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Synthesis and evaluation of hyperbranched phenolic antioxidants of three different generations

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Abstract

Antioxidant-modified Boltorn® of 2nd, 3rd and 4th generation were synthesised. 3-(3,5-Di-*tert*-butyl-4-hydroxy-phenyl)-propionic acid was the active group attached to the three different hyperbranched polyesters. The syntheses were successful with high degrees of substitution. The antioxidants were evaluated in squalane and in polypropylene (PP) films using differential scanning calorimetry (DSC) to determine the oxidation induction time (OIT). They were compared to the commercial antioxidant Irganox 1010, which was added in an amount of 0.1 wt.%. All the synthesised antioxidants were superior to Irganox 1010 in squalane but did not contribute much to the stability of PP. The conclusion was drawn that the low antioxidative performance in PP is due to low mobility in combination with low solubility of the hyperbranched antioxidants.

Keywords: Antioxidants; Hyperbranched antioxidants; Boltorn; Polymer-bound antioxidants; Hindered phenols; Polypropylene; Squalane

1. Introduction

Dendritic polymers, i.e. dendrimers and hyperbranched polymers, are highly branched, tree-like structures. They are built from AB_x monomers, which gives them one or more possible branching points per repeating unit in the polymer. The dendrimers are perfectly branched molecules, whereas hyperbranched polymers have irregularities in their structure (Fig. 1 shows a schematic picture of a hyperbranched polymer). The dendritic polymers have a large number of end groups, which affects the properties of the polymer. The nature of the end groups determines the properties to a great extent, for example the T_g and melt behaviour [1]. Dendritic polymers have high solubility compared to linear analogues [1] and the end groups can be chemically modified. They can for example be used as macroinitiators or have polymerisable groups to facilitate crosslinking [2]. The highly branched structure makes the dendritic polymers compact and spherical. This compact structure results in a lack of entanglements, which leads to a low viscosity [3] and Newtonian behaviour in the molten state, but also renders poor mechanical properties, giving brittle polymers [1]. The properties mentioned make them attractive in many applications. Dendrimers can be used in medicine as drug carriers [4] and hyperbranched polymers can be used as blend components, additives, catalysts [4] and as processing aids in polyolefins [5]. In the last application, they eliminate surface defects and improve processability, which is suggested to be due to their migration to the surface of the processed plastic [5].

Polymers are subjected to heat and shearing forces during processing. The polymers are exposed to oxygen, light, heat and water during their service life. All of these factors cause oxidative degradation of the polymer, resulting in changes of chemical, physical, mechanical and esthetical properties.

To avoid polymer degradation antioxidants are added to polymers in small amounts, usually in the range 0.05–0.5 wt.%. There are several different types of antioxidants. The most common ones are hindered phenols and hindered amines [6]. Antioxidants are eventually consumed, either by chemical loss due to their antioxidant action or more often by physical loss through

