

Functionalization of polymer surfaces by radiation-induced grafting

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Abstract. The mutual radiation grafting of acrylic acid (AAc) onto polyethylene (PE), polypropylene (PP) and polystyrene (PS) films was performed. At first stage of investigations, the influence of ionizing radiation on the trunk polymers was studied, i.e. the level of radicals stable at room temperature and radiation yield of evolved hydrogen were estimated for each polymer. The measurements were carried out using electron paramagnetic resonance (EPR) spectroscopy and gas chromatography (GC), respectively. Radiation yields of radicals as well as hydrogen emission increased in the following order PS < PP < PE. Under comparable conditions, the same relationship was found for the yield of radiation-induced grafting of AAc. A distinct correlation between content of radicals generated by ionizing radiation in polymeric matrices and grafting degree was confirmed for the studied materials. The effect of monomer and inhibitor concentrations on the efficiency of processes were studied as well.

Key words: radiation grafting • EPR • radicals • radiation yield

Introduction

In the past various techniques have been developed for radiation-induced grafting. In the pre-irradiation method polymeric matrix is first irradiated in order to generate active sites either in inert atmosphere or in vacuum. The radicals have to be stable at ambient temperature in order to initiate covalent bonds with monomers after irradiation [6, 15]. The procedure results in elimination of homopolymerization, however the yield of grafting is in this case relatively low. Other variation of such a method is an application of air atmosphere during exposure to ionizing radiation. Both techniques are suitable if only formed radicals are stable enough to react with monomers in post-irradiation effect [5]. In such a case grafting, depending on the system, might be performed after long storage time.

The most frequent method used for grafting consists in irradiation of monomer solution in contact with the surface of polymer. Theoretically, radicals produced both in polymer and in monomer might initiate covalent bonds between the reagents. However, the contribution of active sites situated in polymeric matrices in grafting processes has not been determined yet. We made an effort to determine the role of radicals produced in selected polymers on radiation-induced grafting. The investigations were performed for polymers of different resistance towards irradiation thus various amounts of paramagnetic species were expected at particular dose; applied procedures, experimental conditions and kind of monomer, were the same.

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In our studies three types of polymers, PP, PE and 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.

In the past polyolefines were extensively investigated as potential backbones in grafting processes. A few water soluble monomers: acrylic acid (AAc), methacrylic acid (MAA), acrylamide (AAM), N,N-dimethyl acrylamide (NDAAm) and 1-vinyl-2-pyrrolidone (NVP), were grafted by Aydinli and Tincer [2] on UHMWPE by a direct method. They found that increase in the grafting degree with absorption dose is limited by the formation of intractable homopolymer. The relationship between the pH of a monomer solution and the grafting degree was found for the AAc-PE system [20]. Detailed investigations concerning grafting of some copolymers on LDPE were carried out by Hegazy *et al.* [13, 14]. Copolymerization grafting of binary monomers (AAc was always used as one of the components) results in obtaining promising membranes for the removal of heavy metals from water. An important conclusion was that the membranes preserve good mechanical properties necessary for practical uses. Polyethylene matrix, upon filling with starch, might be also grafted by vinyl monomers, e.g. AAm, and the process is more efficient than in blank LDPE [3]. The AAm grafting is twice more efficient on an EVA copolymer than on PE [1]. Taher *et al.* [18] investigated AAm and NVP grafting depending on the following factors: solvent, inhibitor, dose, dose rate and monomer concentration. A large effort was devoted to the optimization of solvents used in the process. The most promising seems to be dioxane that enhances grafting of NVP as well as AAm. Sidorova *et al.* [17] completed researches on the profiles of PAAc distribution on the LDPE backbone. Surface of the film is entirely covered with PAAc if grafting degree exceeds 10% and then the concentration profile of PAAc is non-diffusional. Due to the chemical stability and excellent mechanical strength, PE is used also as a backbone for preparation of biomaterials of modified surface [9]. It was confirmed that the grafting yield of HEMA in solution in equilibrium with air and in the system free from oxygen is comparable.

