

The photopolymerization rate and activation energy of C₆₀ rotations in fullerene and its molecular complexes

K. P. Meletov

To cite this article: K. P. Meletov (2020) The photopolymerization rate and activation energy of C₆₀ rotations in fullerene and its molecular complexes, Fullerenes, Nanotubes and Carbon Nanostructures, 28:2, 93-96, DOI: [10.1080/1536383X.2019.1680973](https://doi.org/10.1080/1536383X.2019.1680973)

To link to this article: <https://doi.org/10.1080/1536383X.2019.1680973>



Published online: 25 Oct 2019.



Submit your article to this journal [↗](#)



Article views: 29



View related articles [↗](#)



View Crossmark data [↗](#)

The photopolymerization rate and activation energy of C_{60} rotations in fullerene and its molecular complexes

K. P. Meletov

Institute of Solid State Physics RAS, Chernogolovka, Russia

ABSTRACT

The temperature dependence of the photopolymerization rate in pristine C_{60} and fullerene molecular complexes $\{Pt(dbdtc)_2\} \bullet C_{60}$ and $\{Pt(nPr_2dte)_2\} \bullet (C_{60})_2$ was studied. The Raman spectra measured in the temperature region 190–323 K exhibit an intensity increase of the dimer-related $A_g(2)$ mode of the C_{60} molecule and a decrease of the monomer's one under long laser irradiation. The photopolymer content grows exponentially with the laser exposure time while the growth time constant decreases with the increase of temperature. Since the polymerization via the 2 + 2 cycloaddition reaction necessitates the parallel orientation of double C=C bonds of neighboring C_{60} molecules, the acceleration of fullerene rotations at elevated temperatures affects the polymerization rate. The photopolymerization rate under fixed conditions of laser power, excitation wavelength and beam focusing exhibits an activation-type dependence on temperature. The activation energy E_A , obtained from the Arrhenius dependence of the polymer growth time constant on the temperature, increases from (0.13 ± 0.01) eV and (0.18 ± 0.01) eV for $\{Pt(nPr_2dte)_2\} \bullet (C_{60})_2$ and $\{Pt(dbdtc)_2\} \bullet C_{60}$ molecular complexes to (0.24 ± 0.04) eV for pristine C_{60} .

ARTICLE HISTORY

Received 5 June 2019

Accepted 13 October 2019

KEYWORDS

Fullerene molecular complexes; photopolymerization; Raman spectra

Introduction

The photo-induced polymerization of C_{60} was observed, for the first time, under intense illumination by visible or ultraviolet light and the [2 + 2] cyclo-addition mechanism was proposed to explain the creation of covalent bonds among adjacent fullerene molecules.^[1,2] The photopolymerization effectively occurs in thin films or surfaces of bulk samples resulting in creation of various disordered oligomers, that cannot be studied by traditional structural analysis and Raman spectroscopy becomes very important in this case.^[3] The structural analysis is effective in the study of the ordered crystalline polymers of C_{60} obtained under various conditions of high-pressure and high-temperature treatment of C_{60} .^[4,5] X-ray diffraction studies of these polymeric phases prepared under carefully controlled conditions have established their crystal structure while the IR absorption and Raman scattering studies have identified important changes in their vibrational spectra, related to the splitting and softening of phonon modes caused by intermolecular covalent bonding.^[4–8] The Raman identification of the C_{60} polymers is based on the downshift of the $A_g(2)$ mode in all C_{60} polymers. The softening depends on the number of intermolecular covalent bonds per C_{60} molecule: the $A_g(2)$ mode shifts from 1468 cm^{-1} in monomer to 1464 , 1458 , 1446 and 1408 cm^{-1} in dimers, linear chains, planar tetragonal and rhombohedral polymers, respectively.^[8] Photopolymerization within the C_{60} layers takes place also in some fullerene molecular complexes at ambient

conditions.^[9,10] In other cases, the photopolymerization at ambient conditions does not occur but it may appear at elevated pressure.^[11–13]

