



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-butyl, 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.

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1. Introduction

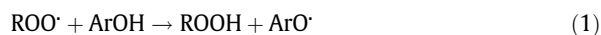
Polymeric materials are commonly exposed to heat, oxygen, radiation, water, metal catalyst residues and

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

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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 Eq. (1)), and thus preventing the hydrogen abstraction from polymer chains (RH) by the peroxy radicals (see Eq. (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 bio-friendly 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.

2. Experimental

2.1. 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/10 min (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 18–22 g/10 min, particle size 500 µm, Vicat 84 °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.

2.2. 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 alkanic 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 h. The precipitated dicyclohexylurea was filtered and the filtrate was concentrated by rotary evaporator. The crude products

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