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Comparative Raman study of photo-oligomer stability in the donor-acceptor fullerene complex $\{\mathrm{Pt(dbdtc)_2}\}\cdot\mathrm{C_{60}}$ and pristine C_{60}

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The photopolymerization process and the stability of the C_{60} photo-oligomers at elevated temperature in the molecular donor-acceptor fullerene complex $\{\mathrm{Pt(dbdtc)_2}\}\cdot\mathrm{C_{60}}$ (C_{60} complex with platinum dibenzyldithiocarbamate) and pristine fullerite C_{60} are studied by Raman spectroscopy. Fast polymerization, manifested by the appearance of additional peaks in the frequency region of the $A_g(2)$ pentagon-pinch (PP) mode of the C_{60} molecule, was observed upon sample illumination at 514.5 and 532 nm, even at low laser power density as well as at 785 nm at higher power density. The frequencies of the new peaks are in accordance with the empirical dependence of the PP-mode frequency on the number of the sp^3-like coordinated carbon atoms per molecular cage. The temperature dependence of the polymer content under constant laser power density reveals the decomposition of the photo-oligomers to monomers at $\sim$ 350 K in the fullerene complex $\{\mathrm{Pt(dbdtc)_2}\}\cdot\mathrm{C_{60}}$ and at $\sim$ 410 K in the case of the pristine C_{60}. These values are considerably smaller than the decomposition temperature of 525 – 565 K for the crystalline polymers of C_{60}.

Keywords: fullerene, molecular complexes, Raman spectroscopy, photopolymerization.

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1. Introduction

The photo-induced polymerization of C_{60} was observed, for the first time, under intense illumination by visible light. To explain this reaction, a [2+2] cyclo-addition mechanism was proposed for the creation of covalent bonds among adjacent fullerene molecules [1,2]. The photopolymerization effectively occurs in thin films or surfaces of bulk samples, owing to the small light penetration depth (~ 1 μm near 500 nm), resulting in rather disordered materials consisting of various oligomers [3,4]. Therefore, structural analysis techniques are relatively inefficient for studying the photopolymers and thus, Raman spectroscopy become very important. In contrast to photopolymers, X-ray diffraction (XRD) measurements are very effective in the study of the ordered crystalline C_{60} polymers obtained by the treatment of C_{60} fullerite under various conditions of high pressure and high temperature (HPHT) [5, 6]. XRD studies of the polymeric phases prepared under carefully controlled conditions of HPHT treatment have identified their crystal structures as follows: one-dimensional orthorhombic (1D-O), two-dimensional tetragonal (2D-T) and two-dimensional rhombohedral (2D-R). IR absorption and Raman scattering studies have revealed important changes in the vibrational spectra of the HPHT polymers with respect to that of the C_{60} fullerite precursor, related to the splitting and softening of the intramolecular modes due to the lowering of the C_{60} molecular symmetry caused by intermolecular covalent bonding [5–9]. The spectroscopic identification of the C_{60} polymers is mainly based on the behavior of the $A_g(2)$ PP-mode of the C_{60} cage, corresponding to the in-phase stretching vibration that involves tangential displacements of carbon atoms with a contraction of the pentagonal rings and an expansion of the hexagonal rings. The PP-mode downshifts in all C_{60} polymers are due to the decrease of the mean intramolecular bond strength. Its softening depends on the number of the sp^3-like coordinated carbon atoms per C_{60} molecular cage that arise due to intermolecular covalent bond formation. In the case of the *fcc* crystal structure of the C_{60} monomer, the $A_g(2)$ mode is observed at 1468 cm^{-1}. In the 1D-O polymer (linear polymer, 4 sp^3-like coordinated carbon atoms) this mode is observed at 1458 cm^{-1}. In the 2D-T polymer (planar tetragonal polymer, 8 sp^3-like coordinated carbon atoms), the peak downshifts to 1446 cm^{-1}, while in the case of the 2D-R phase (planar rhombohedral polymer, 12 sp^3-like coordinated carbon atoms) the $A_g(2)$ mode exhibits the strongest softening and is observed at 1408 cm^{-1} [9].