In this work, we report a comparative study of the photopolymer formation kinetics in the fullerene layers of the molecular complexes $\{Pt(dbdtc)_2\} \bullet C_{60}$ and $\{Pt(nPr_2dte)_2\} \bullet (C_{60})_2$ and pristine C_{60} under long laser irradiation. Spectra were recorded at fixed conditions of laser wavelength and power, beam focusing and spot location. The photopolymerization, manifested by the appearance of a number of new peaks in the frequency region of the $A_g(2)$ mode, is rather fast at room temperature but becomes much slower at lower temperature. The frequencies of the newly appearing $A_g(2)$ mode components are close to those of the various crystalline polymers.^[7,8] The intensity of these bands gradually increases with illumination time, while the photopolymer content can be inferred by the ratio of the sum of the integrated intensities of the new $A_g(2)$ mode components to the total spectral intensity in the frequency region of the $A_g(2)$ mode. The photopolymer output grows exponentially with the laser irradiation time while the exponential growth time constant exhibits an activation type of temperature dependence. The activation energy E_A , obtained from the Arrhenius dependence of the polymer growth time constant on temperature, increases from (0.13 ± 0.01) eV and (0.18 ± 0.01) eV for $\{Pt(nPr_2dte)_2\} \bullet (C_{60})_2$ and $\{Pt(dbdtc)_2\} \bullet C_{60}$ molecular complexes to (0.24 ± 0.04) eV for pristine C_{60} .

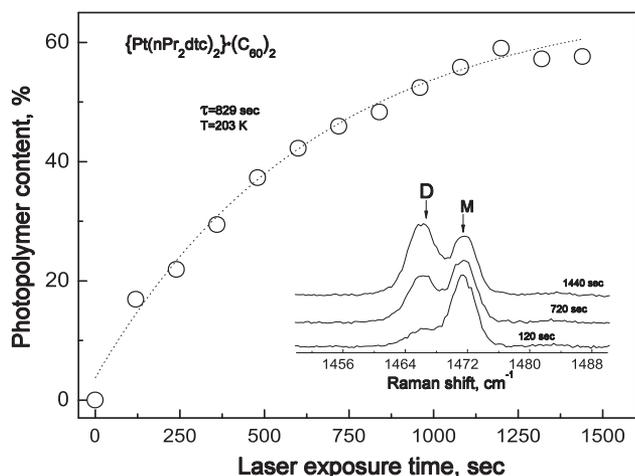


Figure 1. Raman spectra of the $\{Pt(nPr_2dtc)_2\} \bullet (C_{60})_2$ complex in the region of the $A_g(2)$ mode recorded during 120 sec scans at 203 K after continuous irradiation for 120, 720 and 1440 sec. Open circles: the dependence of the photopolymer content on the laser exposure time, dotted line: fitting of data by exponential growth function.

Experimental details

The samples of the donor–acceptor complexes ($\{Pt(dbdtc)_2\} \bullet C_{60}$ and $\{Pt(nPr_2dtc)_2\} \bullet (C_{60})_2$) were obtained by evaporation of solutions containing fullerenes and corresponding donors. The complexes possess layered structure in which the close-packed fullerene layers alternate with layers of molecular donor.^[14] For Raman measurements, small samples of complexes of about 60 μm in diameter and microcrystals of commercial C_{60} powder were used. The spectra were recorded in the back-scattering geometry using a micro-Raman set-up composed of a spectrograph Acton SpectraPro-2500i and a CCD Pixis2K detector system cooled to $-70^\circ C$. The 532 nm line of a single mode YAG CW diode pumped laser was focused on the sample by means of Olympus 10 \times and 50 \times objectives, the elastically scattered light was suppressed by a super-notch filter with suppression efficiency $OD=6$ and bandwidth $\sim 140\text{ cm}^{-1}$, while the beam intensity on the sample was $100 \div 300\ \mu W$. Raman measurements at various temperatures were carried out by the use of an optical liquid nitrogen cryostat, operating in the $80 \div 400\text{ K}$ temperature range.

