Available online at www.sciencedirect.com
ScienceDirect
Chemical Physics Letters 428 (2006) 298–302
CHEMICAL PHYSICS LETTERS
www.elsevier.com/locate/cplett

Influence of pressure on the photopolymerization rate of the linear orthorhombic polymer of C_{60}

K.P. Meletov [a], V.A. Davydov [b], A.V. Rakhmanina [b], V. Agafonov [c], J. Arvanitidis [d], D. Christofilos [d], K.S. Andrikopoulos [d], G.A. Kourouklis [d,*]

[a] *Institute of Solid State Physics of RAS, Chernogolovka, Moscow region 142432, Russia*
[b] *Institute of High Pressure Physics of RAS, Troitsk, Moscow region 42092, Russia*
[c] *Laboratoire de Chimie Physique, E.A. CIME 2098, Universite de Tours, 37200 Tours, France*
[d] *Physics Division, School of Technology, Aristotle University of Thessaloniki, 54124 Thessaloniki, Greece*

Received 13 June 2006; in final form 18 July 2006
Available online 26 July 2006

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 ~3200 W/cm^2, while at high pressure the transformation rate increases and the required intensity drops to ~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 (~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].

---

[*] Corresponding author. Fax: +30 2310 995928.
E-mail address: gak@gen.auth.gr (G.A. Kourouklis).

0009-2614/$ - see front matter © 2006 Published by Elsevier B.V.
doi:10.1016/j.cplett.2006.07.057

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 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 $P = 0.8$ GPa and at room temperature show irreversible changes in the Raman spectra at $\sim$470 W/cm^2, indicating a large decrease of the laser intensity necessary for photopolymerization. The increase of laser intensity to $\sim$4700 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_{mnn}: $a = 9.098$ Å, $b = 9.831$ Å, and $c = 14.72$ Å). The specimens used for the high pressure measurements had dimensions of $\sim$100 μm 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 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 100× and 20× objectives with a spatial resolution of $\sim$1 and $\sim$2.7 μm, 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 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 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 $P = 0.08$ GPa and intensity $\sim$4700 W/cm^2 for the 514.5 nm Ar^+ laser line (Fig. 1a). Measurements in various pressure runs at laser intensity exceeding 470 W/cm^2 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

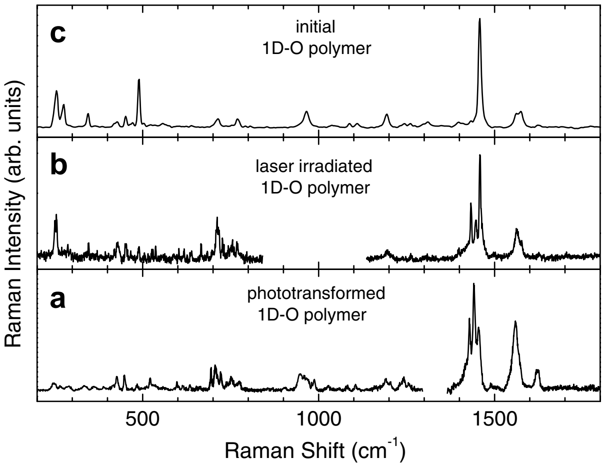

Fig. 1. (a) Raman spectrum of the phototransformed 1D-O polymer recorded at $P \approx 0.08$ GPa and excited with the 514.5 nm line at an intensity of $\sim$4700 W/cm^2. (b) Raman spectrum of the initial 1D-O polymer recorded at ambient conditions and excited with the 514.5 nm line at an intensity of $\sim$3200 W/cm^2. (c) Raman spectrum of the initial 1D-O polymer recorded at ambient conditions and excited with the 1064 nm line at an intensity of $\sim$100 W/cm^2.

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).

