

PHOTOLUMINESCENCE STUDIES ON POLYMERIC FORMS OF SOLID C₆₀

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Simultaneous application of high pressure and high temperature has been shown to induce polymerization in solid C₆₀. [1] In contrast to the charged alkali metal doped C₆₀ polymers [2] (MC₆₀, M = Rb, K) with orthorhombic structure [3], pressure-induced fullerene polymers are neutral. The structure of the pressure-polymerized C₆₀ depends on the conditions of synthesis. Four distinct phases -- orthorhombic (O), rhombohedral (R), tetragonal (T), and compacted fcc -- have been identified. [4,5] The C₆₀ molecules are connected as one dimensional (1D) linear chains in the O-phase and as two-dimensional (2D) square or hexagonal networks in the T- and R-phases, respectively. [4] Nuclear magnetic resonance study on the R-phase polymer [6] has shown that the C₆₀ molecules are connected by 2+2 cycloaddition, as proposed originally for photopolymerized C₆₀. [7]

In all neutral polymeric structures, lineshape analysis of the Raman spectra in the region between 1380 to 1480 cm⁻¹ revealed six distinct modes with nearly the same

frequency in all samples. [8] However, the variation in the relative intensities of the Raman modes was found to be sensitive to the specific polymeric phase. In this paper, we present evidence that the temperature dependence of the photoluminescence (PL) spectra can also be used to distinguish between the O-, T-, and R- phases.

C₆₀ polymers were synthesized by subjecting microcrystalline C₆₀ powder to different high pressure and high temperature treatments. [4] Structure of the polymers were confirmed by simulations of the x-ray diffraction data by Núñez-Regueiro *et al.* [4] Powder samples of the polymer were mixed with 20 weight % KBr and pressed into pellets for PL studies. PL was excited with less than 3 mW of 488 nm laser line focused to a size of ~ 3 mm x 0.5 mm. The PL spectra were measured using a cooled photomultiplier detector and photon counting electronics.

Figures 1 and 2 show, respectively, the normalized PL spectra of O- and R-phase polymers at four temperatures. The experimental data are shown as dots. A sum of several

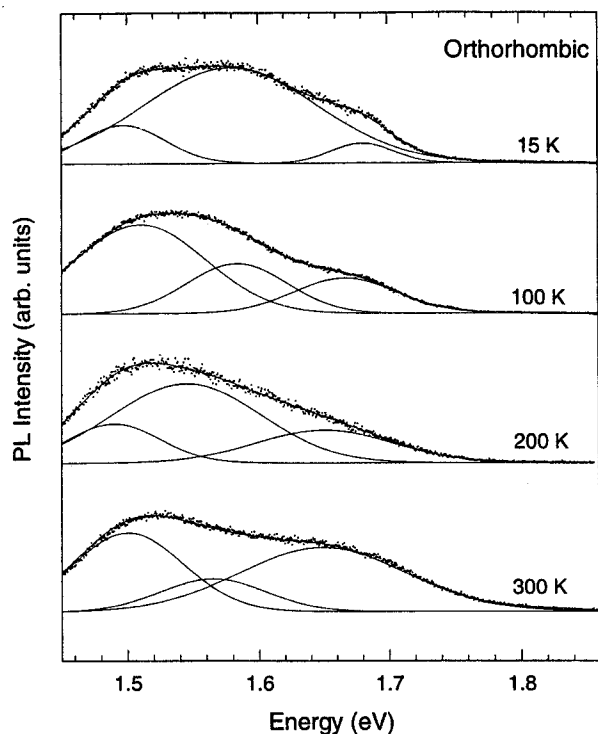


Fig. 1 PL spectra at different temperatures in the 1D orthorhombic phase of pressure-polymerized C₆₀.

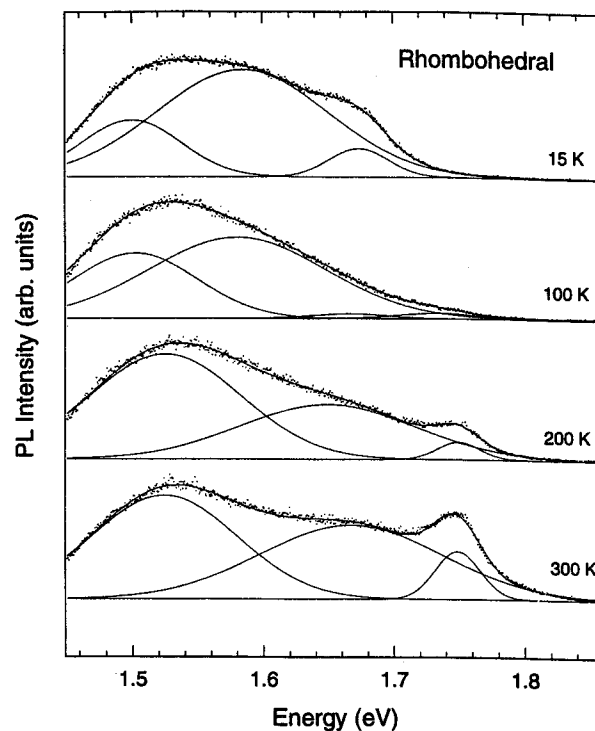


Fig. 2 PL spectra at different temperatures in the 2D rhombohedral phase of pressure-polymerized C₆₀.