Results and discussion

Figure 1 shows the Raman spectra of the $\{Pt(nPr_2dtc)_2\} \bullet (C_{60})_2$ complex in the region of the $A_g(2)$ mode recorded during 120 second scans at 203 K after continuous laser irradiation of sample for 120, 720 and 1440 sec with $\lambda_{exc} = 532\text{ nm}$ at a power of $100\ \mu W$. The spectra consist of two bands centered at 1471.5 and 1466 cm^{-1} , which are related to the $A_g(2)$ mode of the C_{60} monomer and dimer, respectively. The intensity of the dimer band gradually increases with irradiation time, while the ratio of the integrated intensity of the dimer band to the total spectral intensity in the frequency region of the $A_g(2)$ mode provides a measure for the photopolymer content. The dependence of the photopolymer content on the laser exposure time is

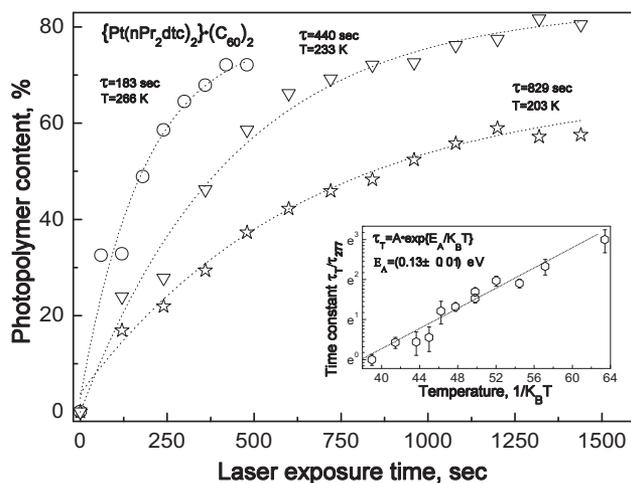


Figure 2. The dependence of the photopolymer content on the laser exposure time for the $\{Pt(nPr_2dtc)_2\} \bullet (C_{60})_2$ complex at various temperatures. Circles, triangles and stars – data obtained at 266, 233 and 203 K, respectively; the dotted lines are fits by an exponential growth function. Inset: Arrhenius dependence of the exponential growth time constant τ_T/τ_{277} on temperature.

shown in Figure 1 by open circles along with the fitting of the data by an exponential growth function:

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

Here, $P(t)$ is the time-dependent content of the photopolymer, $P_{sat} = 67\%$ is the content of the photopolymer attained after saturation of the photopolymerization, and $\tau = 830\text{ sec}$ is the exponential growth time constant. In fact, the time constant depends on the laser power and focusing conditions; the increase of laser power leads to the acceleration of photopolymerization and the exponential growth time constant decreases. This implies the necessity of careful control of the laser power, beam focusing and spot location during all Raman measurements.

Figure 2 shows the dependence of the photopolymer content on the laser exposure time for $\{Pt(nPr_2dtc)_2\} \bullet (C_{60})_2$ complex at various temperatures. Circles, triangles and stars represent the data obtained at 266, 233 and 203 K, respectively; the dotted lines are fits of the data by an exponential growth function. The temperature of the sample was stabilized with an accuracy $\pm 0.3\text{ K}$ by the use of a liquid nitrogen cryostat equipped with a temperature controller. As expected, the photopolymerization inhibits at lower temperatures and the exponential growth time constant increases. Note, that this series of Raman spectra were measured at different sites of the same sample under carefully controlled conditions of laser power, beam focusing and spot location. The temperature dependence of the relative exponential growth time constant τ_T/τ_{277} , where the τ_{277} is the time constant at 277 K, is shown in the inset of Figure 2. The experimental data are represented in the Arrhenius plot by hexagons while the dotted line is their linear best squares fit. The temperature dependence is well described by the Arrhenius equation:

$$\tau(T) = A \times \exp(E_A/k_B T) \quad (2)$$

where E_A is the activation energy, A is a dimensionless constant, k_B is the Boltzmann constant, T is the temperature

