

Pressure-assisted photopolymerization in the molecular donor-acceptor fullerene complex $\{\text{Cd}(\text{dedtc})_2\}_2 \cdot \text{C}_{60}$

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The pressure-assisted photopolymerization in the fullerene complex $\{\text{Cd}(\text{dedtc})_2\}_2 \cdot \text{C}_{60}$ (fullerene complex with cadmium diethyldithiocarbamate) observed in the pressure region between 2.24 and 5.99 GPa was studied in detail. After a phase transition near ~ 2 GPa, the Raman spectra exhibit time-dependent changes under prolonged laser illumination regarding the appearance of new peaks in the frequency region of the $A_g(2)$ mode of the C_{60} monomer. These peaks are related to the fullerene oligomers with a different number of sp^3 -like coordinated carbon atoms per molecular cage. The polymer content increases with the laser power density and exposure time, while for a fixed laser power, its saturated value is independent of pressure. Outside the pressure range 2.24 – 5.99 GPa, photopolymerization is suppressed.

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1. Introduction

The high pressure behavior of donor-acceptor fullerene complexes is of interest due to their layered structure in which the close-packed fullerene layers are alternated with layers of the molecular donor. At high pressures, the reduction of intermolecular distances in fullerene complexes increases the overlap of the highest occupied molecular orbital (HOMO) of the molecular donor and the lowest unoccupied molecular orbital (LUMO) of the fullerene acceptor. This may cause charge transfer, particularly in the case where the molecular complex at ambient conditions is close to the ionic state. Alternatively, the decrease of intermolecular distances within the fullerene layers may result in the formation of covalent inter-cage bonds. The X-ray diffraction (XRD) and Raman studies of ionic and neutral donor-acceptor complexes of C_{60} have revealed the formation of covalent bonds between fullerene molecules at low temperature or elevated pressure [1–8]. Recently, the photo-induced transformations at high pressure were observed in the Raman spectra of the molecular complex $\{\text{Cd}(\text{dedtc})_2\}_2 \cdot \text{C}_{60}$ which take place immediately after the pressure-induced phase transition near 2 GPa [9]. The time-dependent changes in the $A_g(2)$ mode region are reminiscent of those in the Raman spectra of C_{60} fullerene under light irradiation [10].

The ability of C_{60} to form inter-cage covalent bonds is due to the existence of 30 unsaturated double $\text{C}=\text{C}$ bonds in the C_{60} molecule. C_{60} fullerite polymerizes under illumination [10], alkali metal doping [11] and high-pressure/high-temperature (HPHT) treatment [12, 13]. The polymerization of C_{60} is realized through the creation of covalent bonds among adjacent fullerene molecules via a [2+2] cyclo-addition mechanism that necessitates the rotation of molecules to attain a suitable mutual orientation [10, 14]. The photopolymerization is efficient in thin films or the surfaces of bulk samples, owing to the small light penetration depth

($\sim 1 \mu\text{m}$ near 500 nm); the photo-transformed material is rather disordered and contains various oligomers [15, 16]. For these reasons, the XRD method is unsuitable for the analysis of the photopolymers and the role of the Raman spectroscopy becomes crucial. Unlike the case of the photopolymers, XRD is very useful in the study of the ordered crystalline C_{60} polymers obtained by HPHT treatment of the C_{60} fullerite whose structures have been identified as one-dimensional orthorhombic (1D-O), two-dimensional tetragonal (2D-T) and two-dimensional rhombohedral (2D-R) [12, 13]. The Raman spectra of the crystalline polymers exhibit splitting and softening of the bands related to the lowering of the C_{60} molecular symmetry caused by the intermolecular covalent bonds [12, 13, 17]. An important probe of the C_{60} polymers is the behavior of the $A_g(2)$ pentagonal pinch (PP) mode of the C_{60} molecule, related to the in-phase stretching vibration that involves tangential displacements of carbon atoms with contraction of the pentagonal rings and expansion of the hexagonal rings. The PP-mode frequency is downshifted due to the lowering of the average cage stiffness with an increase in the number of the sp^3 -like coordinated carbon atoms per C_{60} molecule, associated with the inter-cage bonds. Thus, the $A_g(2)$ mode of the C_{60} monomer, observed at 1468 cm^{-1} , shifts to 1458 cm^{-1} in the linear chains (1D-O polymer, 4 sp^3 -like coordinated carbon atoms), while in the planar polymers, the peak downshifts further to 1446 cm^{-1} (2D-T polymer, 8 sp^3 -like coordinated carbon atoms) and 1408 cm^{-1} (2D-R polymer, 12 sp^3 -like coordinated carbon atoms) [17].