The stability of the HPHT C_{60} polymers at elevated temperature has been studied by differential scanning calorimetry (DSC) [10–12]. Under a heating rate of 10 – 20 K/min, DSC measurements show a strong endothermic peak between 525 and 565 K, but no signal was observed during the cooling scan [10]. The transition temperature depends on the polymeric phase and somewhat on the scanning rate, indicating that the polymer decomposition process is kinetically-controlled. The change of enthalpy related to the complete polymer decomposition is the highest for the C_{60} dimers, decreases for the linear polymeric chains and attains its smallest value for planar polymeric networks. The decomposition kinetics of the planar C_{60} polymers was studied by IR absorption and Raman scattering and the formation of intermediate oligomeric states was observed in the case of the rhombohedral polymer [12, 13]. Note that in the case of photopolymers, their small amount on the surfaces of bulk samples makes the DSC measurements practically impossible. Thus, Raman spectroscopy becomes very important in the study of their stability at elevated temperatures.

We report the comparative Raman study of photopolymerization in the molecular donor-acceptor fullerene complex $\{Pt(dbdtc)_2\}\cdot C_{60}$ and pristine C_{60}. The fullerene complex $\{Pt(dbdtc)_2\}\cdot C_{60}$ possesses a layered structure in which the close-packed fullerene layers with nearly hexagonal arrangement of C_{60} molecules alternate with layers of molecular donor. In the fullerene layer, each C_{60} molecule is surrounded by six C_{60} neighbors with the shortest distances between the centers of molecules being 9.97 Å (four neighbors) and 10.02 Å (two neighbors). Fast photopolymerization, manifested by the appearance of a number of new peaks in the frequency region of the PP-mode, was observed in the fullerene layers of the $\{Pt(dbdtc)_2\}\cdot C_{60}$ under low laser power density at $\lambda_{exc} = 514.5$ nm which becomes much slower under $\lambda_{exc} = 785$ nm even at high laser power. The frequencies of the new bands are in accordance with the empirical dependence of the crystalline polymer's PP-mode frequencies on the number of the sp^3-like coordinated carbon atoms per C_{60} cage [14]. The polymer content can be inferred by the ratio of the sum of the integrated intensities for the new PP components to the total spectral intensity in the frequency region of the PP-mode. This value grows exponentially with laser exposure time while the time constant decreases with increasing laser power. The stabilities of the photo-induced oligomers in the fullerene complex $\{Pt(dbdtc)_2\}\cdot C_{60}$ and pristine C_{60} were studied at elevated temperatures after saturation of the phototransformation process under constant laser power density. The temperature dependence of the polymer content probed by the same constant laser power density shows the decomposition of photo-oligomers to monomers near $\sim$ 350 K in the fullerene complex and at $\sim$ 410 K in the pristine C_{60}. These values are considerably smaller than the decomposition temperature of 525 – 565 K for crystalline polymers of C_{60} [10].

2. Experimental details

The samples of the donor-acceptor complex $\{Pt(dbdtc)_2\}\cdot C_{60}$ were obtained by evaporating solutions containing fullerene C_{60} acceptors and platinum dibenzyldithiocarbamate donors by the technique described in Ref. [15]. The $\{Pt(dbdtc)_2\}{\cdot}C_{60}$ complex adopts a monoclinic structure (space group $P2_1/c$). The parameters of the unit cell are $a = 15.957(5)$, $b = 17.241(5)$, $c = 10.018(5)$ Å, $\beta = 92.356(5)$ °, $V = 2753.7(5)$ Å^3. The fullerene molecules are in monomeric form under ambient conditions. No covalent or coordination bonds were found between the platinum dibenzyldithiocarbamate molecules and the fullerenes; furthermore these structures were arranged such that the benzyl substituents of $Pt(dbdtc)_2$ were adjacent to the C_{60} [16].