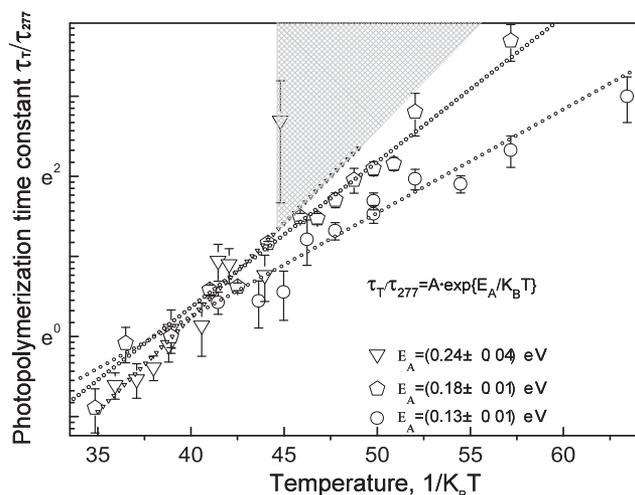


Figure 3. The temperature dependence of the exponential growth time constant τ_T/τ_{277} for the $\{Pt(dbdtc)_2\} \bullet C_{60}$, $\{Pt(nPr_2dtc)_2\} \bullet (C_{60})_2$ and pristine C_{60} (open hexagons, circles and triangles, respectively). The linear fittings of the experimental data are shown by appropriate small symbols. Shaded triangle area: the orientational ordering phase transition in pristine C_{60} near ~ 260 K.

and τ the decay time constant. The activation energy $E_A = (0.13 \pm 0.01)$ eV obtained is rather small.

Similar measurements were carried out for the fullerene complex $\{Pt(dbdtc)_2\} \bullet C_{60}$ and pristine C_{60} . The combined results from all these measurements are shown in Figure 3. The open circles, hexagons and triangles are experimental data related to the dependence of the exponential growth time constant τ_T/τ_{277} on temperature for the $\{Pt(nPr_2dtc)_2\} \bullet (C_{60})_2$, $\{Pt(dbdtc)_2\} \bullet C_{60}$ and pristine C_{60} , respectively. The linear fittings of experimental data are shown by appropriate small symbols. All the experimental data are well described by the Arrhenius equation. Note that the pristine C_{60} undergoes an orientational ordering phase transition near ~ 260 K associated with an fcc-to-sc structural transformation (shaded triangle area in Figure 3).^[15] At a lower temperature, the nearly free rotations of the C_{60} molecules are frozen and the photopolymerization rates, as well as the accuracy of its determination, drastically drop. The activation energy E_A derived from the Arrhenius plots is (0.13 ± 0.01) eV, (0.18 ± 0.01) eV and (0.24 ± 0.04) eV for the $\{Pt(nPr_2dtc)_2\} \bullet (C_{60})_2$ complex, the $\{Pt(dbdtc)_2\} \bullet C_{60}$ complex and the pristine C_{60} , respectively. It is interesting that the larger activation energy of the photopolymerization is consistent with the higher energy barrier between the monomer and polymer states for $Pt(dbdtc)_2 \bullet C_{60}$ complex with respect to the $Pt(nPr_2dtc)_2 \bullet (C_{60})_2$ complex.^[9,10] Since the photopolymerization takes place due to laser irradiation and molecular rotations, the activation energy of photopolymerization under fixed conditions of laser power, excitation wavelength and beam focusing have to be related to the activation energy of the molecular rotations. In view of this, the activation energy (0.24 ± 0.04) eV for the pristine C_{60} is remarkably close to the calculated energy barrier of ~ 0.3 eV between the P and H relative orientations of the C_{60} molecule in solid state.^[16] In the P and H orientations the double C=C bond is faced to the center of pentagon or hexagon of a neighboring molecule, respectively. The smaller values of the photopolymerization activation energy in C_{60}

molecular complexes could be ascribed to the incorporation of the donor molecular layers in the fullerene structure and the weakening of the interfullerene interaction, resulting in the lowering of the energy barrier between the P and H orientations of the C_{60} molecule.

