

## SELECTION OF POLYMER MATRICES FOR RADIATION GRAFTING

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Development of the chemical industry, purification and concentration of valuable materials in dilute solution, or difficult separation system have become important research topic. On the other hand, the effective treatment of heavy metals in the environment has become one of the major issues of public interest due to their toxicity. One of many techniques used for this purpose is an ion exchange method based on cation exchange adsorbents. Radiation-induced grafting of vinyl monomers onto polymer substrates has attracted considerable interest because it imparts some desirable properties, such as chelation and ion exchange.

In our studies three types of polymers, *i.e.* polypropylene (PP), polyethylene (PE) and polystyrene (PS), were applied as matrices. It is well known that these polymers are inert, hydrophobic, mechanically strong and following irradiation produce long-lived paramagnetic species. Therefore, it seems that all of them are appropriate matrices for radiation-induced grafting. At first stage of in-

vestigations, the influence of ionizing radiation on the trunk polymers was studied, *i.e.* level of radicals stable at room temperature and radiation yield of evolved hydrogen were estimated for each polymer. Grafting yield might depend on the level of radicals initiated in polymeric matrix. The analysis of paramagnetic species performed by EPR (electron paramagnetic resonance) spectroscopy enables to estimate the ability of particular polymers to radiation-induced formation of radicals and reveals indirectly the ability to construct covalent bonds with monomer molecules.

PS is considered as the most radiation resistant polymer due to the efficient conversion of absorbed radiation energy into heat by aromatic rings. Thus, radiation processes are very limited and radiation

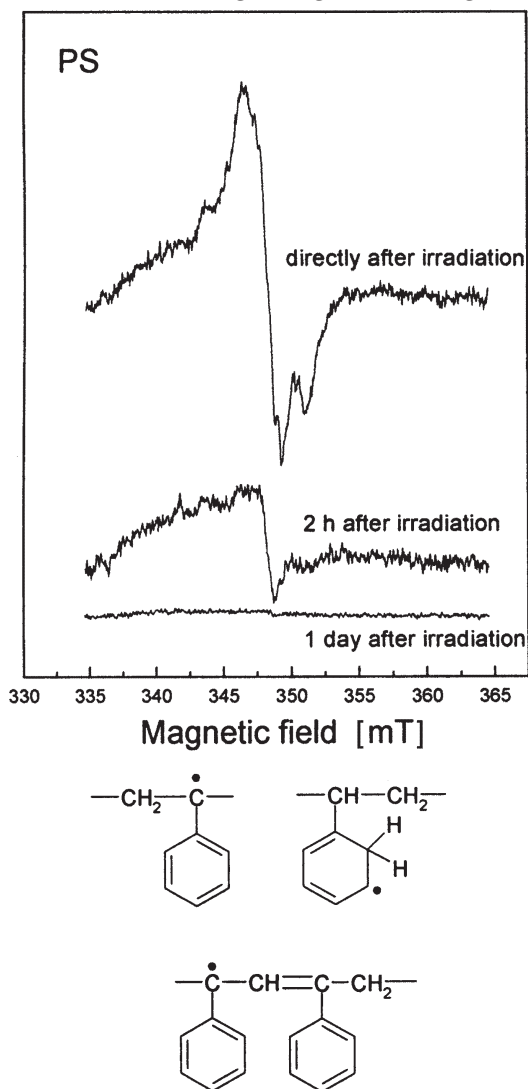


Fig.1. EPR spectra of radicals formed in PS by ionizing radiation with a dose of 25 kGy (electron beam, air atmosphere) and expected radical structures.

