

Raman study of the photopolymer formation in the fullerene complex $\{\text{Pt}(\text{dbdtc})_2\} \cdot \text{C}_{60}$ and kinetics of the photo-oligomers decomposition

The Raman spectra evolution during the radiation of the complex fullerene $\{\text{Pt}(\text{dbdtc})_2\} \cdot \text{C}_{60}$ with laser beam at 633 or 785 nm, is characterized by significant intensity reduction of the $A_g(2)$ vibrational mode of the C_{60} monomer. Simultaneously, in the same frequency region, new peaks corresponding to the C_{60} polymeric structures (linear chains and planar polymers) appear, with the dimers peak being dominant. Polymer thermal treatment results in their gradual decomposition and reestablishment of the monomer phase. Upon temperature increase, the decomposition process becomes faster. This behavior is typical for chemical reactions and it has been observed for the thermal decomposition of all the fullerene polymers. The reaction's activation energy, or equally the energy barrier for the covalent bonds breaking, was estimated based on the experimental data. The resulting activation energy value is 1.12 eV/molecule, much lower than that in the C_{60} crystalline dimers and polymers, derived from the fullerite thermal treatment under high pressure (1.7-1.9 eV/molecule), but very close to the corresponding value for the photopolymerized one (1.25 eV/molecule). The temperature for the total decomposition of the $\{\text{Pt}(\text{dbtc})_2\} \cdot \text{C}_{60}$ photo-oligomers is estimated to be ~ 120 °C, while for the crystalline C_{60} dimer is ~ 180 °C and for the polymers ~ 280 °C. The reduced stability of the fullerene complex can be ascribed to the presence of the organometallic molecules between the C_{60} planes that increase the intermolecular distances and weaken the covalent bonds.