Influence of pressure on the photopolymerization rate of the linear orthorhombic polymer of C$_{60}$


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Abstract

The photopolymerization of the orthorhombic C$_{60}$ polymer has been studied by Raman spectroscopy as a function of laser intensity at ambient and high pressure conditions. The Raman spectra at ambient pressure, excited by 514.5 nm, show irreversible changes at intensity $\approx 3200$ W/cm$^2$, while at high pressure the transformation rate increases and the required intensity drops to $\approx 470$ W/cm$^2$. Raman spectra recorded after pressure release, indicate that non-irradiated sample sites do not exhibit any changes. In addition, ambient pressure X-ray diffraction measurements on high-pressure treated, non-irradiated samples show no structural modification, revealing the dominant role of light in the polymerization processes.

1. Introduction

It is known that the polymerization of the monomeric fcc phase of C$_{60}$ can be performed by various ways of sample treatment. In particular, the polymerization of fullerene C$_{60}$ caused by light illumination from an Ar$^+$ laser beam at 514.5 and 488 nm with a power density exceeding 5 W/cm$^2$ has been observed [1–5]. Photopolymerization is related to covalent bonding between adjacent C$_{60}$ molecules via [2+2] cycloaddition reactions that results to the creation of fullerene dimers and/or oligomers (C$_{60}$)$_n$, with $n = 2$–20 [1,2,5]. The formation of dimers, linear polymeric chains or polymeric networks results in distinct changes in the Raman and IR spectra related to the lowering of the C$_{60}$ molecular symmetry, which leads to the splitting of the bands, as well as to their softening due to the decrease of the mean intramolecular bond strength [1–4]. Because of the small light penetration depth ($\approx 1$ μm), polymerization is only effected in thin films or surfaces of bulk samples, making the X-ray analysis of the photopolymer structure rather uncertain [6].

Contrary to the photopolymerization of the fcc phase of C$_{60}$, products of the high pressure/high temperature (HPHT) polymerization, proceeding basically through the [2+2] cycloaddition reaction, are bulk samples based on various both low- and high-molecular mass 1D, 2D or 3D polymers of C$_{60}$ [7–11]. The structural ordering of the high-molecular mass 1D and 2D polymers gives rise to the formation of crystalline polymeric phases of C$_{60}$: orthorhombic (1D-O) in the case of the 1D polymers and tetragonal (2D-T) or rhombohedral (2D-R) in the case of the 2D polymers depending on the C$_{60}$ coordination within the polymeric layers [4,5,7,8]. According to numerical calculations, the crystalline packing of linear and planar polymers can be transformed to three-dimensional polymeric networks by the application of high pressure [12,13]. However, up to now well-ordered three-dimensional crystalline polymeric networks were obtained only when high pressure was applied to the tetragonal polymeric phase of C$_{60}$ [14,15].

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Investigations on the stability and photochemical conversion of the C_{60} monomeric phases have shown that high pressure drastically increases the rate of the C_{60} photopolymerization [16,17]. Recently, in a high pressure study of the C_{60} crystalline polymeric phases, we have reported that the orthorhombic phase of C_{60} undergoes irreversible transformation under simultaneous application of pressure and laser irradiation [18]. This transformation is related to a phase transition of the initial orthorhombic phase and was associated with the pressure-assisted photopolymerization of the material.