Another hydrophobic polymer frequently applied as a matrix in radiation-induced grafting is PP. In some cases the process is recommended in order to achieve sufficient adhesion required in various, e.g. medical, applications. If the treatment is performed in air atmosphere oxidative degradation following irradiation is expected. Some monomers were grafted by a pre-irradiation method, e.g. acrylonitrile [11], AAc [8], AAc and NIPAAm (N-isopropylacrylamide) [16]. In the systems grafting yield reaches only a few percent, that reveals that this method is appropriate predominantly for creation of thin layers changing physicochemical characteristic of the surface.

Reported preliminary studies were focused on the grafting of a model vinyl monomer, acrylic acid, on three various matrices – PE, PP and PS via the gamma radiation-induced direct method. Used polymers are extensively studied because of their commercial significance. The behavior of each polymer upon exposure to ionizing radiation is distinctively different. For reported

investigations, Mohr's salt was used as an inhibitor of homopolymerization, what was recommended by many authors, e.g. Gargan *et al.* [10].

Experimental

Materials

Materials used in this work were commercially available LDPE – Malen FGNX 23D-022, PP-Malen P J601 and PS-GPPS-Owispol 525 0001TH were from PKN Orlen S.A. Acrylic acid, ferric chloride and Mohr's salt were purchased from Aldrich Chemical Company Inc. and used without any purification. Methanol was delivered from Chempur Co. Influence of Mohr's salt concentration on grafting was investigated for two concentrations of AAc.

Grafting process

The films prepared by press molding with a thickness of ca. 0.20 mm were used as matrices. They were cut into ca. 2 × 3 cm pieces and ultrasonically washed in methanol solution for 1 h and dried under vacuum to constant weight. Subsequently, the samples were immersed in the solvent containing aqueous solution of inorganic salt, $\text{Fe}(\text{SO}_4) \times (\text{NH}_4)_2(\text{SO}_4)$, of various concentrations and methanol comprising AAc, in the volume proportion of 2:5, and deaerated by bubbling nitrogen. The samples were kept in solution for 24 h at room temperature and then irradiated with a ^{60}Co gamma source Issledovatel with a dose rate of 1.156 kGy/h. After grafting the samples were removed from the solution and four times washed ultrasonically at 40°C. Metal ions present in the samples were extracted with 0.1 M hydrochloric acid. Upon successive washing with distilled water, the samples were dried under vacuum at 60°C to constant weight. Degree of grafting was determined gravimetrically and calculated as a percentage of ratio between the growing weight and initial weight. Quantitative analysis of ferric ion uptake was assayed using a UV-Vis spectrophotometer by detecting the absorption band of $\text{Fe}(\text{SCN})_3$ at 480 nm.

Methods

The samples of PP and PS used for free radical investigations (EPR spectroscopy) were irradiated with an electron beam (accelerator Elektronika 10/10) in air, whereas PE in vacuum (due to very fast oxidation of paramagnetic species to peroxy radical). The EPR measurements were performed at ambient temperature with a Bruker ESP 300 spectrometer equipped with a rectangular X-band TE 102 microwave cavity.

The yields of hydrogen in the gas phase evolved from irradiated polymers were determined with a gas chromatograph Shimadzu-14B. 1 m long column was packed with molecular sieves of 5 Å; the thermoconductivity method was used for detection. The carrier gas was argon, calibration was performed with hydrogen of purity 99.99%.