In this paper, we present the detailed study of the pressure-assisted photopolymerization in the fullerene complex $\{\text{Cd}(\text{dedtc})_2\}_2 \cdot \text{C}_{60}$. We have carefully defined the pressure region in which the phototransformation takes place; we have studied the photopolymerization kinetics and its dependence on pressure, and identified the final products of the reaction as fullerene photo-oligomers. Starting at a pressure of 2.24 GPa, immediately after the pressure-induced phase transition [9], photopolymerization occurs up to 5.99 GPa, after which it is abruptly suppressed. In this pressure range, the Raman spectra exhibit time-dependent changes associated with the appearance of new bands in the frequency region of the $A_g(2)$ mode of the C_{60} monomer. Their intensity increases exponentially with the laser exposure time and saturates at a value that does not depend on pressure. The peak frequencies indicate that the new peaks are related to photo-oligomers with four and six sp^3 -like coordinated carbon atoms per molecular cage.

2. Experimental details

Samples of the donor-acceptor complex $\{\text{Cd}(\text{dedtc})_2\}_2 \cdot \text{C}_{60}$ were obtained by evaporation of a solution containing fullerene acceptors and cadmium diethyldithiocarbamate donors by the method described in [18]. The XRD data show that the $\{\text{Cd}(\text{dedtc})_2\}_2 \cdot \text{C}_{60}$ complex acquires a monoclinic structure, space group $P2_1/c$ with unit cell parameters $a = 16.368(3)$, $b = 17.056(2)$, $c = 10.6650(15) \text{ \AA}$, $\beta = 100.058(14)^\circ$ and $V = 2931.63 \text{ \AA}^3$ [7]. In the fullerene layers, each C_{60} molecule is surrounded by six neighbors in a nearly hexagonal manner with the shortest distances between the centers of the fullerene molecules being 10.058 \AA (four neighbors) and 10.665 \AA (two neighbors). No C–C bonds were found between the fullerenes and, therefore, the fullerene molecules of the complex are monomeric at ambient conditions. The Raman spectra were recorded in the back-scattering geometry using a LabRam HR micro-Raman setup equipped with a Peltier cooled (-70°C) CCD detector. The 514.5 nm laser line was used for Raman excitation and the activation of the phototransformation. The laser beam was focused on the sample by a 50 objective with a laser power of $\sim 200 \mu\text{W}$, before the diamond-anvil cell (DAC). Measurements of the Raman spectra at high pressure were carried out using a Mao-Bell type DAC. The 4 : 1 methanol/ethanol mixture was used as pressure transmitting medium and the ruby fluorescence technique for pressure calibration [19].