The samples of the $\{Pt(dbdtc)_2\}{\cdot}C_{60}$ complex were flat, well-facetted crystals with typical in-plane dimension of ~ 50 μm. The samples of 99.98 % purity pristine C_{60} were vapor-grown small single crystals with typical dimensions of ~ 100 μm, nearly mirror-like surface and truncated cubic outline. The crystal structure of the C_{60} fullerite at room temperature is face-centered cubic with lattice parameter 14.17 Å and a nearest-neighbor $C_{60} - C_{60}$ distance of 10.02 Å [17]. The Raman spectra were recorded in the back-scattering geometry using LabRam HR and LabRam ARAMIS micro-Raman setups as well as an Acton SpectraPro-2500i spectrograph, all equipped with Peltier cooled (-70 °C) CCD detectors. The 514.5, 532 and 785 nm laser lines and Olympus 50×/100× objectives were used for the Raman scattering excitation and activation of the phototransformation.

3. Results and discussion

Raman data related to the phototransformation in the $\{Pt(dbdtc)_2\}{\cdot}C_{60}$ complex are shown in Fig. 1. The top right inset shows five Raman spectra in the PP-mode region recorded consecutively at $\lambda_{\text{exc}} = 785$ nm, laser power 16 μW and 100× objective during 3000 s with 600 s exposure time for each spectrum. These spectra do not show any changes while the spectra recorded under similar conditions but with a laser power of 160 μW (bottom right inset) clearly show the appearance of new bands at lower frequencies. These bands are related to various photo-oligomers of C_{60} with different number of the sp^3-like coordinated carbon atoms per molecular cage. The phototransformation is accompanied by the splitting of the Hg degenerate modes of the C_{60} molecule (not shown in the figure). The ratio of the sum of the integrated intensities for the new PP 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):

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

Here, $P(t)$ is the time-dependent content of the photopolymer, 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 are $P_{\text{sat}} = 44.5$ % and $\tau = 320$ s for the illumination conditions shown in the bottom right inset, while the increase of the laser power results in an increase in P_{sat} and a decrease in τ. In fact, the time constant τ depends on the laser power density, which implies the necessity for careful and reproducible focusing of the laser beam on different sample sites. The top left inset of Fig. 1 shows the Raman spectrum of the $\{Pt(dbdtc)_2\}{\cdot}C_{60}$ complex recorded under $\lambda_{\text{exc}} = 514.5$ nm, laser power 25 μW and 100× objective. Four spectra recorded consecutively under continuous laser illumination during 360 seconds with 60 seconds exposure time for each spectrum show very fast transformation despite the relatively low laser power. In this case, the polymerization rate increases drastically due to the considerably higher absorption of the C_{60} layers near 514.5 nm than at 785 nm, leading to a vanishingly small exponential growth time constant while the saturated polymer