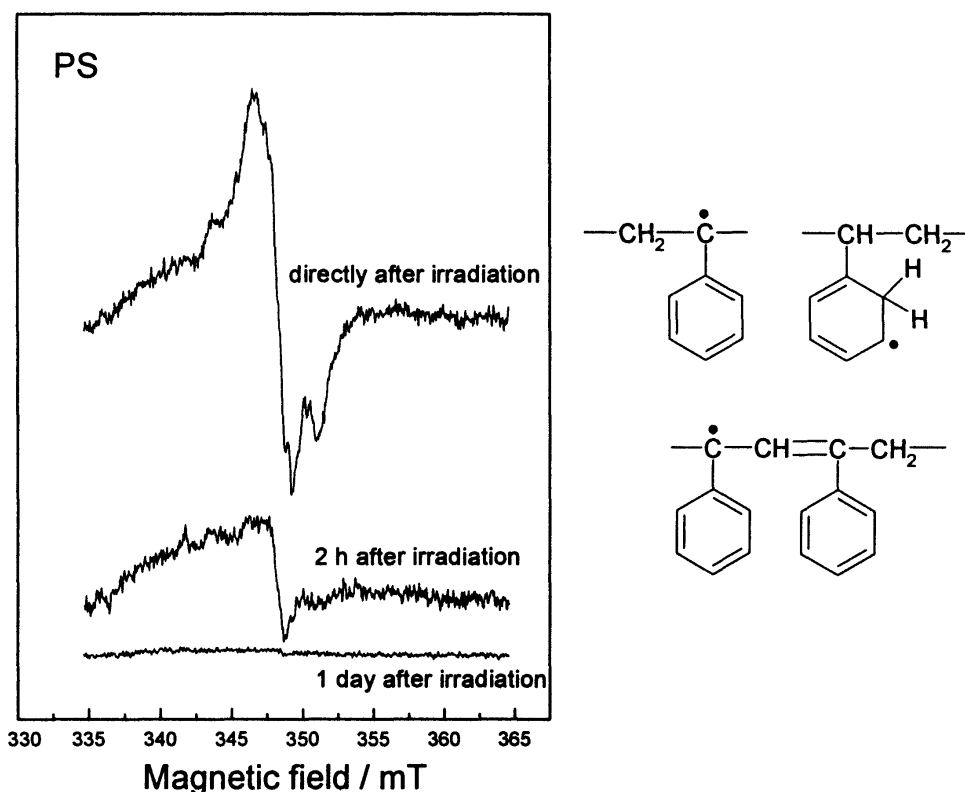


Fig. 1. EPR spectra of radicals formed in PS by ionizing radiation with a dose of 25 kGy (electron beam, air atmosphere) and expected radical structures.

DSC measurements were carried out with a TA Instruments differential scanning calorimeter (MDSC 2920) at a heating/cooling rate of 10°C/min in nitrogen atmosphere. The crystallization and melting behavior of the samples were studied after erasing of the thermal and mechanical history of materials, i.e. in the second run. Measurements were performed in the temperature range from 25°C to 200°C. About 5 mg of the sample inserted in the pan was heated, then kept for 5 min at 200°C and gradually cooled. Afterwards, the second run was performed applying the same conditions as for the first cycle.

Results and discussion

Grafting yield might depend on the level of radicals initiated in polymeric matrix. The analysis of paramagnetic species performed by EPR spectroscopy enables to estimate ability of particular polymers to radiation induced formation of radicals and reveals indirectly ability to construction of covalent bonds with monomer molecules.

PS is considered as the most radiation resistant polymer due to efficient conversion of absorbed radiation energy into the heat by aromatic rings. Thus, radiation processes are very limited and radiation yield of the radicals in PS is much lower than in other polymers. According to Clough *et al.* [7] 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 radiation 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. The 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 the 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 the double integration of the 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 main chains that occurs in the amorphous phase. Except effective crosslinking, ionizing radiation induces residual radicals in the crystalline phase. The experimental spectrum 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 the secondary alkyl radical; less populated are the allyl type radical and polyenyl radical that might be selected upon partial decay of the