3. Results and discussion

Figure 1 illustrates the peculiarities of the pressure-assisted photo-induced transformation in the $\{\text{Cd}(\text{dedtc})_2\}_2 \cdot \text{C}_{60}$ complex as evidenced in its Raman spectra and their pressure and exposure time dependence. The bottom inset shows the time evolution of the Raman spectra of the $\{\text{Cd}(\text{dedtc})_2\}_2 \cdot \text{C}_{60}$ complex recorded at pressures 1.63, 4.37 and 6.37 GPa in the region of the PP-mode under fixed excitation conditions of $\lambda_{\text{exc}} = 514.5$ nm, laser power 200 μW and 50 objective. For each pressure, a different, fresh site of the sample was used to probe the spectra evolution with the illumination time. Raman spectra were recorded consecutively at 1.63 GPa under continuous laser illumination for 1800 s and with 300 s exposure time for each spectrum. The spectra do not evolve with time regarding their structure and intensity distributions. The Raman spectra at 4.37 GPa, recorded under continuous laser illumination for 9900 s and 900 s exposure time for each spectrum, exhibit gradual time-dependent changes associated with the appearance of new bands shifted to lower energies with respect to the $A_g(2)$ mode of the C_{60} monomer. The initial Raman spectrum, recorded with 900 s exposure time is similar to the Raman spectra at 1.63 GPa, while longer time laser illumination leads to a photo-induced transformation manifested by changes in the band structure and intensity distribution. Similar changes were also observed in a number of the degenerate H_g modes for the fullerene molecule. The Raman spectra at 6.37 GPa were recorded under the same laser illumination conditions as the spectra at 4.37 GPa but they do not show any time-dependent changes. The series of Raman measurements at various pressures have shown that the photo-induced transformation takes place in the pressure region 2.24 – 5.99 GPa. The relative intensities of the new bands increase with exposure time, indicating an increase in the photo-oligomers content in the fullerene layers, as in the case for photopolymerization in pristine C_{60} and $\{\text{Pt}(\text{dbdte})_2\} \cdot \text{C}_{60}$ complex at ambient conditions [14,20]. The ratio for the sum of the integrated intensities of the new PP-mode components to the total spectral intensity in the frequency region of the PP-mode provides a measure for the polymer content. The dependence of the photopolymer content on the laser exposure time is shown in Fig. 1 (circles) along with the fitting of the data by an exponential growth function (dotted line):

$$P(t) = P_{\text{sat}} \{1 - \exp(-t/\tau)\}. \quad (1)$$

where $P(t)$ is the time-dependent content of the photopolymers, P_{sat} is the content of the photopolymer attained after saturation of the phototransformation, and τ is the exponential growth time constant. The phototransformation parameters at 2.77 GPa are $P_{\text{sat}} = 64$ % and $\tau = 889$ s. As shown earlier in the photopolymerization study of $\{\text{Pt}(\text{dbdte})_2\} \cdot \text{C}_{60}$ complex at ambient conditions [20], the parameter P_{sat} increases, while the time constant τ decreases with an increase in the laser power. In fact, these parameters depend on the laser power density, which implies that it is necessary to carefully focus the laser beam during measurements. The top inset shows the dependence of the photopolymer content P_{sat} on pressure. The Raman measurements in all pressure values were performed under the same conditions. The photopolymerization was initiated abruptly at 2.24 GPa after the phase transition near 2 GPa [9], occurs up to 5.99 GPa and disappears at 6.37 GPa. The value of P_{sat} varies between 60 % and 80 % despite the fixed illumination conditions, which may be attributed to somehow different focusing of the laser beam in different measurements.

Figure 2 illustrates the pressure dependence of the Raman bands of the $\{\text{Cd}(\text{dedtc})_2\}_2 \cdot \text{C}_{60}$ complex at pressures up to 6.5 GPa. The open circles mark the frequencies of the peaks related to the $H_g(7)$ and $A_g(2)$ modes recorded after short exposure time in the time-dependent set of Raman measurements, whereas the semi-filled circles correspond to the frequencies of the