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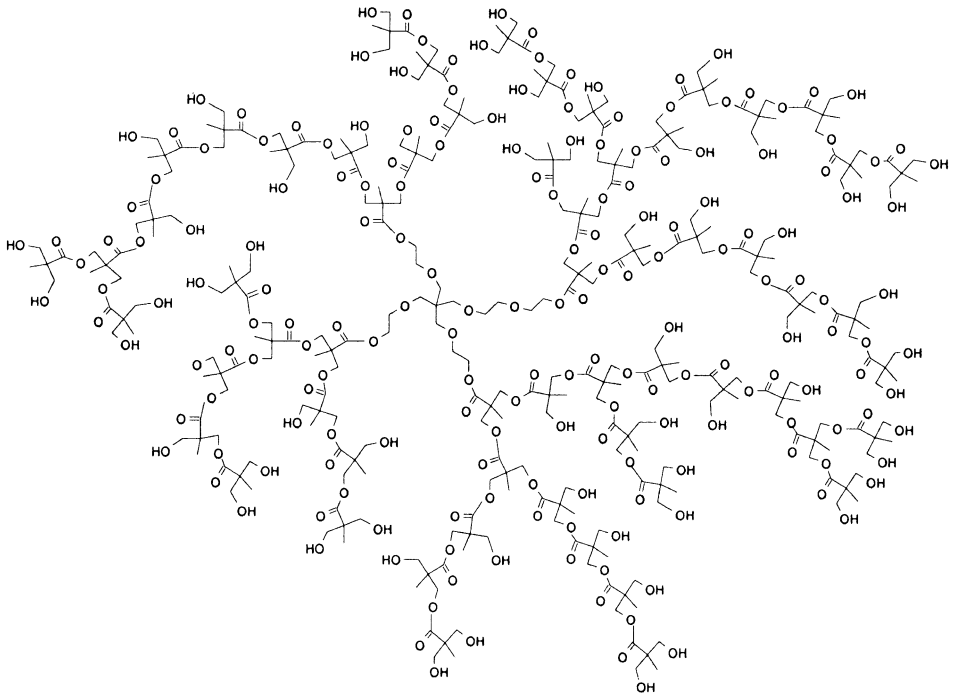


Fig. 1. Schematic drawing of Boltorn®, a hyperbranched polyester.

migration to the surroundings, both leading to loss of polymer stability [7]. Physical loss, which is due to factors such as volatilisation, poor solubility and migration, is a well-known problem [6]. It usually occurs when the polymer is in contact with a flowing medium (e.g. hot water in a pipe) or in contact with food. Adding a larger amount of the antioxidant from the beginning can compensate for the loss. However, that approach brings about some disadvantages, for example, the antioxidants have limited solubility and are relatively expensive [8]. One approach to minimise the physical loss would be to attach the antioxidant to the polymer by grafting the antioxidant onto the polymer backbone. One way is to attach the antioxidant photochemically to the polymer by exposure to UV light [8].

The hyperbranched antioxidant molecules are large and this should make them less prone to physical loss by migration and volatilisation. They would also have a large number of antioxidant groups attached to the same molecule, unlike linear polymers. Both of these factors indicate that hyperbranched antioxidants may prove to be better than their conventional low molecular weight analogues. This article reports the synthesis and evaluation of three hyperbranched antioxidants.

The antioxidants are based on a hyperbranched polyester, Boltorn®, which is commercially available from Perstorp Polyols, Perstorp AB. Boltorn is based on pentaerythritol and 2,2-bis-(methylol)-propionic acid (bis-MPA). Boltorn® has a large number of hydroxyl end groups, which can be chemically modified to meet the desired properties.

2. Experimental

2.1. Materials

Hyperbranched polyesters, Boltorn® H20, H30 and H40 (2nd, 3rd and 4th generation) were obtained from Perstorp Polyols, Perstorp AB. 3-(3,5-Di-*tert*-butyl-4-hydroxy-phenyl)-propionic acid (AG) was purchased from Avocado Research Chemicals Ltd. Oxalyl chloride (Acros), dimethylaminopyridine (DMAP) (Sigma-Aldrich), triethylamine (TEA) (Acros), dichloromethane (DCM) (Lab-Scan), tetrahydrofuran (THF) (Lab-Scan), dimethylformamide (DMF) (Lab-Scan), sodium hydrogen carbonate ($NaHCO_3$) (KEBO Lab), hydrochloric acid (HCl) (Acros), sodium chloride (NaCl) (J.T. Baker), anhydrous magnesium sulfate ($MgSO_4$) (Mallinckrodt), Irganox 1010 (Ciba Specialty Chemicals AB), ethyl acetate (Lab-Scan), ethanol (95%) (Kemetyl AB) and sodium hydroxide (NaOH) (EKA Chemicals) were all used as received. Squalane (2,6,10,15,19,23-hexamethyl tetracosane) 99% was purchased from Sigma-Aldrich and was stored in the dark at room temperature. Unstabilised isotactic polypropylene was kindly supplied by DSM Research and was stored in the dark in a freezer.