Acknowledgements

This work is carried out within the state task of ISSP RAS and partial support of the RAS Presidium Program “Physics of condensed matter and new generation materials”.

References

- [1] Rao, A. M.; Zhou, P.; Wang, K.-A.; Hager, G. T.; Holden, J. M.; Wang, Y.; Lee, W.-T.; Bi, X.-X.; Eklund, P. C.; Cornett, D. S.; et al. Photoinduced Polymerization of Solid C_{60} Films. *Science* **1993**, *259*, 955–957. DOI: [10.1126/science.259.5097.965](https://doi.org/10.1126/science.259.5097.965).
- [2] Zhou, P.; Dong, Z.-H.; Rao, A. M.; Eklund, P. C. Reaction-Mechanism for Photopolymerization of Solid Fullerene C_{60} . *Chem. Phys. Lett.* **1993**, *211*, 337–340. 1993). DOI: [10.1016/0009-2614\(93\)87069-F](https://doi.org/10.1016/0009-2614(93)87069-F).
- [3] Pusztai, T.; Oszlanyi, G.; Faigel, G.; Kamaras, K.; Granasy, L.; Pekker, S. Bulk Structure of Phototransformed C_{60} . *Solid State Commun.* **1999**, *111*, 595–599. DOI: [10.1016/S0038-1098\(99\)00267-7](https://doi.org/10.1016/S0038-1098(99)00267-7).
- [4] Iwasa, Y.; Arima, T.; Fleming, R. M.; Siegrist, T.; Zhou, O.; Haddon, R. C.; Rothberg, L. J.; Lyons, K. B.; Carter, H. L.; Hebard, A. F.; et al. New Phases of C_{60} Synthesized at High Pressure. *Science* **1994**, *264*, 1570–1572. DOI: [10.1126/science.264.5165.1570](https://doi.org/10.1126/science.264.5165.1570).
- [5] Nunez-Regueiro, M.; Marques, L.; Hodeau, J.-L.; Bethoux, O.; Perroux, M. Polymerized Fullerite Structures. *Phys. Rev. Lett.* **1995**, *74*, 278–281. P. DOI: [10.1103/PhysRevLett.74.278](https://doi.org/10.1103/PhysRevLett.74.278).
- [6] Rao, A. M.; Eklund, P. C.; Hodeau, J.-L.; Marques, L.; Nunez-Regueiro, M. Infrared and Raman Studies of Pressure-Polymerized C_{60} . *Phys. Rev. B.* **1997**, *55*, 4766–4773. DOI: [10.1103/PhysRevB.55.4766](https://doi.org/10.1103/PhysRevB.55.4766).
- [7] Senyavin, V. M.; Davydov, V. A.; Kashevarova, L. S.; Rakhmanina, A. V.; Agafonov, V.; Allouchi, H.; Ceolin, R.; Sagon, G.; Szwarc, H. Spectroscopic Properties of Individual Pressure-Polymerized Phases of C_{60} . *Chem. Phys. Lett.* **1999**, *313*, 421–425. DOI: [10.1016/S0009-2614\(99\)01050-7](https://doi.org/10.1016/S0009-2614(99)01050-7).
- [8] Davydov, V. A.; Kashevarova, L. S.; Rakhmanina, A. V.; Senyavin, V. M.; Céolin, R.; Szwarc, H.; Allouchi, H.; Agafonov, V. Spectroscopic Study of Pressure Polymerized Phases of C_{60} . *Phys. Rev. B.* **2000**, *61*, 11936–11945. DOI: [10.1103/PhysRevB.61.11936](https://doi.org/10.1103/PhysRevB.61.11936).
- [9] Meletov, K. P.; Velkos, G.; Arvanitidis, J.; Christofilos, D.; Kourouklis, G. A. Raman Study of the Photopolymer Formation in the $\{Pt(Dbdtc)_2\} \bullet C_{60}$ Fullerene Complex and the Decomposition Kinetics of the Photo-Oligomers. *Chem. Phys. Lett.* **2017**, *681*, 124–129. DOI: [10.1016/j.cplett.2017.05.065](https://doi.org/10.1016/j.cplett.2017.05.065) DOI: [10.1016/j.cplett.2017.05.065](https://doi.org/10.1016/j.cplett.2017.05.065).
- [10] Meletov, K. P. Photopolymerization in the Fullerene Layers of the Molecular Donor-Acceptor Complex $\{Pt(nPr_2dtc)_2\} \bullet (C_{60})_2$. *Phys. Solid State* **2018**, *60*, 2103–2108. DOI: [10.1134/S1063783418100190](https://doi.org/10.1134/S1063783418100190).
- [11] Meletov, K. P.; Konarev, D. V.; Tolstikova, A. O. Phase Transitions and Photoinduced Transformations at High Pressure in the Molecular Donor-Acceptor Fullerene Complex $\{Cd(Dedtc)_2\} \bullet C_{60}$. *J. Exp. Theor. Phys.* **2015**, *120*, 989–997. DOI: [10.1134/S1063776115050167](https://doi.org/10.1134/S1063776115050167).
- [12] Kato, K.; Murata, H.; Gonnokami, H.; Tachibana, M. Polymerization in Ferrocene-Doped C_{60} Nanosheets under High Pressure and Light Irradiation. *Carbon* **2016**, *107*, 622–627. DOI: [10.1016/j.carbon.2016.06.042](https://doi.org/10.1016/j.carbon.2016.06.042).
- [13] Kuzmin, A. V.; Konarev, D. V.; Khasanov, S. S.; Meletov, K. P. Crystal Structure and Raman Spectra of Molecular Complex