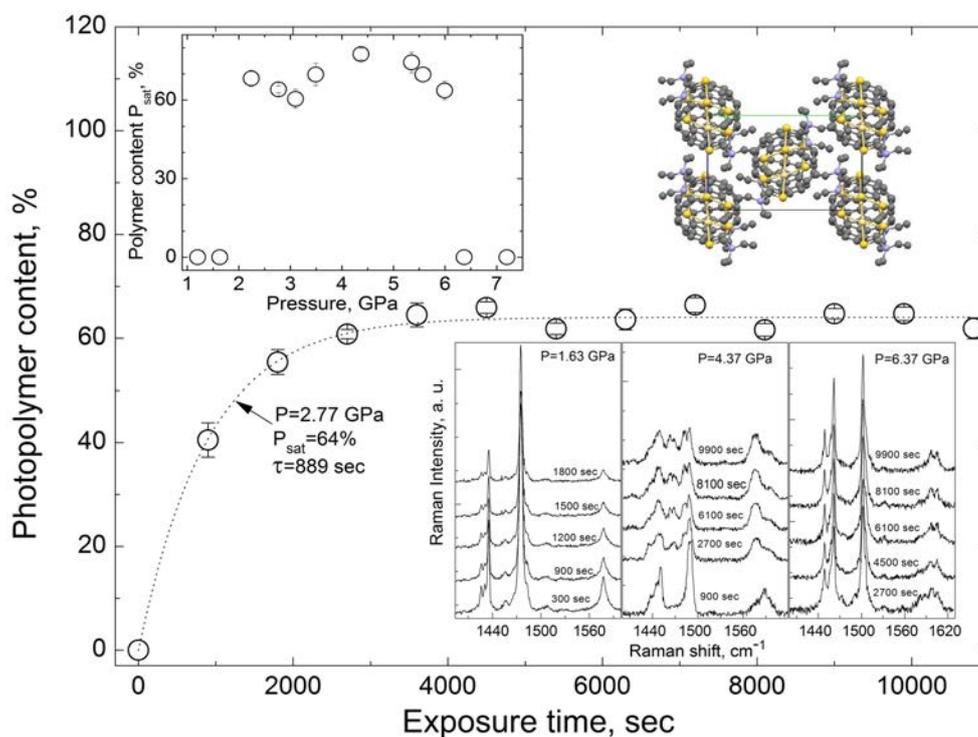


FIG. 1. Photopolymer content in the $\{\text{Cd}(\text{dedtc})_2\}_2 \cdot \text{C}_{60}$ complex at 2.77 GPa, excited with $200 \mu\text{W}$ at 514.5 nm, as a function of the illumination time and fitted by an exponential growth function (dotted line). The molecular arrangement in the fullerene complex viewed along the a -axis of the unit cell is also included. Bottom inset: Time evolution of the Raman spectra of the $\{\text{Cd}(\text{dedtc})_2\}_2 \cdot \text{C}_{60}$ complex in the region of the PP-mode at 1.63 GPa (left), 4.37 GPa (center) and 6.37 GPa (right). Top inset: Pressure dependence of the saturated photopolymer content

split PP-mode components recorded after long exposure time when the photopolymer content is saturated. The solid lines are linear fits of the experimental data related to the $H_g(7)$ and $A_g(2)$ modes, while the dotted lines are fits of the split PP-mode components. Stars denote the frequencies of the split PP-mode components extrapolated to ambient pressure. The pressure evolution of the main PP-mode frequency exhibits an irregularity near ~ 2 GPa: the pressure coefficient between 2 and 3 GPa is almost zero, whereas before and after this region it is $\sim 5 \text{ cm}^{-1}/\text{GPa}$. Thus, the Raman data recorded after short laser exposure time show the pressure-induced phase transition near ~ 2 GPa was most likely associated with covalent bonding between C_{60} molecules in fullerene layers. The phase transition was confirmed independently by XRD measurements which showed a distinct change in the material compressibility along the fullerene layers [9]. The intriguing result of the high pressure Raman study is that the pressure-induced phase transition activates the photo-induced transformation as it follows from the appearance of the split PP-mode components under prolonged laser illumination.