2.2. Characterisation

^{1}H- and ^{13}C NMR were recorded on a Brüker 400 MHz spectrometer using the solvent signal as a reference. Infrared spectra were recorded on a Perkin-Elmer

Spectrum 2000 FTIR equipped with a MKII Golden Gate™, Single Reflection ATR System from Specac Ltd, London, UK. The ATR-crystal was a MKII heated Diamond 45° ATR Top Plate. Oxidation induction time measurements were performed on a Mettler Toledo DSC 820, with Mettler Toledo STAR^{e}® software.

2.3. Synthesis—general procedures

2.3.1. AG-reagent

The AG-reagent was prepared by dissolving 3-(3,5-di-*tert*-butyl-4-hydroxy-phenyl)-propionic acid (AG) and oxalyl chloride in dichloromethane (DCM) and leaving the reaction for 3 h at room temperature (amounts—see Table 1).

2.3.2. Antioxidant-modified Boltorn®

An amount of Boltorn® (see Table 2) was heated to 140 °C in an oil bath (Table 2—"Heating time"), then cooled to 50 °C. Tetrahydrofuran (THF) was added and the THF-Boltorn® solution was heated to reflux until the Boltorn had dissolved (ca. 1 h). A solution of triethylamine (TEA) and dimethylaminopyridine (DMAP) (catalytic amount) in 5 ml THF was prepared.

The TEA–DMAP-solution was added to the Boltorn® solution (cooled to 50 °C) and the resulting solution was placed on an ice bath. The AG-reagent was carefully added drop by drop and the reaction was left overnight (20 h) at room temperature.

The solvents (THF and DCM) were removed by rotary evaporation and the solid residue was dissolved in 20 ml DCM. TEA and DMAP salt were removed by extraction, two times with $NaHCO_3$ (10% solution), two times with HCl (0.5 M) and finally one time with brine. The organic phase was dried over anhydrous $MgSO_4$ and filtered. After rotary evaporation of the solvent and drying, the crude product was obtained as a white-yellow solid.

The crude product was washed with a 1:1 solution of ethanol and 1 M NaOH. The solid product was ground, mixed with the washing-solution in a beaker, stirred for a few minutes and filtered. It was washed three times using 15 ml of the washing-solution each time. Between each wash it was rinsed with water in order to remove residues of the washing solution. The product was then dried and obtained as a yellow solid.

Table 1
Amounts of the reagents used in the preparation of the AG-reagent

Synthesis no.	AG	Oxalyl chloride	DCM
1	2.28 g (8.19 mmol)	1.08 g (8.51 mmol)	20 ml
2	2.27 g (8.15 mmol)	1.04 g (8.20 mmol)	20 ml
3	1.08 g (3.88 mmol)	0.485 g (3.82 mmol)	10 ml

Table 2
Amounts of reagents and heating time for modifying Boltorn® with the active group

Synthesis no	Boltorn®		Heating time (h)	TEA
	Generation	Amount		
1	H20	0.359 g (0.205 mmol)	1.5	0.705 g (6.97 mmol)
2	H30	0.364 g (0.101 mmol)	1	0.695 g (6.87 mmol)
3	H40	0.365 g (0.050 mmol)	1	0.442 g (4.37 mmol)

2.4. Sample preparation

2.4.1. Antioxidants in squalane

Stock solutions of antioxidants in squalane were prepared. Since all antioxidants were insoluble in squalane, they were pre-dissolved in ethyl acetate and then mixed with squalane. A stock solution of ten times the final concentration of the antioxidant in ethyl acetate was prepared and one tenth of the solution was added to the squalane (Table 3). The antioxidant concentration in the stock solutions was 1435 ppm with respect to the active groups (mol active groups/mol squalane).