In this Letter, we report the results of an extended study of the pressure-assisted photopolymerization of the 1D-O polymer induced by laser irradiation and applied pressure. We investigate the influence of laser irradiation intensity on the Raman spectra of the polymer excited by the 514.5 nm Ar\(^+\) laser line. Raman spectra at ambient conditions show irreversible changes at laser intensity \(\sim 3200 \text{ W/cm}^2\). Further increase of intensity results in an almost instantaneous transformation of the 1D-O polymer to a new phase, whose Raman spectra resemble those of the pressure-assisted photopolymerized sample [18]. Measurements at \(P = 0.8 \text{ GPa}\) and at room temperature show irreversible changes in the Raman spectra at \(\sim 470 \text{ W/cm}^2\), indicating a large decrease of the laser intensity necessary for photopolymerization. The increase of laser intensity to \(\sim 4700 \text{ W/cm}^2\) leads to an almost instantaneous transformation of the material to a new phase. Raman spectra recorded after pressure release reveal that the transformation to a new phase takes place only at the sample sites that have been irradiated by laser beam at 0.8 GPa, whereas non-irradiated sites do not exhibit any changes. In line with these observations, the X-ray diffraction (XRD) data from the 1D-O polymer before and after high pressure treatment show that no structural changes occur when the sample was not irradiated by laser at high pressure.

2. Experimental

Samples of the initial 1D-O phase were prepared from sublimed 99.98% pure C_{60} powder treated at 1.2 GPa and 573 K in a ‘toroid’-type device. The preliminary XRD analysis has confirmed that the samples have the orthorhombic packing of linear polymeric chains (space group \(P_{mmm}\): \(a = 9.098 \text{ Å}, b = 9.831 \text{ Å}, \text{ and } c = 14.72 \text{ Å}\)). The specimens used for the high pressure measurements had dimensions of \(\sim 100 \mu\text{m}\) and have been selected from the batch material by means of micro-Raman probing for their intense, clear and spatially uniform Raman spectra, typical of the 1D-O polymeric phase [9,19].

Raman spectra were recorded in the back-scattering geometry using a micro-Raman system equipped with a triple monochromator (DILOR XY) and a CCD liquid-nitrogen cooled detector system. The spectral width of the system was \(\sim 3 \text{ cm}^{-1}\). The 514.5 nm line of an Ar\(^+\) laser with beam intensity in the range 0.005–0.5 mW was used for excitation. The laser line was focused on the sample by means of 100x and 20x objectives with a spatial resolution of \(\sim 1\) and \(\sim 2\mu\text{m}\), respectively. Measurements of the Raman spectra at high pressures were carried out using a Mao-Bell type diamond anvil cell (DAC) [20]. The 4:1 methanol–ethanol mixture was used as pressure transmitting medium and the ruby fluorescence technique was used for pressure calibration [21].

3. Results and discussion

Raman spectra of the orthorhombic phase measured at various laser intensities and pressures are illustrated in Fig. 1. The reference spectrum in Fig. 1c shows the Raman features typical for the linear orthorhombic polymer of C_{60} both in the number of bands as well as in their positions [9,19]. This spectrum was recorded at ambient conditions with intensity \(\sim 100 \text{ W/cm}^2\) for the 1064 nm excitation line of a Nd:YAG laser. Note that, the 1D-O polymer is transparent to infrared light, thus the photopolymerization of the material is prevented for this wavelength at any laser intensity. Fig. 1b depicts the Raman spectrum of a sample from the same batch recorded at ambient conditions and excited with the 514.5 nm Ar\(^+\) laser line at intensity \(\sim 3200 \text{ W/cm}^2\). The spectrum shows significant changes marked by the appearance of a number of new peaks and the shift of the Raman peaks corresponding to the initial 1D-O polymer. Drastic changes in the Raman spectrum of the initial 1D-O polymer were also observed at \(P = 0.08 \text{ GPa}\) and intensity \(\sim 4700 \text{ W/cm}^2\) for the 514.5 nm Ar\(^+\) laser line (Fig. 1a). Measurements in various pressure runs at laser intensity exceeding 470 W/cm² show identical results and demonstrate the irreversible transformation of the 1D-O polymer. It was not possible to determine the threshold pressure for this transformation in the

![Fig. 1](image-url)
high-pressure Raman measurements as it occurs at pressure even as low as \(~0.08\) GPa.

