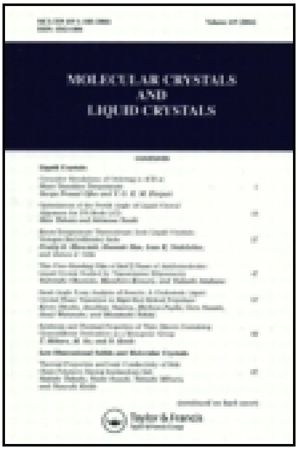

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Can Two-Dimensional Fullerene Polymers Be Intercalated?

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Can Two-Dimensional Fullerene Polymers Be Intercalated ?

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Two-dimensional C_{60} polymers can be produced by treatment at high T and high p. Attempts have previously been made to intercalate these layered materials by alkali metals using the gas phase method but the polymers have always decomposed. We investigate here whether intercalated 2D polymers can be formed by other methods, such as by polymerization in the presence of alkali metals. Preliminary x-ray and Raman data can be interpreted to indicate the presence of an alkali metal intercalated tetragonal fullerene polymeric structure.

Keywords: Tetragonal C_{60}; Alkali metal intercalation; High pressure; Raman scattering

INTRODUCTION

It is now well known that fullerenes such as C_{60} and C_{70} can be polymerized by radiation[1] or by treatment at combined high temperatures and high pressures[2-4]. While radiation polymerized material is usually structurally disordered, pressure polymerized C_{60} can under suitable conditions form well ordered structural phases where the C_{60} molecules are linked together through a [2+2] cycloadition mechanism to form linear chains (1D polymer) or planes (2D polymers). Two 2D polymerized phases are known, a tetragonal phase formed below 3 GPa and a rhombohedral phase formed above 4 GPa[3-5]. Since these materials contain stacked layers of strongly bound C_{60} molecules, intercalation of foreign atoms or molecules between these planes should be a definite possibility. 1D polymers can be obtained by either doping C_{60} with alkali metals or by treating C_{60} under pressure. The doped 1D polymer is a good metal, and an alkali metal doped 2D material should have interesting new properties. In fact, one 2D polymerized doped polymer, Na_4C_{60}, is already known but differs from the 2D polymers produced under pressure by having single bonds between molecular neighbours[6]. Several unsuccessful attempts to intercalate 2D pressure polymerized C_{60} by the gas phase method have already been reported[7], and we here discuss results obtained by this and other methods. Preliminary results indicate that 2D C_{60} polymers can indeed be intercalated while still retaining its polymeric structure.

EXPERIMENTS AND DISCUSSION

Polymerization under pressure

The tetragonal C_{60} polymer used as the starting material for our intercalation experiments at normal pressure was produced by treating sublimed, nominally 99.98% pure C_{60} for several hours at $T > 800$ K and $p > 2$ GPa. The temperature was always increased to the reaction temperature in the fcc phase before the final pressure increase to the reaction conditions in order to bypass the p-T zone where the orthorhombic phase is formed[8]. The polymer produced was characterized by Raman spectroscopy and x-ray diffraction which both indicated the presence of an almost pure tetragonal phase[8].

Intercalation of polymeric fullerenes at normal pressures

Fullerenes are easily intercalated by alkali metals such as K and Rb, which often donate electrons to the conduction band of the resulting compound. The most common method to insert alkali metals into carbon materials is to use gas phase transport in a two-bulb glass tube, where one bulb contains the host and the other molten metal. To avoid condensation of metal on the host the latter is usually kept at a higher temperature than the metal. Because the 2D polymers break down into molecular C_{60} at relatively low temperatures[2,4] it is difficult to find a temperature range where the metal vapour pressure is high enough for intercalation while still keeping the polymer intact. Previous experiments have shown that intercalation occurs but that the polymer breaks down to molecular form during the process such that the end products are non-polymeric intercalation compounds of the type A_nC_{60}[7]. We have attempted to use this method but our results agree with previous observations.

Graphite can also be intercalated by direct contact with liquid alkali metals. This "brute force" approach results in very rapid intercalation which allows little control over the result, but has the advantage that the temperature need not be raised above the melting point of the metal. We have therefore tried this method on a tetragonal polymeric sample. Again, Raman data indicate that intercalation occurs, but we have not yet been able to identify the phases formed and we cannot prove that the polymer structure remains intact.

Intercalation during polymerization

To complement attempts to intercalate the C_{60} polymer at zero pressure we have tried intercalating C_{60} during the polymerization process by premixing the C_{60} samples with either pieces of alkali metal or with alkali halide salts.

For technical reasons, the simplest way to include alkali metal ions with the C_{60} during the polymerization reaction is to use alkali metal salts which can be handled in air. However, most alkali metal salts have melting points under pressure that are comparable with the stability limit of C_{60}, and in order to bring down the melting point we have used a mixture of 65 at% RbCl with 35 at% CuCl which has a melting point near 150°C at zero pressure. The salts were mixed with C_{60} powder in a Rb/C_{60} ratio of 4:1 and reacted for 14 h at 2.5 GPa and 430 K. After the reaction Raman spectra showed a strong broadening of the H_g modes, indicating that intercalation had occurred and that the material was doped and "metallic". However, an XRD analysis was inconclusive and did not prove whether the polymer was still intact. Further experiments with a higher reaction temperature gave similar results.

