

earlier observed in a similar system [4]. Anisotropic doublet with similar EPR parameters was observed in gamma-irradiated H-Y/ ^{13}C O zeolite

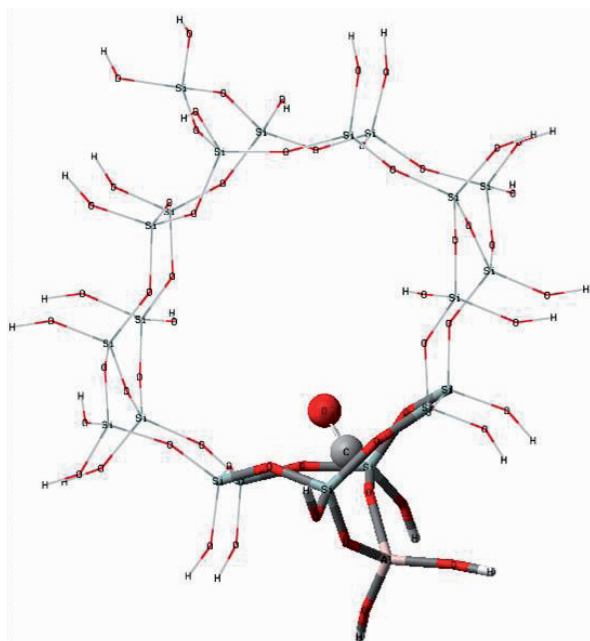


Fig.2. $^{13}\text{CO}^+$ radical situated in H-ZSM-5 lattice (structure I).

by Vedrine and Naccache [5] and assigned to $^{13}\text{CO}^+$ radical cation. As a working hypothesis, we assumed that anisotropic doublet A represents $^{13}\text{CO}^+$ interacting with zeolite framework, whereas the isotropic doublet is a spectrum of freely rotating radical. We applied DFT calculation to test that hypothesis.

We optimized two structures: the first one with $^{13}\text{CO}^+$ radical cation located close to zeolite lattice (Table). Fermi constant coupling value [mT] for structures I and II.

Basis set	DGDZVP	DG2CF	TZVP	IGLO-III
Structure I	25.84	24.64	27.34	27.0
Structure II	25.82	24.83	27.49	27.12

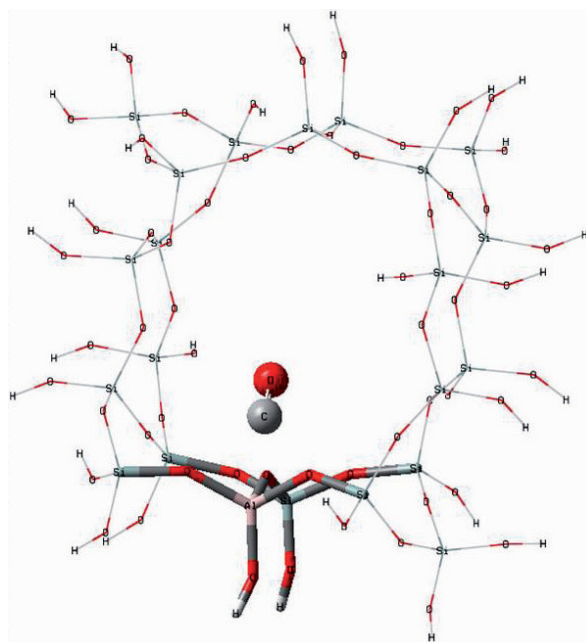


Fig.3. $^{13}\text{CO}^+$ radical situated in H-ZSM-5 lattice (structure II).

(Fig.2) and the second one with $^{13}\text{CO}^+$ at a distant site interacting weaker with lattice nuclei (Fig.3). We expected that those two structures would correspond to the EPR doublets A and B. Unexpectedly, for both sites we received very similar values for ^{13}C hyperfine splitting (Table). Those values are in very good agreement with the experimental value for signal A. That allowed us to assign univocally signal A to $^{13}\text{CO}^+$ radical cation. However, the isotropic signal B remains unidentified.