Figure 3 shows the frequencies of the $A_g(2)$ PP-modes of various crystalline polymers of C_{60} (circles) vs. the number of the sp^3 -like coordinated carbon atoms per fullerene molecular cage [17, 21]. The Raman frequencies of the photo-oligomers in C_{60} fullerite (hexagons) are also included [20]. The structural arrangements of the intermolecular covalent bonds in different HPHT crystalline polymers, as deduced by detailed XRD measurements, are also illustrated in the insets [12, 13, 22]. The empirical dependence of the PP-mode frequencies of crystalline

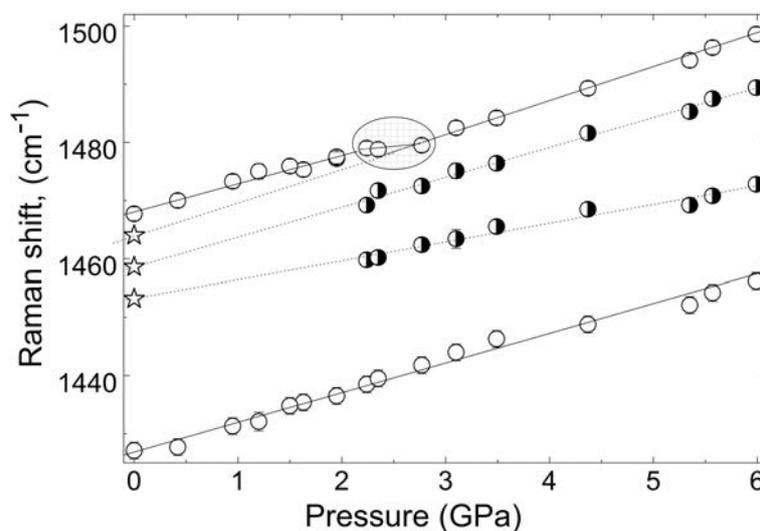


FIG. 2. Pressure dependence of the $\{\text{Cd}(\text{dedtc})_2\}_2 \cdot \text{C}_{60}$ complex Raman peaks related to the $H_g(7)$ and $A_g(2)$ modes of the C_{60} molecule at pressure up to 6.1 GPa. The open circles denote the peak frequencies recorded under short exposure time, while the semi-filled circles the frequencies of the split components of the PP-mode recorded under long exposure time. The lines are linear fits of the experimental pressure dependencies, while the stars show the extrapolated frequencies of the split PP-mode components to ambient pressure

C_{60} polymers and the photo-oligomers in C_{60} fullerite exhibits a monotonic decrease with an increase in the number of the sp^3 -like coordinated carbon atoms per C_{60} molecule. Note, that the Raman band at $\sim 1452 \text{ cm}^{-1}$ in phototransformed C_{60} is related to the conjugated linear chains that were first observed in the pressure-assisted photo-induced transformation of the linear orthorhombic C_{60} polymer [21–23]. The frequencies of the pressure-induced dimers, as well as the pressure-assisted photo-induced oligomers in the $\{\text{Cd}(\text{dedtc})_2\}_2 \cdot \text{C}_{60}$ complex extrapolated to ambient pressure are also shown in Fig. 3 (stars). These data agree well with those of the HPHT crystalline polymers and the photo-oligomers of C_{60} fullerite and may be attributed to dimers, fragments of linear chains and conjugated linear chains.