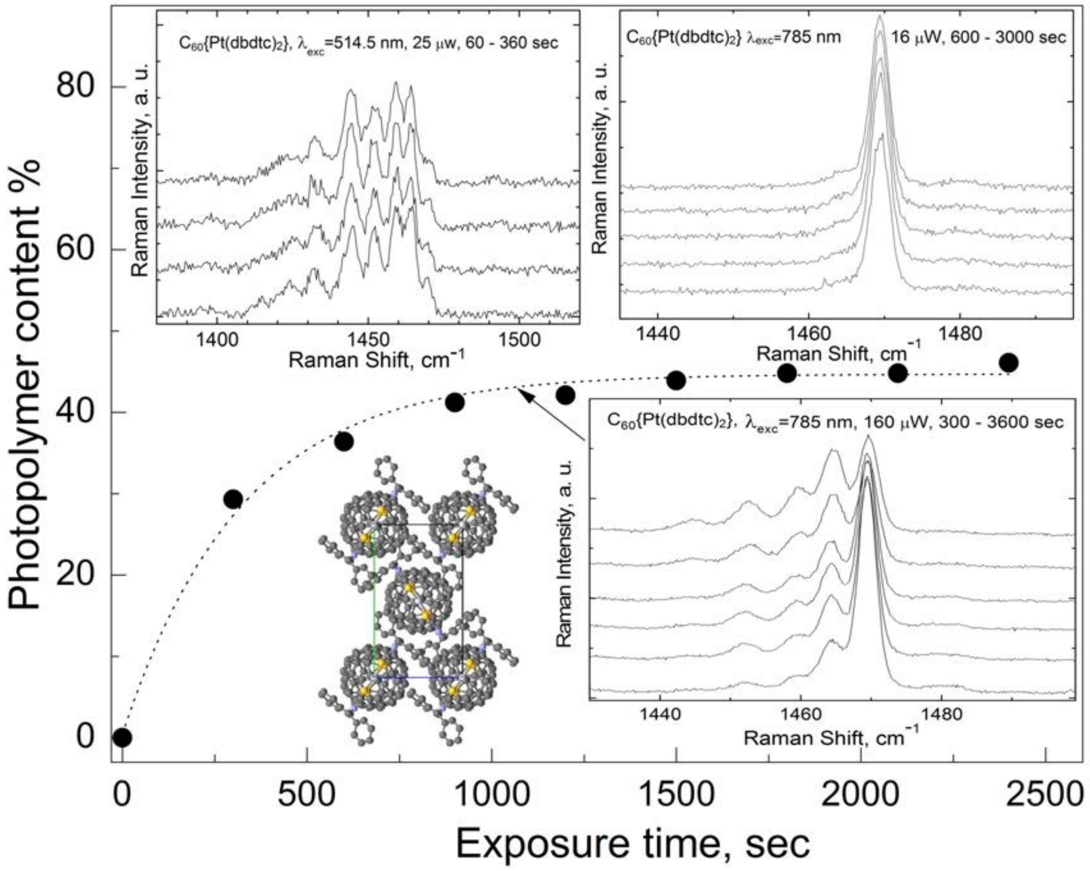

FIG. 1. Photopolymer content in the $\{Pt(dbdtc_2)\}\cdot C_{60}$ complex, excited at $\lambda_{exc} = 785$ nm and a power of 16 μW, as a function of the illumination time (circles) fitted by an exponential growth function (dotted line). The molecular arrangement in the fullerene complex viewed along the a-axis of the unit cell is also included. Insets: Time evolution of the Raman spectra of the $\{Pt(dbdtc_2)\}\cdot C_{60}$ complex in the region of the PP-mode excited through a 100× objective and $\lambda_{exc} = 785$ nm, laser power 16 μW (top right), $\lambda_{exc} = 785$ nm, laser power 160 μW (bottom right), as well as $\lambda_{exc} = 514.5$ nm, laser power 25 μW (top left)

content reaches $P_{sat} = 96.1$ %. This is in accordance with the much smaller penetration depth for C_{60} crystals at 514.5 nm than at 785 nm [18].