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RADIATION-INDUCED EFFECTS IN SEGMENTED POLYURETHANES

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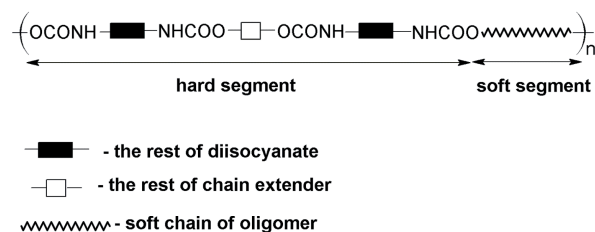
The purpose of the presented study was to investigate the effect of ionizing radiation on selected physicochemical properties of segmented polyurethane (PU). Polyurethane was characterized by electron paramagnetic resonance (EPR), measurement of dynamic contact angle and investigation of thermal and mechanical properties. The results obtained by these techniques revealed an insignificant influence of radiation on the structure and features of investigated polymer up to 112 kGy. Thus, it was confirmed that upon exposition to a sterilization dose of about 25 kGy polyurethane does not change chemical and mechanical properties.

Polymeric materials used in medicine as biomaterials for the fabrication of medical devices and tissue engineering scaffolds have to fulfil many requirements [1]. Firstly, they ought to possess good mechanical and physical properties, be reproducible and should not change properties upon processing and sterilization. Secondly, they should not induce adverse inflammatory reaction, be toxic and carcinogenic. This requires adequate control of implant properties (such as degradation rate and mechanical strength) and creating optimal conditions for cell survival, proliferation, and subsequent tissue formation. Among the known methods of sterilization, two of them are recommended for

polymer biomaterials: radiation sterilization and chemical treatment using ethylene oxide as a sterilization agent. On the other hand, the polymers might be also exposed to ionizing radiation to improve their properties.

Biomedical polyurethanes are used in a broad range of applications. Because of their excellent mechanical properties and biocompatibility, they have been frequently used in the medical devices as blood contacting materials, such as artificial heart, catheters and mammary implants [2].

Segmented polyurethane (Scheme 1) based on poly(1,4-butylene adipate)diol end-capped by -OH group (PBA) of molecular weight MW = 1000,

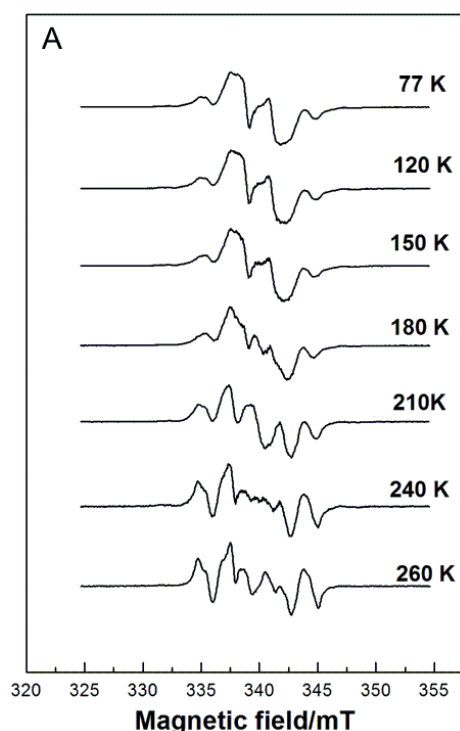


Scheme 1. Structure of segmented polyurethane.

isophorone diisocyanate (IPDI) and 1,4-butanediol (BDO) were synthesized in bulk by a two-step reaction. The weight ratio between hard and soft segment was 30:70. A polycondensation process was carried out without catalyst.

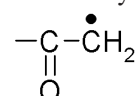
Segmented polyurethane samples were irradiated at ambient temperature with a high energy electron beam generated in a linear electron accelerator Elektronika 10/10 to a dose of 112 kGy.

The polymer studied by the EPR method was irradiated by gamma rays in a ^{60}Co source Issledovatel (dose rate 1.036 kGy/h) at 77 K. EPR spectra were recorded using a Bruker ESP 300 spectrometer with rectangular cavity TE 102.



