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EUROPEAN POLYMER JOURNAL 68: pp. 609-617. (2015)

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**Synthesis of hyperbranched poly(ethyleneimine) based macromolecular
antioxidants and investigation of their efficiency in stabilization of polyolefins**

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ABSTRACT

Macromolecular antioxidants with highly suppressed leaching to the environment, based on hyperbranched poly(ethyleneimine) carrier with bonded sterically hindered phenol and

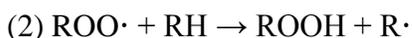
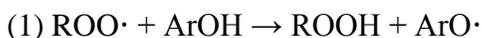
alkyl compatibilizing groups with various chain length were synthesized and tested for their efficiency in stabilization of polyolefins. The synthesis of the macromolecular antioxidants was carried out by amidation of the amine groups present in poly(ethyleneimine) with various carboxylic acids containing sterically hindered phenol and compatibilizing groups, such as n-butyryl, lauryl or stearyl. The structure of the resulting polymers was analyzed by ^1H NMR and by GPC. The antioxidant content of the samples was determined by UV-Vis spectroscopy. The efficiency of the synthesized antioxidants in thermooxidative stabilization of polypropylene was determined by chemiluminescence. The efficiency in photostabilization of polypropylene and polyethylene was investigated by using FT IR and UV-Vis spectroscopies. It was found that the macromolecular antioxidant which did not contain any compatibilizing groups shows the best stabilizing efficiency in both thermooxidative and photooxidation tests. The extent of extraction of the synthesized macromolecular antioxidants from polypropylene films was investigated as well. Low extent of extraction of the macromolecular antioxidants from the polypropylene films was observed in contrast to the high level of leaching of commercially used low molecular weight phenolic antioxidant. These results indicate the environmental advantage of the investigated poly(ethyleneimine) based macromolecular antioxidants over the widely applied low molecular weight compounds.

Keywords:

macromolecular antioxidant, polymer-bound antioxidant, hindered phenols, chemiluminescence, thermooxidation, photooxidation

Introduction

Polymeric materials are commonly exposed to heat, oxygen, radiation, water, metal catalyst residues and mechanical stress during processing and application. These external effects cause oxidative degradation of the polymers which results in deterioration of their chemical, physical and mechanical properties. To avoid polymer degradation various stabilizers (e.g. antioxidants, UV-stabilizers) are usually added to the polymers. The most commonly used antioxidants are hindered phenols (e.g. Irganox[®]1010, Irganox[®]1076 and Irganox[®]HP-136) and hindered amines (e.g., Tinuvin[®], Omnistab[®], SABO[®]STAB) [1], mostly in the form of low molecular weight additives, and they are usually added to the polymers in small amounts in the range of 0.05-0.5 wt% (based on recommendation of producers according to applications and type of polymer). Sterically hindered phenols (ArOH) are the most commonly used class of antioxidants. [2] These stabilizers act by efficient trapping of peroxy radicals (see equation 1), and thus preventing the hydrogen abstraction from polymer chains (RH) by the peroxy radicals (see equation 2). [3, 4]



Antioxidants with low molecular weight (M_w) are sensitive to physical loss through migration, evaporation and extraction. [5, 6] These events occur when the product contacts with food or environment (e.g. in agriculture) and a flowing medium. [7] Physical loss of antioxidants therefore constitutes a major concern in environmental issues and safety regulation, as well as in long-term use of polymers. [4, 8] In order to reduce the physical loss of antioxidants, various high molecular weight antioxidants were

developed. [9-12] In addition, various polymer-bound antioxidants were prepared either by copolymerization of monomers with antioxidant-functionalized monomers or by postfunctionalization of reactive groups on polymer chain with antioxidants. [4, 13-19] Due to the low diffusion the macromolecular antioxidants, it is expected that macromolecular stabilizers can be considered as biofriendly polymer additives, and such additives are more appropriate for polymeric materials applicable mainly in food packaging and agriculture. The sterically hindered phenol antioxidants were bound to several types of linear polymers, such as chitosan [18], polybutadiene [20, 21], polystyrene [22], polyethylene [23-25], polypropylene [26, 27] and polyisobutylene [28].

Compared to the linear polymers, their branched (mainly highly branched) analogues have compact structure and lower viscosity which has significant advantages in processing. They also have high number of functional groups which can be modified easily by different synthetic reactions. These advantages make them to be attractive in many fields of applications. So far, there has been only one work describing the use of a hyperbranched polyester as a carrier for sterically hindered phenol antioxidants, but it was inefficient in polymers. [29]

In our investigations, a hyperbranched poly(ethyleneimine) (PEI) was used as a core for bonding of sterically hindered phenol antioxidant, as an analogue of butylated hydroxytoluene (BHT). The advantage of the hyperbranched PEI based macromolecular antioxidants in comparison with hyperbranched polyester based ones should be their lower polarity and thus better compatibility with polyolefins. Moreover, the formed amide bonds between the PEI carrier and BHT and/or compatibilizer groups are more stable against hydrolysis than ester linkages. In order to further improve the compatibility

with polyolefins, the functionalization of PEI with a BHT-type molecule was also performed in the presence of alkanic acids with different alkyl chain. The thermal stability of the synthesized new macromolecular antioxidants as well as their efficiency in stabilization of polyolefins was investigated. The extractability of the macromolecular antioxidants from polypropylene was studied as well.

Experimental:

Materials

The hyperbranched poly(ethyleneimine) (PEI) ($M_n = 1.8$ kDa, PDI=1.1) was purchased from Sigma-Aldrich as a 50 wt% water solution. Prior to use the PEI was precipitated into THF and dried at 50 °C under vacuum until constant weight. 3-(3,5-Di-tert-butyl-4-hydroxy-phenyl)propionic acid (AoxAc) was purchased from Creasyn Finechem and purified by recrystallisation from diethylether/hexane 20/80 vol% solvent mixture. The white crystals were filtered and washed with cold hexane and dried under vacuum. The dicyclohexylcarbodiimide (DCC), 1-hydroxybenzotriazole (HOBt), butyric acid (ButAc), lauric acid (LaAc) and stearic acid (StAc) were purchased from Sigma-Aldrich and were used without purification. Irganox 1010 was provided by BASF and was used as received. Unstabilized polypropylene (PP; TATREN® FF500, Slovnaft Density 0.903 g cm⁻³, Melt Mass-Flow Rate (MFR) 2–1 g/10min (230 °C/2.16 kg); Tensile Modulus 1500 MPa, Tensile Stress 32 MPa, Tensile Strain (yield) 9.0%; Vicat Softening Temperature 153 °C) and unstabilized low density polyethylene (LDPE; Arcoplast Slovakia a.s.; Density 0.913-0.917 g cm⁻³, MFR 18-22g/10 min, particle size

500 μm , Vicat 84 $^{\circ}\text{C}$) were used as polymer matrices. The solvents for the syntheses and purifications (dimethylformamide (DMF), tetrahydrofuran (THF) and methanol (MeOH)) were purchased with analytical reagent grade from Molar Ltd. and were used without purification. THF (a.r. from Molar Ltd.) for GPC analysis and UV spectroscopy was distilled from KOH under nitrogen atmosphere prior to use.

