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Hyperbranched polyglycerol nanoparticles based multifunctional, nonmigrating hindered phenolic macromolecular antioxidants: synthesis, characterization and its stabilization effect on poly(vinyl chloride)

Dedicated to Professor Axel H. E. Müller on the occasion of his 70th birthday

by

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Abstract

A facile synthesis of multifunctional hindered phenolic macromolecular antioxidants based on hyperbranched polyglycerol (HbPG) nanoparticles as cores with different molecular weights is reported. The structure of the resulting polymers was verified by ^{1}H NMR and UV–Vis spectroscopies indicating 64-77% antioxidant functionalizations of the hydroxyl groups of the HbPGs. GPC analyses show that polymeric antioxidants with PDI of 1.33-1.66 are formed. DSC and TGA measurements revealed T_g of ~40 °C and high thermal stability up to ~300 °C of the multifunctional HbPG-antioxidant conjugates, respectively, confirming that these materials are liquids and stable at usual polymer processing temperatures. The efficiency of the synthesized antioxidants in thermooxidative stabilization of PVC was investigating, keeping in mind that although the importance and wide application of PVC, especially in biomedical fields are incontestable, the utilization of macromolecular antioxidants for the stabilization of PVC has not been examined so far. It was found that the macromolecular antioxidants show similar stabilizing efficiency as the tetrafunctional industrial Irganox1010. Very low extent of leaching of the HbPG-antioxidant from PVC blends, investigated by extraction tests in both water and hexane, was observed in both extracting agents in contrast to the case of the low molecular weight hindered phenolic antioxidant. Thus, the obtained results confirm the advantages, i.e. high efficiency and highly suppressed leaching, of HbPG-based macromolecular antioxidants in a variety of application fields.

Keywords

Hyperbranched polyglycerol nanoparticle; Macromolecular antioxidant; Polymer-bound antioxidant; Hindered phenols; Thermooxidation; PVC

1. Introduction

Hyperbranched polymers are unique nanoparticles, many of which possess multiple functional terminal sites, some of them pendant functionalities as well, capable to function as starting materials for new nanostructured substances not existed before [1-8]. Among such highly branched macromolecules, hyperbranched polyglycerol (HbPG) with average diameter in the few nanometer range (~2-20 nm) and with both chain end and pendant hydroxyl functionalities offers a variety of new derivatization processes to obtain materials with advantageous application possibilities, ranging from biomedicine to nanotechnologies and large scale commodities as well [9-18]. HbPG is a polyether polyol, which has favorable properties, namely low cytotoxicity, biocompatibility, water solubility and low viscosity [19-21]. The hydroxyl groups of HbPG were transformed to different functional groups and were modified by imaging or drug molecules to develop macromolecular supports for organic syntheses or biomaterials for biomedical applications [22-29]. Based on these benefits, HbPG is a promising candidate as carrier molecule for the synthesis of multifunctional macromolecular nanosized assemblies with targeted applications. One such possibility can be related to the utilization of the hydroxyl groups of HbPG to attach hindered phenol moieties in order to obtain multifunctional hyperbranched antioxidants with HbPG cores.

Sterically hindered phenols, especially 3,5-di-*tert*-butyl-4-methylphenol (butylated hydroxytoluene, BHT) and its derivatives, such as Irganox1010, are the most commonly used class of antioxidants [30] and have been widely applied in the stabilization of polymers during processing and use (for the structure of BHT and Irganox1010, see Scheme S1 in the Supporting Information). However, most of these antioxidants, and other polymer stabilizers and additives as well, with low molecular weights are sensitive to physical loss by evaporation, extraction and migration [31,32]. Therefore, a major concern has evolved in environmental and biomedical issues and safety regulations, as well as in long-term use of polymers containing

such antioxidants [33,34]. In order to reduce the physical loss of antioxidants, intensive research has been conducted worldwide, and various high molecular weight antioxidants were developed [35-38]. Another possible route is the application of polymer-bound antioxidants with low extent of migration to the environment. Due to the slow or completely retarded diffusion of macromolecular antioxidants, it is expected that these materials can be considered as more bio- and environmental friendly polymer additives than their low molecular weight counterparts, and may be applied advantageously in wide application ranges, mainly in biomedical fields, food packaging and agriculture. Macromolecular antioxidants have already been prepared either by postmodification of the reactive sites on polymer chains or copolymerization of monomers with antioxidant-functionalized monomers [33,39-45]. The sterically hindered phenolic antioxidants were bonded to variety of substrates, such as silica nanoparticles [46,47], carbon nanotubes [48,49] and several types of linear polymers, e.g. polybutadiene [50,51], polystyrene [52], polyethylene [53-55], polypropylene (PP) [52,56] and polyisobutylene [57]. Although, polymers with complex topology, such as star and branched structure, have numerous advantageous properties compared to their linear analogues, namely lower intrinsic viscosity and high number of modifiable functional groups, only one seven-arm star polymer [58] and few hyperbranched polymer based macromolecular antioxidants were described in previous literature [59-61]. However, the efficiency investigations of the reported hyperbranched polyester based sterically hindered phenol antioxidants showed that these macroadditives are more efficient in squalane than in PP matrix [59]. Recently, phenolic antioxidant-functionalized dendritic polyethylene was also prepared by copolymerization of ethylene with an olefin containing hindered phenol moiety [60]. In our previous report, hyperbranched poly(ethyleneimine) based hindered phenol-type macromolecular antioxidants were reported [61]. Our findings showed that these additives are effective antioxidants in

polypropylene and polyethylene matrices. Moreover, their lower extent of leaching than that of BHT and Irganox1010, a tetrafunctional industrial antioxidant, was also proved.