2.4.2. Antioxidants in polypropylene

The antioxidants were dissolved in DCM and the solutions were poured over polypropylene powder (unstabilised PP) (amounts in Table 4). The solvent was allowed to evaporate for 20 min during stirring. 0.5 g of the now stabilised PP powder was pressed into films (4 min at 200 °C at 50 bar and 20 s at a 100 bar). The resulting films were about 4×4 cm with an average thickness of 0.15 mm. Two films with each antioxidant and two films with unstabilised PP were made. The antioxidant concentration was 3.4 μmol active groups/g PP.

Table 3
Amounts of antioxidants in squalane

Antioxidant	Amount (mg)	EtOAc (ml)	Squalane (g)
Irganox 1010	3.05	0.1	3.007
1	3.79	0.2	3.002
2	3.83	0.2	3.003
3	4.09	0.2	3.004

Table 4
Amounts of antioxidants in PP

Antioxidant	Amount (mg)	DCM (ml)	PP (g)
Irganox 1010	5.2	2.5	5.09
1	6.4	4	5.01
2	6.3	4	4.99
3	7.0	3	5.02

2.5. Oxidation induction time—OIT-test

2.5.1. Antioxidants in squalane

The method used for the OIT tests was based on ASTM D 3895–95 "Oxidation-Induction Time of Polyolefins by Differential Scanning Calorimetry". The method was modified, as described by Breese et al. [10] to allow for liquid samples instead of solid polyolefin samples as the oxidisable material. Instead of shallow 40 μl aluminium pans, deeper 100 μl aluminium pans were used. The sample size was 30 ± 1 mg and the added ethyl acetate was allowed to evaporate prior to the measurements. The standard ASTM method specified the gas flow and temperature ramping. First the sample was held at room temperature (25 °C) for 5 min with a nitrogen flow of 50 ml/min. The sample was then heated to 190 °C at a rate of 20 °C/min, still under a flow of nitrogen. Then, once at 190 °C, the sample was held for another 5 min, at which point the gas was switched to oxygen at a flow rate of 50 ml/min. The oxidation was observed as an increase in heat flow. Triplicate samples of each antioxidant were analysed and after each antioxidant, a burnout was performed in order to remove any remaining oxidation products. The burnout was performed at 400 °C with oxygen flow (50 ml/min) for 30 min. Unstabilised squalane was run as a control sample.

2.5.2. Antioxidants in polypropylene

The same method as with squalane was used to evaluate the OITs for the PP films, but the standard 40 μl aluminium pans were used. Pieces of the PP films were punched and the sample sizes were 6–7 mg. Three samples of each antioxidant were run and after each antioxidant, a burnout was performed in order to remove any remaining oxidation products. Unstabilised PP was run as a control.

3. Results and discussion

3.1. Synthesis

3.1.1. AG-reagent

3-(3,5-Di-*tert*-butyl-4-hydroxy-phenyl)-propionic acid (AG) was transformed into the corresponding acid chloride by the use of oxalyl chloride. The acid chloride is more reactive than the acid itself towards hydroxyl groups, but it does not attack the phenolic hydroxyl group on AG, due to steric hindrance.

3.1.2. Antioxidant-modified Boltorn®

Boltorn® forms strong intermolecular hydrogen bonds and this is the reason for heating the Boltorn® prior to the synthesis, the hydrogen bonds break when the polymer is heated. They are also hygroscopic, i.e. bind moisture, and bonded water is also removed by the heating step.

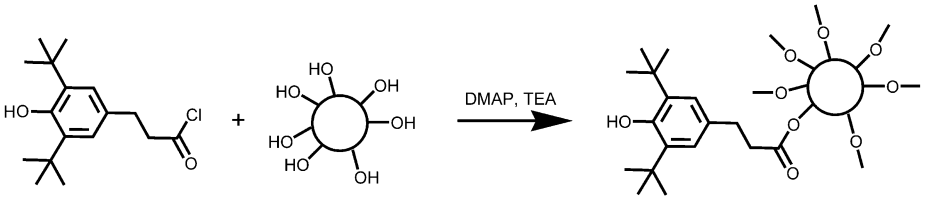
The active group was attached to Boltorn by mixing the AG-reagent and the dissolved Boltorn® (Scheme 1).

