

Isolation and Structure of Fullerene Photodimer, C_{120}

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Abstract. Photopolymerization of C_{60} was performed on a gram scale via a new monomer transport method. After subsequent extractions of the raw polymer in organic solvents, 100mg dimer and 10mg mixture of soluble oligomers were yielded. The structures of the soluble fractions and the insoluble polymer were studied by optical spectroscopy and x-ray diffraction methods. According to IR and UV-VIS spectroscopic data, the obtained photodimer is identical to the (2+2) cycloadduct C_{120} prepared previously. In contrast to previous crystallization studies, a fast precipitation of the dimer from toluene gives rise to the formation of a solvent-free microcrystalline solid. The crystal structure of the pure dimer is fcc ($a=14.05\text{\AA}$) consisting of closely packed balls with the cycloadduct bonds oriented randomly along the 12 nearest neighbor directions. A linear relationship is found to exist between the fcc lattice parameter (a) and the average number of bonded neighbours (n_B) in various photopolymerized structures. For insoluble polymers $n_B=2$ is estimated, supporting previous photopolymer models of small ring or branched clusters.

INTRODUCTION

The pioneering work of Rao *et al.* [1] on the photopolymerization of C_{60} initiated a series of extended studies, which resulted in the discovery of various neutral and ionic fullerene polymers [2]. In spite of the vast amount of experimental and theoretical data accumulated so far, the structure of phototransformed C_{60} is still not well understood. Raman spectroscopy [3] and theoretical [4,5] studies indicate that the C_{60} photopolymer is a disordered mixture of short cycloadduct oligomers with various molecular geometries. X-ray diffraction studies [6] showed that the fcc lattice of the precursor C_{60} is preserved with a somewhat contracted unit cell, in agreement with the above model. On the other hand, the microscopic structures of the proposed oligomers are unknown since none of them were experimentally detected. Large-scale production of the polymer and the isolation of its components would be necessary to isolate the proposed oligomers and determine their structures.

The first preparative photopolymerizations were performed on small pre-existing particles either in a suspension [7] or in a fine powder [6], yielding no more than 10 mg of polymerized material. Recently, we described a novel dynamical method [8]: with a liquid phase transport of the monomer, we preserved a steady state condition of polymerization and increased the yield up to gram scale. Here we describe the isolation of the pure dimer and the structures of the photopolymerized phases produced by this method.

PHOTOPOLYMERIZATION METHOD

Details of the photopolymerization are described elsewhere [8]. Briefly, a suspension of solid C₆₀ (800 mg) in its saturated solution of toluene (20 ml) was sealed in a Pyrex tube and illuminated with two 23 W luminescent light sources. The temperature was controlled by air cooling. The photopolymerization took place in the surface regions of the monomer. At the same time, the thermal convection in the tube induced a continuous dissolution-recrystallization of C₆₀. Thus, the surface of the monomer was refreshed while the insoluble polymer accumulated gradually in the solid phase. The reaction mixture was occasionally homogenized by sonication. After a reaction time of a few weeks, the products were separated and the dimer was purified.

The soluble components of the photopolymer were separated by selective extractions in hexane, toluene and 1-methylnaphtalene. We monitored the concentrations of the solutions by visible spectroscopy, then precipitated the materials with pentane and characterised the solids by infrared spectroscopy and x-ray diffraction. Most of the unreacted C₆₀ was extracted by hexane, while the toluene extract contained predominantly the dimer. Since the rate of solubility decreases with increasing molecular mass, the first methylnaphtalene fractions contained the dimer while the following ones the various mixtures of higher oligomers. The residue after subsequent extractions was a purified insoluble polymer.

The dimer-rich fractions were purified by column chromatography (toluene/silica gel). After the separation, we obtained the pure dimer phase by fast evaporation of the solvent. We could not obtain higher oligomers by this method.

STRUCTURE OF THE DIMER AND THE POLYMERS

The visible spectrum of the purified dimer is the same as that prepared by a mechano-chemical method [9] previously. It has a characteristic peak at 700 nm which disappears in the spectra of higher oligomers. The latter ones resemble the polymer spectra obtained in suspension [7].

The IR spectra of the typical photopolymer fractions are shown in Fig. 1. The purified dimer can be unambiguously identified by the IR spectrum. All peaks of its spectrum were assigned as dimer lines by comparing the data with those of dimers prepared by different methods previously [9,10]. Thus, we produced the cycloadduct C₁₂₀ dimer by the above photopolymerization method in spectroscopically pure form.

The broader and less characteristic IR lines of the soluble oligomers are somewhat different from those of the dimer and the polymer. The spectra of the subsequent oligomer fractions vary slightly, indicating the change of their composition [8]. On the other hand, they have features characteristic of either the dimer or the polymer. Further HPLC separation will be necessary to isolate the pure oligomer components.