Antioxidants are widely used for protecting of a large variety of polymers against degradation and simultaneous deterioration of their physical and chemical properties during processing and use in the presence of air, i.e. oxygen. Among commercial polymers, poly(vinyl chloride) (PVC), due to its advantageous properties, is one of the most widely used polymers in broad ranges of industrial and medical applications. However, it is also one of the most sensitive polymers to heat, thermooxidation and photooxidation during processing and use [62-76]. Thermal degradation of PVC occurs by an autocatalytic dehydrochlorination reaction with simultaneous formation of reactive conjugated double bond containing sequences along the polymer chain [64-67]. This process causes unacceptable discoloration of the polymer and drastic changes in its chemical, physical and mechanical properties. [64-68,75]. Therefore, various additives, such as antioxidants, thermal and photo-stabilizers, are used to reduce the adverse external effects and avoid chain scission and cross-linking reactions during processing and application of this useful polymer [62-67]. In spite of its importance, it is surprising that thermooxidation of PVC and its stabilization process by antioxidants have rarely been investigated. As was found by us recently [70,71], even low extent of thermooxidation of PVC results in severe chain scission and to significant decrease of the thermal stability of this polymer. Therefore, efficient stabilization against oxidative and thermal degradation is essential for processing and use of PVC and related polymers. To the best of our knowledge, multifunctional macromolecular antioxidants for PVC stabilization have not been explored at all so far.

Taking into account the beneficial properties of HbPG as multifunctional nanoparticle [9-29,77-80], we aimed at the synthesis and exploration of HbPG-based multifunctional antioxidants. It has to be mentioned that only one case is known in the course of which HbPG-

based supramolecular antioxidant assemblies were studied [77]. These antioxidant complexes showed enhanced antioxidant capacity, proved by oxygen radical absorbance capacity assay. However, the phenolic active groups were not linked by covalent bond to the HbPGs, and these HbPG-based macromolecular antioxidants were not tested in polymer matrices. In our investigations, the HbPGs were synthesized by ring-opening multibranching polymerization [78,79], with different molecular weights and functionalized with sterically hindered phenolic antioxidant by an esterification reaction to obtain a macromolecular analogue of butylated hydroxytoluene (BHT). The good miscibility and compatibility of polyesters and polyethers with PVC matrices are well-known [81,82], therefore the application of HbPG-based macromolecular antioxidants is expected to be advantageous for stabilization of PVC. Herein, the results of our investigations on the synthesis, molecular characteristics and thermal properties of new macromolecular antioxidants with HbPG cores, as well as their stabilization efficiencies are reported. The extractability of the macromolecular antioxidants from PVC with the antioxidants was studied as well.

2. Experimental

2.1. Materials

Glycidol was obtained from Sigma-Aldrich and it was purified by vacuum distillation prior to use. 3-(3,5-Di-*tert*-butyl-4-hydroxyphenyl)propionic acid (AoxAc) was purchased from Creasyn Finechem and purified by recrystallization in Et_2O/hexane 20/80 (by volume) solvent mixture. The white crystals were filtered and washed with cold hexane and dried in vacuum. Pentaerythritol, potassium methoxide (KOMe) solution, *N*,*N*'-dicyclohexylcarbodiimide (DCC), 4-dimethylaminopyridine (DMAP), butylated hydroxytoluene (BHT) (all from Sigma-Aldrich) and Irganox1010 (from BASF) were used as received. A suspension PVC (BorsodChem, ONGROVIL® S-5070, M_n=68,800 g/mol, PDI =

2.26) was used in our experiments. Dimethylformamide (DMF), tetrahydrofuran (THF), methanol (MeOH), abs. ethanol (EtOH), 1,2,4-trichlorobenzene (TCB), diethyl ether (Et_2O) and *n*-hexane (all purchased from Molar Ltd.) were used without purification.

2.2. Synthesis of HbPG-based macromolecular antioxidants (HbPG-*l*-AoxAc)

HbPGs with three different molecular weights were applied as multifunctional core for producing macromolecular antioxidants. The HbPG starting materials were synthesized by ring-opening multibranching polymerization of glycidol according to the literature [78,79] initiated by pentaerythritol with three different monomer/initiator ratios (M/I = 80, 130, 330). The pentaerythritol initiator (0.2415 g, 0.1579 g and 0.0620 g) was placed in a three-necked round bottom flask equipped with a septum, a mechanical stirrer and connected to the vacuum line. Subsequently, the KOMe (0.4 eq. to the initiator) was added and stirred for one hour at 50 °C. After the deprotonation, the methanol was removed by vacuum, and the mixture was heated to 95-100 °C under nitrogen atmosphere. Then the glycidol monomer (10 mL, 11.17 g, 0.1508 mol) was added with a syringe pump by 2 mL/h dosing rate. After the completed monomer addition, the stirring was continued for three hours. Then the reaction mixture was cooled to room temperature and was dissolved in methanol and passed through a column filled with a cation exchange resin (Amberlite® IR120 hydrogen form). The products were precipitated into large excess of Et_2O two times and dried in vacuum at 80 °C. The produced HbPG samples were applied for the synthesis of macromolecular antioxidants without characterization.