Synthesis methods

General procedure of synthesis of PEI based macromolecular antioxidants: The base PEI (1 g, 0.55 mmol what contain about 5.5 mmol primary amine group) was dissolved in 25 mL DMF and placed into a dry 100 mL, round-bottom flask with magnetic stirring bar. Then HOBt (1.8579 g, 13.75 mmol) and AoxAc (3.8225 g, 13.75 mmol, 2.5 fold excess to primary amines) was dissolved in 25 mL DMF and added to the PEI solution. In some cases, a part of AoxAc was replaced with alcanoic acid, while the molar ratio of antioxidant and compatibilizer was kept to be 1:1 (except in the case when lauric acid was used, AoxAc:Lauric acid 2:1 ratio). The total amount of carboxylic acids was every time kept to 13.75 mmol. Finally DCC (2.8370 g, 13.75 mmol) was dissolved in 10 mL DMF and added to the reaction mixture. The reaction flask was sealed and the reaction mixture was stirred at room temperature at least for 40 hours. The precipitated dicyclohexylurea was filtered and the filtrate was concentrated by rotary evaporator. The crude products were dissolved in THF, filtered, precipitated twice into large excess of MeOH/Brine (95:5) and washed with cold hexane. The solid residues were collected and dried under vacuum at 60 $^{\circ}\text{C}$ until constant weight. The products were solid and the colors varied from a sandlike yellow to pale brown. The yields of bonding of carboxylic

acids were in the range of 59-79%. The yield of bonding of carboxylic acid (conv) (%) was calculated as follows:

$$\text{conv (\%)} = \frac{(m_p - m_{0(\text{PEI})}) / (A \times M_{(\text{acid}1)} + B \times M_{(\text{acid}2)})}{(A \times n_{0(\text{acid}1)} + B \times n_{0(\text{acid}2)}) / (A+B)} \times 100$$

where m_p and $m_{0(\text{PEI})}$ are weight of final macrostabilizer and weight of initial PEI, respectively, $M_{(\text{acid}1)}$ and $M_{(\text{acid}2)}$ are molecular weights, after subtraction of molecular weight of water, for AoxAc and compatibilizer (i.e. ButAc, LaAc or StAc), respectively, $n_{0(\text{acid}1)}$ and $n_{0(\text{acid}2)}$ are initial moles of AoxAc and compatibilizer, respectively, and A/B is molar ratio of AoxAc and compatibilizer determined in macrostabilizer by ^1H NMR.

Characterization

Average molecular weights and molecular weight distribution (MWD) of the PEI-based antioxidants were measured by gel permeation chromatography (GPC). The GPC equipped with differential refractive index and viscosity detector (Agilent Infinity 1260) was used with 5 μm particle size PLGel Mixed-C columns (HR 1, 2, and 3 with different molecular weight ranges from 100 Da to 600 kDa) and a PLGel guard column thermostated at 35 $^\circ\text{C}$. THF was used as eluent under a flow rate of 1 mLmin^{-1} . The molecular weights and MWD were determined using a universal calibration based on linear polystyrene (PS) standards.

The macromolecular antioxidants were characterized by ^1H NMR spectroscopy. ^1H NMR spectra were recorded on Bruker-Avance 250 spectrometer operating at 250 MHz. The samples were measured at room temperature in CDCl_3 .

The BHT content of the samples was determined by UV-Vis spectrophotometer (Jasco V-650 spectrophotometer) equipped with Jasco MCB-100 mini Circulation Bath and Peltier thermostat heating and cooling system. The samples were dissolved in abs. THF and measured with standard 1x1 cm quartz cuvette thermostated at 23 °C. The reference was abs. THF. PEI control sample was investigated in abs. EtOH. The BHT content was determined based on the calibration curve prepared from various concentrations of AoxAc in abs. THF. The photooxidation of polyolefin films was followed by FT IR (Nicolet 6700 FTIR spectrometer) and UV-Vis spectrometer UV 1650PC (Shimadzu, Japan).

The thermogravimetric measurement was made with Mettler TG50 instrument under dry nitrogen atmosphere. The results were evaluated with Mettler Toledo Stare System software. In all cases, the heating rate was 10 °Cmin⁻¹ from 35 °C to 750 °C. The flow rate of the nitrogen was 100 mLmin⁻¹.

Preparation of polyolefin films

All the additives (0.2 wt% of BHT groups) were solvent blended into the polymer powder using THF as solvent. After evaporation of the solvent under stirring, the impregnated polymer powders were mixed and homogenized in the 30 mL mixing chamber of blending machine (Brabender Plasticorder PLE 331) (Germany) at 185 °C and 135 °C for PP and PE, respectively, for 5 min in air at a mixing speed of 35 rpm. The bulk polymer was then pressed into the required shape of c.a. 0.1 mm films in an electrically heated laboratory press (Fontijne SRA 100, (Netherlands) at 190 °C and 135 °C for PP and PE, respectively, for 5 min.

Chemiluminescence

Chemiluminescence measurements were performed in a Lumipol 3 photon-counting instrument manufactured at the Polymer Institute of the Slovak Academy of Sciences. The film samples (from 5 to 7 mg) were weighed on an aluminium pan (9 mm in diameter) and placed in the sample compartment. The gas flow (oxygen or nitrogen) through the sample cell was set to 3.0 Lh⁻¹. The purging of the gas through the compartment was set 10 minutes before the start of measurement. The temperature in the sample cell of the apparatus was increased linearly with time from 40 °C up to 220 °C at the rate 5 °Cmin⁻¹. The signal of the photocathode was recorded at a 10-second data collection interval. Repeated experiments do not differ on the temperature axis more than by 2 °C and by 5% in chemiluminescence intensity.

Photooxidation of polyolefin films

The photooxidation was performed using the merry-go-round type set up, equipped with a medium pressure 250 W mercury arc with luminophore envelope (RVL, Tesla Holešovice, Czech Republic) as source of irradiation. The temperature of photooxidation was 30 °C. The course of photooxidation was followed by FT IR spectroscopy monitoring the increase of carbonyl absorption, in 1700-1740 cm⁻¹ region, caused by formation of oxidation products.

Extraction of antioxidants from polypropylene films

The PP films containing antioxidants were extracted either in hexane at room temperature for 70 hours or in water at 65 °C for 27 hours. After extraction the films were

dried on a filtration paper for 1 hr and subsequently under vacuum at room temperature for 3 hrs. The extent of the extraction of antioxidant from PP film was followed by UV-Vis spectroscopy.

