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The Stability of the Linear Orthorhombic Polymer of C₆₀: A High-Pressure Study

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Abstract: The phonon modes of the linear orthorhombic polymer of C₆₀ and its stability as function of pressure have been studied by in-situ Raman scattering and X-ray measurements. The Raman data show an irreversible transition to a new phase at any small pressure while the independent X-ray study does not reveal structural changes even at pressure up to 3 GPa. This may be the indication of the pressure assisted photopolymerization resulting in the formation of the planar polymeric sheets via further bonding between adjacent polymeric chains.

Keywords: Fullerene C₆₀, polymerization under high pressure, orthorhombic C₆₀ phase, X-ray diffraction, Raman characterization

The treatment of C₆₀ under high pressure and high temperature leads to its polymerization related to intermolecular covalent bonding via *sp*³-like coordinated carbon atoms. The crystal structures of these polymers have been identified as the one-dimensional orthorhombic (1D-O), two-dimensional tetragonal (2D-T), and rhombohedral (2D-R), and three-dimensional face-centred cubic (1–3). Raman and X-ray studies of the 2D-T polymer at high

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pressure have revealed an irreversible transition above 20 GPa (4, 5), related to its further three-dimensional polymerization by the formation of covalent bonds between the molecules belonging to adjacent polymeric sheets. In this paper, we have studied the Raman spectra and the stability of 1D-O polymer of C_{60} at high pressure and at room temperature by in-situ Raman scattering and X-ray measurements. The experiments were undertaken to check the possibility for further pressure-induced polymerization via covalent bonding between the adjacent polymeric chains.

Samples of the initial 1D-O phase were prepared from sublimed 99.98% pure C_{60} powder at 1.2 GPa at 573 K in a "toroid"-type device. The preliminary X-ray analysis confirmed that the samples have the orthorhombic packing of linear polymeric chains (space group P_{mmn} : $a = 9.098$ Å, $b = 9.831$ Å, and $c = 14.72$ Å). The in-situ Raman measurements at high pressure were carried out using a diamond anvil cell of Mao-Bell type, a triple

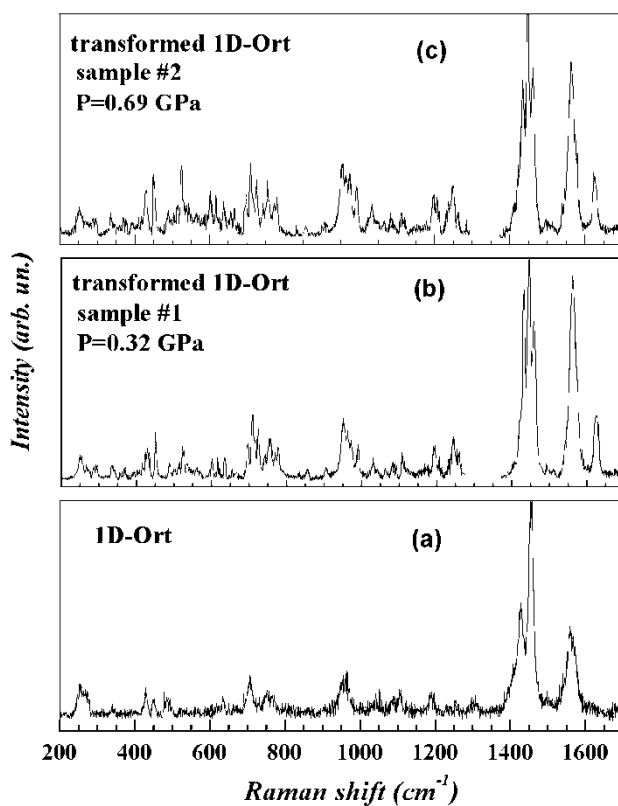


Figure 1. Raman spectra of the initial 1D-O polymer at normal conditions (Figure 1a), as well as of the same sample subjected to 0.69 GPa (Figure 1c). A different sample of the material has been already transformed at a pressure of 0.32 GPa (Figure 1b).

monochromator DILOR XY-500 equipped with a liquid-nitrogen cooled CCD detector system, and the 514.5 nm emission line of an Ar^+ laser.

The Raman spectrum of the initial 1D-O polymer at ambient conditions is shown in Figure 1a. The number of the Raman active modes and their frequencies are typical for 1D-O polymer and has been reported earlier (6). The spectrum of the same sample at ~ 0.69 GPa (Figure 1c) has quite different structure: the number of peaks and their positions differ from those of the initial spectrum. We have not been able to find any threshold pressure for this transformation: it occurs at pressure even as low as 0.32 GPa (Figure 1b). The Raman spectra of the transformed 1D-O polymer along with those of the planar 2D-R and 2D-T polymers are shown in Figures 2c, 2b, and 2a, respectively. The ambient pressure X-ray and Raman characterization studies of the 1D-O samples, which have been treated under the same P, T conditions with those used for the in-situ high pressure Raman measurements, do not show any changes in the crystal structure of the polymer. These observations show the importance of the simultaneous pressure application and light irradiation for the transformation observed in the Raman spectra indicating that it is associated with pressure-assisted photopolymerization of the linear 1D-O polymer. In conclusion, it is important to note, that at ambient conditions the 1D-O polymer is stable with respect to light irradiation. The transformation of the 1D-O polymer of C_{60} at high pressure

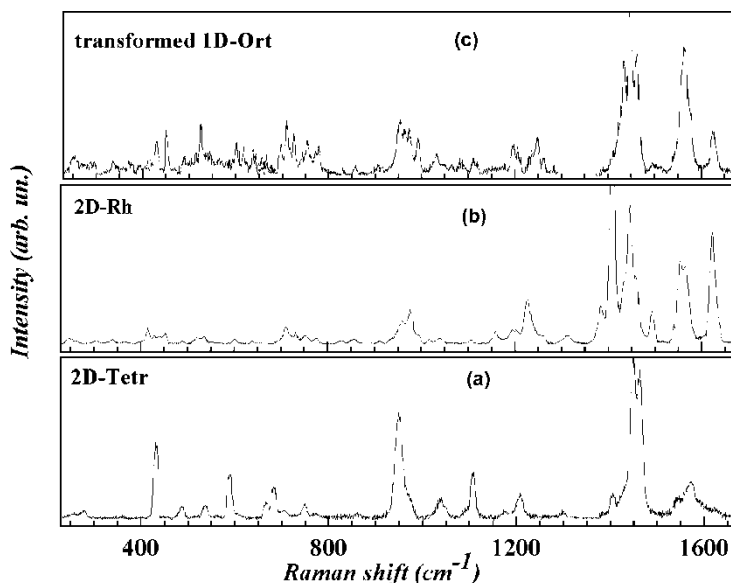


Figure 2. Raman spectra of the various planar polymers of C_{60} : (a) 2D-T polymer, (b) 2D-R polymer, (c) transformed 1D-O polymer.

and laser irradiation may be related to further polymerization via covalent bonding between molecules belonging to adjacent polymeric chains.

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