For the functionalization of HbPG to obtain macromolecular antioxidants, a Steglich type esterification reaction was performed. The HbPGs (1 g, 10.9 mmol repeating unit) were dissolved in DMF (10 mL) and placed into a dry 100 mL round-bottom flask with magnetic stir bar. Then AoxAc (6.0519 g, 21.7 mmol, 2 eq. to repeating units) and DMAP (2.9296 g, 23.98 mmol, 2.2 eq. to repeating units) dissolved in DMF (20 mL) was added to the polymer solution.

Subsequently DCC (4.9478 g, 23.98 mmol, 2.2 eq. to repeating units) dissolved in DMF (20 mL) was added to the reaction mixture. The reaction flask was sealed and the reaction mixture was stirred overnight at room temperature. The formed dicyclohexylurea was removed by filtration and the filtrate was concentrated by rotary evaporator. The crude products were dissolved in cold THF, filtered and precipitated two times into large excess of MeOH/brine (95/5 by volume) and washed with cold hexane. The products were dried in vacuum at 50 °C until constant weight.

2.3. Characterization

Molecular weight and molecular weight distribution (polydispersity index, PDI) of the produced macromolecular antioxidants were measured by gel permeation chromatography (GPC). The GPC equipped with differential refractive index and viscosity detector (Agilent Infinity 1260) was used with three 5 μm particle size PlGel Mixed columns (HR1, HR2 and HR3 with different molecular weight ranges from 100 Da to 600,000 Da) and with a PlGel guard column thermostated at 35 °C. THF eluent was used with a flow rate of 1 mL/min. The molecular weight and PDI were determined using universal calibration based on linear polystyrene standards (from PSS Standards, Germany).

For the investigation of the functionalization efficiency and quantitative determination of the conversion of hydroxyl groups of HbPGs, solution state ^{1}H NMR spectra were obtained by a Varian NMR System spectrometer operating at the ^{1}H frequency of 600 MHz. The measurements of the macromolecular antioxidants were performed in deuterated chloroform ($CDCl_3$) at 25 °C and the unmodified HbPG control sample (HbPG1) was investigated in DMSO-d_6.

The BHT content of the produced 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 1×1 cm quartz cuvette, thermostated at 23 °C. The reference was abs. THF. The unmodified HbPG control sample (HbPG1) was investigated in abs. EtOH. The determination of the BHT content was based on the BHT calibration curve measured in abs. THF. The applied polymer concentrations are listed in the Supporting Information (see Table S1).

The thermal behaviour of the antioxidant molecules was investigated with differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA). The DSC investigation was performed on a TA Instruments Q2000 instrument under nitrogen atmosphere. The heating and cooling cycles were between -60 to 180 °C, and the first heating was made to eliminate the thermal history of the samples. The heating rate was 10 °C/min, and the nitrogen flow was 50 mL/min. The T_g values were calculated from the inflexion point of the DSC curves. The TGA measurements were carried out on a TA Instruments Q500 equipment under nitrogen atmosphere. The heating rate was 10 °C/min in the range of 35 to 750 °C. The nitrogen flow was 100 mL/min. The thermal stability was determined as the temperature of the 5 wt% weight loss.

2.4. Investigation of the antioxidant efficiency

The antioxidative properties of the produced macromolecular additives were investigated in the course of the thermooxidative degradation of PVC and compared to the commercially available Irganox1010 tetrafunctional antioxidant. The degradative treatment of PVC solutions (0.2 g PVC dissolved in 20 ml TCB) was carried out by using a Metrohm PVC Thermomat 763 instrument. The eliminated HCl was monitored on-line with the same equipment. The degradation was carried out under oxygen with a flow rate of 4 L/h at 200 °C in presence of different amounts of antioxidants (0.14, 0.29, 0.59, 1 eq. BHT/100 vinyl chloride

(VC) repeating units). The oxidation induction times (OIT) and the standard deviations (SD) were determined by two parallel measurements. After degradation, the samples were precipitated in hexane and dried until constant weight under vacuum at room temperature. The precipitations were repeated one more times from THF to hexane. The effect of the antioxidants on the changes of molecular weight of PVC was investigated by GPC using the above mentioned equipment and conditions.

2.5. Extraction of antioxidants from PVC blends

PVC films containing either Irganox1010 or HbPG-l-AoxAc_1 were prepared by the solvent casting technique. The components, i.e. PVC (25 mg/mL) and Irganox1010 (25 mg/mL) in one case, and PVC (40 mg/mL) and HbPG-l-AoxAc_1 (25 mg/mL) for the other film were dissolved in distilled tetrahydrofuran separately. Then, 1 mL of the additive stock solutions were added to 12.5 mL of PVC solution in both cases. The solutions were stirred continuously for 24 h to obtain homogenous mixtures at room temperature. Then, 11 mL of the obtained solutions were cast on a glass Petri dish and were allowed to stand in air overnight at room temperature to allow slow evaporation of THF. The remaining THF residue was removed by further drying in vacuum for 6 hours at 50 °C. Thin films with ~0.25 mm thickness were obtained after casting. The films were sliced for the same size and weight (around 30 mg) and were extracted either in hexane (100 mL) and water (100 mL) at room temperature for 240 hours. After predetermined extraction times (24, 48, 96, 168, 240 hours), the films were removed and dried on a filtration paper for 1 h, and subsequently under vacuum at room temperature for 5 h. The extent of the extraction of the investigated antioxidants from PVC film was followed by ^{1}H NMR spectroscopy. The measurements were performed on a Bruker Avance 500 operating at 500 MHz ^{1}H frequency in deuterated tetrahydrofuran (THF-d_8) at 30 °C.

