

Study of structural changes in irradiated polycarbonate by positron annihilation spectroscopy, NMR spectroscopy and nanoindentation

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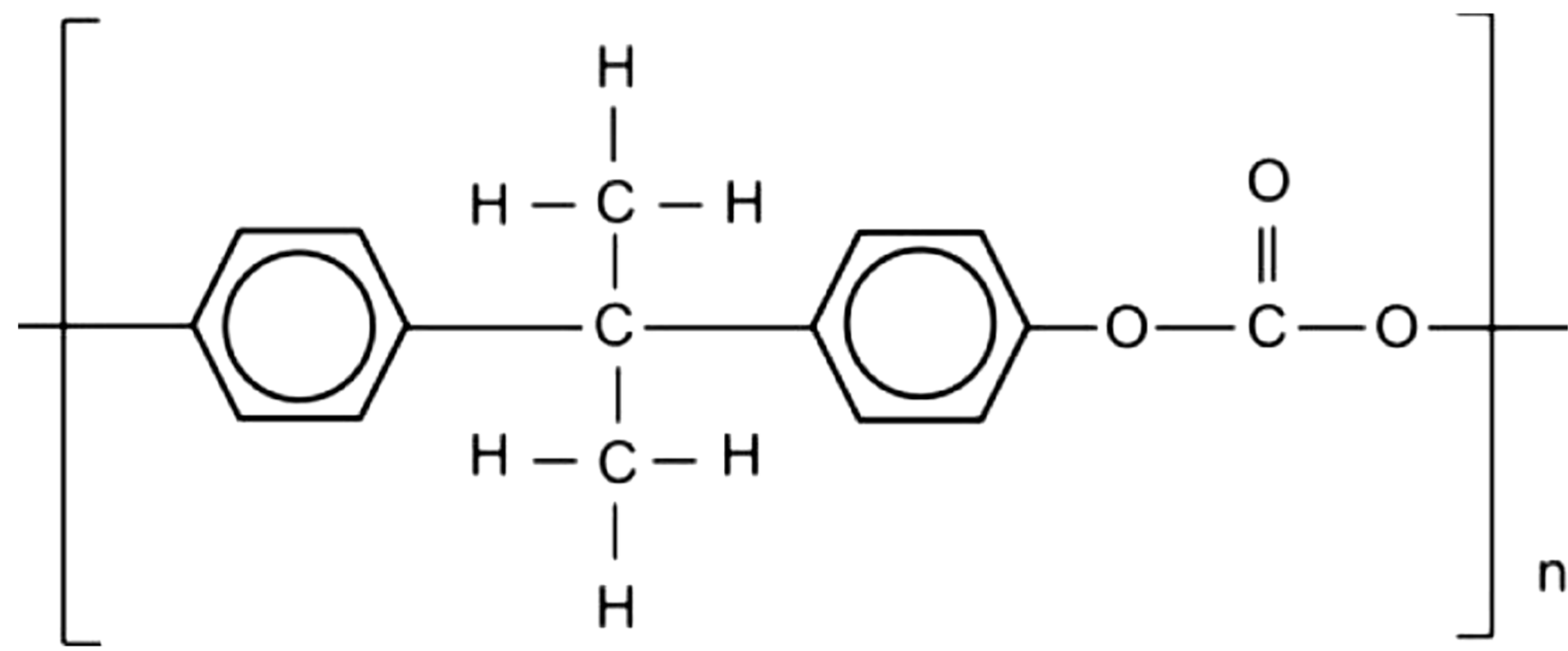


Figure 1: The molecular scheme of polycarbonate made from bisphenol A.