In all the reactions the active group (AG) was used in excess, which means there was unreacted AG left in the crude product. This could be seen in the infrared spectra as a shoulder at 3000 cm^{-1} and also as double carbonyl peaks at 1700 cm^{-1} in the FTIR spectra (Fig. 2). The unreacted AG was removed by washing the solid product with a 1:1-solution of EtOH:NaOH (1 M). The IR spectra also indicated that the antioxidants in synthesis no. **1** and **2** were fully substituted as the broad hydroxyl peak at 3400 cm^{-1} had disappeared. The ^{13}C NMR spectra also indicated whether the products were fully substituted or not. A peak at 46 ppm corresponds to fully substituted repeating unit in Boltorn®, whereas a peak at 49 ppm corresponds to Boltorn® that is not fully substituted [9]. Also the ^{13}C NMR spectra showed that in synthesis **1** and **2** the antioxidants were fully substituted, but in synthesis **3** it was not and only about 80% of the end groups were substituted with AG. The full substitution of **2** theoretically corresponds to 32 attached active groups and 16 active groups on **1**. **3** had 51 active groups attached on average.

3.2. Sample preparation

To evaluate the efficiency of the synthesised antioxidants, they were compared to the commercial antioxidant Irganox 1010. The chemical structure of the active group is identical to that of Irganox 1010 (Fig. 3) and they should therefore behave similarly in radical scavenging reactions.

Besides the stabilisation of PP, the antioxidants were mixed with a model compound, squalane, which is a viscous liquid. Its chemical structure resembles the structure of polypropylene (Fig. 4), they have similar solubility parameters and they are thought to oxidise by similar a mechanism [10].



Scheme 1. Conceptual scheme showing how the active group is attached to Boltorn®.

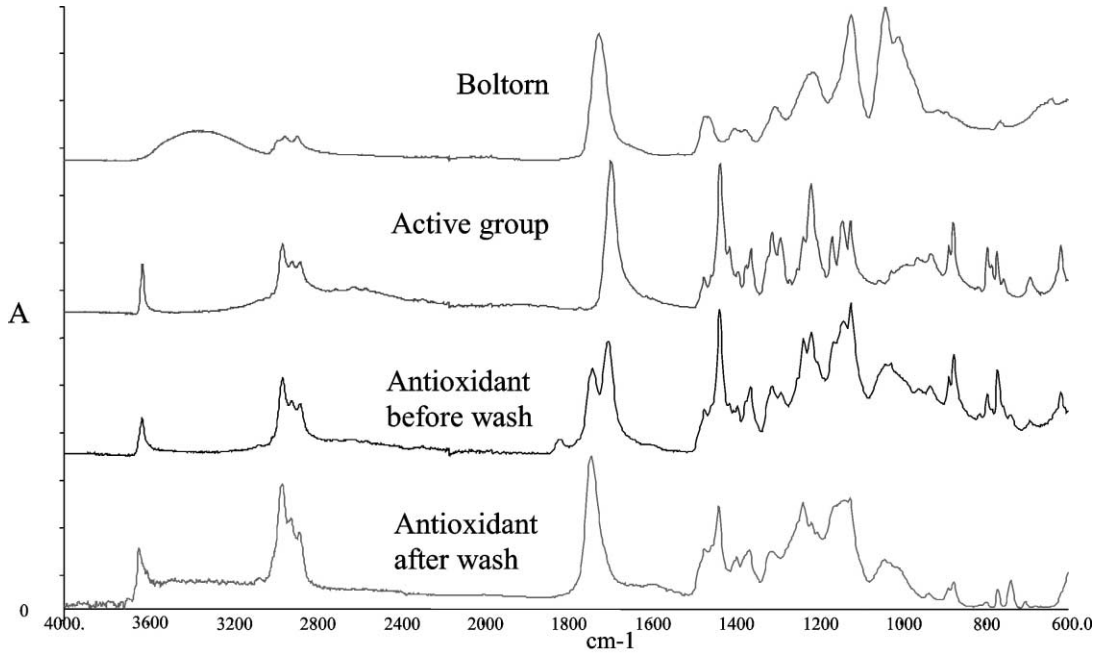


Fig. 2. Infrared spectra of Boltorn®, the active group and antioxidants before and after washing.