Results and discussion

Synthesis of hyperbranched poly(ethyleneimine) based macromolecular antioxidants

The purpose of this work was the synthesis of macromolecular antioxidants with low diffusion out of the polymer matrix and with good compatibility with polyolefins. The synthetic approach is presented in **Figure 1**. A hyperbranched poly(ethyleneimine) possessing primary and secondary amine groups, which can be easily functionalized, was used as a polymeric carrier. Hindered phenols are cheap and widely used antioxidants, therefore derivative of BHT with functional carboxylic group was used for bonding the BHT moiety to the PEI carrier through amidation reaction. The reaction of amines with carboxylic acids catalysed by DCC and HOBT is a simple and well-known synthetic approach giving high conversions of the resulting amides. [30] Furthermore, it enables simultaneous reaction of amines with different carboxylic acids. Therefore, this synthetic approach was used to functionalize simultaneously the PEI carrier with both BHT antioxidant and compatibilizer (butyric, lauric and stearic acid). In all cases, the carboxylic acids were used in 2.5 fold excess to the primary amines present in the PEI. It was expected that due to the lower reactivity and higher sterical hindrance of the secondary amines, preferentially primary amines will be functionalized.

FIGURE 1

Characterization of hyperbranched poly(ethyleneimine) based macromolecular antioxidants

All synthesized antioxidants were insoluble in water and highly soluble in common organic solvents, such as DMF, DMSO and unlike PEI also in CHCl_3 and THF. Thus the macromolecular antioxidants were characterized by GPC, ^1H NMR and UV spectroscopies. In addition, the new macromolecular antioxidants bearing also lauric and stearic compatibilizing groups were slightly soluble also in hexane, suggesting possible improvement of the compatibility of these macromolecular stabilizers with polyolefins.

The MWD and average molecular weights of the resulting polymers were determined by gel permeation chromatography (GPC). The results, presented in **Figure 2** and **Table 1**, show that the molecular weight and polydispersity of the synthesized samples were higher than that of the starting polymer, i. e. PEI ($M_n = 1.8$ kDa, PDI = 1.1). The changes in molecular weights and improved solubility in THF proved that the modification of PEI by the BHT-type antioxidant and compatibilizers was successful in all cases. In addition, the GPC results showed that no detectable residues from the reactants was present in the macromolecular antioxidants, except one sample, when AoxAc:LaAc in ratio of 2:1 was used. In this case, a small amount of low molecular weight impurities was detected.

FIGURE 2

TABLE 1

In the ^1H NMR spectra of the macromolecular antioxidants, the signals of protons of main chain of PEI at around 2.5-3 ppm region and the signals of the aromatic and tert-butyl protons at around 6.8 ppm and 1.2 ppm, respectively, and the methylene protons next to the formed amide groups in the 3-3.5 ppm region can be observed (**Figure 3**). In addition, when compatibilizers were also bound onto the PEI carrier, the signal of the alkyl chain end methyl protons is observed in the 0.7-1.7 ppm region. It should be mentioned that small amount of impurities (mainly remained solvents: THF at 3.75 ppm and DMF at 2.8 and 2.9 ppm) can be observed in the recorded spectra as well.

FIGURE 3

The ratio of BHT and compatibilizer bonded to the PEI carrier was determined by the ratio of integrals of the aromatic protons of BHT and methyl protons of the chain end of the compatibilizer (**Table 1**). It can be stated that the BHT and compatibilizer ratios fit well to the feed ratio of the BHT and compatibilizer reactants. Thus the ratio of the BHT and compatibilizer in the macromolecular antioxidant can be easily controlled by the feed ratio of the reactants. The total content of both the BHT and compatibilizer groups bonded to the PEI carrier was estimated from the ratio of integrals of aromatic protons and the total amount of protons (**Table 1**). Knowing the exact ratio of the BHT and compatibilizer groups, their content was calculated also from the increase of the weight of PEI after its modification. The BHT content determined this way fits very well with the BHT content determined from the ^1H NMR spectra.

Finally, the macromolecular antioxidants were investigated by UV spectroscopy, which can provide the most accurate information on the BHT content bonded on the PEI carrier. As depicted in **Figure 4**, UV spectra of macromolecular antioxidants showed the presence of absorption peaks in the aromatic region (260-290 nm) in contrast to that of the unmodified PEI, which has only one peak at about 209 nm. The BHT content (**Table 1**) was determined from the absorbance at 275 nm, where the polymer main chain does not absorb. As shown in Table 1, the BHT content calculated from the UV spectra fits quite well with the values determined by the other two methods, described above, with error lower than 10%.

Based on the BHT content determined by both UV and NMR spectroscopy and the ratios of BHT and compatibilizer contents, the conversion of carboxylic acids in the amidation reaction was calculated and it ranged from 59 to 79%. Taking into account that the carboxylic acids were used in 2.5 fold excess to primary amines present in the PEI structure, only 40% conversion could be expected when only primary amines react with the carboxylic acids. Since the conversion of carboxylic acids was higher, it can be concluded that in addition to primary amines, also part of the secondary amines was converted to amide groups during the reaction with the carboxylic acids.

Based on the results of functionality investigations, it can be concluded that we reached high active group content by amidation of PEI as carrier for AoxAc (3.18 mmol BHT/g macromolecular antioxidant) which is only slightly below the functionality of commercially available antioxidant IRGANOX[®] 1010 (3.4 mmol BHT/g antioxidant).

FIGURE 4

Efficiency of hyperbranched poly(ethyleneimine) based macromolecular antioxidants in stabilization of polyolefins

Thermal stability of the macromolecular antioxidants is an important factor during processing. Therefore, before mixing with polyolefins the thermal behavior of the new polymeric antioxidants was examined by thermal gravimetric analysis (see **Figure S1** in the Supporting Information). The main data about the functionalized polymer is the temperature of the 5% weight loss, because this is the end point of the thermal stability (**Table S1**). To eliminate the effect of residual solvents, the thermal decomposition temperatures were calculated at 5 wt% weight loss from 150 °C. For all the synthesized antioxidants, the $T_{5\%,wt.loss}$ temperature was found to be over 240 °C, and for the antioxidants containing stearyl and lauryl groups even at higher temperatures, about 290 °C. These results clearly indicate that all the synthesized new macromolecular antioxidants are stable at temperatures used for both polyethylene and polypropylene processing. Due to the presence of relatively high amount of compatibilizing agent in some synthesized samples, the amount of the synthesized antioxidants added to the polymers was calculated to achieve 0.2 wt% concentrations of BHT groups in the polymer matrices.

The novel PEI-based macromolecular antioxidants were first tested for their efficiency in thermooxidative stabilization of polypropylene (PP) and their inhibition efficiency was compared to the thermooxidative stability of pure PP. The thermooxidative stability of the PP films was evaluated by chemiluminescence (**Figure 5**). As expected, the induction period of thermal oxidation was shortest in the case of pure

PP. The best stability against the thermooxidation of PP was achieved in the case of macromolecular antioxidant PEI-*l*-AoxAc bearing no compatibilizing group. All the other tested antioxidants bearing some compatibilizing groups showed almost the same stabilizing efficiency against thermooxidation of PP, which was lower than in the case of PEI-*l*-AoxAc.