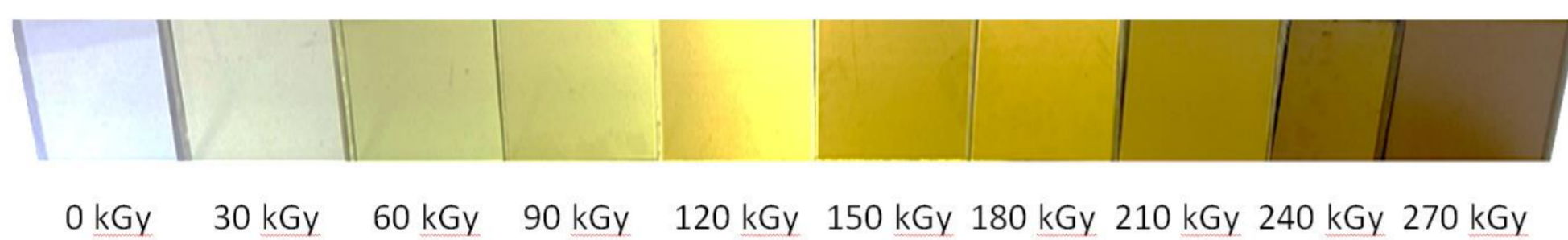


Figure 2: The colorization of polycarbonate after irradiation by different doses of gamma radiation.