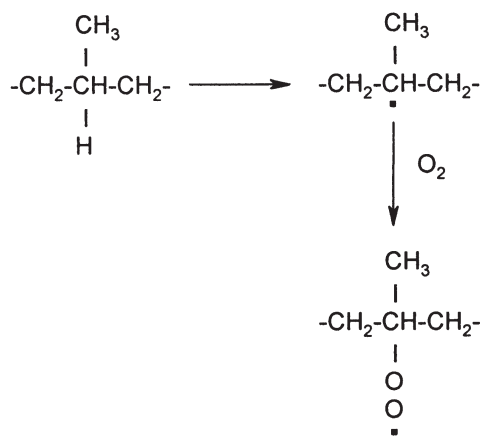
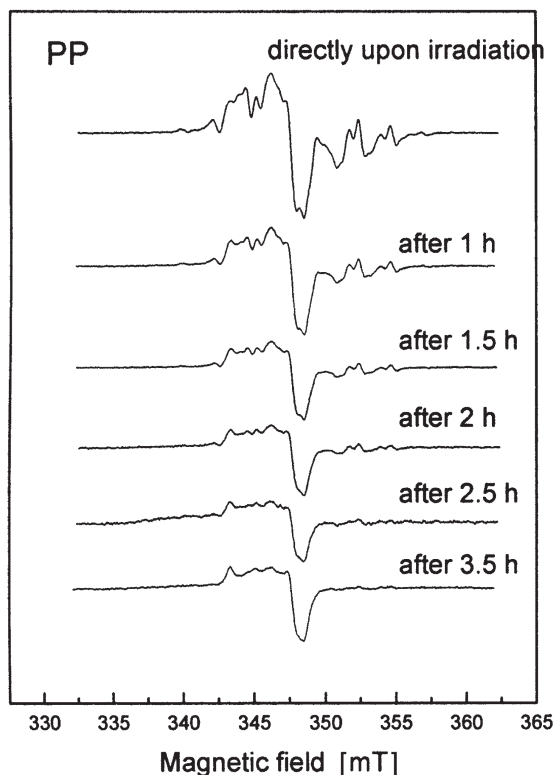


Fig.2. EPR spectra of radicals formed in PP by ionizing radiation with a dose of 25 kGy (electron beam, air atmosphere) and expected radical structures.

yield of the radicals in PS is much lower than in other polymers. According to Clough *et al.* [1] three radicals can be produced – two formed upon abstraction of hydrogen and one created *via* addition of hydrogen atom to the aromatic ring.

The EPR spectrum measured upon irradiation with a dose of 25 kGy (Fig.1) is uncharacteristic and of low intensity. The shape of signals points out that oxidative degradation must be limited as the contribution of peroxy radical signal is insignificant. This is another reason for unusual radia-

trum of PE is a composite signal arising from the various contribution of several radical individuals (Fig.3). Deconvolution of the experimental spectra leads to the conclusion that eventually alkyl, allyl and polyenyl radicals are produced under vacuum. The dominant intermediate is a secondary alkyl radical; less populated are allyl type radical and polyenyl radical that might be selected upon partial decay of the main product. Significant level of paramagnetic species should facilitate the formation of covalent bonds during grafting. The