3. Results and discussion

3.1. Synthesis and characterization of hyperbranched polyglycerol based macromolecular antioxidants

The goal of this work was the synthesis of effective macromolecular antioxidants with multifunctional HbPG nanoparticles as cores with low diffusion out of polymer matrices. The synthetic approach is presented in Fig. 1. In addition to its outstanding biocompatibility, HbPG possesses primary and secondary hydroxyl groups, which can be modified with various desired functionalities. Therefore, HbPG can be utilized as a starting material for the preparation of complex multifunctional macromolecular nanoparticles. As shown in Fig. 1, the carrier HbPGs were synthesized by ring-opening multibranching polymerization of glycidol using pentaerythritol as initiator with three different monomer/initiator ratios according to a previously applied method [78,79]. Hindered phenols with BHT moieties are widely used antioxidants, even as food additives, therefore a carboxylic derivative of BHT (AoxAc) was used for bonding it to the HbPG carrier by applying the Steglich esterification reaction assisted with DCC and DMAP (Fig.1). All the synthesized antioxidants, i.e. HbPGs with AoxAC conjugates (HbPG-*l*-AoxAc, where *"l"* stands for *"linked to"*), were insoluble in water and highly soluble in common organic solvents, such as DMF, DMSO and unlike HbPG also in $CHCl_3$, THF and diethyl ether. The resulting macromolecular antioxidants were characterized by various methods, such as GPC, ^{1}H NMR and UV spectroscopies, TGA and DSC.

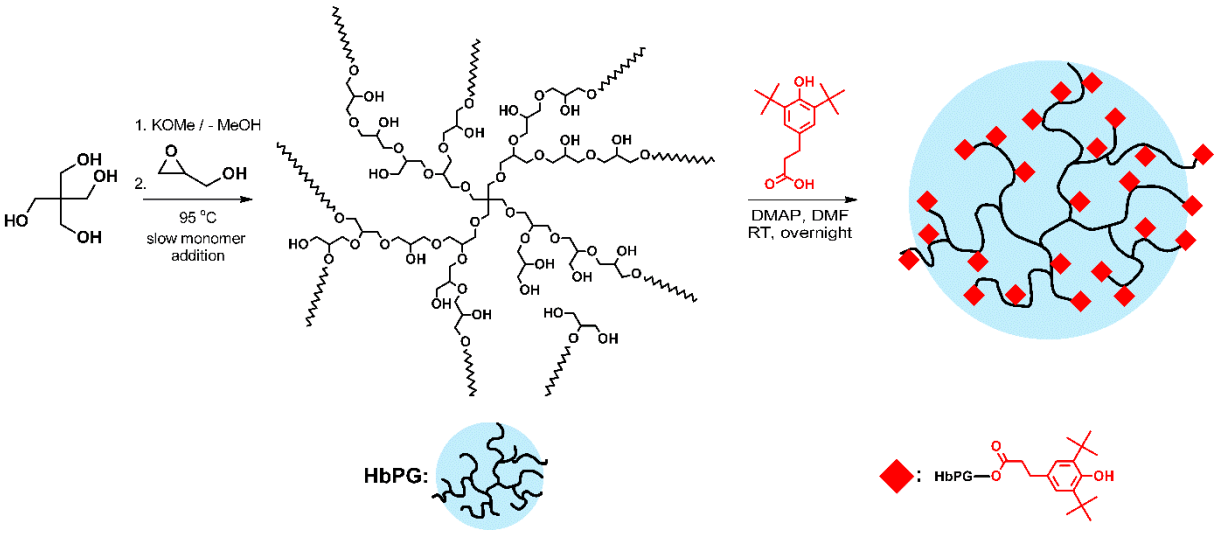

Fig. 1. The reaction scheme of the synthesis of HbPG-based macromolecular antioxidants (HbPG-*l*-AoxAc) by ring-opening multibranching polymerization of glycidol followed by functionalization with AoxAc.

The molecular weight distributions and thus the number average molecular weights (M_n) and PDI values of the produced macromolecular antioxidants were determined by GPC. The results are presented in Fig. 2 and Table 1. Based on the GPC results, it can be stated that HbPG based macromolecular antioxidants (HbPG-*l*-AoxAc) were successfully synthesized with three different M_n (between 20 – 100 kg/mol) and low PDI (around 1.2 – 1.6).

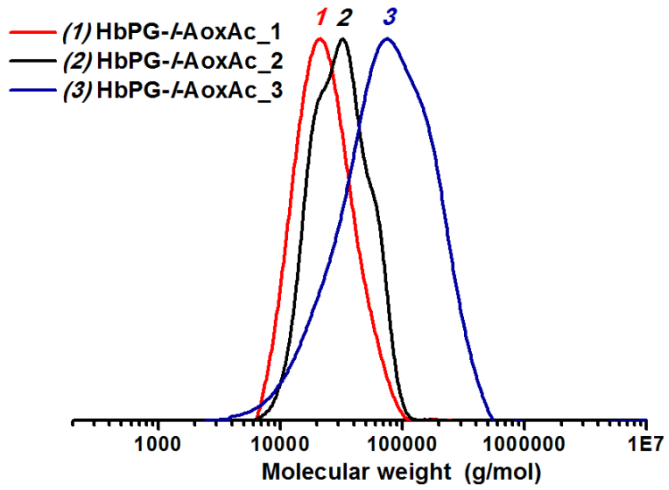

Fig. 2. Molecular weight distribution curves of HbPG-based macromolecular antioxidants (HbPG-*l*-AoxAc) (for sample identification see Table 1).