Gaussians is fit to each spectrum. The resulting curve, shown as solid lines through the dots, fits the data very well and is almost indistinguishable in the figures. The individual Gaussians are also shown below each of the PL spectra. At room temperature, there are three broad PL peaks at 1.51, 1.57, and 1.65 eV in the O-sample, and at 1.52, 1.67, and 1.75 eV in the R-sample. The peak at 1.75 eV is specific only to the R-phase and is seen most strongly at room temperature. At low temperatures, the intensity of this PL peak observed in the R-phase, decreases gradually until it disappears around 100 K; its energy position, however, remains essentially the same between 300 K and 100 K. Below 100 K, both the O- and R-phase samples contain three peaks at approximately the same energies but with different relative intensities.

The temperature dependence of the PL in the range between 15 K and 300 K was also studied in pristine and photopolymerized C₆₀ films, and pressure-polymerized 50% O + 50% T (O+T) phase and another R-phase sample with about 20% interlayer bonding to form a three dimensional network (R+3D)[9]. A comparison of the room temperature PL spectra of all samples is shown in Fig. 3. The overall PL intensity in the R + 3D sample is weak compared to all other samples. However, it is interesting to note that R+3D phase also has a moderate PL peak at 1.75 eV which disappears at low temperatures, similar in behavior to the 2D-R phase PL peak discussed above. Although not as pronounced as in the R-phase samples, the PL spectra of O + T phase also contain a PL

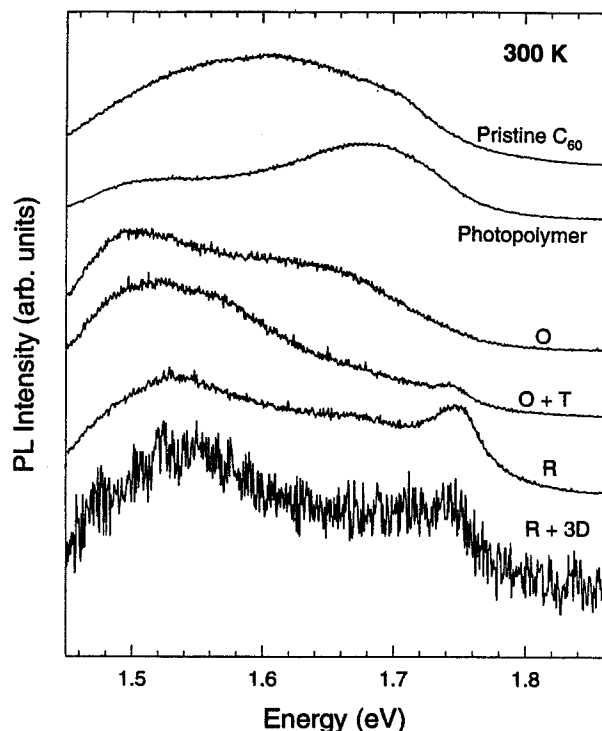


Fig. 3 Comparison of the room temperature PL spectra in pristine and photopolymerized C₆₀ films with several pressure-polymerized phases of solid C₆₀.

peak at ~ 1.75 eV. However, this peak in the O + T sample persists with almost the same intensity at all temperatures down to 30 K and a slight *increase* in intensity at 15 K. Therefore, PL spectra measured at room temperature *and* at a temperature below 100 K, could be used as a method of identifying the presence of O, R, or T phases in pressure-polymerized C₆₀ samples.

Lineshape analysis similar to the one shown in Figs. 1 and 2 for O- and R-phase polymers, has been performed on the PL spectra of pristine and photopolymerized C₆₀ films as well. In pristine C₆₀, the room temperature PL spectrum is best fit with three Gaussians while the 15 K PL spectrum reveals five or more better resolved peaks: the PL peak at 1.69 eV in the 15 K spectrum has been interpreted as the intrinsic emission from bulk C₆₀ and all other peaks are associated with X-traps.[10,11] The PL spectra of the photopolymer at all temperatures can be resolved into three Gaussian peaks. The larger widths of the PL transitions seen even at low temperatures in polymerized structures may be due to inhomogeneous broadening caused by the presence of defects and/or a distribution in the size of the polymer chains. It is worth noting that the Gaussians fitted to the 15 K PL spectra of the photopolymer, O, and R phase polymers are at roughly the same energy positions which show an overall redshift compared to the PL spectrum of pristine C₆₀. This trend is in agreement with a recent electronic structure calculation for the R-phase polymer[12], which predicts a 0.7 eV reduction in the fundamental energy gap.[12] A discussion of the details of the PL energy shifts in fullerene polymers compared to pristine C₆₀ and the correlations in the electronic properties of different polymeric phases will be presented.

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