It is interesting to compare the photopolymerization in the $\{Pt(dbdtc)_2\}\cdot C_{60}$ complex with that of the pristine C_{60} with respect to the photo-oligomer content and stability at elevated temperatures. The Raman spectra recorded in the region of the $A_g(2)$ PP-mode under excitation by $\lambda_{exc} = 532$ nm, laser power 60 μW and 50× objective are shown in the bottom right inset of Fig. 2. The initial spectrum recorded with 600 s exposure time contains only the $A_g(2)$ PP-mode of the C_{60} monomer. The following spectra recorded with 3600 s exposure time after continuous laser illumination for 7200, 14400, 21600 and 28800 s show a gradual decrease of the PP-mode intensity of the monomer as well as the appearance and gradual increase in the intensities of the corresponding photo-oligomer modes. The intensity distribution between the PP-modes of the photo-oligomers differs from that of the $\{Pt(dbdtc)_2\}\cdot C_{60}$ complex but the peak frequencies for both materials are similar. The experimental dependence of the photopolymer content on the laser exposure time is shown in Fig. 2 by circles while the dotted line is the exponential growth fitting. Its time constant is relatively high (~ 6000 s), suggesting that the almost instantaneously transformed complex is more sensitive to light. However, the time constant of C_{60} being longer, may also be partly related to the larger laser spot under the 50× objective focusing as well as to the somewhat higher transmittance of C_{60} near 532 nm with respect to 514.5 nm. The dependence of the exponential growth time constant on the laser power is shown in the bottom left inset. The measurements were performed at a number of neighboring sites of the same C_{60} sample and under reproducible focusing conditions. The dependence is quasi-linear and the time constant decreases with increasing laser power as in the case of the fullerene complex.

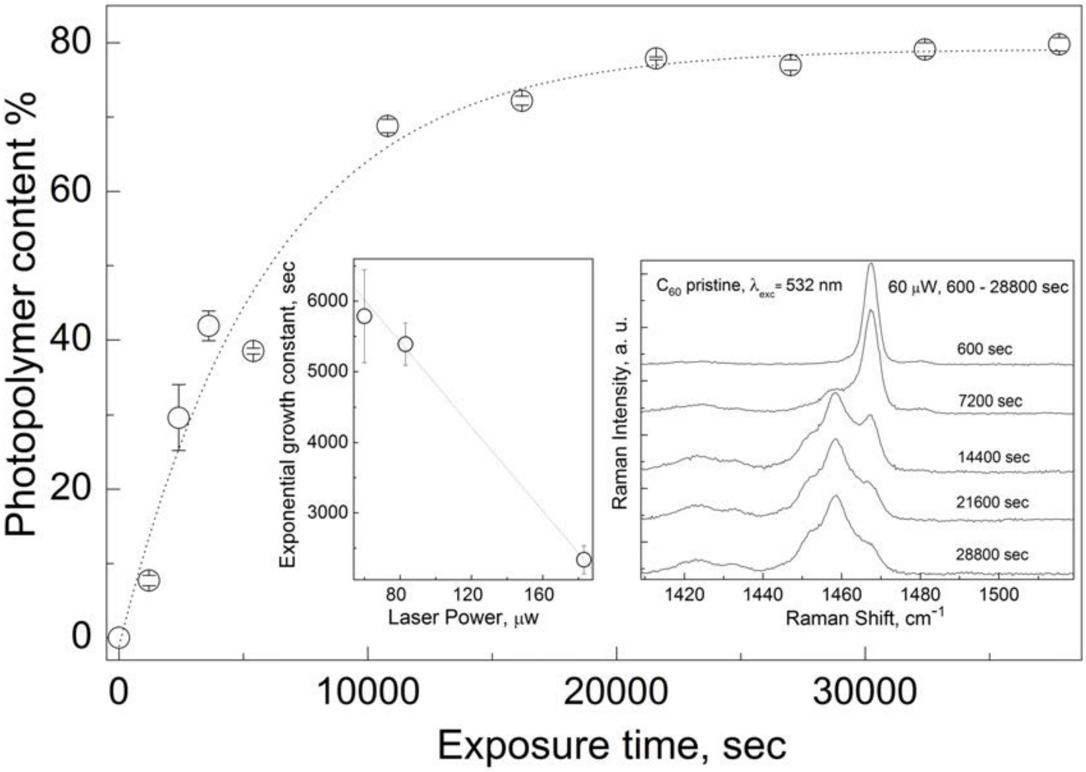

FIG. 2. Photopolymer content in the fullerite C_{60}, excited through a 50× objective at $\lambda_{\text{exc}} = 532$ nm and laser power 60 μW, as a function of the exposure time (circles) fitted by an exponential growth function (dotted line). Right inset: Time evolution of the Raman spectra in the region of the PP-mode. Left inset: Laser power dependence of the exponential growth time constant (circles) fitted by a linear function (dotted line)