The obvious alternative to this procedure is to include pure alkali metals with the C_{60} sample during intercalation. 2D polymerization of C_{60} occurs at pressures and temperatures above the melting line of K[9], and any K in contact with the C_{60} sample should thus be liquid and easily diffuse into the lattice during polymerization under pressure. We have also carried out experiments of this type, mixing the C_{60} sample with fine pieces of K metal under Ar in the atomic ratio 1:3 before filling the pressure capsule. High pressure treatment was carried out under conditions similar to those mentioned above, i.e. 770-825 K at 2.5 GPa for 12-16 h.

After treatment, direct resistance measurements under Ar showed that the resistance was at least six orders of magnitude lower than for the pure tetragonal phase under similar conditions. The Raman spectrum of one sample

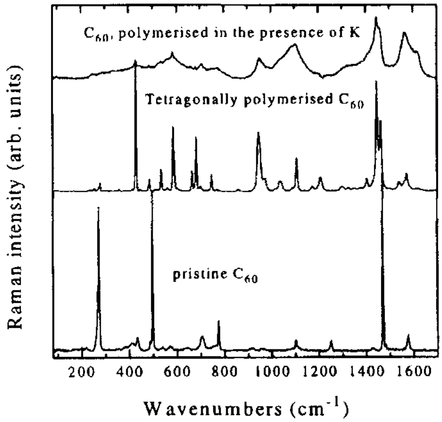

FIGURE 1 Raman spectra of pristine, tetragonal, and K doped C_{60} obtained using Ar^+-ion laser excitation.

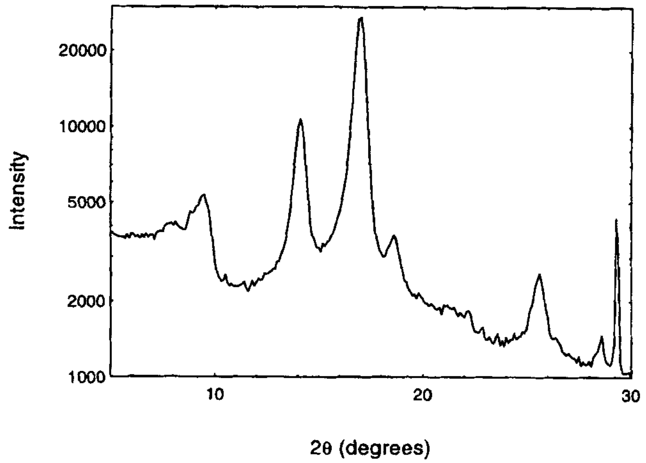

FIGURE 2 X-ray diffraction diagram for a K doped specimen. The sharp peak near 29.5° is believed to be due to an impurity.

treated in this way is shown in Figure 1, together with Raman spectra of pristine C_{60} and of a tetragonal polymer specimen. The Raman spectrum of the tetragonal phase shows a number of typical features, such as a doublet at 742 and 748 cm^{-1}, (weak) intermolecular modes at 139 and 154 cm^{-1}, modes around 950 cm^{-1} characteristic for the intermolecular four-carbon rings, a strong enhancement of the $H_g(2)$ mode near 430 cm^{-1} and a characteristic shift of the $A_g(2)$ mode to 1463 and 1447 cm^{-1}. The spectrum of the doped material still shows these features but also clear features of doping, such as a larger downshift of the $A_g(2)$ mode indicating charge transfer and very broad H_g peaks possibly arising from a strong electron-phonon interaction[10].

A second sample treated under similar, but not identical, conditions was studied by X-ray diffraction with the results shown in Figure 2. (For the first sample, X-ray diffraction gave similar results but with a much lower signal-to-noise ratio.) The diagram is very different from diagrams obtained for either pristine or tetragonal C_{60}. We expect that intercalation of the tetragonal phase would expand its c-axis lattice parameter[8] c = 15.04 Å but leave the in-plane parameter[8] a = 9.10 Å basically unchanged. An analysis of the peaks in Figure 2 shows that their positions are, in fact, compatible with a tetragonal structure with a = 9.2 ± 0.3 Å and c = 17.0 ± 0.4 Å, indicating that the latter has increased by about 13 % on intercalation. We see no Raman or XRD peaks that can clearly be attributed to undoped cubic or tetragonal C_{60} (except for (*hk0*) lines), which suggests (but does not prove) we have a single phase sample.

We conclude that there are strong indications that polymerization of C_{60} under pressure in the presence of K metal can result in the production of intercalated tetragonal C_{60} containing K ions, although we have not yet found the exact composition of the samples. As expected, the new compound is metallic. However, there is a small possibility that the materials consist of mixed phases, with an intercalated phase co-existing with an undoped fullerene polymer phase and further studies are necessary to find out whether we have indeed produced an intercalated 2D fullerene polymer.

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