range of 1 Å have been reported at low temperatures for bilayers of C_{60} over Au(110) [7].

Optical microscopy [11] showed that after toluene dissolution the polymerized KC_{60} consists of bundles of fibres. X-ray measurements [12] evidenced linear polymerization with a molecular spacing of 9.138 Å along the fibre axis. The purpose of this work was to check the existence of polymer fibres in the as-grown material and to investigate structural details of the fibres.

2. Experimental results and discussion

Polycrystalline samples were prepared by a co-evaporation method described previously [11]. Stoichiometric amounts of C_{60} and the alkali metal were sealed in silica tubes and heated in a gradient furnace. The temperatures of C_{60} and the alkali metals were kept at 600 and 100–150 °C, respectively. A shiny black microcrystalline film of fulleride salt coats the wall of the tubes at about the 250–400 °C region within a few hours, and larger crystals grow in the inner surface of the film within days. The samples were slowly cooled in the furnace to room temperature within 8 h.

Typically 100–300 μm isometric rectangular or octahedral crystals were found, embedded in a microcrystalline matrix. Room-temperature ESR measurements indicate around 10% polymerized KC_{60} .

If the crystals are immersed in toluene, the shiny surfaces turn dull and cracks, parallel to some edges of the crystals, are visible within a few minutes. After 1 day etching a considerable amount of C_{60} is dissolved; the partially disintegrated crystals are soft and can be smashed easily to individual fibres. In contrast to our preliminary suggestion [11], the fibrillar material forms under anaerobic conditions as well, indicating that the structure of the pre-existing fibres does not change due to etching.

STM examination was carried out in ambient atmosphere in constant current mode using mechanically prepared Pt tips. Tip quality was checked against the highly oriented pyrolytic graphite (HOPG), the substrate of the sample. Tunnelling currents in the range of 1–0.1 nA were used. Low tunnelling

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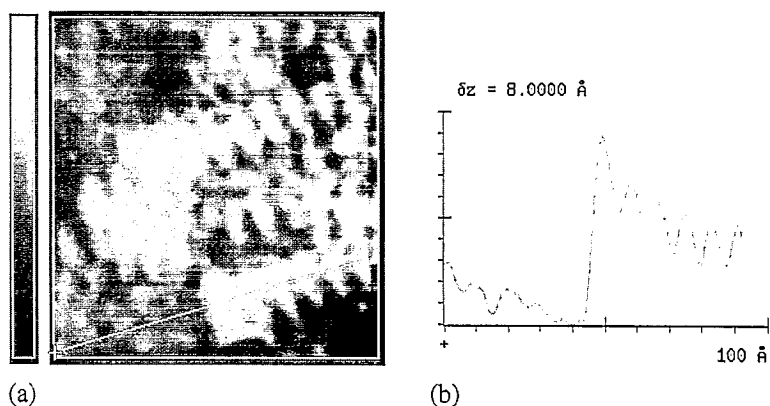


Fig. 1. (a) Polymer fibre in the as-grown sample. The scan range is $93 \times 94 \text{ \AA}^2$; the gray scale at the left-hand side corresponds to 10.1 \AA . (b) The line cut along the white line.

currents were used for the as-grown samples because of the large differences in the z direction. Bias values around 100 mV were used. Bias polarity did not have a significant influence on the acquired images.

On terraces of the as-grown (AG) sample, STM imaging with molecular resolution was possible; nevertheless, IMC was not achieved. Regions of regular distributions of embedded C_{60} molecules have been found; however, structural details could not be revealed. Most frequently, single or associated 'finger like' formations emerge from the surface under an angle of a few tens of degrees. One characteristic image is shown in Fig. 1. Measuring the distances of consecutive maxima associated with C_{60} molecules and averaging these values one gets $8.2 \pm 0.2 \text{ \AA}$. The fibres do not lie in plane but have various declinations; an angle of approximately 27° can be calculated from Fig. 1. Hence the value $9.2 \pm 0.2 \text{ \AA}$ as intermolecular distance is obtained in good agreement with X-ray measurements [12]. In a few regions of the AG sample, a regular rhombohedral-type arrangement of the fullerene molecules was found, as shown in Fig. 2. As these regions are not flat enough to allow the use of larger areas for lattice