Table 1. Characterization results of HbPG-based macromolecular antioxidants: the extent of esterification (C), the number average molecular weight (M_n), polydispersity (PDI), BHT functionality, the glass transition temperature (T_g) and the decomposition temperature (T_d).

Sample	C[(a)] %	M_n (g/mol)	PDI	Functionality (mmol BHT / g)		T_g (°C)	T_d[(c)] (°C)
				NMR[(b)]	UV		
HbPG-*l*-AoxAc_1	77	26200	1.33	2.88	2.51	42	316
HbPG-*l*-AoxAc_2	64	34900	1.28	2.71	2.65	40	300
HbPG-*l*-AoxAc_3	73	101100	1.66	2.77	2.68	42	296

(a) hydroxyl group conversion determined by ^{1}H NMR spectroscopy
(b) calculated by Eq. 1-3.
(c) 5% weight loss

The synthesized macromolecular antioxidants were characterized by ^{1}H NMR spectroscopy in order to reveal the functionalization and to determine the conversion of hydroxyl groups of the HbPG molecules. In the recorded ^{1}H NMR spectra (Fig. 3.), the signals for aromatic protons (6.91-7.08 ppm), protons of the *tert*-butyl groups (1.23-1.55 ppm) and methylene protons (2.35-2.67 ppm and 2.71-2.93 ppm) of the BHT analogue are all observed. The signals for the methylene and methine groups next to the ester bonds appear in the 3.95-4.22 and 4.22-4.47 ppm regions, but these signals do not separate well from each other. The signals of the chemical shifts of the protons of the polyether main chain (-OC*H*$_2$- and -OC*H*-) appear in the region of ~3.2-3.9 ppm. This clearly indicates that the functionalization reactions were successful. However, the chemical shifts for aromatic hydroxyl group and non-functionalized hydroxyl groups overlap in the region of 4.92-5.24 ppm. Taking into account these observations, the conversion of the hydroxyl groups to ester groups can be determined from the integral ratio of the region of the hydroxyl and the aromatic protons in the ^{1}H NMR spectra. As presented in Table 1, the applied esterification process led to 64-77% conversion of the hydroxyl groups of the HbPG to the ester attaching the BHT moieties to the hyperbranched core.

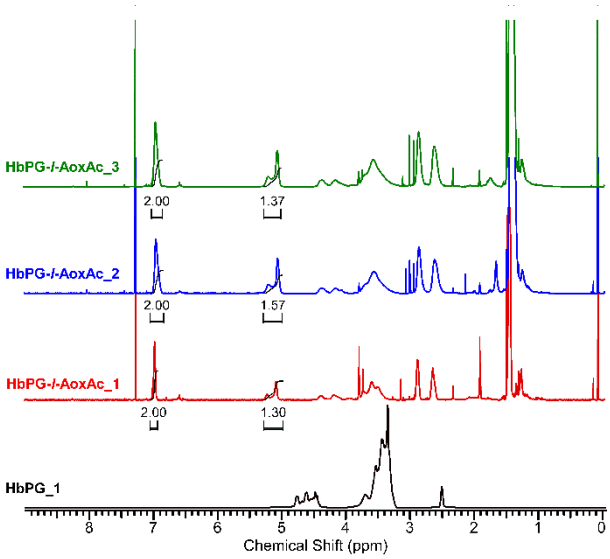

Fig. 3. ^{1}H NMR spectra of the HbPG-based antioxidants (in $CDCl_3$) and one representative starting HbPG (in DMSO-d_6) as control sample (HbPG_1).

By using the determined hydroxyl conversion values, the number average degree of polymerization and the number average molecular weight of the base hyperbranched polyglycerols and the BHT content were calculated by the following equations (Eq. 1-3.):

$$DPn = \frac{M_{n,GPC} - M_{inic} - C \cdot (M_{AoxAc} - 18)}{M_{mon} + C \cdot (M_{AoxAc} - 18)} \quad (1)$$

$$M_{HbPG} = M_{inic} + DPn \cdot M_{mon} \quad (2)$$

$$n_{BHT} = \frac{C \cdot (DPn + 4)}{M_{n,GPC}} \quad (3)$$

where DP_n is the number average degree of polymerization, C is the conversation calculated from the ^{1}H NMR spectra, $M_{n,GPC}$, M_{inic}, M_{AoxAc}, M_{mon} are the molecular weights of the macroantioxidants determined by GPC, pentaerythritol (136 g/mol), AoxAc (279 g/mol), and glycol (74 g/mol), respectively, and n_{BHT} is the amount of the BHT equivalent in 1 g macromolecular antioxidants. The theoretical and the calculated molecular weight is close to each other, so the synthesis of the HbPG macromolecules and also their functionalization by the BHT containing AoxAc antioxidants were successful.

The BHT contents of the HbPG-*l*-AoxAc macromolecular antioxidants were also measured by UV spectroscopy, which can provide the accurate information on the BHT content bonded to the HbPG carriers. The UV spectra of BHT, Irganox1010, a HbPG without any chromophore and the HbPG-*l*-AoxAc samples are depicted in Fig. 4. As displayed in this Figure, the UV spectra of macromolecular antioxidants as well as BHT and Irganox1010 show the presence of absorption peaks in the aromatic region (260–290 nm) in contrast to that of the unmodified HbPG. The BHT content (Table 1) was determined from the absorbance at 275 nm, where the polymer main chain does not absorb. For the measured absorbance values and the calculation of the BHT group content of the produced macromolecular antioxidants see Table S1 in the Supporting Information. As shown in Table 1, the BHT content determined from the UV spectra fits quite well with the values obtained from the ^{1}H NMR spectra of the HbPG-*l*-AoxAc samples (Fig. 3).