FIGURE 5

All the synthesized macromolecular antioxidants as well as the commercially available hindered phenolic antioxidant Irganox 1010 (0.2 wt% concentrations of BHT groups) and 0.2 wt% of unmodified PEI were further tested as light stabilizer in both PP and polyethylene (PE) films. The extent of photooxidation of PP and PE films was followed by FT IR spectroscopy (**Figs. 6 and 7**). As shown in Figure 6, the pure PP started to oxidize shortly after the beginning of irradiation. There was practically no induction period. For quantification of the stabilizing effect, usually the time when the carbonyl absorption reached the value of 0.2 was taken into account (**Table 2**). This value was determined by Gugumus et al. to be roughly adequate to the 50% loss of tensile strength of PP and PE films. [31] The value $A_{CO} = 0.2$ for non-stabilized PP was reached after 220 hrs. Slight stabilizing effect was observed when unmodified PEI was mixed to the PP, probably due to presence of amine groups enable to react with radicals. The value of $A_{CO} = 0.2$ in this sample was reached after 340 hrs. The stabilizing efficiency of the new macromolecular antioxidants depend on the presence and structure of the compatibilizing groups. Surprisingly, the best efficiency, reaching $A_{CO} = 0.2$ after 740 hrs, was obtained for the sample PEI-*l*-AoxAc bearing no compatibilizing groups, but

only the BHT groups on the PEI carrier. The presence of butyl groups on the PEI carrier beside the active BHT in PEI-*l*-AoxAc/ButAc sample led to 25% decrease of the stabilizing efficiency in comparison with the PEI-*l*-AoxAc sample without compatibilizer, and the $A_{CO} = 0.2$ was reached after 570 hrs. The lauryl and stearyl groups on the PEI carrier decreased the stabilizing efficiency even in higher extent, and $A_{CO} = 0.2$ was reached after 450 hrs and 480 hrs for lauryl for stearyl derivatives, respectively. It should be mentioned that increasing the BHT/lauryl compatibilizer ratio from 1/1 to 2/1 for the lauryl derivatives led to increased stabilizing efficiency. While for BHT/lauryl compatibilizer ratio 1/1 the $A_{CO} = 0.2$ was reached after 450 hrs, for the ratio 2/1 it was after 500 hrs.

TABLE 2

FIGURE 6

The photooxidation of PP is a heterogeneous process taking place mainly in amorphous and semi-crystalline domains. There are some weak sites in the polymer chain where oxidation starts during processing resulting in the formation of hydroperoxide, sometimes also ketone, groups. This could be the reason for higher efficiency of the more polar antioxidant bearing no compatibilizer, such as PEI-*l*-AoxAc, which can concentrate preferably in these polar regions. On the other hand, the n-butyl, lauryl and stearyl groups bonded to the macromolecular antioxidants can diminish accumulation in the polar preoxidized regions. Another explanation could be partial steric effect, especially long alkyl chains, such as lauryl or stearyl, on the active BHT parts.

The best efficiency was reached for the commercially available sterically hindered phenol (Irganox 1010). The better efficiency in comparison with PEI-*l*-AoxAc may be due to the much lower molecular weight of the Irganox 1010 (1178 Da) than that of the macromolecular PEI-*l*-AoxAc (8800 Da) sample.

The photooxidation of PE films containing synthesized macromolecular antioxidants are shown in Figure 7. Naturally, the photostability of pure PE is much higher in comparison with pure PP. As the data in Table 2 indicate, the value of $A_{CO} = 0.2$ was reached in the case of pure PE after 420 hrs, that is double time as in the case of pure PP. On the other hand, the relative stabilizing efficiencies of all synthesized macromolecular antioxidants as well as the commercially available antioxidant (Irganox 1010) were lower in comparison with their stabilizing efficiencies in PP. The best stabilizing efficiency among the synthesized stabilizers was obtained for PEI-*l*-AoxAc bearing no compatibilizing groups, and for PEI-*l*-AoxAc/ButAc, bearing short butyryl group. For both samples, the $A_{CO} = 0.2$ was reached after about 720 hrs. Similarly to PP, also in the case of PE stabilization, the efficiency of antioxidants with long alkyl chains, such as lauryl and stearyl, was lower than for antioxidant with no compatibilizing group, and the samples reached the $A_{CO} = 0.2$ within the irradiation period of 540-630 hrs. The samples containing the commercially available antioxidant (Irganox 1010) were slightly more stable than the samples containing the most efficient macromolecular antioxidants, and the $A_{CO} = 0.2$ for Irganox 1010 was reached after about 870 hrs.

FIGURE 7

The photooxidation of the polyolefin films was followed also by UV-Vis spectroscopy. Figure 8 shows a representative example of the UV-Vis spectra of PE film containing PEI-*l*-AoxAc antioxidant before irradiation and after various irradiation times. As can be seen in this Figure, the absorption peaks from the antioxidant at about 235 and 280 nm progressively decrease during the irradiation, and almost disappear after 112 hours of irradiation. Subsequently, after prolonged irradiation period for more than 350 hours, progressive increase of absorption in the 200-300 nm region is observed due to oxidation of the PE matrix. Comparison of the photooxidation of PE for pure PE, PEI-*l*-AoxAc and PEI-*l*-AoxAc/ButAc antioxidants and Irganox 1010 based on evolution of the absorbance at 225 nm with irradiation time is shown in **Figure S2**. The stabilizing efficiency trend determined from the UV-Vis spectra corresponds well with the efficiency trend obtained from the FT IR spectra. Similar agreement between the results from FT IR and UV-Vis was observed also for PP (**Figure S3**).

FIGURE 8

Extraction of antioxidants from PP films

One of the main advantages of macromolecular antioxidants should be their low extractability from the polymer matrices, which makes such stabilizers environmentally advantageous and biofriendly polymer additives. This resistance was tested by using n-hexane and water as extraction agents. Extraction by n-hexane was done at room

temperature for 70 hrs. The leaching of the antioxidants from PP films was followed by UV-Vis spectroscopy. The changes in absorbance for PP films containing Irganox 1010, PEI-*l*-AoxAc and PEI-*l*-AoxAc/StAc are shown in **Figure 9**. As expected, low extractability was observed for all the prepared new additives (the spectra for PEI-*l*-AoxAc and PEI-*l*-AoxAc/StAc samples are shown as examples). Surprisingly, Irganox 1010 was almost completely washed out from PP under the applied conditions. All the synthesized macromolecular antioxidants as well as Irganox 1010 showed no extraction in hot water since there were no changes in the UV spectra after extraction in water at 65 °C for 27 hrs.