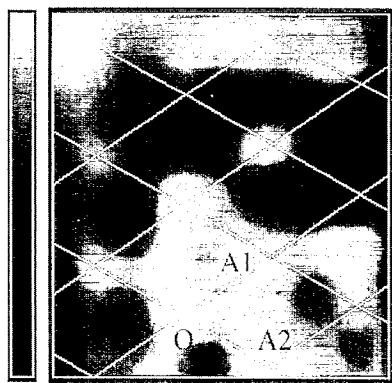


Fig. 2. Rhombohedral arrangement of C_{60} molecules in the as-grown sample. The scan range is $32 \times 32 \text{ \AA}^2$; the gray scale at the left-hand side corresponds to 5.7 \AA . Bright spots at the crossing points of the lattice indicate C_{60} molecules. Lattice vectors: $A1$, length 9.99 \AA ; $A2$, length, 9.38 \AA ; $\theta = 60.0^\circ$; origin is point O.

measurements, the somewhat higher value of vector $A1$ may be attributed to local distortions of the lattice.

The sample prepared by toluene dissolution (TD) reveals a clear fibrous structure (Fig. 3(a)). Images taken at higher resolution show that the fibre pointing in the direction of the lower corner is composed of several smaller fibres. Fibres are at a distance of 14 \AA , i.e., monomolecular fibres can be resolved.

A region with clearly resolved monomolecular fibres is shown in Fig. 3(b). The average distance between the individual fibres is $14.7 \pm 0.3 \text{ \AA}$. This value agrees well with the value 14.32 \AA obtained by X-ray measurements [12]. As one can see from the line cut, the differences in height over the bundle are in the range of 10 \AA ; the z range for the whole area is 35 \AA . The dynamic range of the piezo motion in the z direction makes it impossible to resolve the intrafibre contrast (IFC).

IFC can be resolved only over smaller regions as shown in Fig. 4(a). Even in this case the curvature of the fibre does not allow a straightforward interpretation. The position of three C_{60} molecules can unambiguously be identified from the line cut. Apparently one structural unit is missing from the row. On the basis of the line cut the total distance between the two large maxima is 24.6 \AA , and the distance between the right-hand-side maximum and the small one is 8.8 \AA . Comparing with the value 9.1 \AA , an angle of about 13° to the horizontal can be estimated. The calculated fibre structure is shown in Fig. 4(b). Under the given conditions the molecule situated in the deepest position is barely seen by the STM. The fibres are curved not only in plane as was evident from Fig. 4(a), but also they are curved in a plane perpendicular to that of the image.

In Fig. 5 two fibres are shown, one is assumed to consist of one single molecular (monomolecular) chain, while the broader one is assumed to contain three monomolecular fibres. The diameters are different from those expected from structural data [12]. This is attributed to lateral tunnelling when scanning a cylindrical object on a flat surface. The tip-sample distance, Δ , may change when the tip scans over the