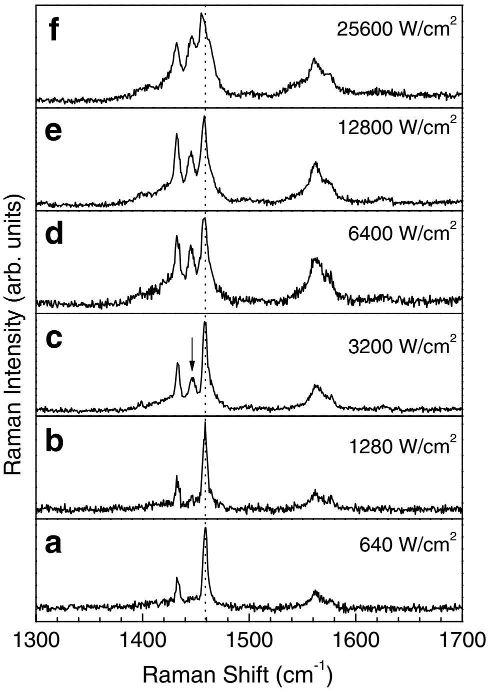

Fig. 2. Raman spectra of the 1D-O polymer recorded at ambient conditions and various excitation intensities of the 514.5 nm Ar^+ laser line. The irreversible transformation of the material starts at laser intensity exceeding 1280 W/cm^2. The intensity enhancement of a new Raman band (marked by the arrow) with increasing laser power indicates the growth of the photopolymer content. Vertical line was drawn to guide the eye.

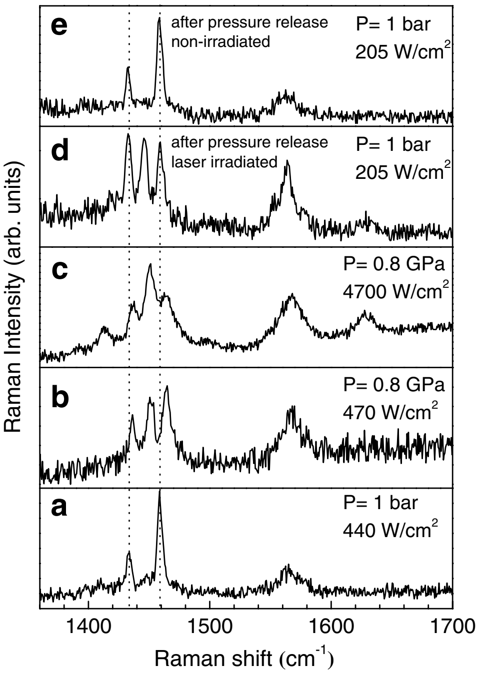

Fig. 3. Raman spectra of the 1D-O polymer recorded at various pressures and excitation intensities of the 514.5 nm Ar^+ laser line. The pressure-assisted photopolymerization starts at relatively low laser power (~470 W/cm^2). After pressure release, the laser treated sites show Raman spectra typical of the photopolymer while non-treated sites do not show any photopolymerization effects. Vertical lines were drawn to guide the eye.

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

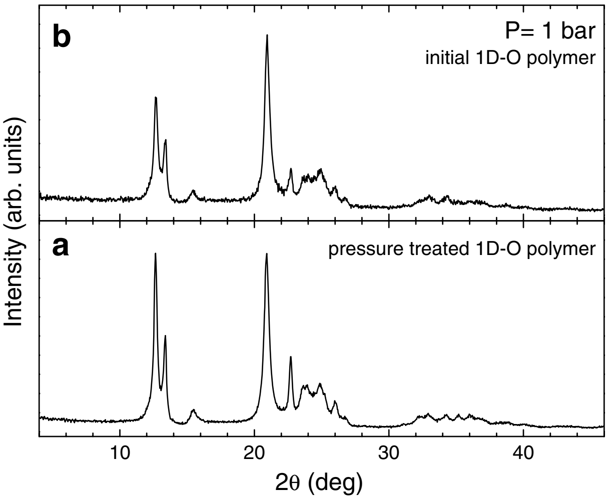

Fig. 4. X-ray diffraction patterns of (a) the pressure-treated 1D-O polymeric phase after pressure release, and (b) the initial 1D-O polymeric phase of C_{60} at normal conditions.