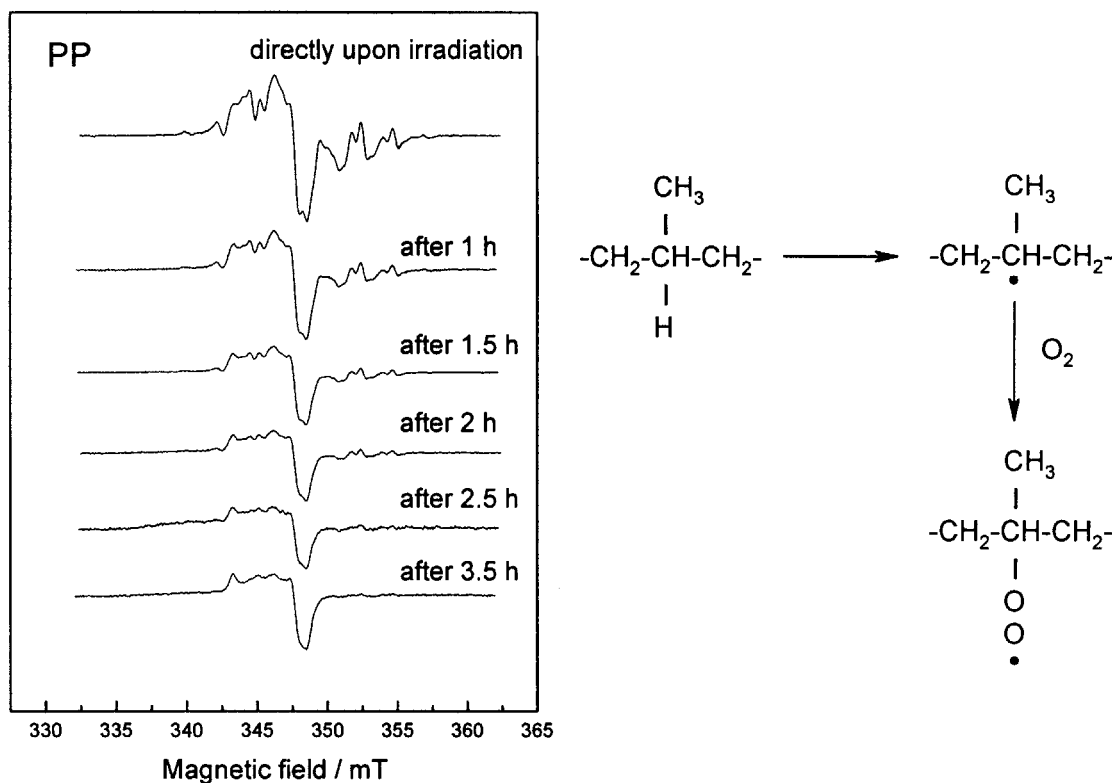


Fig. 2. EPR spectra of radicals formed in PP by ionizing radiation with a dose of 25 kGy (electron beam, air atmosphere) and expected radical structures.

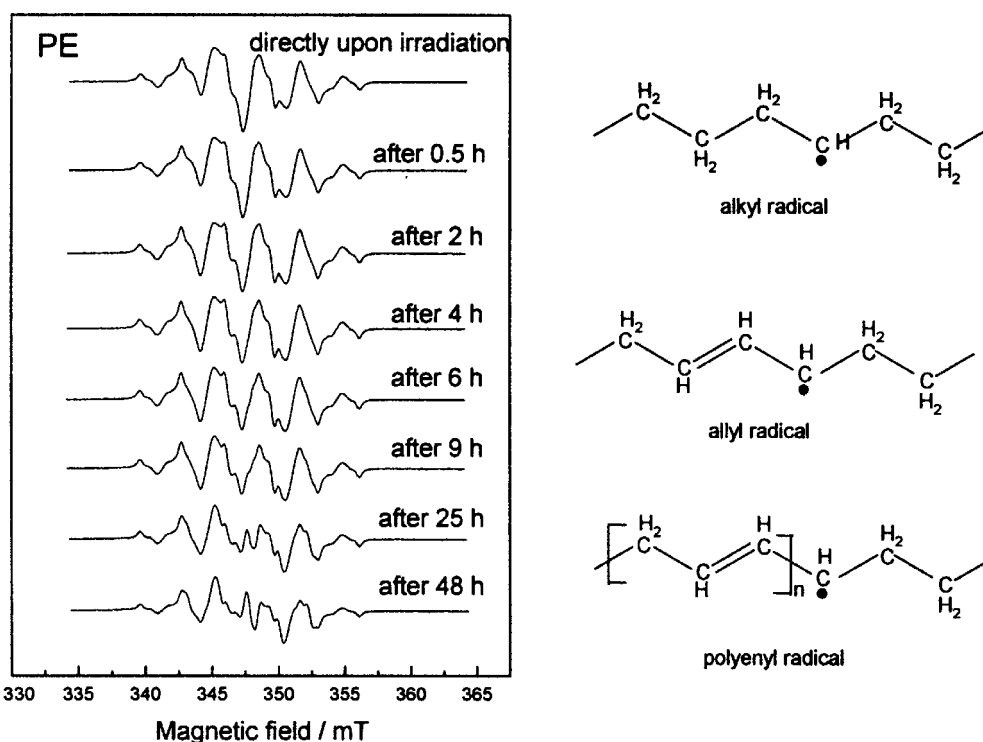


Fig. 3. EPR spectra of radicals formed in PE by ionizing radiation with a dose of 25 kGy (electron beam, vacuum) and expected radical structures.