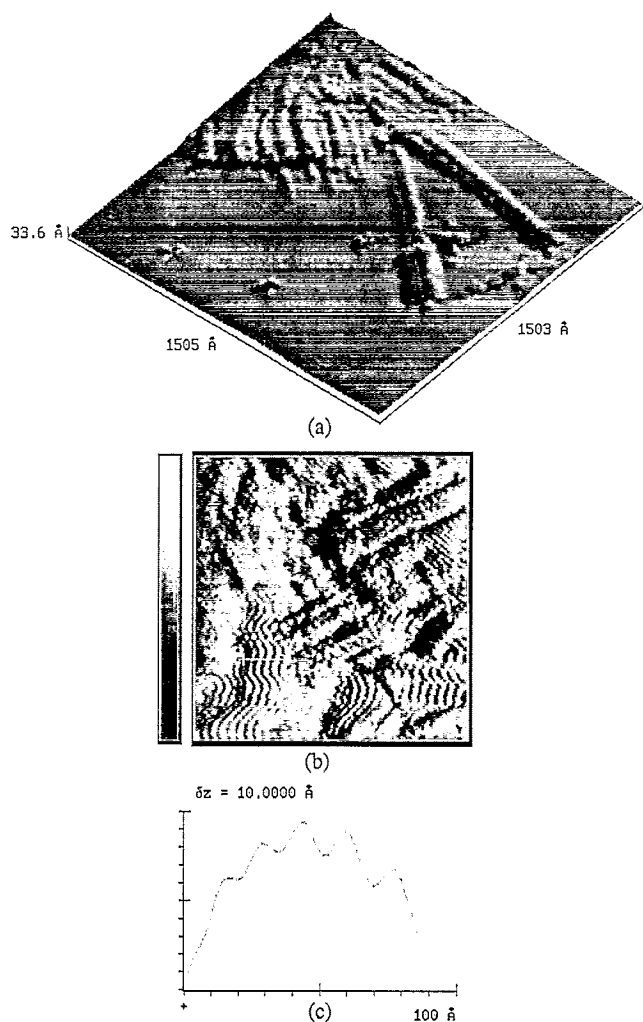


Fig. 3. Bundles of fibres on HOPG from the residue that was not dissolved by toluene: (a) Light-shaded image; illumination from right-hand side at an angle of 20° measured from the horizontal. (b) Bundles of monomolecular fibres; scan range is $524 \times 530 \text{ \AA}$; gray scale corresponds to 35 \AA^2 . (c) Line scan along the white line. Interfibre distance is 14.7 \AA .

HOPG or over the monomolecular fibre. The distortions of diameter and height data depend strongly on the Δ value.

In the case of the monomolecular fibres it was possible to reveal IMC. The distribution of the local maxima in the tunnelling current is regular for a certain fibre. The distances between the maxima may be grouped into three ranges: distances of 4.5 \AA along the fibre axis, characteristic for all fibres in which IMC was observed; a value around 2.5 \AA in rows of transversal maxima, as for the fibre shown in Fig. 5; and a value around 3.3 \AA for fibres that did not show the transversal rows of maxima, as those in Fig. 5. The maxima observed in the IMC images may be attributed to a convolution of the electronic structure of the fibre and that of the substrate [8,9], or to effects due to the electronic structure of the fibre [13].

3. Conclusions

STM examination of AG and TD samples of KC_{60} showed that polymer fibres are present in the AG material. They are

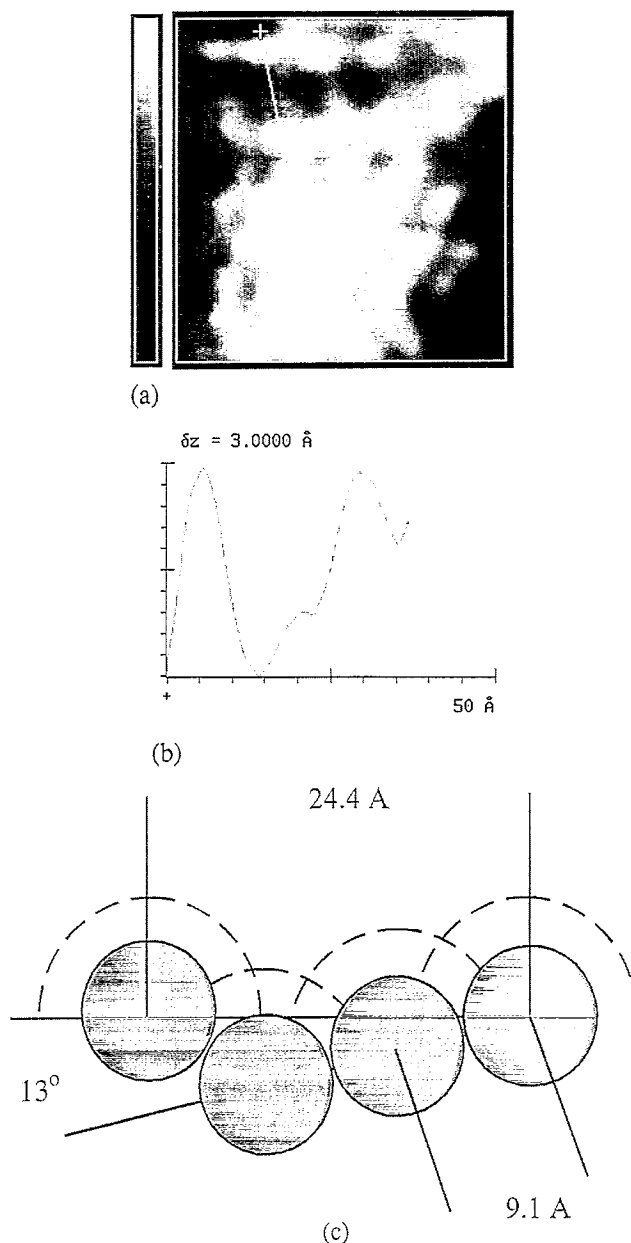


Fig. 4. Intrafibre details over monomolecular fibres: (a) Image. Scan range is $94 \times 95 \text{ \AA}^2$; gray scale corresponds to 9 \AA . (b) Line scan along the white line. (c) Calculated fibre structure along the line cut shown in (a). Shaded spheres indicate the fullerene molecules. The broken line circles represent the tip-sample separation. In the simplest case the tip moves over the envelope of these circles.

embedded in the bulk material that is removed by toluene dissolution. The free fibres may be curved.

