

# **Topochemical reactions of crystalline fullerene derivatives**

PhD thesis abstract

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## Introduction

I did my PhD work in the Research Institute for Solid State Physics and Optics. The main topics of my research are the preparation and study of fullerene photopolymer and fullerene-cubane compounds.

One of my projects was the examination of  $C_{60}$  photopolymerization. Although this reaction has been studied since 1993, the structure of phototransformed material is still ambiguous because of the small amount of available samples. We worked out a new technique to produce polymerized  $C_{60}$  in large quantity. The method is based on the continuous recrystallisation of the monomer from under the poorly soluble polymer phase. A suspension of large quantity of solid  $C_{60}$  in a small amount of solvent was sealed in a pyrex tube and illuminated for several days. Due to the non-uniform illumination, a temperature gradient formed along the tube resulting in thermal convection of the suspension and inducing a continuous dissolution-recrystallization of  $C_{60}$ . Thus, the surface of the monomer was refreshed, retaining steady-state conditions of the polymerization for a long time. While the liquid-state transport recycled the monomer, the practically insoluble polymer accumulated gradually in the solid phase.

Mixtures of the photopolymer's soluble components were extracted, then collected and analyzed by high-performance liquid chromatography (HPLC). The major component of the soluble fractions is the (2+2) cycloadduct dimer,  $C_{120}$ . It was crystallized and obtained in high purity. Several higher oligomers were also detected by HPLC. Based on the decomposition products these molecules are identified as trimers and tetramers. The materials were studied by UV spectrophotometry, IR spectroscopy and X-ray crystallography.

According to our X-ray crystallographic data the crystal structure of the polymer is fcc. It can be built only from small, closed or branched molecules. The molecular structures of the main oligomers were identified based on topochemical and thermodynamic considerations.

We suggested a model to estimate the size of the oligomers based on structural characteristics of the photopolymer. The estimated number of bonded neighbors per  $C_{60}$  is about 2. We examined how the lattice constant of the polymer, the amount and the composition of the soluble oligomers depend on the preparation temperature.

In the second part of my Ph. D. thesis I studied fullerene-cubane compounds. The goal was to build molecules of octahedral symmetry into the same symmetry voids of fullerene crystals. The basic material,  $C_{60}$ , has a face centered cubic crystal structure under ambient conditions. This lattice expands significantly when the cubane molecules are placed into the octahedral voids. The stabilizing factor is the strong fullerene-cubane attraction, which we explain as a molecular recognition between the convex  $C_{60}$  and concave cubane surfaces. Although this strong interaction allows the rotation of fullerenes, it keeps cubane in the equilibrium position and orientation. This characteristic is different from the orientationally ordered and plastic crystals, we call it 'rotor-stator' feature.

We prepared several kinds of these new heteromolecular crystals with 1:1 stoichiometry:  $C_{70}$ ,  $C_{76}$ ,  $C_{78}$  and  $C_{84}$  also form rotor-stator phases. The ball-shaped fullerenes form an fcc. structure with cubane, the elongated molecules compose lower symmetry structures. The lattice parameter depends on the sizes of fullerenes and cubane, and can be predicted accurately.

We studied these materials in a wide temperature range: the materials have rich phase diagrams and unconventional topochemistry. At low temperature the rotation of the fullerenes stops and the systems become orientationally ordered. We followed these structural changes with x-ray diffraction.

At elevated temperature (500K) the stator component of these materials, cubane, decomposes to higher stability  $C_8H_8$  hydrocarbons. This unimolecular isomerization takes also place in the rotor-stator phases, inducing a single phase topochemical reaction with the surrounding fullerenes. The resulting material is a random copolymer that is stable up to high temperature. We followed the polymerization by HPLC, IR and UV-VIS spectroscopy and optical microscopy, and determined the thermal stability by TG-MS analysis.

## Conclusions

### I. C<sub>60</sub> photopolymerization

*I/1. We worked out a new technique to produce polymerized C<sub>60</sub> and prepared several samples in large quantities in the temperature range of 40-100 °C.*

The method is based on the continuous recrystallisation of the monomer and the accumulation of the poorly soluble polymer phase. The refreshed surface of C<sub>60</sub> prevented the slowdown of the reaction, increasing the yield significantly.