main product. Significant level of paramagnetic species should facilitate the formation of covalent bonds during grafting. The concentration of radicals in PE estimated directly upon irradiation overcome that found in PP. We must emphasize that the used polymers are commercial

products, thus observed variations among radical populations concern only these particular materials.

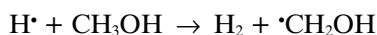
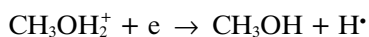
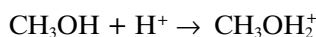
The radicals formed in the studied polymers, PP, PS and PE, are predominantly generated upon abstraction of hydrogen. Consequently, radiation yield of hydrogen

Table 1. Radiation yield of hydrogen G(H₂)

Polymer	Radiation yield of hydrogen (μmol/J)
PP	0.270
PS	0.036
PE	0.460

reflects indirectly the level of formed paramagnetic species. Values of G(H₂) in Table 1 reveal great discrepancies in particular polymers. The most efficient is the emission of hydrogen from PE (0.46 μmol/J), less efficient from PP (0.27 μmol/J) and the least efficient from PS (0.036 μmol/J). Dehydrogenation results in the production of alkyl radicals as well as crosslinking and the last process is the most significant in PE.

Used in the grafting experiments solutions were composed of methanol and water. Grafting procedures were performed using a methanol solution of AAc at concentrations of 25% or 50% mixed with water in proportion of 5:2. Alcohol is one of the dominant component and the following series of reactions is expected:



The mechanism is interfered by the presence of water and ferrous ions. The inhibitor initiates a few various processes: scavenging of oxidative radicals, reduction of vinyl radicals that leads to the reconstruction of monomer, formation of complexes both with polymer matrix and with growing chains created from monomers.

In the solutions free from ferrous salts and at a concentration of Fe(SO₄) × (NH₄)₂(SO₄) below 4 μmol/dm³ acrylic acid undergoes gelation. Separation of the films from the gel of PAAC is then obstructed. Above this limit, viscosity of the solution did not increase indicating that homopolymerization was insignificant. This phenomenon cannot result from the reaction of ferrous ions with hydroxyl radical as (i) rate constant of OH[•] with methanol is much higher than those with Fe²⁺ [19] and (ii) concentration of methanol is considerably higher than the content of iron ions. Sidorova *et al.* [17] suggested that reactivity of ferrous ions with the active sites located in grafted matrices is lower than with radicals situated in growing chains of AAc. Complexes PAAC-Fe²⁺ restrain diffusion of free Fe²⁺ ions towards surface what enables fast grow of macromolecules attached to the polymeric matrices. Further processes enhance viscosity of the grafted layer reducing additionally contact of ferrous ions with the backbone.

AAc displays entirely different grafting efficiency towards the studied polymers. Figures 4a, 4b and 4c illustrate relationships between the grafting degree and the concentration of the agent inhibiting homopolymerization, observed for PS, PP and PE matrices, respectively. For PS, even upon a relatively high absorption dose, 25 kGy, efficiency of the process is insignificant at a concentration of 50% of AAc and negligible at 25%. EPR and GC results indicate that the level of

radicals in PS is very low. Therefore, lack of noticeable changes reveals that radicals occurred in the matrix have a dominant influence on the initiation of monomer grafting. Additionally, life-time of intermediates in PS is shorter than in irradiated PE and PP thus conversion to diamagnetic product concurs with initiation of the grafting processes.

The grafting degree on PP in the function of Mohr's salt concentration is shown in Fig. 4b. If concentration of the inhibitor exceeds 2 μmol/dm³, the degree of grafting was found to be independent of the amount of additive till 8 μmol/dm³ and subsequently diminishes. Probably the fraction of Fe²⁺ contributes to the termination of grafting processes.