FIGURE 9

Conclusions

Macromolecular antioxidants as potentially new environmentally advantageous polymer additives were successfully synthesized *via* functionalization of hyperbranched poly(ethyleneimine) with sterically hindered phenolic antioxidant (BHT analogue) and different compatibilizers. ¹H NMR and UV-Vis spectroscopies as well as GPC showed high degree of functionalization and possibility of control of the molar ratio of BHT and compatibilizer groups by the feed ratio of the reactants. The stabilization efficiency against thermooxidation and photooxidation of polyolefins was found to be higher for the macromolecular antioxidant not bearing any compatibilizing groups than that for antioxidants with long alkyl chain for improving the compatibility with the polymer

matrix. Even though the stabilizing efficiency of commercially available antioxidant Irganox 1010 was only slightly higher than that found for the synthesized novel macromolecular antioxidants, the extraction of the antioxidants from the polypropylene film in hexane resulted in significantly lower extent of diffusion for the macromolecular antioxidants out of the polymer film than that found for Irganox 1010. No extraction was observed in water at 65 °C. The results of this study show the applicability of the synthesized antioxidants in (food) packaging materials and/or in materials used in agriculture, and moreover for organic solvent and reagent packaging or rubber seals, septa etc., where additives with low diffusion from the polymeric materials are required.

Acknowledgements

The authors are grateful for the TGA, ¹H NMR and GPC analyses to J. Szauer, É. Dorko and T. Ignáth, respectively. The authors also thank for financial support to the European Regional Development Fund through the Hungary-Slovakia Cross-Border Cooperation Program 2007-2013 (HUSK/1101/1.2.1/0209).

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FIGURE CAPTIONS

Fig. 1. The reaction scheme of the synthesis of poly(ethyleneimine) based macromolecular antioxidants

Fig. 2. Molecular weight distribution curves of PEI modified with antioxidant and different compatibilizers

Fig. 3. ^1H NMR spectra of PEI based macromolecular antioxidants

Fig. 4. UV spectra of the starting PEI and BHT compared with PEI-antioxidant samples

Fig. 5. Chemiluminescence (CL) intensity as a function of time in oxygen for pure PP and PP containing (1) PEI-*l*-AoxAc, (2) PEI-*l*-AoxAc/ButAc, (3) PEI-*l*-AoxAc/StAc, (4) PEI-*l*-AoxAc/LaAc (AoxAc:LaAc 1:1) and (5) PEI-*l*-AoxAc/LaAc (AoxAc:LaAc 2:1) loaded at 0.2% wt. concentration of BHT groups (the dotted line indicates the temperature increase during the measurements).

Fig. 6. Evolution of changes in FT IR spectra in the carbonyl region for pure PP and PP films containing synthesized antioxidants or commercially available Irganox 1010 as a function of time of irradiation. Additives concentration of BHT groups was 0.2 wt%, film thickness: 0.1 mm.

Fig. 7. Evolution of changes in FT IR spectra in the carbonyl region for pure PE and PE films containing synthesized antioxidants or commercially available Irganox 1010, with time of irradiation. Additives concentration of BHT groups was 0.2 wt%, film thickness: 0.1 mm.

Fig. 8. Changes in the UV spectra for PE film containing synthesized macromolecular antioxidants (PEI-*l*-AoxAc) before irradiation and after various irradiation times.

Fig. 9. Changes in the UV spectra for PP films containing commercially available (Irganox 1010) and synthesized macromolecular antioxidants (PEI-*l*-AoxAc and PEI-*l*-AoxAc/StAc) before and after extraction in hexane at room temperature for 70 hours.

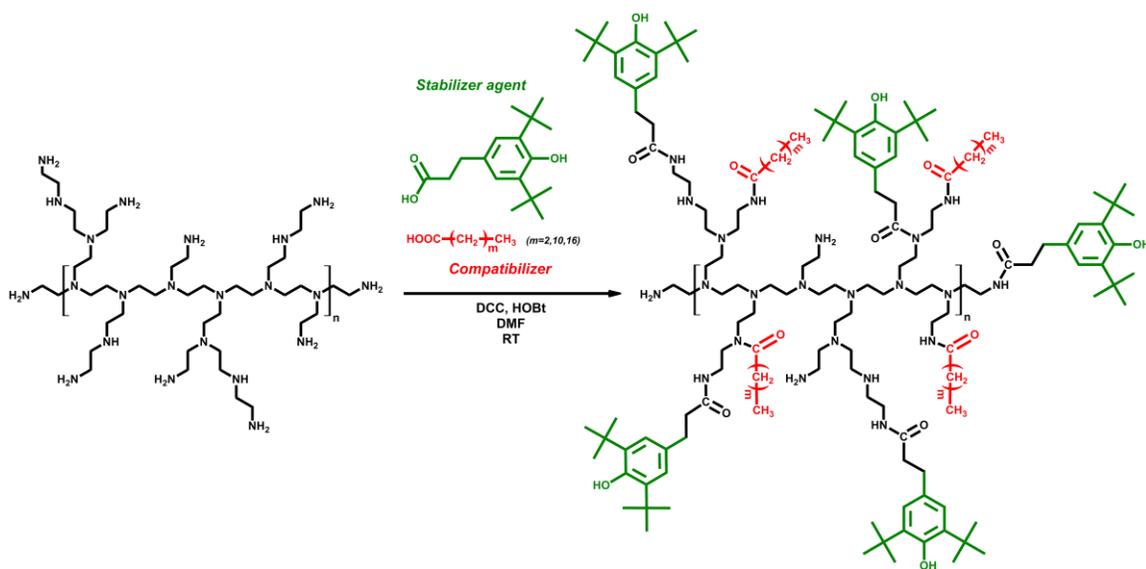


Fig. 1. The reaction scheme of the synthesis of poly(ethyleneimine) based macromolecular antioxidant