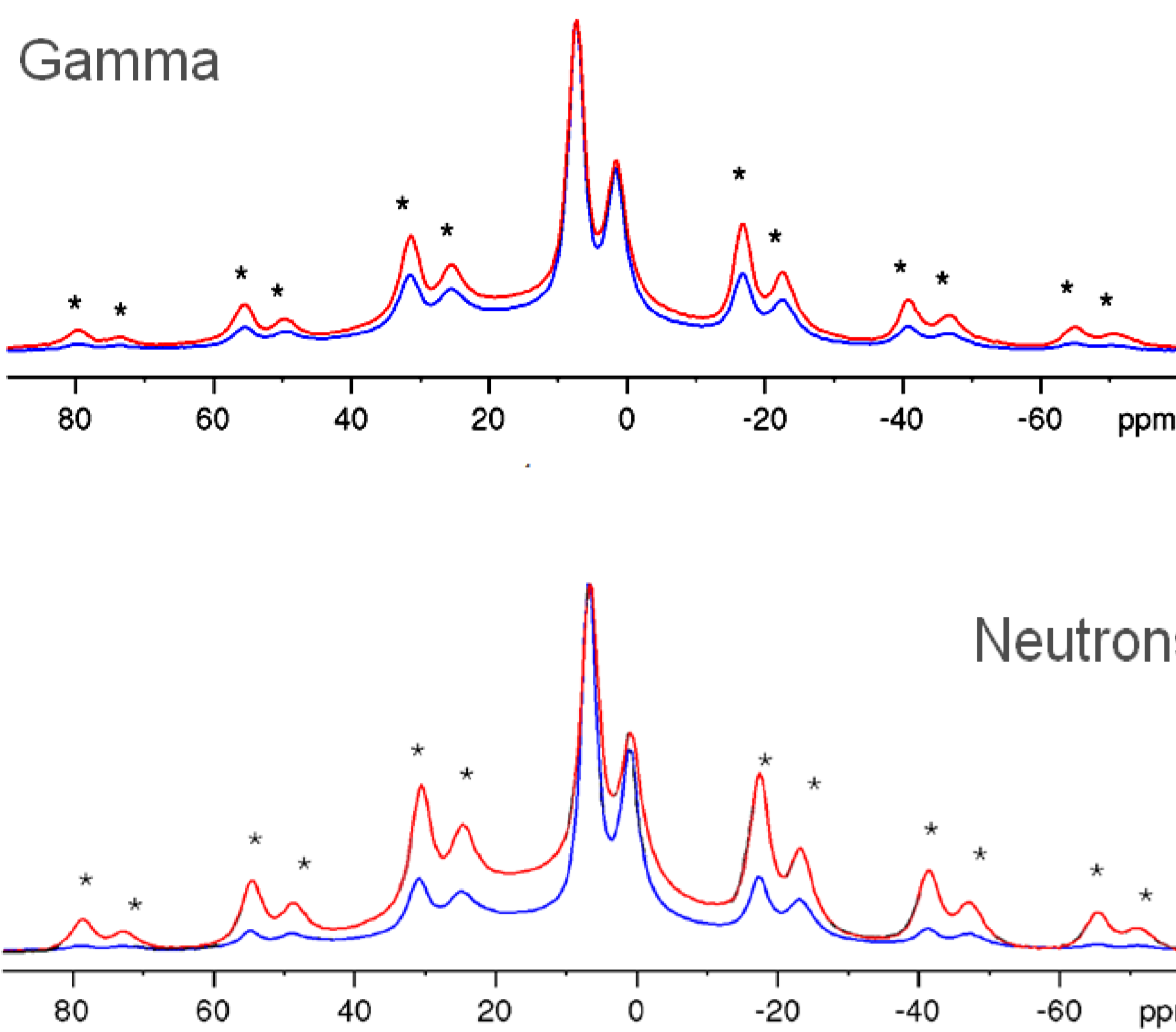


Figure 3: Single-pulse ¹H MAS 12 kHz spectra of non-irradiated (red) and irradiated polycarbonate (100 kGy, blue), scaled for matching the maximal intensities. Top: gamma-irradiated sample, Bottom: reactor-irradiated sample. Asterisks mark Spinning Side Bands (SSB).