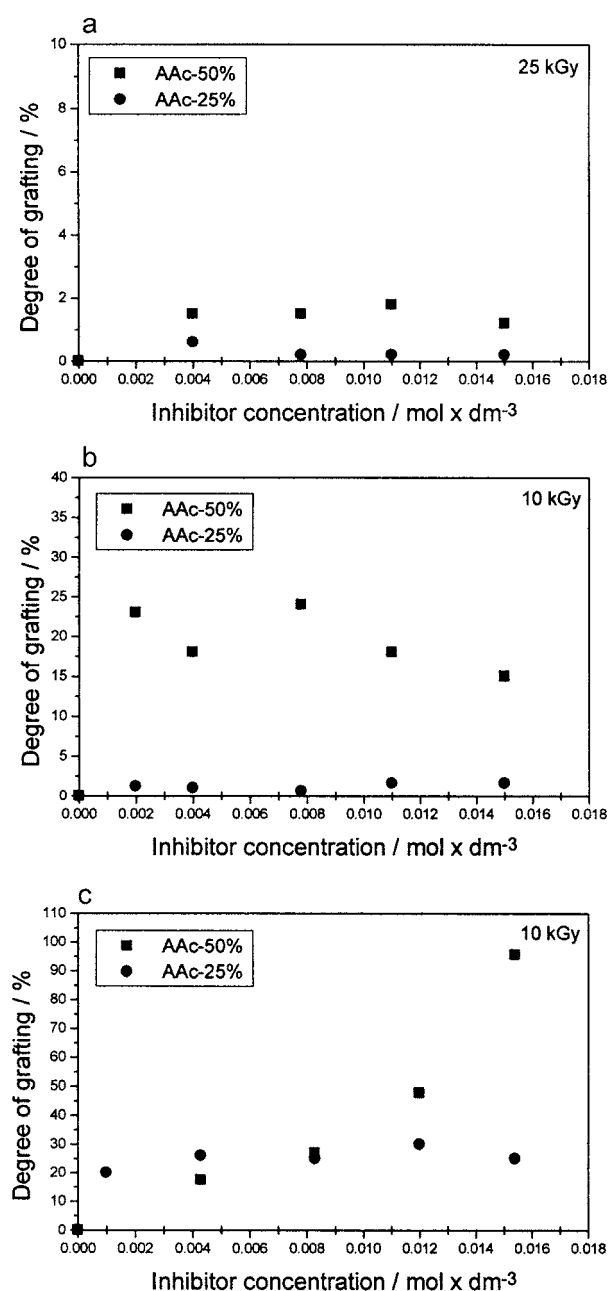
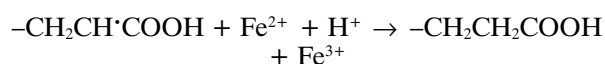


Fig. 4. Effects of Fe(SO₄) × (NH₄)₂(SO₄) concentration on the degree of grafting of AAc onto PS (a), PP (b) and PE (c).