Fig. 2 shows the Raman spectra of 1D-O polymer measured at ambient conditions and various intensities of the 514.5 nm Ar\(^+\) laser line. The spectrum in Fig. 2a, measured at laser intensity \(~640\) W/cm\(^2\), is identical to the Raman spectrum of the initial 1D-O polymer and does not show any traces of phototransformation. The increase of laser intensity to \(~1280\) W/cm\(^2\) (Fig. 2b) does not affect the Raman features, while at a laser intensity of \(~3200\) W/cm\(^2\) a new Raman band appears near \(~1446\) cm\(^{-1}\) (marked by the arrow in Fig. 2c). Further increase of the laser intensity to \(~6400\) W/cm\(^2\) (Fig. 2d) and subsequently to \(~12,800\) W/cm\(^2\) (Fig. 2e) leads to the intensity enhancement of the new band. At the same time, the other two bands near \(1433\) cm\(^{-1}\) and \(1563\) cm\(^{-1}\) become stronger with respect to the main band near \(1458\) cm\(^{-1}\), which is attributed to the ‘pentagon-pinch’ \(A_g(2)\) intramolecular mode of \(C_{60}\) in the 1D-O polymer [9]. At the highest laser intensity of \(~25,600\) W/cm\(^2\) (Fig. 2f) the Raman bands broaden significantly and slightly shift to lower energies indicating the sample heating, which results in its gradual degradation.

Fig. 3 depicts the Raman spectra of the 1D-O polymer measured at various conditions of laser intensity and pressure. The Raman spectrum of the 1D-O polymer shown in Fig. 3a refers to ambient conditions and laser intensity \(~440\) W/cm\(^2\). Apparently, these experimental conditions do not cause changes related to photopolymerization. At pressure \(0.8\) GPa the changes in the Raman spectrum appear even at laser intensity as low as \(~470\) W/cm\(^2\) (Fig. 3b). Further increase of the laser intensity to \(~4700\) W/cm\(^2\) leads to an almost instantaneous transformation of the material to a new phase (Fig. 3c). The Raman spectrum recorded in the DAC, after pressure release, shows the same typical features of the photopolymer as that recorded under pressure of \(0.8\) GPa (Fig. 3c). This indicates that the new phase – appearing at the sample sites treated by laser irradiation at high pressure – remains stable at ambient conditions (Fig. 3d). On the contrary, the sample sites that were not irradiated by laser beam at high pressure show the typical Raman features of the initial 1D-O polymer (Fig. 3e). To avoid any influence of laser irradiation on the Raman spectra acquired after pressure release (Fig. 3d, e) the measurements were performed at laser intensity \(~205\) W/cm\(^2\), considerably lower than the \(3200\) W/cm\(^2\) at which the photopolymerization was observed at ambient pressure (Fig. 2c).

To ensure that the observed transformation is related to pressure-assisted photopolymerization we have compared the X-ray diffraction patterns of the high pressure-treated orthorhombic phase at ambient conditions with those of the initial orthorhombic phase (Fig. 4a, b, respectively). For the high pressure treatment, a sample from the same batch was kept for \(~10\) min at a pressure of \(3\) GPa, at room temperature, before pressure release. As it can be
deduced from Fig. 4, there is no significant difference in the XRD patterns of the 1D-O polymer before and after pressure treatment. The positions of all the observed peaks are the same, while small difference in peak intensities is related to the powder material preparation.