Figure 3 shows the frequencies of the PP-mode for various crystalline polymers of C_{60} (circles) *vs.* the number of the sp^3-like coordinated carbon atoms per fullerene molecular cage [7–9, 19]. The Raman frequencies of the photo-oligomers in the pristine C_{60} crystal (squares) and $\{Pt(dbdtc)_2\}\cdot C_{60}$ complex (open stars) are also shown in Fig. 3. The structural arrangements of the intermolecular covalent bonds in the different HPHT crystalline polymers, as deduced by detailed XRD measurements, are also illustrated [5,6,20]. The empirical dependence of the PP-mode frequency of the crystalline C_{60} polymers shows a gradual decrease with an increase in the number of the sp^3-like coordinated carbon atoms per C_{60} molecule. The Raman data for the photo-oligomers in the $\{Pt(dbdtc)_2\}\cdot C_{60}$ complex and pristine C_{60} agree well with those of crystalline polymers, which clarifies the origin of the new PP-modes as dimers, fragments of linear chains, conjugated linear chains, planar tetragonal and rhombohedral polymeric networks. Note, that the Raman band ~ 1452 cm^{-1} observed in the Raman spectra of the phototransformed $\{$Pt(dbdtc)$_2\}\cdot$C$_{60}$ complex and pristine C$_{60}$ does not exist in the crystalline C$_{60}$ polymers and is related to conjugated linear chains that were observed under pressure- and photo-induced transformations in the linear orthorhombic C$_{60}$ polymer [19–21]. In addition, the phototransformed $\{$Pt(dbdtc)$_2\}\cdot$C$_{60}$ complex and pristine C$_{60}$ exhibit a Raman band near ~ 1432 cm^{-1} which may be related to the PP-mode of an exotic photo-oligomer with 10 sp^3-like coordinated carbon atoms per fullerene molecular cage.