The IR spectra of the insoluble photopolymers are similar to those prepared by other photopolymerization methods [2,6]. The line intensities are characteristic of the preparation conditions [8].

The structures of the photopolymer fractions were also studied by x-ray diffraction. The oligomer mixtures, precipitated from methylnaphtalene, are amorphous,

supporting the assumed structure of the oligomers: the insufficient packing of molecules of various shape and size prevents their recrystallization.

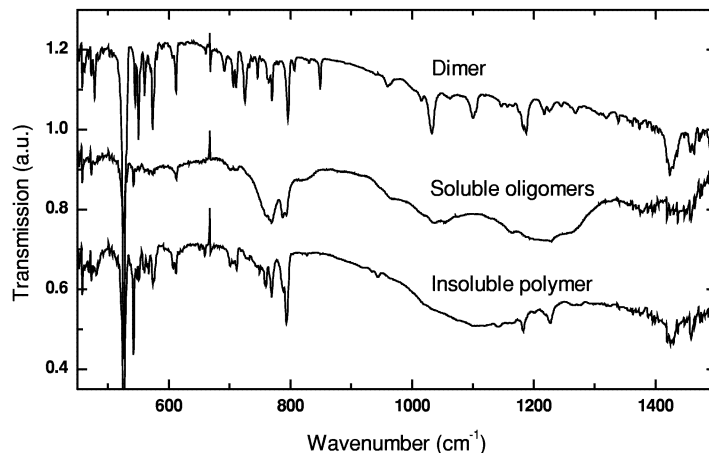


FIGURE 1. Infrared spectra of the separated fractions of C_{60} photopolymer.

The raw dimer, obtained from the same solvent, is crystalline with poor quality and rather complicated diffraction lines, indicating the formation of lower symmetry (probably solvate) crystals. On the contrary, the purified dimer, precipitated from toluene, exhibits broader diffraction lines characteristic of an fcc structure with a contracted lattice parameter: $a=14.05 \text{ \AA}$. The dumbbell-shape dimers can form a disordered fcc lattice if the balls occupy the fcc lattice sites and the cycloadduct bonds are randomly oriented along the 12 nearest neighbour directions. The disorder may give rise to the observed broadening of the diffraction lines. The obtained material is the first solvent-free dimer; only solvate crystals were grown previously [9] from ODCB.

The insoluble polymers also have fcc structure with lattice parameters depending on the preparation temperature [8]. The lower the polymerization temperature, the higher the contraction of the fcc lattice parameter (Table 1). The fcc structure of the photopolymers can be explained by the following model: The polymerization takes place in the lattice of C_{60} . The dimers form randomly along the 12 nearest neighbour directions. 2D oligomers (rings, bended or branched structures) can grow either in the (100) or in the (111) close packed planes. High linear extension or 3D oligomers can be excluded, because their insufficient packing would destroy the fcc structure. The randomly distributed oligomers of various shape and size preserve a disordered fcc structure with the lattice parameter a depending on the average number of bonded neighbours (n_B):

$$\mathbf{a} = \frac{\sqrt{2}}{12} (n_B r_B + (12 - n_B) r_0) \quad (1)$$

where $r_B=9.2 \text{ \AA}$ is the center to center distance of the bonded balls and $r_0=10.01 \text{ \AA}$ is that of the non bonded balls. For the fcc dimer structure, where $n_B=1$, the calculated lattice constant $a_{\text{calc}}=14.05 \text{ \AA}$ is the same as the experimental value, supporting the above model of photopolymer structures. In the knowledge of the lattice parameters, the average number of bonded neighbours, n_B , can be calculated from Equ. 1. For the insoluble photopolymers $n_B \approx 2$ (Table 1.) is much less than that found on surface layers previously [11]. In the absence of long linear molecules, the obtained number of cycloadduct bonds corresponds to the mixture of ring-shape oligomers.

TABLE 1. Structural Characteristics of Crystalline C₆₀ Photopolymers.

Sample	Preparation Method	fcc Lattice Constant (Å)	Average Number of Bonded Neighbors, n_B
Dimer	Monomer Transport, Recrystallized	14.05	1
Polymer	Monomer Transport (80-100 °C)	13.95-14.00	2.0-1.5
Polymer	Monomer Transport (40-60 °C)	13.93-13.95	2.3-2.0
Polymer	Powder Method [6]	13.90	2.6

CONCLUSIONS

We have produced C₆₀ photopolymer in gram quantity and separated its soluble components by selective extractions. For the first time we isolated the cycloadduct dimer from the photopolymer in pure crystalline form. The structure of the solvent-free dimer crystals is fcc with $a=14.05 \text{ \AA}$. Comparing the crystal structures of the dimer and the polymers, we determined the average number of bonded neighbours in various photopolymers.

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