MODIFICATION OF HEXAGONAL PHASE [C60]FULLERITE

E.V. Skokan (1), I.V. Arkhangelsky(1), N.B.Tamm, N.V. Chelovskaya(1), M.M. Nikulin(1), V.M. Senyavin(1), V.A. Davydov(2), A.V. Rakhmanina(2), V.N. Agafonov (3)

(1) M.V. Lomonosov Moscow State University, Chemistry Department, 119992 Moscow, Russia
(2) L.F. Vereshagin Institute of High Pressure Physics, 142092 Troitsk, Moscow area, Russia
(3) F. Rable University, 37200 Tours, France

Introduction

The [60] fullerite exists as a stable cubic (fcc) and hexagonal close-packed (hcp) modification, the hcp being metastable with respect to the fcc. For this reason, the synthesis of hcp modification and its derivatives is not a simple task [1]. Since coordination spheres, packing modes, and orientation of molecules in the hcp and fcc crystals are different, one would expect essential differences in properties of their derivatives, for example, polymers and intercalation products.

By now, polymerization of fcc [60]fullerite under high temperatures and pressures is studied rather well [2]. The structures, properties of polymers, and conditions of their formation, were established. However, the polymerization process might be different, if metastable hexagonal modification of [60]fullerite was used as initial material.

In this work, the hcp [60]fullerite was polymerized under high pressures and temperatures, the properties of the products were studied and compared with the properties of the fcc-based polymers.

According to the deformation theory, two-layered hexagonal structure can be transformed into three-layered cubic structure (phase transition) upon compression. Experimental data supported this statement. Really, it was established that uniaxial or any tangential loads resulted in the hcp-fcc phase transition, while no transition was observed under hydrostatic pressure. This makes it evident that optimal compression conditions should be found to perform high-pressure polymerization.

Experimental

The initial sample of [60]fullerite was obtained by the cryochemical extraction method; it contained 95 % of hcp modification.

Polymers were synthesized in "toroid" high-pressure chambers under quasihyrostatic and hydrostatic pressure in wide intervals of pressure (1.2-5.5GPa) and temperature (100-600 °C). The samples were studied using X-ray diffraction, IR spectroscopy, and DSC methods.

The structure of the obtained polymers was other than that of polymers synthesized on the basis of cubic [60] fullerite under similar conditions.

Results and discussion

According to X-ray analysis, the samples obtained under quasihydrostatic and hydrostatic pressure were different. In the case of quasihydrostatric pressure, polymerization was accompanied with the hcp-fcc phase transition; therefore, only hydrostatic compression was used in our experiments.

The samples with different phase composition were obtained under the pressure of 2.1 GPa and temperatures of 170, 200, 300 and 400 ^{o}C.

The samples obtained at 170^{o}C retained hcp structure but with reduced lattice parameters: a=0.9894 nm, c=1.6147 nm compared to a=1.002 nm, c= 1.638 nm for the initial hcp modification. The IR spectrum of this sample was found to be identical to the spectrum of dimer obtained from fcc modification of [60] fullerite.

The DSC study revealed that the hcp-based polymer depolymerizes; the maximum of the depolymerization effect was equal to 190^{o}C, and its enthalpy, to 8 kJ/mol that is close to the values obtained for the fcc-based dimer. These data unambiguously evidenced the formation of dimeric phase with the hcp structure. The content of dimer in the samples was estimated from the IR spectral data.

When the synthesis temperature was increased to 200°C, noticeable distortion of the hcp structure was observed. The X-ray diffraction analysis showed that the samples obtained at 300 °C and 400 °C are closely allied structurally. Their DSC curves are similar: they revealed one irreversible effect with maximum at 250 °C corresponding to depolymerization.

A comparison between the IR spectra of the samples synthesized in this work and the spectra of high-pressure phase obtained from cubic [60] fullerite indicated that the studied samples are low oligomers with different structures.

Depolymerization of high-pressure phases was found to be kinetically delayed process; at heating rate of 10 K/min, depolymerization can not be completed until 550 °C. The depolymerization product contained initial hcp modification.

Acknowledgment

This work was supported by the Russian Foundation for Basic Researches, project nos. 04-03-32783 and 03-03-32640.

Refereces

1. Arkhangel’skii I., Skokan E., Velikodnyi Yu., Chernyshev V., Sidorov L. Synthesis of Hexagonal Close-Packed Phase of [C60] fullerite. Doklady Acad. Nauk, 1998, v. 363, no. 4-6, p.413-415.
2. Davydov V., Kashevarova L., Rachmanina A., Dzyabchenko A., Senyavin V., Agafonov V., High-Pressure Polymeric Phase of [C60]Fullerite: Synthesis, Identification, Properties, Zh. Phys. Khem (Russian), 2001, v. XLV, no. 4, p.23-34.