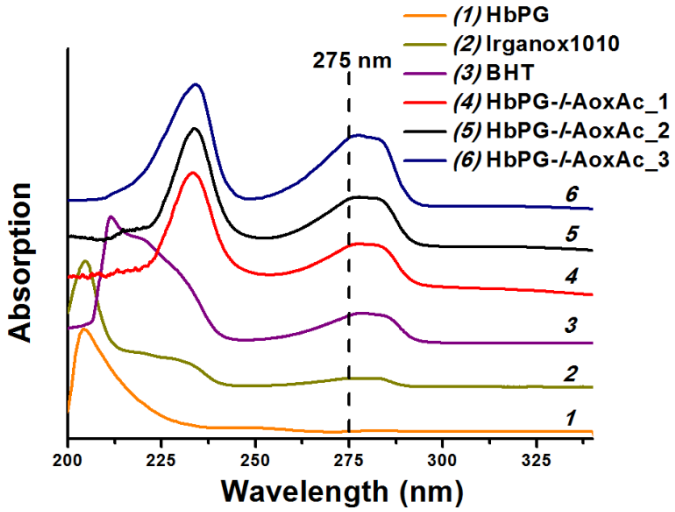

Fig. 4. UV spectra of the HbPG-*l*-AoxAc samples compared with an unmodified HbPG, Irganox1010 and BHT.

Based on the results of functionality investigations, it can be concluded that high active group content was reached by the performed esterification of HbPG as carrier for AoxAc, i.e.

between 2.6-2.7 mmol/g antioxidant functionality. This is only slightly below the phenol functionality of the widely used commercial antioxidant Irganox1010 (3.4 mmol phenol/g antioxidant). It can be also concluded that the molecular weight of the starting HbPG core has no significant influence on the functionalization efficiency.

The thermal properties and stability are also important aspects of the applicability of the synthesized macromolecular antioxidants. Therefore, the produced samples were investigated by DSC and TGA measurements. Based on the DSC curves (Fig. S1), the T_g values of the HbPG-*l*-AoxAc samples are 40-42 °C, and do not depend on the molecular weight of the macromolecular additives. This means that the T_g is over room temperature, but not too high, so the measuring, dosage and mixing can be carried out easily during application and processes, on the one hand. On the other hand, the TGA curves (see Fig. S2) show that the temperature of the 5 wt% weight loss of the antioxidants is at about 270-280 °C, which means that the HbPG-*l*-AoxAc nanoparticles are stable at the usual processing temperature of polymers. Briefly, based on the obtained characterization results, the synthesized HbPG-based macromolecular antioxidants can be suitable for effective thermooxidative stabilization of several polymers.

3.2. Thermooxidative efficiency of the HbPG-based macromolecular antioxidants in stabilization of PVC

The novel multifunctional HbPG-based macromolecular HbPG-*l*-AoxAc antioxidants were tested for their efficiency in thermooxidative stabilization of PVC. Their inhibition efficiency was compared to the Irganox1010 and the pure PVC, respectively. The thermooxidative degradation of PVC in presence of different amount of additives was followed via detecting the evolved free HCl measured by conductometry. Fig. 5a shows the extent of HCl evolution versus degradation time in the case of one representative measurement where

0.59 BHT eq. over 100 VC units was used for all the investigated antioxidants. (The rest of the HCl evolution curves are presented in Fig. S3-S5 in the Supported Information.)

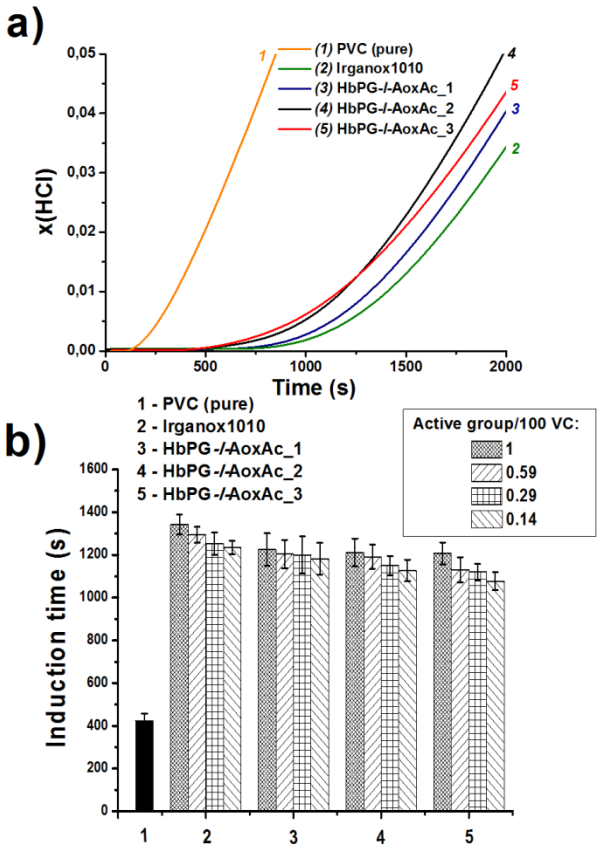

Fig. 5. The extent of HCl elimination as a function of degradation time without and with antioxidants (BHT eq./VC = 0.59/100) (a), and the OIT values for investigated antioxidants with various BHT equivalent contents (b).