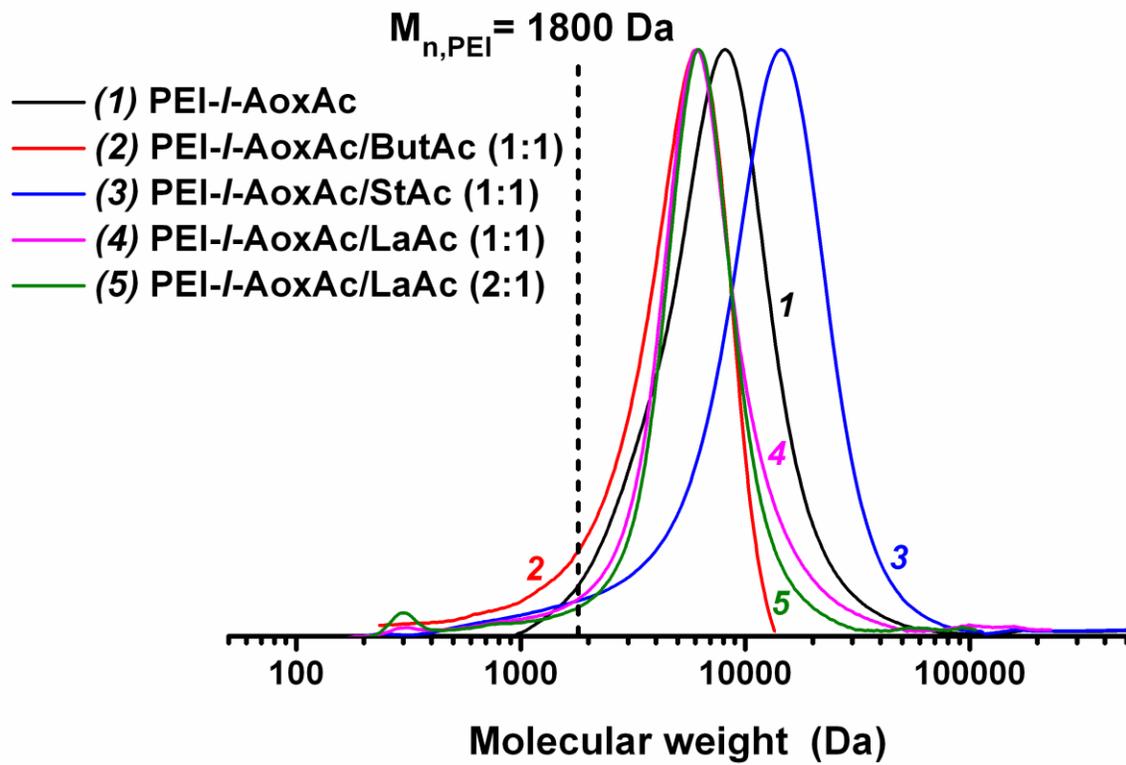


Fig. 2. Molecular weight distribution curves of PEI modified with antioxidant and different compatibilizers

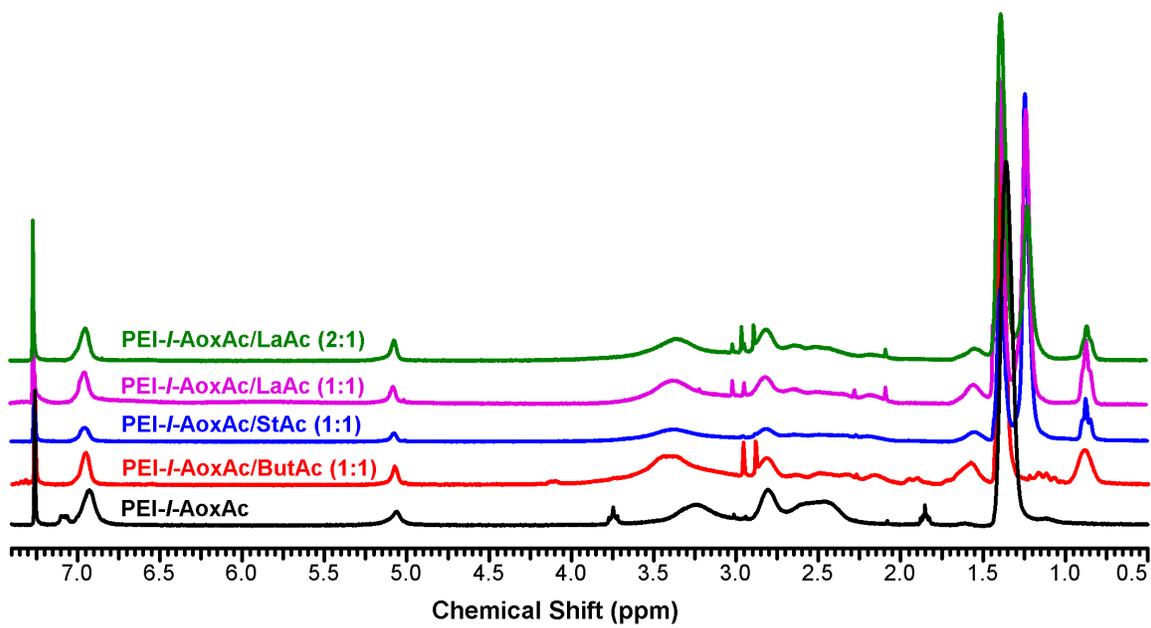


Fig. 3. ¹H NMR spectra of PEI based macromolecular antioxidants

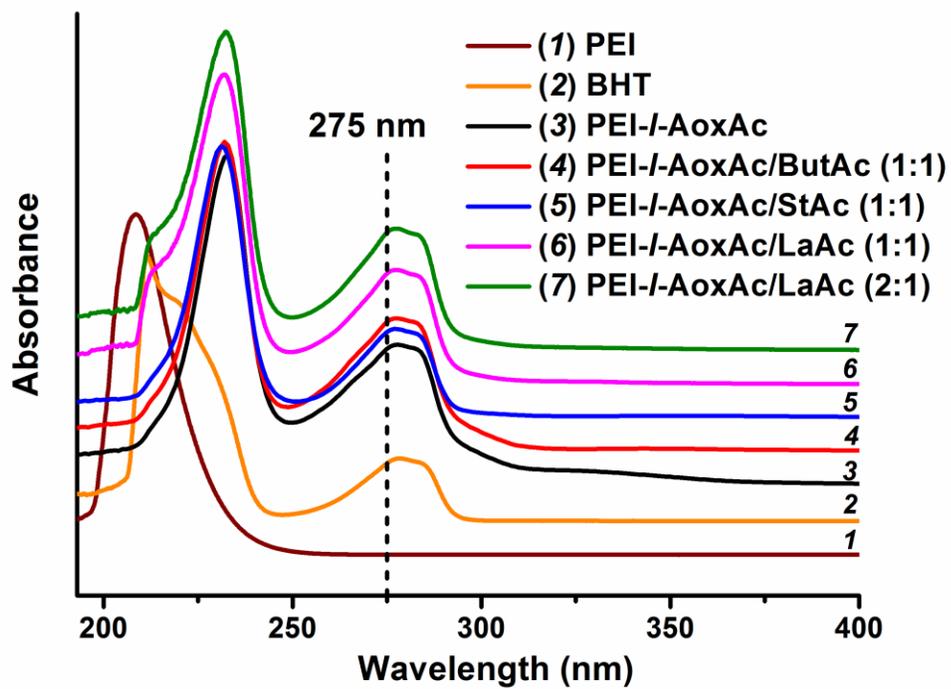


Fig. 4. UV spectra of the PEI-antioxidant samples compared with starting PEI and BHT