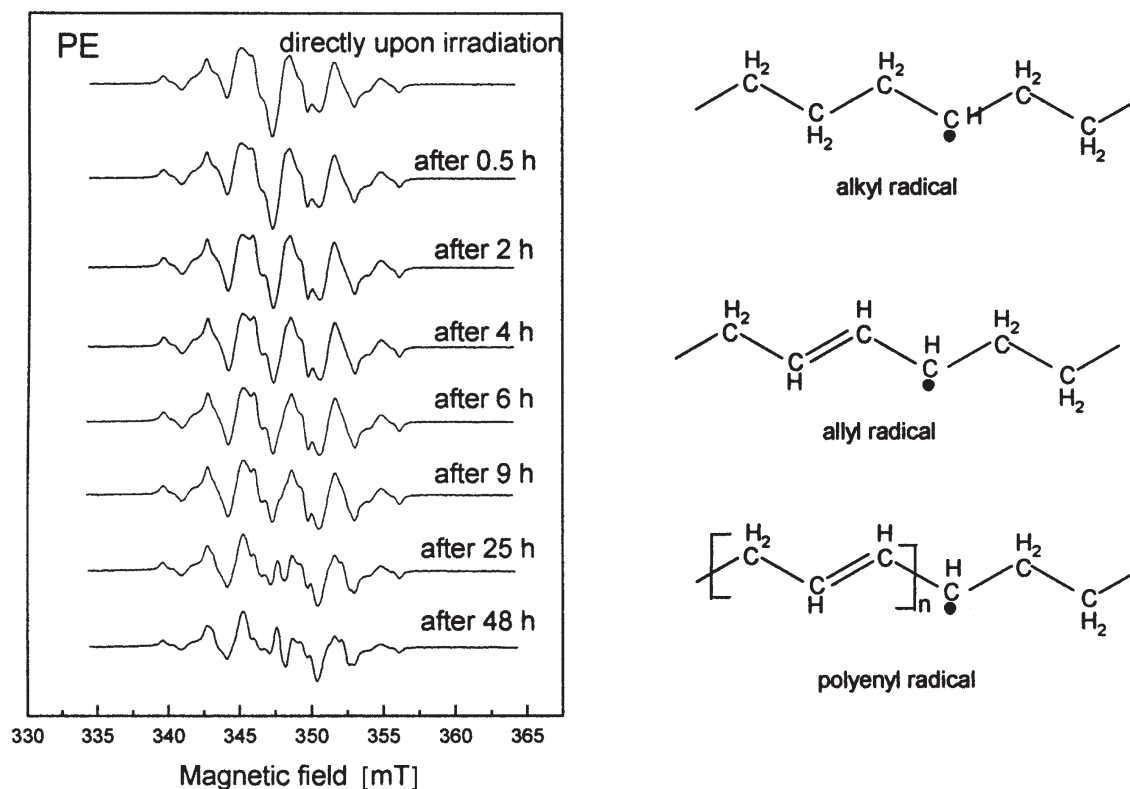


Fig.3. EPR spectra of radicals formed in PE by ionizing radiation with a dose of 25 kGy (electron beam, vacuum) and expected radical structures.

tion resistance of PS. On the other hand, low efficiency of the radical production might inhibit radiation-induced grafting.

Figure 2 shows the EPR spectra of the radicals formed in PP upon exposure to an electron beam. Tertiary alkyl radical is a dominant product that fast undergoes oxidation. Formed peroxy radical is very stable and can be detected even many months upon irradiation thus PP seems to be a proper matrix for applying pre-oxidation method of grafting. However, such a procedure requires exposure of the polymer to much higher doses than in the direct method, thus the risk of polymer degradation increases. The level of radicals, as was roughly determined by double integration of obtained EPR signal is more than 4 times higher in PP than in PS.

PE also is considered as a radiation resistant polymer, but the background of the phenomenon is different than in the case of PS. A dominant factor determining final effect of irradiation is the formation of bonds between the main chains that occur in amorphous phase. Except effective cross-linking, ionizing radiation induces residual radicals in crystalline phase. The experimental spec-

tration of radicals in PE estimated directly upon irradiation overcome that found in PP. We must emphasize that the used polymers are commercial products, thus the observed variations among radical populations concern only these particular materials.

The melting points of crystalline phases of PP and PE before and after grafting processes do not change considerably values (Fig.4). Analysis of the melting endothermic peaks (as well as crystallization exotherms, not shown results) reveals that enthalpies of transitions decrease. These data provide information on the changes in structural order of polymer chains promoted by the grafting. Taking into account enhancement of the total weights by 25% due to AAc grafting, the enthalpy of phase transitions ought to be reduced by 20%. Observed decline of the enthalpies is *ca.* 33 and 20%, respectively for PE and PP. It seems that radiation grafting induces in PE reduction of the degree of crystallinity while proportion between the ordered and disordered phases in PP remains unchanged. Disintegration of crystalline regions in grafted PE was also confirmed by Gupta *et al.* [2].