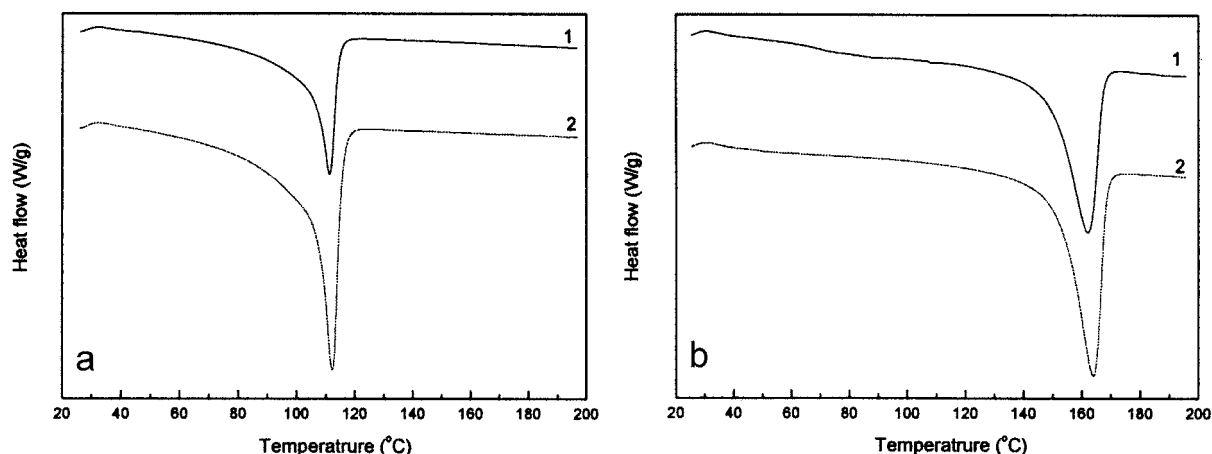


Fig. 5. Endotherms of PE (a) and PP (b) before grafting (2) and after grafting (1). Degree of grafting – 25%.

Table 2. Endothermic transitions determined by DSC method for PE and PP

Sample	Dose (kGy)	Grafting degree (%)	Second cycle	
			Melting point (°C)	Melting enthalpy (J/g)
PE	10	25	111	72
PE	0	0	112	107
PP	10	25	162	66
PP	0	0	164	82

Table 3. Adsorption of ferric ions by grafted layers. Initial concentration of Fe^{3+} feed solution – 200 $\mu\text{g/ml}$. Average degree of grafting was determined on the basis of 5 measurements

Sample	Average degree of grafting (%)	Average uptake ($\mu\text{mol/g}$)
PE	47	65
PP	18	111

Under experimental conditions, the yield of AAC grafting on PP does not exceed 30% in the presence of 50% AAC.

The most pronounced effect of radiation-induced grafting was observed for PE. Increase in the inhibitor concentration results in the gradual grow of the grafting degree. Two various tendencies support the process – high level of AAC monomers that avoid homopolymerization due to raising contents of ferrous ions and large population of radical centers situated in the matrix. As was found by EPR spectroscopy, concentration and stability of radicals generated in this backbone is higher than in irradiated PS and PP. PE is well known as a polymer that efficiently undergoes radiation crosslinking. The phenomenon proceeds exclusively during irradiation and the crosslinking degree does not increase in post-radiation period [4]. Thus, the observed by EPR spectroscopy radicals do not recombine forming interchain covalent bonds and can be consumed in radiation-grafting processes. Therefore, in the reported investigations their population might be compared with the amounts of radicals found in PP and PS.

The melting points of crystalline phases of PP and PE before and after grafting processes do not change considerably the experimental values (Fig. 5 and Table 2). Analysis of 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 the proportion between ordered and disordered phases in PP remains unchanged. Disintegration of crystalline regions in grafted PE was also confirmed by Gupta *et al.* [12].

The ferric ions uptake expressed in μmol per gram of grafted chains is shown in Table 3. After 24 h contact of grafted matrices with feed solution containing 200 $\mu\text{g/ml}$ of FeCl_3 , the adsorption yield of ferric ions by carboxyl groups was determined. The efficiency of iron ions uptake normalized to 1 g of grafted layer is higher for PP than for PE. It seems that the layer structure, i.e. grafting density and thickness, have influence on the observed phenomenon. Since population of radicals is higher in PE than in PP, the distances among grafted chains for PE are shorter for the same grafting degree. The grafting process enhances local viscosity in the vicinity of matrix restraining diffusion of ferric ions to carboxylic groups what results in lowering metal ions absorption by grafted PE.

Conclusions

The degree of radiation-induced grafting of AAC is the highest for PE matrix, lower for PP and insignificant for PS, under comparable conditions. Radiation processes in the solutions are independent of the character of immersed samples of particular polymers. Thus, radicals generated in the matrices have to be responsible for

differences in the yields of grafted monomer. Analyzing population of unpaired spins by double integration of EPR spectra, it was found that concentration of the radicals is consistent with increasing efficiency of grafting. The changes in radiation yield of hydrogen emitted by irradiated PS, PP and PE also confirmed such a tendency.

Adsorption of ferric ions by high density layer grafted on PE is limited by increasing viscosity near the surface. Therefore, for the same degree of grafting, the process is more effective for grafted PP (the grafted layer is in that case composed of longer chains of smaller density) than in the case of PE matrix.

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