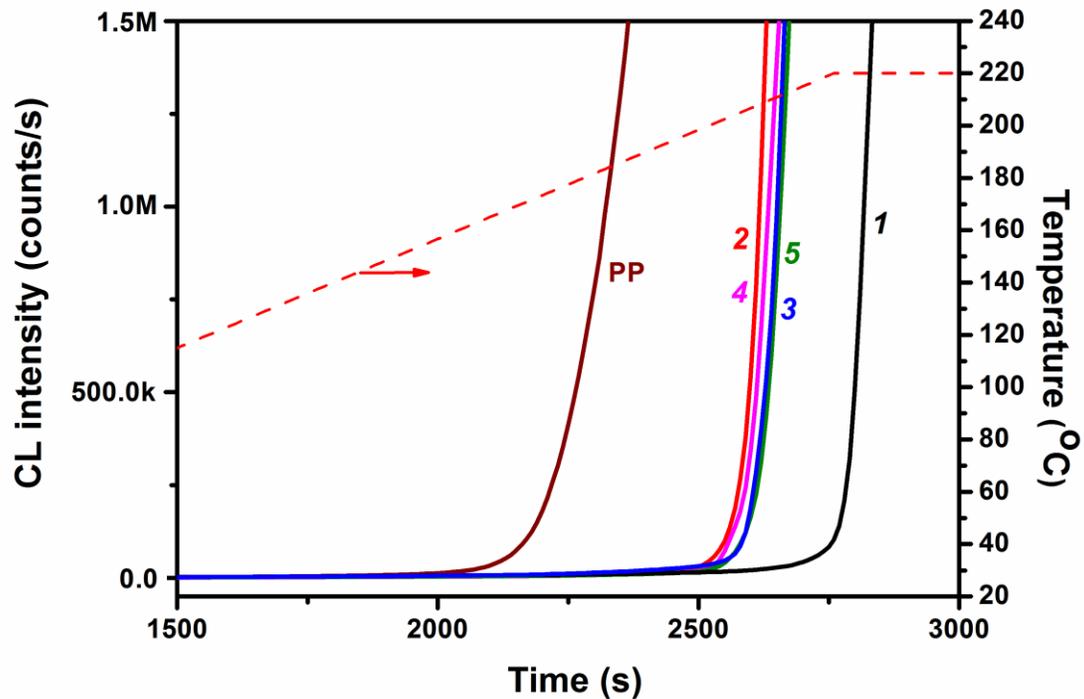


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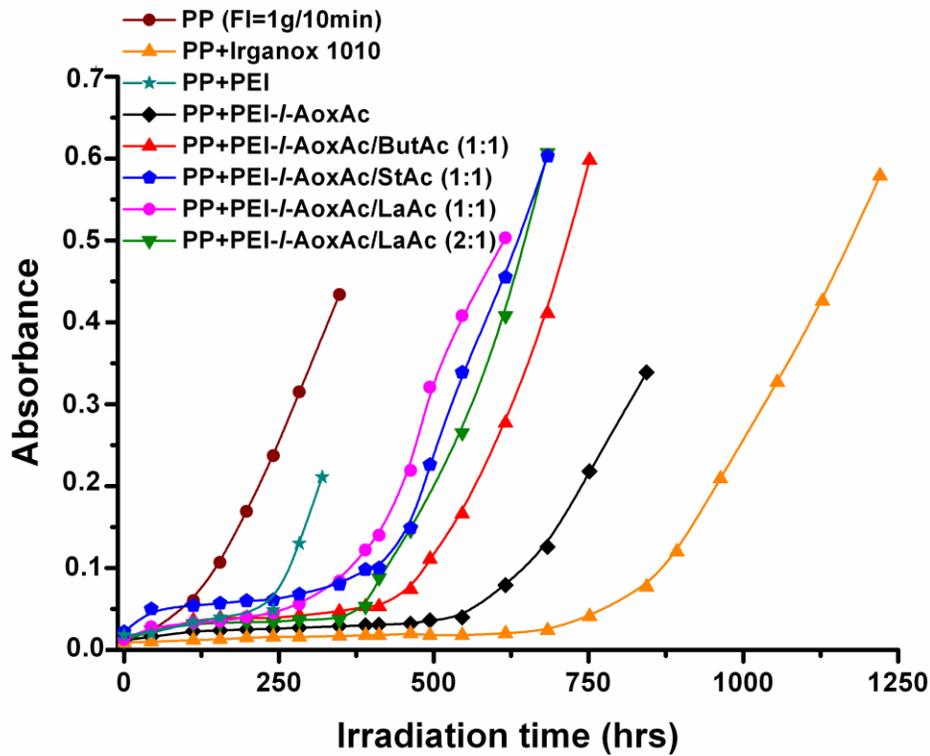


Fig. 6. Evolution of changes in FT IR spectra in the carbonyl region for pure PP and PP films containing synthesized antioxidants or commercially available Irganox 1010 as a function of time of irradiation. Additive concentration of BHT groups was 0.2 wt%, film thickness: 0.1 mm.

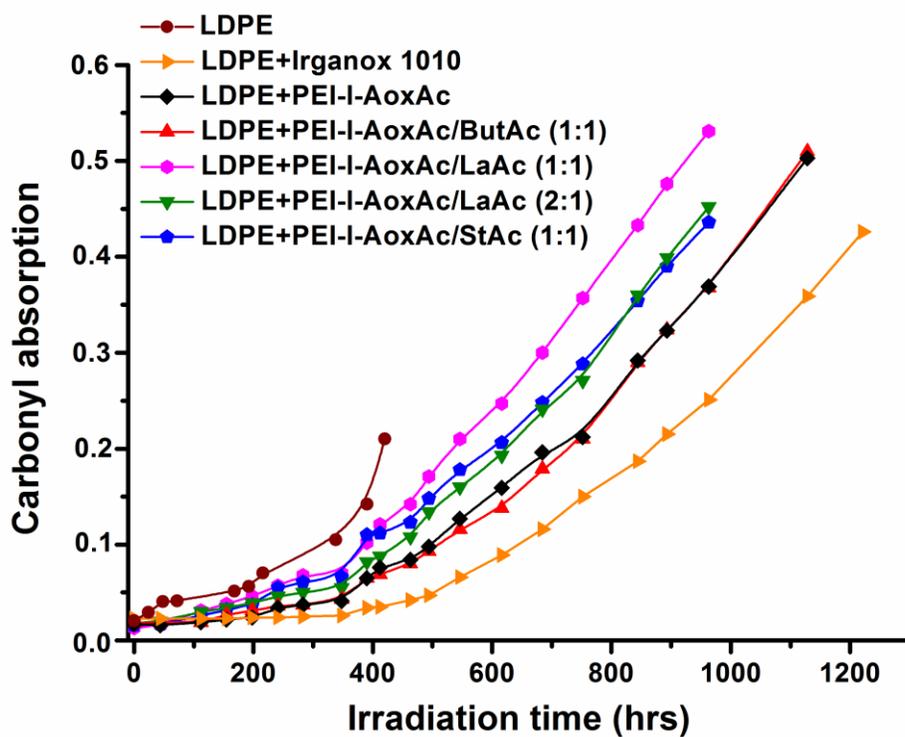


Fig. 7. Evolution of changes in FT IR spectra in the carbonyl region for pure PE and PE films containing synthesized antioxidants or commercially available Irganox 1010, with time of irradiation. Additive concentration of BHT groups was 0.2 wt%, film thickness: 0.1 mm.