*I/2. We extracted, collected and separated large quantities of several higher oligomers from the polymer phase.*

The extracts were analysed by HPLC and proved to consist of small oligomers. The major component of the soluble fractions is the (2+2) cycloadduct dimer, C<sub>120</sub>. Its molecular structure was identified based on its IR spectrum. The dimer was collected and crystallized solvent-free in 99.3% purity. Based on dimer data we proved that the reaction mechanism of the photopolymerization is the previously suggested [2+2] cycloaddition. Besides the dimer, we detected 3 different trimers and several higher oligomers. We assigned these materials according to their stepwise decomposition. Despite the decomposition one trimer isomer was collected in larger quantity.

*I/3. The crystal structure of the photopolymer was studied with X-ray crystallography. Based on it we worked out a model for the reaction mechanism and for the molecular structure of the oligomers.*

The fcc lattice constant of C<sub>60</sub> decreases significantly during the photochemical reaction. This structural change is explained by a topochemical model of the polymerization process. Based on geometric considerations, only the formation of small, branched and two-dimensional oligomers can preserve an fcc lattice. The competition of the photochemical reactions in the intersecting crystallographic planes prevent the formation of larger oligomers. The decrease in the lattice constant is proportional to the number of the formed interfullerene bonds so the sizes of photooligomers can be estimated from the crystallographic data. The

materials detected by HPLC can be assigned based on the structural model of the photopolymer.

*I/4. We established that the lattice constant, as well as the amount and kind of the soluble oligomers, depend on the polymerization temperature*

At lower polymerization temperature the lattice contraction is higher because of the formation of larger, poorly soluble oligomers. The higher the polymerization temperature the smaller the lattice contraction because at elevated temperature competing decomposition reactions become more important besides the polymerization. In this case the crystal can be built only from small, soluble oligomers. Detailed HPLC analysis and topochemical considerations show that V-shaped or triangular trimers are the major soluble oligomer components, depending on the temperature of polymerization.

## **II. Fullerene – cubane supramolecular systems**

*II/1. We prepared heteromolecular crystals of  $C_{60}$ ,  $C_{70}$ ,  $C_{76}$  and  $C_{84}$  with cubane in 1:1 stoichiometry.*

The driving force of the formation is the molecular recognition between the complementary surfaces. The concave cubane and the convex fullerene surfaces match perfectly.

*II/2. We proved that fullerene-cubane compounds form „rotor-stator” phases in certain temperature regions.*

The fullerenes can rotate freely but the cubane is static in a fixed orientation in the crystals. The variation of rotating and fixed molecules in a same crystal structure is a new feature, it differs from both orientationally ordered and plastic crystals. We call these systems „rotor-stator” crystals.

*II/3. We detected several phase transitions in  $C_{60}$ -cubane and  $C_{70}$ -cubane systems.*

At room temperature the structure of  $C_{60}$ -cubane is face centered cubic. We showed that the system undergoes a first order phase transition at 140 K and becomes orthorhombic. In this structure all the molecules are orientationally ordered so the structure is no more „rotor-stator”. The structure of  $C_{70}$ -cubane is

tetragonal at room temperature and becomes face centered cubic at 375 K. Both structures consist of rotating fullerenes and static cubanes. The rotation of C<sub>70</sub> becomes restricted at 150 K, the tetragonal structure changes to monoclinic.

*II/4. At elevated temperature a single phase topochemical reaction occurs in the fullerene-cubane systems. A new family of fullerene copolymer forms with high stability.*

Cubane undergoes a unimolecular isomerization at 200 °C, and in the heteromolecular crystals the resulting reactive intermediers react with the surrounding fullerenes. The product is an insoluble copolymer that decomposes between 400-700 °C. The residue is an amorphous material, consisting of 99% carbon.

*II/5. We proposed a model to predict the structure and properties of higher fullerene-cubane crystals.*

On the basis of the crystal parameters of pure fullerenes we can calculate the properties of the fullerene-cubane compounds. If the size of the fullerene is smaller than C<sub>86</sub>, rotor-stator systems form with rotating fullerenes and static cubanes. At larger ball diameters the materials belong to the host-guest systems, consisting of an fcc framework of fullerenes with orientationally disordered cubane guests in the octahedral voids.