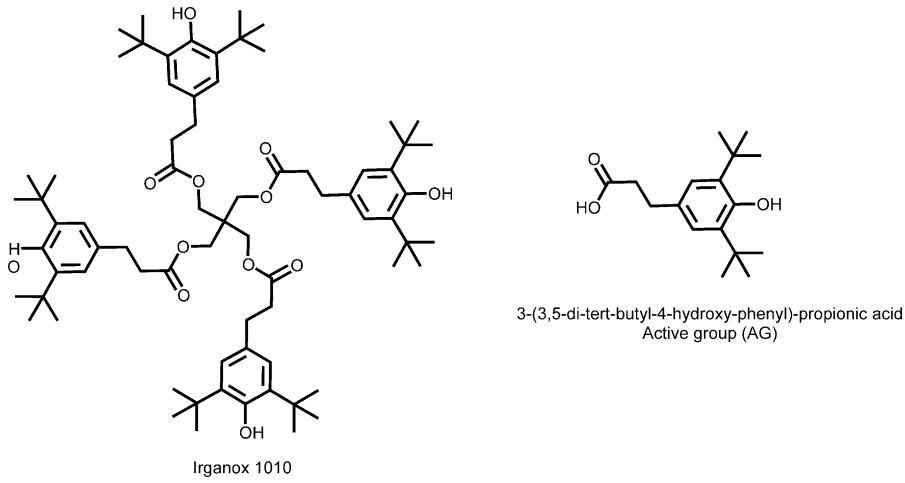


Fig. 3. The commercial antioxidant Irganox 1010 and the active group.

The use of a liquid compound as oxidisable material makes the sample preparation easier and faster. The amount of the commercial antioxidant was 0.1 wt.% in both PP and squalane and the amounts of the synthesised antioxidants had to be corrected to account for their larger molecular weight and number of active groups, giving equal concentrations of active groups for all antioxidants.

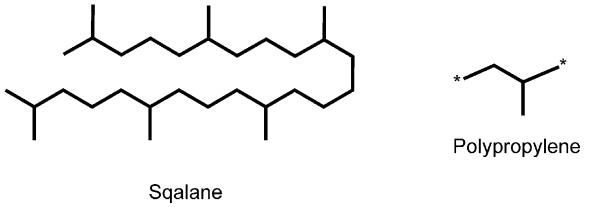


Fig. 4. The model compound squalane and one repeating unit of polypropylene.

3.3. OIT-tests

The oxidation induction time (OIT) is the time it takes before the sample starts to oxidise. The more resistant the sample is to oxidation, the longer the OIT. An earlier study using squalane [10] showed that there was no significant vaporisation of squalane at the temperature used in the study and that the addition of ethyl acetate did not affect the OIT-results. The OIT-values were determined from the DSC thermograms. The computer was used to calculate the second derivative of the enthalpy