The contact angle was measured with a tensiometer K100C (Krüss) by using the Wilhelmy method. The mechanical properties: tensile stress and elongation at break were measured using an Instron 3366 machine, according to PN-EN ISO 527-1:1998 technical standard.

The EPR studies were carried out under cryogenic conditions since the radicals generated at ambient temperature were unstable and decay fast to diamagnetic species. The spectra of PU (Fig.1) detected after irradiation with a dose of 6 kGy show predominantly triplet of hyperfine splitting about 1.3 mT (hfs). Character of the signal suggests an interaction between unpaired electron and hydrogen atoms. It seems that the radical centre is situated in α position towards -CO groups (Scheme 2) as such a type of intermediate is stabilized by neighbouring double bond by resonance.



Scheme 2. The most probable radical.

Upon thermal annealing, the polyurethane spectrum is converted to a signal similar to that detected for diol oligomers (PBA). The influence of hard segments on radiation-induced processes is less significant, thus the soft domains determine the microscopic effects of irradiation.

It was found that ionizing radiation increases the value of dynamic contact angle measured in water (Fig.2). It was expected that the contact angle ought to decrease after irradiation since ionizing radiation induces formation of polar groups, *e.g.* hydroxyls, carbonyls and carboxyls. However, it was found that irradiated PU is slightly more hydrophobic than non-irradiated one. It seems that hydrophobic soft segment domains migrate towards

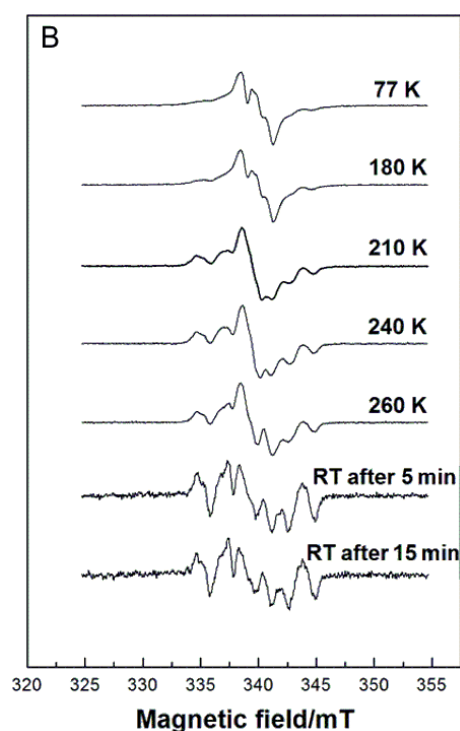


Fig.1. EPR spectra of PBA (A) and PU (B) upon irradiation with a dose of 6.0 kGy under cryogenic conditions and gradual annealing to indicated temperatures.

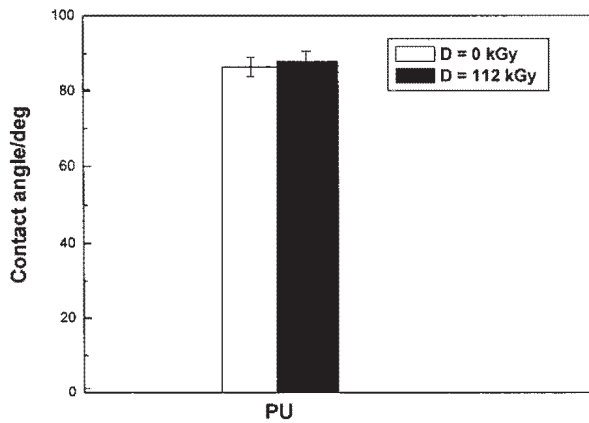
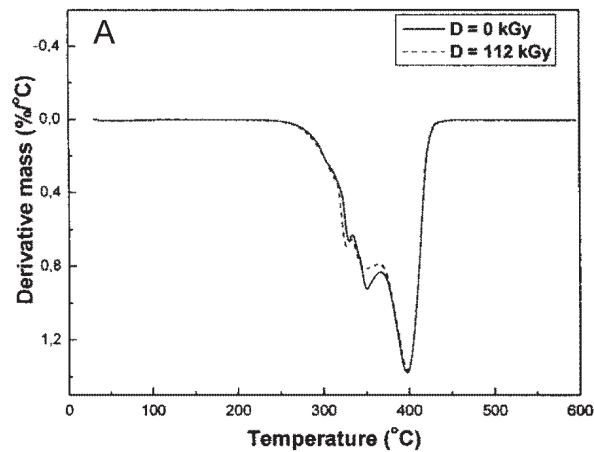