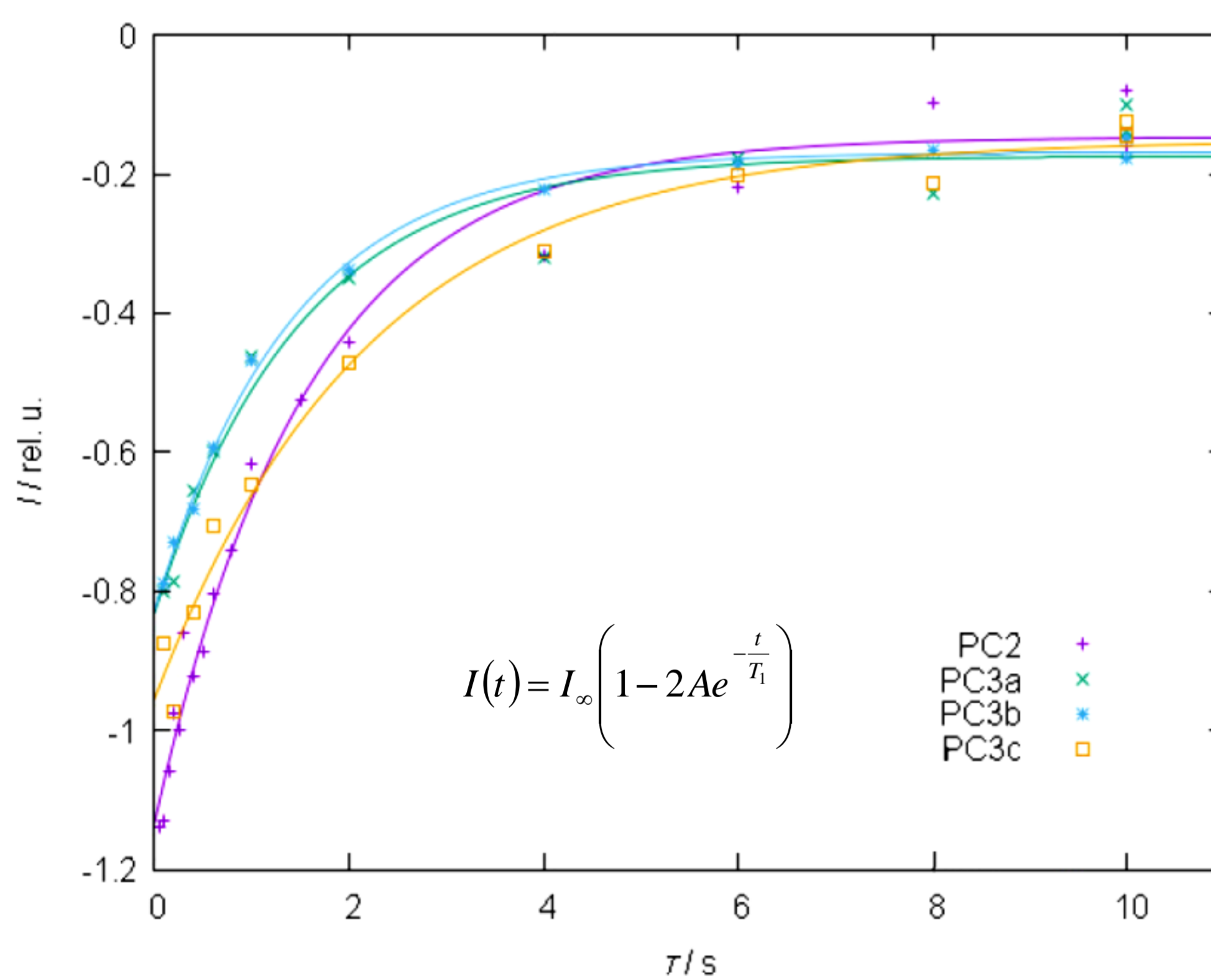


Figure 4: ¹³C CP MAS inversion recovery with the delay t between the pulses. Cumulated integral intensities of carbons 3 and 10 together with their fits by exponential function. After irradiation, a shortening of relaxation times for quaternary carbons at position 6 (to which the two methyl groups are attached) was observed. The original ¹³C $T_1 = 7.0$ s of the pristine PC decreased to 3.5 s and to 4.1 s after irradiation by ⁶⁰Co and LVR-15, respectively. On the other hand, the relaxation enhancement is not significant for other carbon nuclei. Therefore, we expect that paramagnetic radicals that accelerate the relaxation processes are formed, but only at a relatively low concentration.

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Polycarbonate (PC) shown in Figure 1 is a polyester of carbonic acid, which is produced by the gradual polymerization of Bisphenol A with phosgene. It is a transparent polymer with a large index of refraction ($n = 1.584$) and a large light transmission (at least 80% transmittance for 10 mm thick plate). It reacts to irradiation by changing the optical density. The changes first occur predominantly in the UV region of the spectrum (10 - 380 nm), for higher doses they extend into the visible region (380 - 760 nm) - Figure 2. The determination of dosimetrically monitored changes is carried out by spectrophotometry.

For the dosimetry of high doses of neutron and gamma radiation, the change in optical density is an easily and inexpensively measurable parameter. It can be used even in the field, using a handheld portable densitometer. Therefore, the use of solid-state organic radiochromic dosimeters is much easier than using alanine or gel dosimeters, which require very time-consuming and costly laboratory methods (electron paramagnetic resonance or nuclear magnetic resonance) for their evaluation.

The aim of this work is to investigate the possibilities of replacing the above-mentioned costly methods of evaluation, by about two orders of magnitude less expensive optical densitometry, which will provide the necessary results in minutes, either through a desktop scanner or even a portable hand densitometer.

In this study we focused on (i) radiation-induced changes in the material at the molecular level, by methods of nuclear magnetic resonance (NMR) spectroscopy and positron annihilation spectroscopy (PAS) (ii) changes in the mechanical properties of polycarbonate after irradiation with different doses, utilizing tensile tests and nanoindentation.

All tested PC samples were cut by a diamond disc from MAKROCLEAR polycarbonate sheets (Omniplast). In order to compare response of PC on different type of radiation PC samples were irradiated in two facilities:

(i) a gamma ray irradiation facility equipped with a ⁶⁰Co radioisotope source with a high activity of 200 TBq. Decay of ⁶⁰Co radioisotope is accompanied by emission of gamma rays with energies of 1.173 and 1.333 MeV. PC samples were irradiated in the ⁶⁰Co irradiation facility for a short time periods (hours to days). Irradiation was performed to various doses gradually increasing from 0 to 1000 kGy. All doses were measured by certified method using alanine dosimeters, with a total uncertainty of 3%.

(ii) the research nuclear reactor LVR15. Samples in the reactor were irradiated in a mixed field of neutrons (continuous energy spectrum from epithermal to fast) and gamma rays. Approximately 70% of dose is caused by neutrons and 30% by gamma ray. During irradiation in the nuclear reactor the samples heat up rapidly, so irradiation has been performed only up to doses of approx. 100 kGy. All doses were measured by certified method using alanine dosimeters, with a total uncertainty of 3%. The ratio of doses from neutrons and photons was determined using neutron activation analysis with an uncertainty in the range of 5% - 10%.