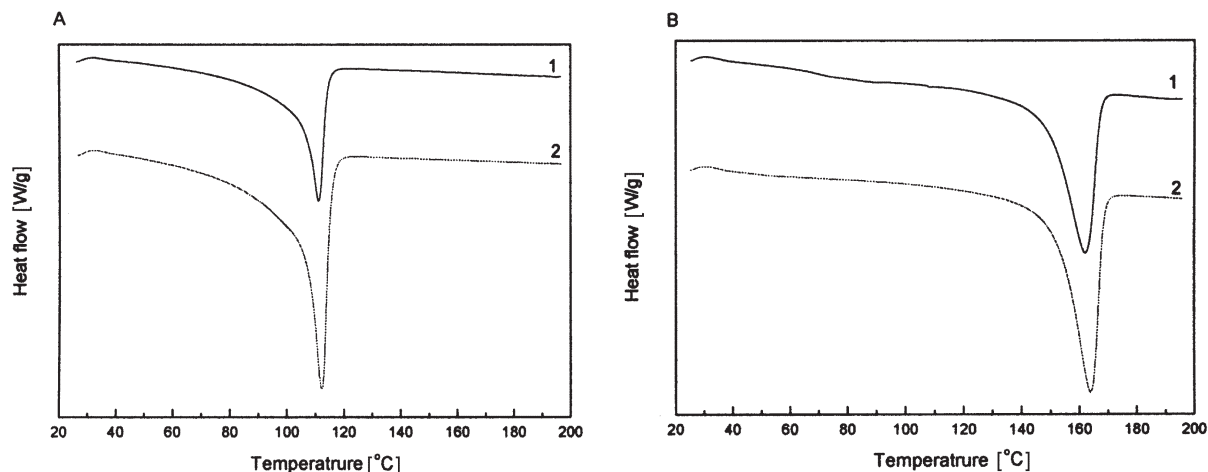


Fig.4. Endotherms of PE (A) and PP (B) before grafting (2) and after grafting (1). Degree of grafting – 25%.

Finally, we found by EPR spectroscopy that concentration of radicals generated in PE backbone is higher than in PP, and much higher than in irradiated PS. Additionally, lifetime of the intermediates in PS is shorter than in the irradiated PE and PP thus conversion to diamagnetic product might concur with initiation of the grafting processes.

On the basis of the above data, polyethylene was chosen as the most promising matrix for radiation grafting.

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### References

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## UNIT PROCESSES AND UNIT OPERATIONS IN RADIATION PROCESSING

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The concept of unit processes and operations has been introduced early in the history of chemical technology, already at the beginning of the XX century. Elements of the technological procedures were divided into unit processes and unit operations. The intention was a rationale and economic combination of, e.g. operation of liquid-liquid separation in the process of extraction, with the reduction of time of contact of two liquid phases. Such contact has to be reduced as much as possible during the process of separation of radioactive constituents in the processing of spent nuclear fuel. Unexpectedly, a unique operation involving centrifuge in the extraction, developed in the Institute of Nuclear Research (now the Institute of Nuclear Chemistry and Technology – INCT) in the early seventies by Professor Przemysław Hoffmann, has shown advantage in the production of antibiotics, where the contact of the extractant with the basic solution has to be reduced to avoid the decay of the antibiotic.

More examples of advantages, which are reached by matching proper unit operation to most strange unit process can be found in the history of rapid and successful separation of constituents, plutonium mainly, of spent reactor fuel in Hartford, USA in the years 1943-1945, with the purpose of construc-

tion of the A-bomb. Authors of the success were chemists from DuPont, experienced with critical stages of polymer production, in that case of the specific polyamid, later called nylon.

There is no need to list the usefulness of application of the idea of unit operations and processes in more cases in chemistry. One of the present authors, Zagórski [1], has indicated the usefulness of the idea in analytical chemistry, where proper combination of processes (chemical reactions running with high rate constant and without secondary reactions) combined with proper operations (mainly separations) yielded best results, especially in automation of industrial control [2] and in distant operations, like present day robotic devices performing chemical research in far places, like the planet of Mars.

It is not difficult to see unit processes and unit operations in the technology of radiation processing. Unit processes are chemical, ionizing radiation-induced reactions and secondary phenomena, e.g. applied in radiation sterilization. They are defined by the dose/effect value, which has to be achieved by matching proper unit operation. The latter is the source of radiation and mode of its operative delivery. A unit process in radiation processing, as above, has to be developed with the