As expected, the elimination of HCl in the case of unstabilized PVC begins rapidly and increases sharply during the thermooxidative treatment (Fig. 5a). The obtained results show that the HCl elimination curves are shifted towards higher degradation times by using the antioxidant additives, namely longer induction periods and lower rates of HCl evolution are detected in the presence of antioxidants than that for the virgin PVC. The oxidation induction times (OIT) were determined as the interception of the two straight lines fitted to the beginning and the increasing section of the elimination curves. The OIT values are depicted in Fig. 5b.

The OIT of the unstabilized PVC is around 400 s and increases to around 2.5-3 times higher degradation times by the application of Irganox1010. As it can be seen in Fig. 5b, the OIT increases only negligibly with increasing the BHT eq./VC ratio. Furthermore, it can be concluded that the OIT values for the synthesized HbPG-*l*-AoxAc antioxidants are close to the values obtained for Irganox1010. These findings clearly indicate that the HbPG-*l*-AoxAc macromolecular antioxidants are close as efficient as the industrially used Irganox1010.

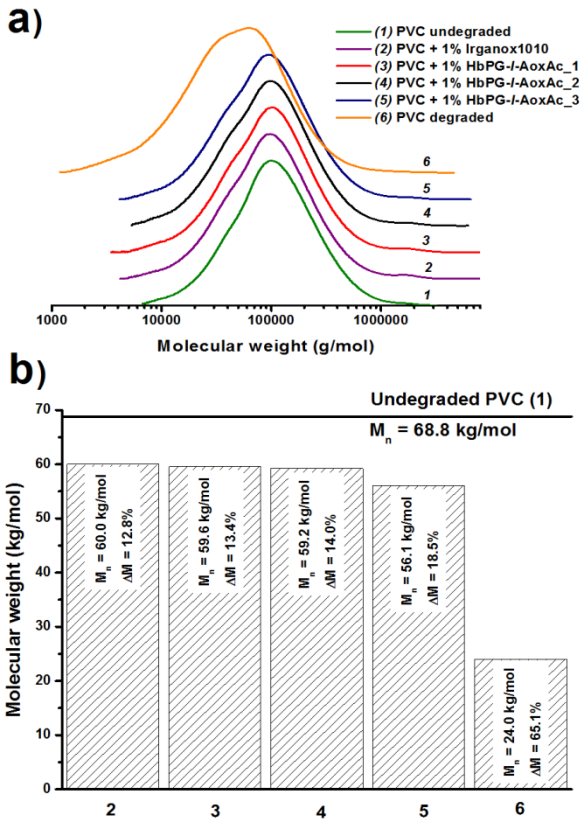

Fig. 6. The molecular weight distribution curves (a) and the comparison of the change in the number average molecular weights (M_n) of the undegraded PVC (1), degraded PVC stabilized with Irganox1010 (2) and the synthesized HbPG-*l*-AoxAc macromolecular stabilizers (3-5), and unstabilized degraded PVC (6). The stabilizer contents were 1 BHT eq./100 VC units, the degradation time was 4 hours.

In addition to HCl elimination and discoloration by the simultaneous formation of conjugated double bond containing sequences, another essential aspect of the thermooxidative degradation of PVC is the oxidative chain scission in this process [64,69,70]. The effect of the HbPG-based phenolic antioxidants in comparison to that of Irganox1010 on the change of molecular weight of PVC was investigated by GPC. The molecular weight distribution (MWD) curves of the unmodified and additive containing (1 BHT eq./100 VC) PVC after 4 hours thermooxidative degradation, as well as that of the initial unstabilized PVC, and the number average molecular weights are presented in Fig. 6a and 6b, respectively. As can be seen in Fig. 6a, the MWD curve of the unstabilized PVC is significantly shifted to the lower molecular weight region. This leads to more than 60% decrease of the number average molecular weight of the unstabilized PVC, i.e. from 68.8 kg/mol to 24.0 kg/mol (Fig. 6b), even at relatively low level of HCl elimination, which is 3.4% after four hours degradation time (see Fig. S6 in Supporting Information). This indicates remarkable oxidative chain scission of the polymer main chain in the absence of any antioxidants in accordance with our recent report on this phenomenon [69,70]. In contrast, in the case of using antioxidants, the MWD curves are only shifted slightly to lower molecular weights upon thermooxidative treatment. The shape and the position of the MWD curves remain similar to that of the undegraded PVC. The decrease of the number average molecular weight of PVC in the presence of the macromolecular HbPG-*l*-AoxAc antioxidants is between only 13-19%, and this slightly increases by the increasing molecular weight of the macrostabilizers. In case of using antioxidants, the extent of HCl elimination after treatment for four hours is only around 1%, namely HbPG-*l*-AoxAc_1: 1.05%, HbPG-*l*-AoxAc_2: 1.27%, HbPG-*l*-AoxAc_3: 1.36% and Irganox1010: 0.96%. The low level of the decrease of molecular weights in the presence of antioxidants compared to that of the unstabilized PVC indicates efficient suppression of chain scission by these stabilizers, on the one hand. On the other hand, the M_n values of PVCs stabilized with HbPG-*l*-AoxAc are close

to the molecular weights obtained by using Irganox1010 (Fig. 6b). These findings mean that the HbPG-*l*-AoxAc macromolecular antioxidants can inhibit not only the HCl elimination from the PVC chain, but can significantly suppress the radical chain scission of this polymer as well during thermooxidative degradation, similar to the commercially applied Irganox1010. Based on these results, it can be concluded that the synthesized macromolecular HbPG-*l*-AoxAc hindered phenolic antioxidants are effective stabilizers for PVC against thermooxidative degradation.