The changes observed in ¹H and ¹³C using NMR spectroscopy indicate that the irradiation of PC with a dose of 100 kGy causes higher mobility of the molecules - Figure 3. It means that the polymers are cleaved into shorter chains. In addition, radicals are formed - Figure 4.

Positron annihilation spectroscopy further revealed that at a dose of 200 kGy the material undergoes structural changes in the form of cross-linking. This can be facilitated by the decomposition of the polymer to form radicals, which at also facilitates crosslinking into more branched structures. While the destructive effect is dominating for neutrons (forming substantial part of the reactor radiation), the cross-linking is more efficient in the case of the gamma radiation - Figure 5.

Repeated measurements performed after 40 days demonstrated the material's ability to partially regenerate its radiation damage and recombine radiation-induced free radicals - Figure 6. However, the material will never return to the initial state after such a high dose of radiation, which fully corresponds to the results of observations by optical absorption spectroscopy.

The observed disintegration and subsequent reconnection of the polymer chains correspond well with the relatively wild oscillations of the mechanical parameters, indicated by the nanoindentation within the indicated dose range - Figure 7.

Future studies will be aimed on the methods of proton beams dosimetry.

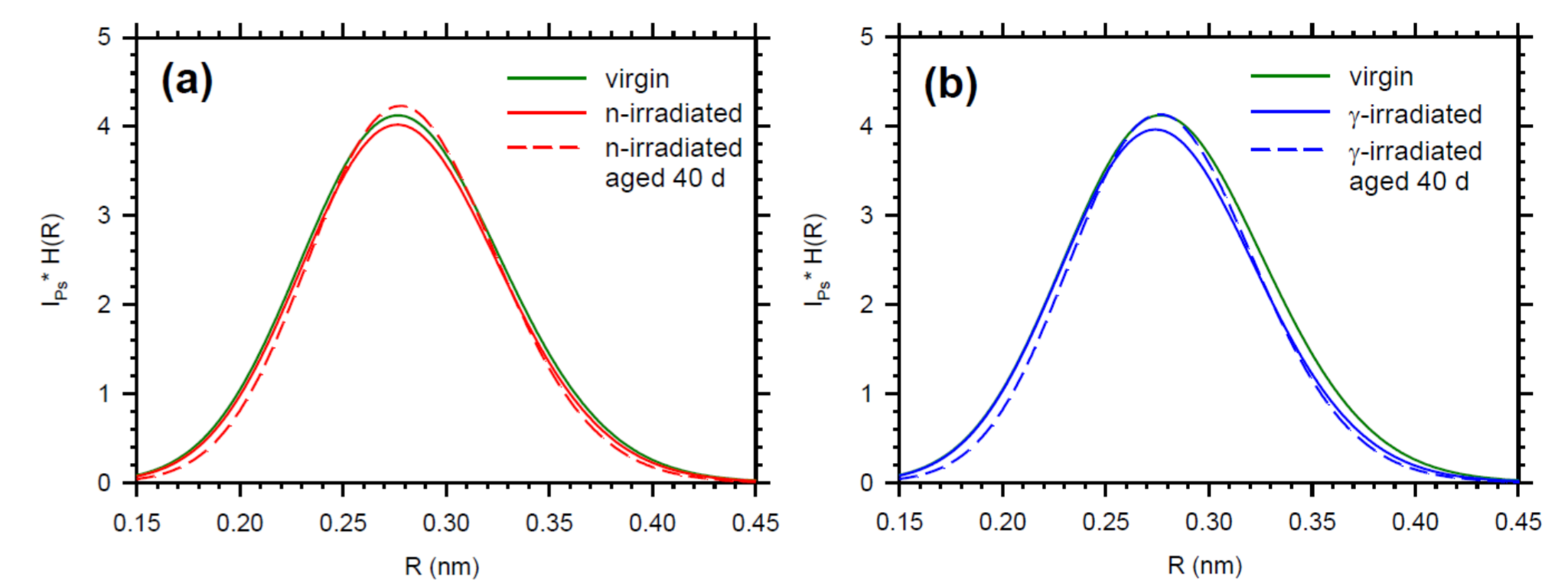


Figure 5: Comparison of the size distribution of free volumes $H(R)$ multiplied by the intensity I_{Ps} of the Ps contribution: (a) the sample irradiated with neutrons and gamma-rays in the nuclear reactor, (b) the sample irradiated with ⁶⁰Co gamma-rays.