Summarizing, we have studied in detail the pressure-assisted photopolymerization of the fullerene molecules in the C_{60} layers of the molecular donor-acceptor complex $\{\text{Cd}(\text{dedtc})_2\}_2 \cdot \text{C}_{60}$, activated immediately after the pressure-induced phase transition near 2 GPa. The phototransformation process occurs at pressures ranging from 2.24 – 5.99 GPa. The photopolymerization rate and the saturated polymer content depend on the laser excitation wavelength, laser power and focusing but they are independent of pressure within this region. The photo-oligomers are, most likely, fragments of linear chains and conjugated linear chains whereas the pressure-induced phase transition results in the creation of C_{60} dimers. The photopolymerization of C_{60} , which requires the rotation of the molecules in order to attain a suitable mutual orientation of the neighboring cages necessitated in the [2+2] cycloaddition reaction [14], may serve as the basis for the interpretation of the observed behavior. Then, the stability of the studied complex upon laser illumination at ambient and low pressure suggests that the molecular rotations are hindered. However, in the high pressure phase (above 2 GPa), the inter-cage distances are redistributed due to the pressure induced formation of dimers, leading to relatively large inter-dimer distances. This may allow some rotational degree of freedom that would explain the

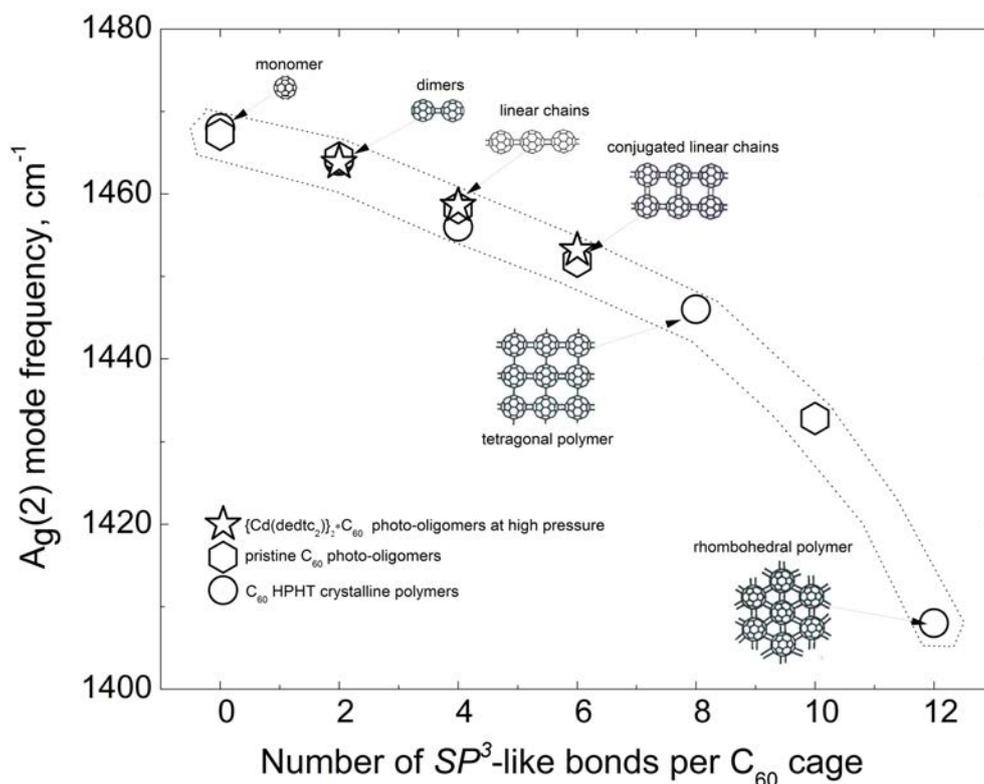


FIG. 3. The frequencies of the PP-modes of the HPHT crystalline polymers of C_{60} (circles), the photo-transformed C_{60} fullerite (hexagons) and the ambient pressure extrapolated frequencies of the photo-induced oligomers in $\{Cd(dedtc)_2\}_2 \cdot C_{60}$ complex at high pressure (stars) vs. the number of the sp^3 -like coordinated carbon atoms per C_{60} molecular cage. The arrangement of the intermolecular covalent bonds in HPHT crystalline polymers is also shown

photosensitivity of the material. Further volume reduction, for pressure above 6 GPa, freezes the rotations and renders the dimer phase immune to the laser irradiation.

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