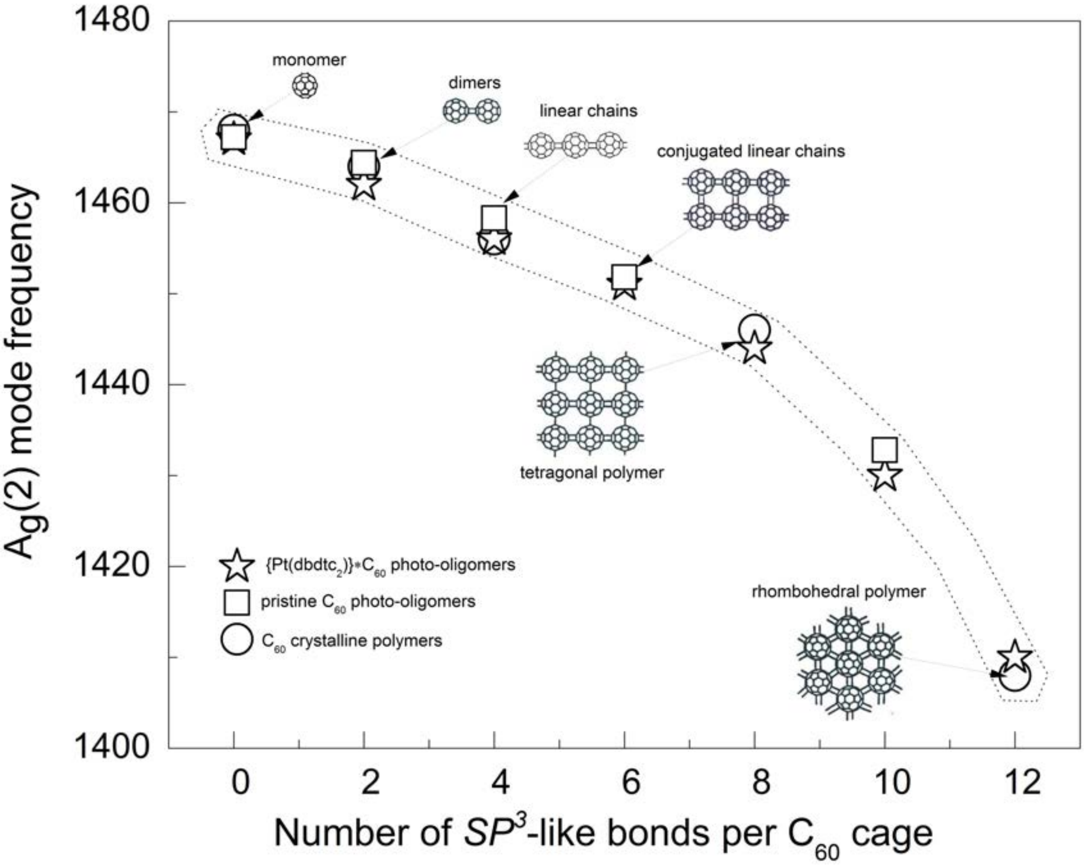

FIG. 3. The frequencies of the PP-mode of the HPHT crystalline polymers of C$_{60}$ (circles), the photo-transformed pristine C$_{60}$ (squares) and $\{$Pt(dbdtc)$_2\}\cdot$C$_{60}$ complex (stars) *vs.* the number of the sp^3-like coordinated carbon atoms per C$_{60}$ molecular cage. The arrangement of the intermolecular covalent bonds in HPHT crystalline polymers is also shown

The stability of the photo-oligomers at elevated temperatures was also studied in a series of Raman measurements under excitation by $\lambda_{\text{exc}} = 514.5$ nm, laser power 20 μW and 50× objective. The photopolymer content attained after saturation of the phototransformation process is shown as a function of temperature in Fig. 4 for the $\{$Pt(dbdtc)$_2\}\cdot$C$_{60}$ complex (solid circles) and pristine C$_{60}$ (open circles). The inset in Fig. 4 shows the Raman spectra of the $\{$Pt(dbdtc)$_2\}\cdot$C$_{60}$ complex in the region of the PP-mode recorded with 240 s exposure time for each spectrum at various temperatures from 318 to 413 K. The data were acquired after 1440 s illumination time, where the saturation of the photopolymer content has occurred. The spectrum recorded at the lowest temperature of 318 K exhibits the typical photopolymer features and is characterized by a suppressed monomeric PP-mode. The maximum content of polymer at this temperature is ~ 90 % and decreases to ~ 7 % at the highest temperature of 413 K, where the PP-mode of the monomer becomes dominant. The rapid reduction of the photopolymer content begins at ~ 340 K and is halved at ~ 350 K. This temperature can be considered as the temperature limit of the photo-oligomer stability in the $\{Pt(dbdtc)_2\}\cdot C_{60}$ complex. Similar Raman measurements were also performed at elevated temperatures for the pristine C_{60}. The photo-oligomers in pristine C_{60} show somewhat higher stability: the rapid decrease of the photopolymer content begins near ~ 400 K and becomes half at 410 K. These data are very close to those obtained in a previous Raman study of the thermal decomposition of photopolymerized C_{60} thin films [22].