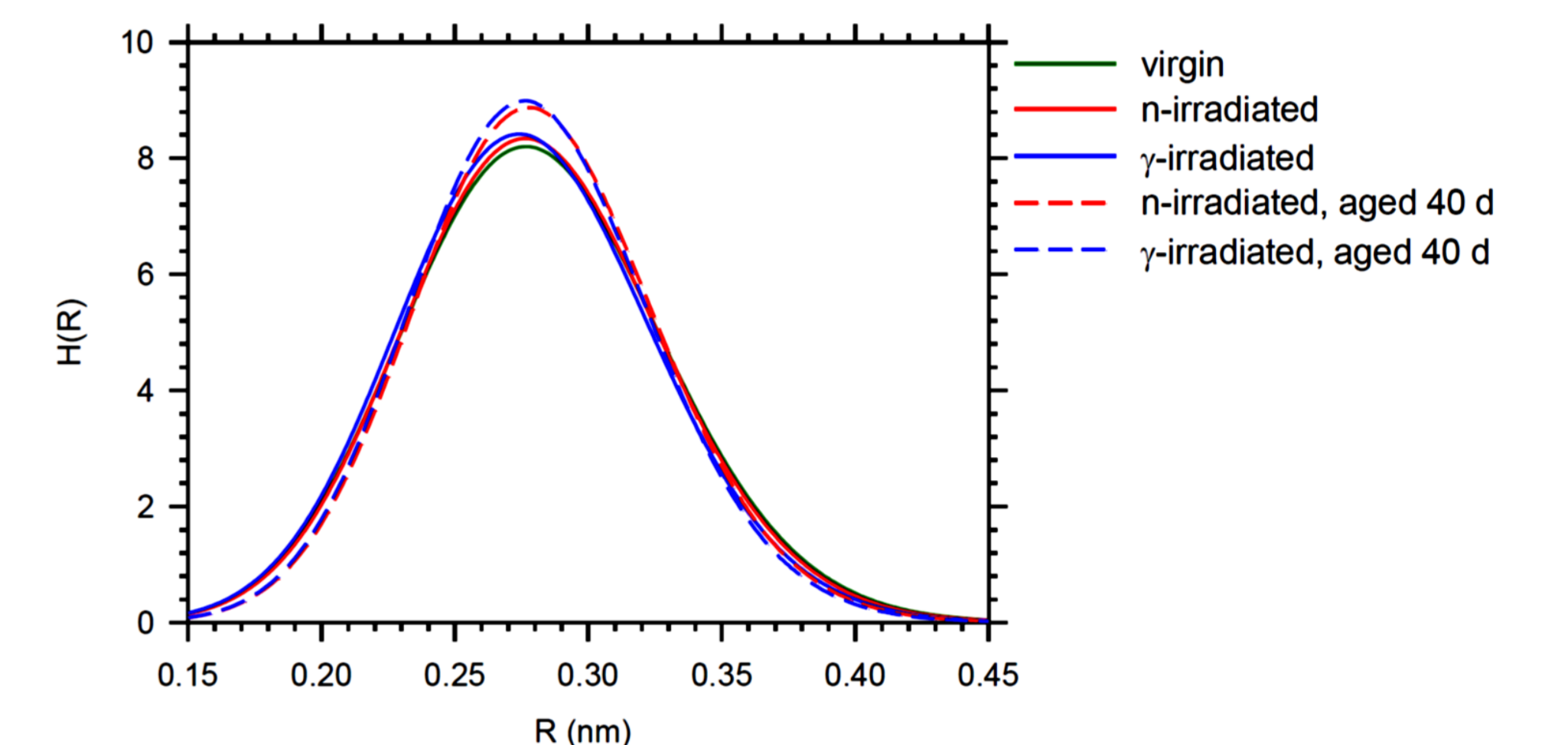


Figure 6: Size distribution (radii R) of free volumes in the initial sample, shortly after irradiation at the dose of 200 kGy and after subsequent aging of samples for 40 days at room temperature.