- [Cd(Et₂dtc)]₂·DABCO]·C₆₀·(DABCO)₂ at High Pressure. *Nanosyst. Phys., Chem., Math.* **2018**, 9, 23–37. DOI: [10.17586/2220-8054-2018-1-33-37](https://doi.org/10.17586/2220-8054-2018-1-33-37).
- [14] Konarev, D. V.; Khasanov, S. S.; Lopatin, D. V.; Rodaev, V. V.; Lyubovskaya, R. N. Fullerene Complexes with Divalent Metal Dithiocarbamates: structures, Magnetic Properties, and Photoconductivity. *Russ. Chem. Bull.* **2007**, 56, 2145–2160. DOI: [10.1007/s11172-007-0339-y](https://doi.org/10.1007/s11172-007-0339-y).
- [15] Heiney, P. A.; Fischer, J. E.; McGhie, A. R.; Romanow, W. J.; Denenstein, A. M.; McCauley Jr, J. P.; Smith, A. B.; Cox, D. E. Orientational Ordering Phase Transition in Solid C₆₀. *Phys. Rev. Lett.* **1991**, 66, 2911–2914. DOI: [10.1103/PhysRevLett.66.2911](https://doi.org/10.1103/PhysRevLett.66.2911).
- [16] Burgos, E.; Halac, E.; Bonadeo, H. Intermolecular Forces and Phase Transitions in Solid C₆₀. *Phys. Rev. B.* **1994**, 49, 15544–15549. DOI: [10.1103/PhysRevB.49.15544](https://doi.org/10.1103/PhysRevB.49.15544).