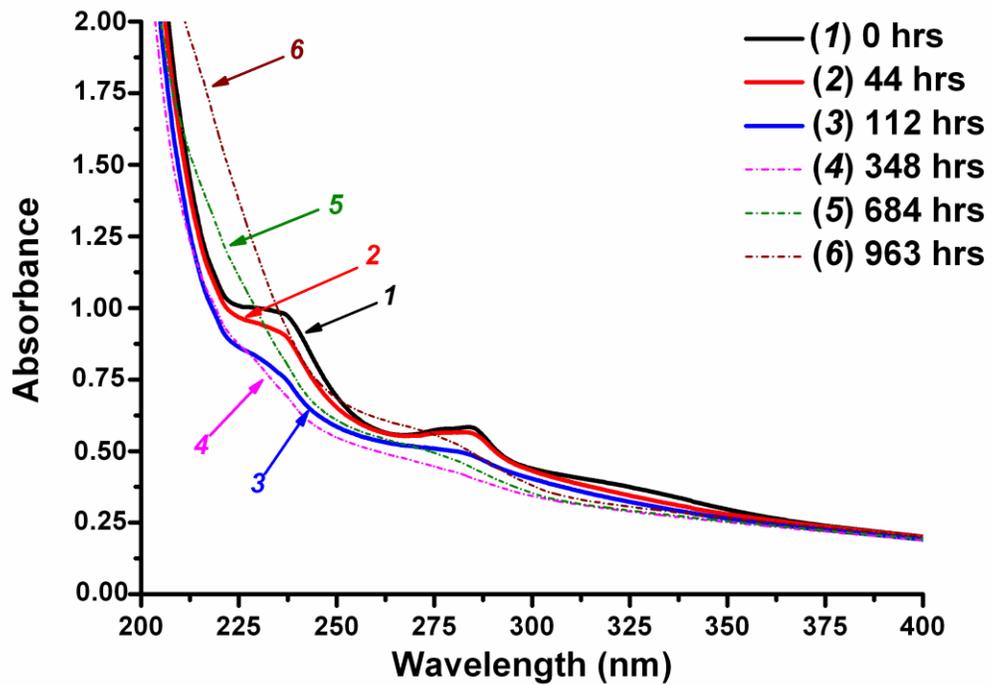


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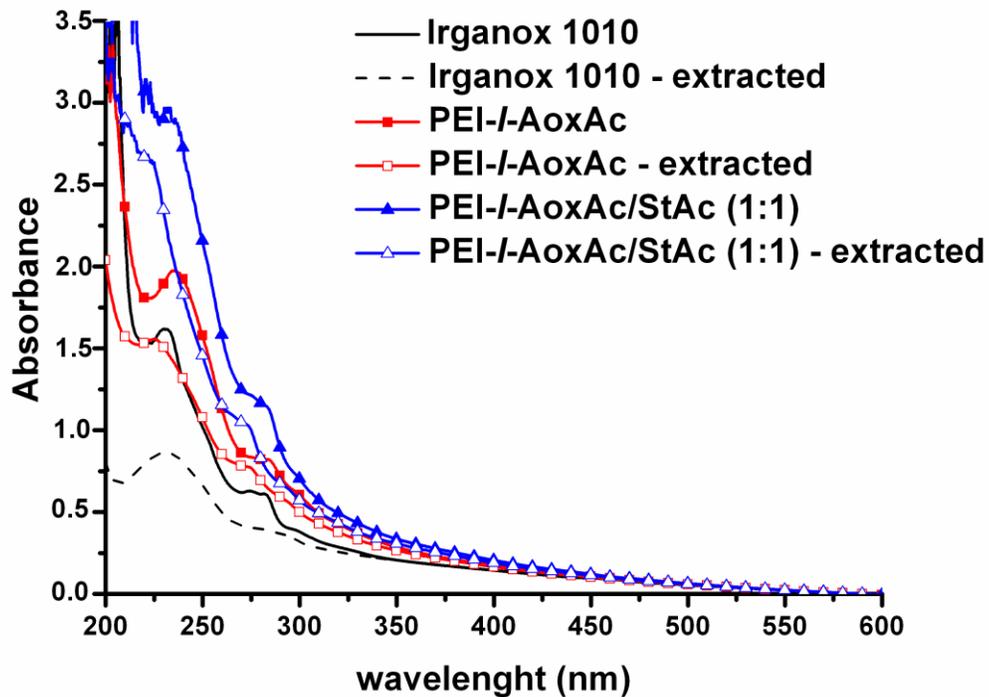


Fig. 9. Changes in the UV spectra for PP films containing commercially available (Irganox 1010) and synthesized macromolecular antioxidants (PEI-*l*-AoxAc and PEI-*l*-AoxAc/StAc) before and after extraction in hexane at room temperature for 70 hours.

Tables

Table 1. Results of characterization of the synthesized hyperbranched poly(ethyleneimine) based macromolecular antioxidants

Sample	f ^a	F ^b	M _n (Da)	PDI	Conv ^c (%)	BHT content based on (mmol BHT / 1g stabilizer)		
						conv	¹ H NMR	UV
PEI- <i>l</i> -AoxAc	1:0	1:0	8800	1.43	79	2.84	3.07	3.18
PEI- <i>l</i> -AoxAc/ButAc	1:1	1:1	5300	1.21	70	1.85	1.90	1.87
PEI- <i>l</i> -AoxAc/LaAc	1:1	1:1	6800	1.23	79	1.59	1.78	1.56
PEI- <i>l</i> -AoxAc/LaAc	2:1	2:1	7400	1.42	62	1.90	2.14	1.94
PEI- <i>l</i> -AoxAc/StAc	1:1	1:1.2	14900	1.40	59	1.21	1.29	1.13

^a Feed ratio of the antioxidant and compatibilizer

^b Molar ratio of the BHT and compatibilizer determined by ¹H NMR spectroscopy

^c Conversion of carboxylic acids during functionalization of PEI carrier

Table 2. The irradiation times when the carbonyl absorption in the FT IR spectra in the 1700-1740 cm⁻¹ region reaches the value of 0.2 ($t_{A(C=O)=0.2}$) for PP and LDPE in the absence and presence of the stabilizers. Additive concentration of BHT groups was 0.2 wt%, film thickness: 0.1 mm.

Antioxidant	$t_{A(C=O)=2}$ (hours)	
	PP	LDPE
no antioxidant	220	420
Irganox 1010	950	870
PEI	340	not tested
PEI-/-AoxAc	740	715
PEI-/-AoxAc/ButAc (1:1)	570	725
PEI-/-AoxAc/LaAc (1:1)	450	540
PEI-/-AoxAc/LaAc (2:1)	500	630
PEI-/-AoxAc/StAc (1:1)	480	600

Graphical abstract