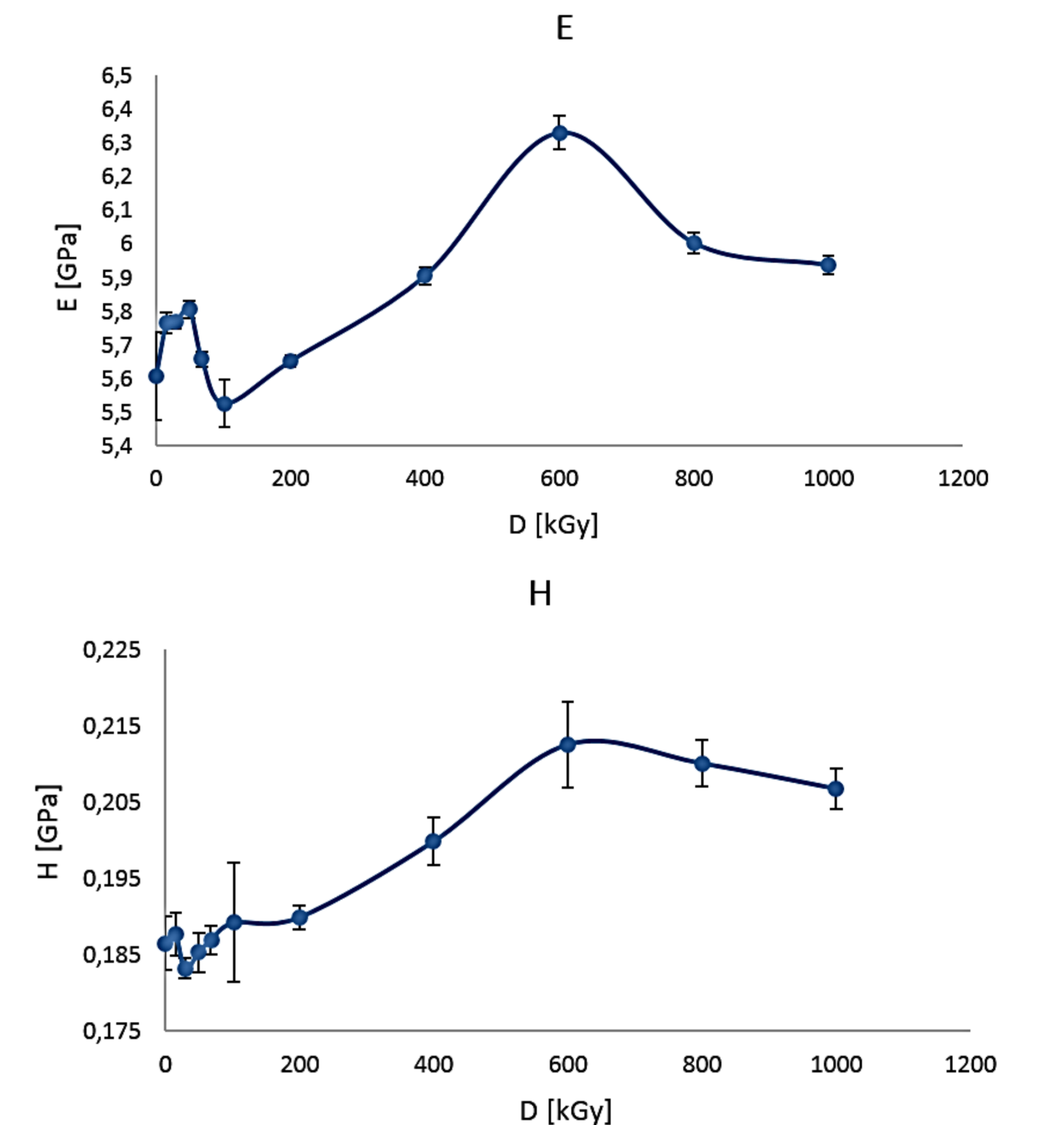


Figure 7: The results of nanoindentation of irradiated PC. Young's modulus E (top panel) and hardness H (bottom panel) as a function of ⁶⁰Co gamma ray dose.