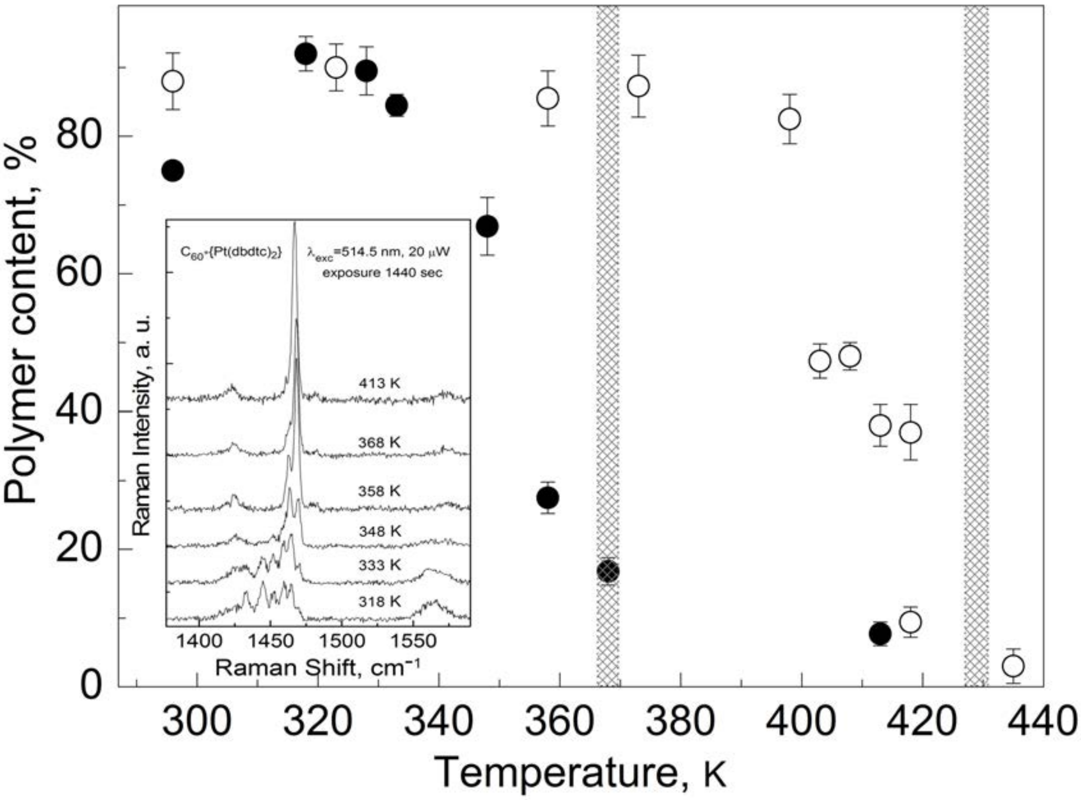

FIG. 4. The photopolymer content attained after saturation of the phototransformation process as a function of temperature for the $\{Pt(dbdtc)_2\}\cdot C_{60}$ complex (solid circles) and pristine C_{60} (open circles). Shaded areas indicate the decomposition temperature of the photo-oligomers. Inset: Raman spectra of the $\{Pt(dbdtc)_2\}\cdot C_{60}$ complex in the PP-mode region recorded at various temperatures

Summarizing, we have revealed the photopolymerization of the C_{60} layers in the molecular donor-acceptor complex $\{Pt(dbdtc)_2\}\cdot C_{60}$. Various aspects of this process were comparatively studied by Raman spectroscopy with those of the pristine C_{60}. The photopolymerization rate and polymer content attained after phototransformation saturation depended on the laser excitation wavelength, laser power and focusing. The photo-oligomers are, most likely, dimers, fragments of linear chains, conjugated linear chains, as well as planar tetragonal and rhombohedral polymeric networks. The stability study of photo-oligomers at elevated temperatures showed that their decomposition to a monomer occurred near 350 K in the fullerene complex $\{Pt(dbdtc_2)\}\cdot C_{60}$ and at ~ 410 K in pristine C_{60}. These values are considerably smaller than the decomposition temperature 525 – 565 K for crystalline C_{60} polymers [10]. This difference, to a significant extent, may be related to the structural transformations and the deformation of the fullerene molecular cage during the creation of the HPHT crystalline polymers, whereas the photopolymerization is less energetically demanding because of the disordered structure of the photo-oligomers and their small fragment size.

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