Fig.2. Dynamic contact angle vs. water.

surface. This phenomenon was earlier observed by Górna and Gogolewski [3].

Thermal properties of PU were investigated upon exposure to ionizing radiation by differen-



The thermogravimetric analysis revealed that the polymer is slightly more stable before than after irradiation with a dose of 112 kGy. Polyurethane remains thermally resistant up to 270°C and above this temperature the first stage of decomposition is observed. Character of thermograms points out for a multi-stage mechanism of the decomposition.

On the basis of the mechanical measurements, it was found that the irradiation with a dose twice higher than the sterilization dose has insignificant influence on mechanical properties of the investigated polyurethane. After irradiation, a small reduction of tensile stress was revealed and practically the same value of elongation at break as for the neat sample (Fig.4).

Polymers for biomedical applications might be exposed to ionizing radiation to carry out sterilization and/or to improve their properties. Irradiation affects physicochemical and mechanical properties of polymers leading usually to crosslinking and/or

Fig.3. DTG (A) and DSC (B) thermograms of PU before and after irradiation with a dose of 112 kGy.

tial scanning calorimetry (DSC) and thermogravimetric analysis (TGA), (Fig.3).

degradation. Segmented polyurethane is radiation stable at least up to 112 kGy as such a dose has a

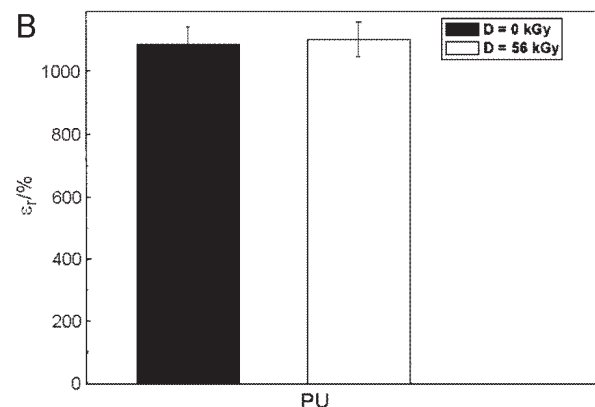
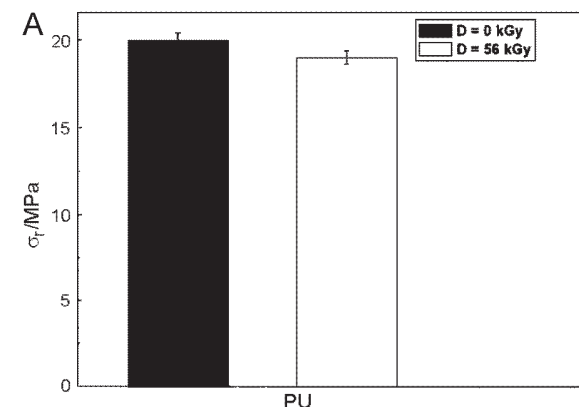


Fig.4. Tensile stress (A) and elongation at break (B) of polyurethane before and after irradiation.

The DSC studies showed that glass transition of the soft segment chains were observed at -31.3°C and -32.4°C for neat and irradiated polyurethane, respectively. The endothermic peaks that correspond to the melting transition of the hard segment were observed at 100.1°C and 111.0°C, respectively for non-irradiated and irradiated PU. The significant enhancement of temperature results from crosslinking of polyurethane initiated by ionizing radiation.

small impact on changes in properties of investigated polyurethane.

References

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