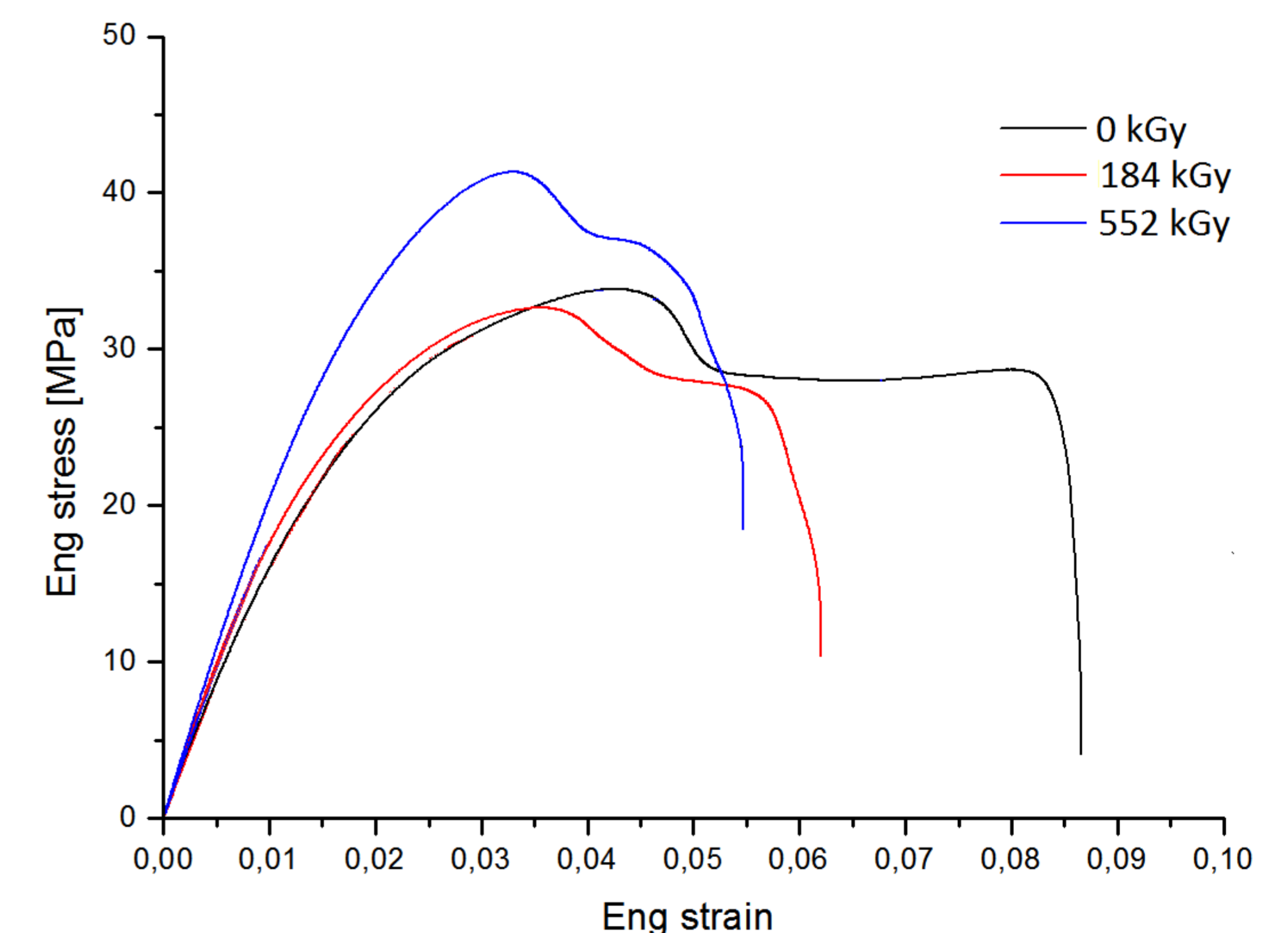


Figure 8: Engineering stress-strain curves of the non-irradiated and irradiated polycarbonate. The tests were performed with a constant extension rate of 2 mm/min; engineering stress is calculated as the applied load divided by the original cross-sectional area of a material and engineering strain is the amount that a material deforms per unit length during a tensile test.