Both for AD and TD samples the intermolecular distance along the fibre axis is found to be around 9 \AA , in good agreement with X-ray data. In the AG material regions of rhombohedral symmetry were found.

IMC was possible only on TD monomolecular fibres, with a regular distribution of tunnelling current maxima of periodicity of 4.5 \AA along the axis. Very likely, this is a consequence of the electron density distribution along the fibre axis.

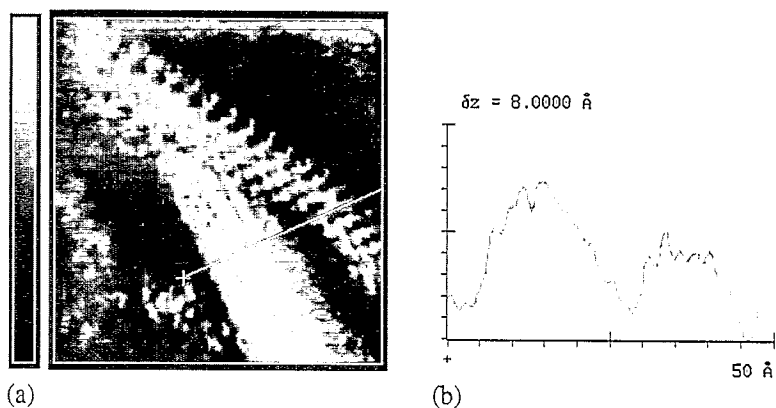


Fig. 5. (a) Monomolecular fibre, and a fibre consisting of three monomolecular fibres. The scan range is $73 \times 74 \text{ \AA}^2$; the gray scale corresponds to 8.8 \AA . (b) The line cut along the white line. The measured values for the diameters and heights of the two different fibres are $12.0, 2.0 \text{ \AA}$, and $24.1, 4.7 \text{ \AA}$, respectively.

Acknowledgements

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References

- [1] H.W. Kroto, J.R. Heath, S.C. O'Brien, R.F. Curl and R.E. Smalley, *Nature*, **318** (1985) 162.
- [2] S. Iijima, *Nature*, **354** (1991) 56.
- [3] D. Ugarte, *Chem. Phys. Lett.*, **198** (1992) 596.
- [4] S. Pekker, L. Forró, L. Mihály and A. Jánosy, *Solid State Commun.*, **90** (1994) 349.
- [5] M. Núñez-Regueiro, L. Marques, J.-L. Hodeau, O. Béthoux and M. Perroux, *Phys. Rev. Lett.*, **74** (1995) 278.
- [6] Ting Chen and D. Sarid, *Mod. Phys. Lett. B*, **6** (1992) 967.
- [7] R. Gaisch, R. Berndt, J.K. Gimzewski, B. Reihl, R.R. Schlitter, W.D. Schneider and M. Tschudy, *Appl. Phys. A*, **57** (1993) 207.
- [8] C. Chavy, C. Joachim and A. Altibelli, *Chem. Phys. Lett.*, **214** (1993) 569.
- [9] T. Hashizume, X.D. Wang, H. Shinohara, Y. Saito, M. Maruyama, K. Ohno, Y. Kawazoe, Y. Nishima, H.W. Pickering, Y. Kuk and T. Sakurai, *Phys. Rev. Lett.*, **71** (1993) 2959.
- [10] N. Ohmae, M. Tagawa and M. Umeno, *J. Chem. Phys.*, **97** (1993) 11 366.
- [11] S. Pekker, A. Jánosy, L. Mihály, O. Chauvet, M. Carrard and L. Forró, *Science*, **256** (1994) 1077.
- [12] P.W. Stephens, G. Bortel, G. Faigel, M. Tegze, A. Jánosy, S. Pekker, G. Oszlányi and L. Forró, *Nature*, **370** (1994) 636.
- [13] P.R. Surján, L. Udvardi and K. Németh, *Synth. Met.*, **77** (1996) 107.