The obtained data imply that the irreversible changes in the Raman spectra of the initial 1D-O polymer are related to the laser irradiation of the samples, which leads to the photopolymerization. Note that, photopolymerization of the HPHT 1D-O polymer, observed for the first time at ambient conditions, takes place at a laser intensity of \( \sim 3200 \text{ W/cm}^2 \) that exceeds more than two orders of magnitude the intensity of \( \sim 5 \text{ W/cm}^2 \) where the photopolymerization of the monomeric C\(_{60}\) was reported. The application of high pressure promotes the transformation process, resulting in the drastic increase of the photopolymerization rate and in a consequent reduction of the laser intensity required for the transformation (\( \sim 470 \text{ W/cm}^2 \)). It is important to note that the molecules in the ground state cannot take part in the polymerization process that implies as a first step the formation of C\(_{60}\) dimers through [2+2] cycloaddition reaction. According to the Woodward–Hoffmann rule the straightforward coupling of the C\(_{60}\) molecules in their ground state is not favoured due to the symmetry of the highest occupied orbitals of C\(_{60}\) [22,23]. However, the molecular orbital of the excited state of C\(_{60}\), being populated by light absorption, has favourable symmetry for dimer formation. On the contrary, the formation of dimers at high pressure takes place even at room temperature without light irradiation [24], which means that the occupied molecular orbitals of C\(_{60}\) at high pressure are out of symmetry limitations on the pair interaction related to the Woodward–Hoffmann rule. In view of this, the simultaneous effect of pressure and light irradiation can stimulate the polymerization process, which results in considerable increase of the polymerization rate. The results of this work confirm this suggestion: the 1D-O polymer indeed becomes more sensitive to photochemical reactions when high pressure is applied.

The structural features of the pressure-assisted photopolymerization of the orthorhombic phase are not clear but one can imply that it relates to the bonding between the linear polymeric chains. The distinction of the Raman spectrum of the transformed 1D-O polymer from those of the 2D polymerized tetragonal and rhombohedral phases of C\(_{60}\) may be indicating that the novel chemical bonds in the transformed orthorhombic phase are not the typical [2+2] cycloaddition bonds but rather single bonds between polymeric chains [18]. In the case of cross-linking of the pristine orthorhombic polymer, the lowering of symmetry indicated by the appearance of a new Raman peak can be associated with the formation of new intercage covalent bonds between the C\(_{60}\) molecules that belong to the neighbouring polymeric chains in the structure of the orthorhombic phase. Note that this process, which can give rise to the formation of both the 2D and 3D polymeric structures of C\(_{60}\), must be accompanied by an appropriate distribution of the positions of the single and double bonds into the C\(_{60}\) molecular cages. Nevertheless, one cannot exclude that the new phase may be formed also via conventional [2+2] cycloaddition reaction between the molecules belonging to the adjacent polymeric chains resulting in formation of planar polymeric network. Then, the distinction of the Raman spectrum of the transformed 1D-O polymer from those of the known planar C\(_{60}\) polymers may be related to the structural distortion of the planar polymeric network obtained under specific conditions of photopolymerization in thin surfaces. In any case, the unambiguous determination of the structural properties of the new phase requires further experimental and theoretical investigations.

As for the possible mechanism of the high pressure photoinduced transformation of the 1D-O polymer of C\(_{60}\), one can speculate that it may be similar to the mechanism of high pressure photoinduced transformation of other molecular carbon compounds with unsaturated bonds. In particular, the combined action of pressure and laser irradiation reduces the pressure threshold of the chemical transformation of crystalline benzene from 23 to 16 GPa [25]. According to this report, high pressure induces a distortion of the benzene ring that resembles the molecule in the first excited electronic state S\(_1\). The change of molecular geometry relates to the pressure-induced mixing of the excited S\(_1\) state with the S\(_0\) ground state. That is, the distortion of the molecule at high pressure speeds up the photochemical transformation related to the selective pumping of the system in the S\(_1\) excited state.

In conclusion, the linear orthorhombic polymeric phase of C\(_{60}\) is not stable with respect to laser irradiation and transforms to a new photopolymer phase. The laser intensity necessary for the photopolymerization at ambient conditions is considerably higher than that needed for the C\(_{60}\) monomer. The application of high pressure promotes the transformation and the photopolymerization rate increases drastically. The photopolymerization may be accomplished...
by covalent bond formation between molecules belonging to adjacent polymeric chains resulting in the formation of a new 2D or 3D polymerized state of C_{60}.

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