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 ~3200 W/cm^2 that exceeds more than two orders of magnitude the intensity of ~5 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 (~470 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}.

Acknowledgements

The support by the Russian Foundation for Fundamental Research, grant #06-03-32050, and the support of the General Secretarial for Research and Development, Greece, under the bilateral Greek–Russian collaboration program, are greatly acknowledged. V.A.D. and A.V.R. also thank US Civilian Research & Development Foundation (CRDF) / Award RUE2-2659-MO-05 /. J.A. and D.C. acknowledge the financial support from the Hellenic Ministry of National Education and Religious Affairs and the European Union through the 'PYTHAGORAS II' program.

References

[1] A.M. Rao et al., Science 259 (1993) 955.
[2] P.C. Eklund, A.M. Rao, P. Zhou, Y. Wang, J.M. Holden, Thin Solid Films 257 (1995) 185.
[3] B. Burger, J. Winter, H. Kuzmany, Z. Phys. B 101 (1996) 227.
[4] M. Sakai, M. Ichida, A. Nakamura, Chem. Phys. Lett. 335 (2001) 559.
[5] E. Kovats, G. Oszlany, S. Pekker, J. Phys. Chem. B 109 (2005) 11913.
[6] T. Puzstai, G. Oszlanyi, G. Faigel, K. Kamaras, L. Granasy, S. Pekker, Solid State Commun. 111 (1999) 595.
[7] Y. Iwasa et al., Science 264 (1994) 1570.
[8] M. Nunez-Regueiro, L. Marques, J.-L. Hodeau, O. Bethoux, M. Perroux, Phys. Rev. Lett. 74 (1995) 278.
[9] V.A. Davydov et al., Phys. Rev. B 61 (2000) 11936.
[10] V.D. Blank, S.G. Buga, G.A. Dubitsky, N.R. Serebryanaya, M.Yu. Popov, B. Sundqvist, Carbon 36 (1998) 319.
[11] V.V. Brazhkin, A.G. Lyapin, S.V. Popova, JETP Lett. 76 (2002) 805.
[12] S. Okada, S. Saito, A. Oshiyama, Phys. Rev. Lett. 83 (1999) 1986.
[13] E. Burgos, E. Halac, R. Weht, H. Bonadeo, E. Artacho, P. Ordejon, Phys. Rev. Lett. 85 (2000) 2328.
[14] K.P. Meletov et al., Chem. Phys. Lett. 341 (2001) 435.
[15] D.H. Chi, Y. Iwasa, T. Takano, T. Watanuki, Y. Ohishi, S. Yamanaka, Phys. Rev. B 68 (2003) 153402.
[16] M. Sakai, A. Nakamura, Phys. Rev. B 64 (2001) 033413.
[17] T. Mitani, K. Matsuishi, S. Onari, Chem. Phys. Lett. 383 (2004) 486.
[18] K.P. Meletov, V.A. Davydov, A.V. Rakhmanina, V. Agafonov, G.A. Kourouklis, Chem. Phys. Lett. 416 (2005) 220.
[19] V.M. Senyavin et al., Chem. Phys. Lett. 313 (1999) 421.
[20] A. Jayaraman, Rev. Sci. Instrum. 57 (1986) 1013.
[21] D. Barnett, S. Block, G.J. Piermarini, Rev. Sci. Instrum. 44 (1973) 1.
[22] J. Fagerstrom, S. Stafstrom, Phys. Rev. B 53 (1996) 13150.
[23] E.A. Halevi, Helvetica Chim. Acta 84 (2001) 1661.
[24] V.A. Davydov, L.S. Kashevarova, A.V. Rakhmanina, V. Agafonov, R. Ceolin, H. Szwarc, JETP Lett. 68 (1998) 928.
[25] L. Ciabini, M. Santoro, R. Bini, V. Schettino, Phys. Rev. Lett. 88 (2002) 085505.