## List of publications

*Articles published in referred journals related to the thesis*

1. S. Pekker, K. Kamarás, *É. Kováts*, T. Pusztai, G. Oszlányi: Soluble Photopolymer: Isolation of cycloadduct oligomers from the phototransformed C<sub>60</sub>, *Synthetic Metals*, **121**, 1109 (2001)
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3. *É. Kováts*, S. Pekker: Separation of the photo-oligomers of C<sub>60</sub>, *Fullerenes, Nanotubes and Carbon Nanostructures*, **13**, 471 (2005)
4. *É. Kováts*, G. Oszlányi and S. Pekker: Structure of the Crystalline C<sub>60</sub> Photopolymer and the Isolation of Its Cycloadduct Components, *J. Phys. Chem. B*, **109**, 11913 (2005)
5. S. Pekker, *É. Kováts*, G. Oszlányi, G. Bényei, G. Klupp, G. Bortel, I. Jalsovszky, E. Jakab, F. Borondics, K. Kamarás, M. Bokor, G. Kriza, K. Tompa, G. Faigel: Rotor-Stator Molecular Crystals of Fullerenes with Cubane, *Nature Materials*, **4**, 764 (2005)
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7. G. Bortel, G. Faigel, *É. Kováts*, G. Oszlányi, S. Pekker: Structural study of C<sub>60</sub> and C<sub>70</sub> cubane, *Phys. Stat. Sol. B*, accepted
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9. C.A. Kuntscher, S. Frank, K. Kamarás, G. Klupp, *É. Kováts*, S. Pekker, Gy. Bényei, and I. Jalsovszky: Pressure-dependent infrared spectroscopy on the fullerene rotor-stator compound C<sub>60</sub>-C<sub>8</sub>H<sub>8</sub>, *Phys. Stat. Sol. B*, accepted

*Articles published in conference proceedings related to the thesis*

1. S. Pekker, K. Kamarás, *É. Kováts*, T. Pusztai, G. Oszlányi: Isolation and structure of fullerene photodimer, C<sub>120</sub>, AIP Conference Proceedings, **591**, 37 (2001)
2. *É. Kováts*, S. Pekker: HPLC separation of soluble (C<sub>60</sub>)<sub>n</sub> oligomers from fullerene photopolymer, AIP Conference Proceedings, **685**, 46 (2003)

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1. *É. Kováts*, S. Pekker: HPLC separation of soluble (C<sub>60</sub>)<sub>n</sub> oligomers from fullerene photopolymer, IWEPNM2003, Kirchberg, Austria, 2003.
2. G. Klupp, K. Kamarás, *É. Kováts*, S. Pekker, T. Pusztai, Z.-T. Zhu, V. C. Long, J. L. Musfeldt, G. B. Adams, J. B. Page: Vibrational spectroscopy of C<sub>60</sub> photopolymer, 1st SIWAN, Szeged, Hungary, 2003.
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8. *É. Kováts*, G. Bortel, G. Oszlányi, I. Jalsovszky, S. Pekker: Formation and structure of higher fullerene-cubane crystals, ICSM 2006, Dublin, Ireland, 2006
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*Articles published in conference proceedings not related to the thesis*

1. G. Klupp, K. Kamarás, N.M. Nemes, P. Matus, D. Quintavalle, L.F., Kiss, *É. Kováts*, S. Pekker and A. Jánossy: Nanosegregation in Na<sub>2</sub>C<sub>60</sub>, *AIP Conference Proceedings*, **786**, 17 (2005)
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2. Á. Pekker, F. Borondics, K. Kamarás, *É. Kováts*, S. Pekker, U. Schade: Optical spectra of self-supporting SWNT films, Hungarian Nanotechnology Symposium, Budapest, Hungary, 2005
3. *É. Kováts*, Á. Pekker, S. Pekker, F. Borondics, K. Kamarás: Carbon nanotube films for optical absorption, NATO ASI, Sozopol, Bulgaria, 2005