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Structure investigations of radiation-modified polymers Polyethylene and Polymethylmethacrylate

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Abstract

Polyethylene and polymethylmethacrylate were irradiated with intense beam of high-energy electrons or with 'white' beam of synchrotron radiation with different doses. Results of changes in structure after irradiation *ex situ* and *in situ* during heating up to melting point for polyethylene are presented using synchrotron radiation X-Ray diffraction. Measurements were performed using SR from the VEPP-3 storage ring

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1. Introduction

The intense electron beam can modify structure and properties of inorganic or organic materials, crystal or amorphous. Ionizing radiation affect on polymer materials in different ways, such as introduction of defects into the crystal structure, breaking the bonds in polymers, that in turn can lead to formation of another bonds in the structure and modify mechanical or physical-chemical (such as solubility etc.) properties of polymer materials, Forgács et al. (1981), Nazmov et al. (2000), Nazmov et al. (2001), Nazmov et al. (2002), Nazmov et al. (2011).

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The structure of polyethylene -(-CH_2-CH_2-)$_n$- consist of zigzag chains of carbon atoms, each of them is connected with two hydrogen atoms. Usually chains tend to form crystalline domains with amorphous surrounding. Crystal structure of polyethylene, Bunn (1945), has orthorhombic symmetry with the space group Pnam (#62), with lattice parameters a=7.41Å; b=4.94Å; c=2.55Å. Polymer chains extend along c-axis in the crystal and each unit cell consists of one formula unit -(-CH_2-CH_2-)$_n$- and contain two perpendicularly zigzagged chains (see the figure 1a).

Structure of polymethylmethacrylate -(-CH_2-C(-CH_3)(-CO-O-CH_3)-)$_n$-is more complicated: each second carbon atom in the chain is bonded both with (-CH_3) and (-CO-O-CH_3) groups. This polymer tends to form amorphous structure (see the figure 1b).

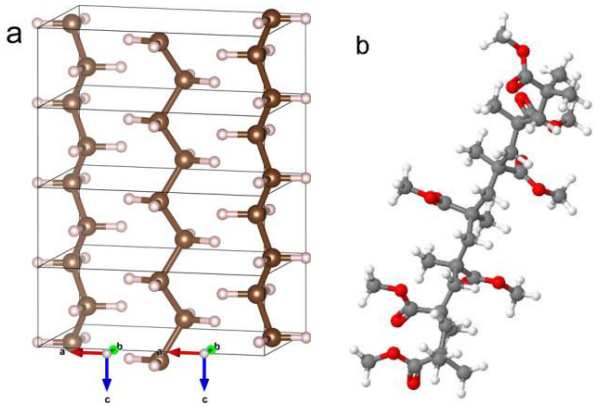

Fig. 1. (a) crystal structure of polyethylene; (b) molecular structure of polymethylmethacrylate.

The irradiation causes two oppositely going processes in the polymers - breaking and crosslinking of the chains, Industrial radiation Processing, 2011. The crosslinking (to a three-dimensional network) prevails in polyethylene resulting in mechanical properties changing. The polymethylmethacrylate demonstrates scissioning prevailing, that property can be useful for artificial creating of microstructures in polymethylmethacrylate, Mohr et al. (1988).

In order to understand the nature of changes of polymers properties, it is necessary to study the changes in local structure after irradiation. The most direct way is to investigate the structure changes with using X-ray diffraction method, especially synchrotron radiation XRD, as the X-Ray scattering on light elements is not intense enough.

2. Experiment

LDPE (Low Density Polyethylene) and GS233 polymethylmethacrylate samples having thicknesses of ~1 and 0.57 mm respectively were tested. The samples of polyethylene were subjected to electron beam treatment with doses of 2, 4, 6, 8, 16 and 40 kGy at room ambient conditions (temperature and pressure). The electron beam was generated by ILU-6 electron accelerator (located in BINP SB RAS, Novosibirsk, Russia), beam parameters were as follows: electron energy of 2.4 MeV, pulse beam current of 320 mA, pulse duration of 0.6 ms, pulse repetition rate of 2 Hz, underbeam transportation velocity of 2 cm/s. The absorbed dose was determined by number of underbeam passages, during one pass sample got the dose 2 kGy during approximately 4-5 seconds under outlet port. The samples temperature was kept below 35ºC to avoid structural changes caused by temperature increase. Time between passing during radiation treatment was not less then 30-40 seconds.

The polymethylmethacrylate samples were irradiated with doses of ~0.6, 1.2, 2.4 and 4.8 MGy; 1 and 2 kGy by 'white' beam of X-Rays at the LIGA experimental station located at the 0th beamline of VEPP-3 storage ring in BINP SB RAS, Goldenberg et al. (2016). Aluminum foil having thickness of 0.6 mm was used to decrease sample's heating during X-Ray irradiation, so the majority (about 90%) of the X-Ray photons had energy 12-30keV.

Ex situ investigations of polymers structure changes in XRD experiments were carried out at the experimental station on the 4th beamline of VEPP-3 storage ring in BINP SB RAS (Ancharov et al. 2001, Levichev 2016). X-rays