3.3. Extraction of antioxidants from PVC blends

One of the major advantages of the application of macromolecular antioxidants is related to their low migration ability from the polymer matrices, which may improve not only their stabilization effects, but can significantly decrease the pollution of the environment and the safety risks. The low migration and leaching ability of the HbPG-*l*-AoxAc macromolecular antioxidants was investigated by extraction tests using *n*-hexane and water as extraction agents at room temperature for 240 h. The leaching of one selected antioxidant (HbPG-*l*-AoxAc_1) from PVC films was followed by ^{1}H NMR spectroscopy and was compared to that of Irganox1010. The recorded ^{1}H NMR spectra are presented in the Supporting Information (Fig. S7). The changes of BHT contents were determined by the integral ratios of the aromatic region (6.91-7.08 ppm) and methine group of PVC (4.23-4.85 ppm) by using the following equation:

$$n_{BHT,t} = \frac{\left(\frac{I_{Ar} \cdot 100}{I_{CH}}\right)_t}{\left(\frac{I_{Ar} \cdot 100}{I_{CH}}\right)_{t=0}} \cdot 100 \qquad (4)$$

where $n_{BHT,t}$ stands for the BHT content after t extraction time, I_{Ar} and I_{CH} mean the relative integrals of the aromatic region and methine region of PVC before ($t=0$) and after (t) extraction. The obtained PVC foils contained 7.8 wt% of Irganox1010 and 4.6 wt% of HbPG-*l*-AoxAc_1

antioxidants on the basis of the ^{1}H NMR spectra of the starting mixtures (see the corresponding spectra at 0 h in Fig. S7 in the Supporting Information) The changes of active group contents in PVC blends as a function of extraction times are displayed in Fig. 7. As shown in this Figure, very low extractability is observed for the prepared novel HbPG-based macromolecular additive in both extracting agents. Namely, after 240 hours, the extracted amount of HbPG-*l*-AoxAc_1 is 8% in hexane and 3% in water. In contrast, in the case of Irganox1010, the extracted amount is higher than 30% in hexane. This finding agrees well with the results of our previous investigations performed with polypropylene [61], but in contrast to PP, here the results show significant leached amounts (~9%) of Irganox1010 from PVC in water as well. It can be stated that the leaching of the synthesized HbPG-*l*-AoxAc macromolecular antioxidant is around three times smaller in both applied solvents than for the commercially available and broadly applied low molecular weight Irganox1010.

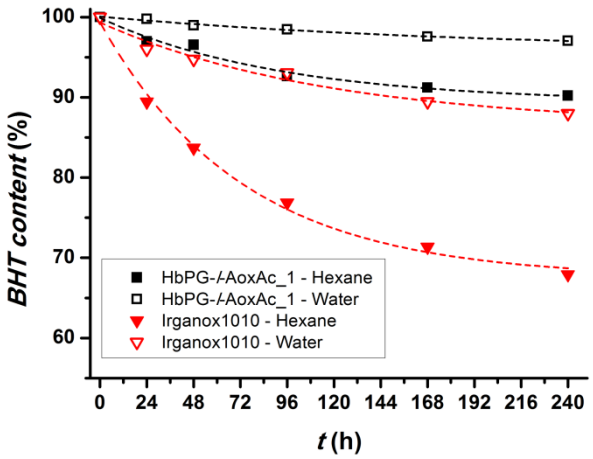

Fig. 7. BHT equivalent contents in PVC containing macromolecular antioxidant (HbPG-*l*-AoxAc_1) and Irganox1010 as a function of extraction time in hexane and water.

4. Conclusions

New macromolecular antioxidants, HbPG-*l*-AoxAc, were synthesized successfully by the functionalization of hyperbranched polyglycerol (HbPG) of different molecular weights, as

multifunctional nanoparticles, with a sterically hindered phenol antioxidant containing BHT moiety. The active group contents of the antioxidants were determined by UV-Vis and ^{1}H NMR spectroscopies, and it was found that the functionalities for the new macromolecular antioxidants can be achieved as high as that of the industrially widely used low molecular weight Irganox1010. The thermooxidative stabilization efficiency of the synthesized HbPG-based antioxidants was investigated in the thermooxidative degradation of PVC. The results show that the oxidation induction time (OIT) approximately doubled for PVC stabilized with either Irganox1010 or the HbPG-based spectroscopy antioxidants compared to that of the unstabilized PVC. The extent HCl elimination from PVC decreases dramatically in the presence of all the investigated antioxidants, i.e. including the HbPG-*l*-AoxAc macroantioxidants as well. The degradative chain scission of PVC during its thermooxidative treatment is also significantly suppressed by the macromolecular antioxidants similar to Irganox1010. Extraction of the antioxidants in hexane and water clearly shows that the HbPG-based macromolecular antioxidants leach out in significantly smaller amounts compared to Irganox1010. The results indicate that the stabilization efficiency of the multifunctional macromolecular HbPG-*l*-AoxAc antioxidants, obtained by the derivatization of the hyperbranched HbPG nanoparticles, is comparable to that of the industrially used Irganox1010. In sum, considering the high antioxidant efficiency and highly suppressed migrating ability of the multifunctional HbPG-based macromolecular HbPG-*l*-AoxAc phenolic antioxidants, it can be concluded that these hyperbranched polymers are excellent candidates as stabilizers for environmentally advantageous applications with a variety of polymers.

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