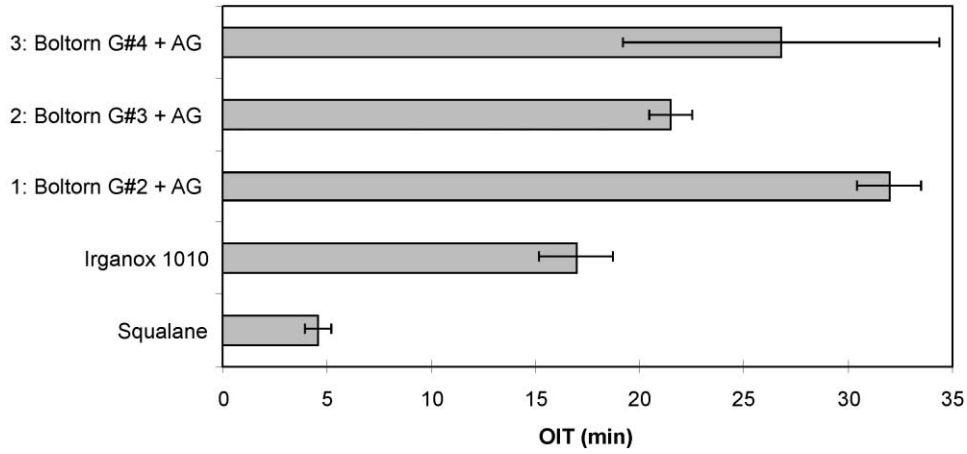


Fig. 5. Results of OIT measurement with antioxidants from synthesis **1**, **2**, **3** and Irganox 1010 in squalane. Antioxidant concentration: 1435 ppm.

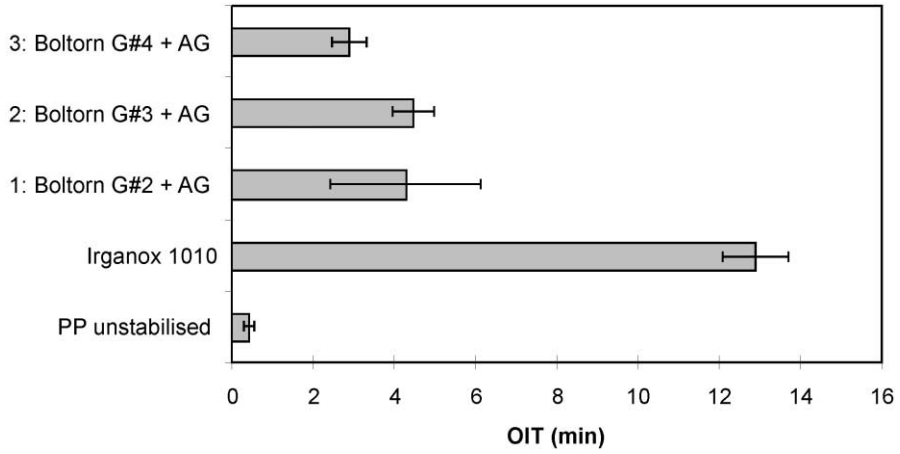


Fig. 6. Results of OIT-measurements with antioxidants from synthesis **1**, **2**, **3** and Irganox 1010 in PP. Antioxidant concentration: 3.4 μmol active groups/g PP.

versus time curve. The first peak of this second derivative was taken as the onset of oxidation (the OIT-value) [10].

The results of the OIT measurements in squalane revealed that all of the synthesised antioxidants were much more effective at stabilising the squalane than the commercial antioxidant (Fig. 5).

In contrast, the results of the OIT measurements in polypropylene revealed that all the synthesised antioxidants were less efficient as stabilisers in PP than the commercial antioxidant, Irganox 1010 (Fig. 6). The OIT values for Irganox 1010 in PP and squalane are approximately the same, indicating that the two methods are comparable, i.e. mixing antioxidants in squalane and PP. One reason for the shorter OIT in PP for the synthesised antioxidants could be due to poor solubility. The antioxidants have a large number of polar hydroxyl end groups, which may form the outer shell of the more or less spherical hyperbranched molecules. PP is hydrophobic (non-polar) and mixing these two compounds could cause phase separation of PP and the antioxidant. However, at 190 °C, which is the temperature the OIT measurements were made at both squalane and PP are in a liquid state having similar solubility parameters. If the solubility had been the only reason for the low efficiency, low antioxidant performance would be observed also in the squalane samples. The lack of efficiency might instead be due to the high viscosity of molten PP compared to squalane causing a restricted mobility of the antioxidant and thereby a low efficiency.

4. Conclusions

The synthesised hyperbranched antioxidants are more effective than the commercial antioxidant in the liquid model compound squalane, but inferior in polypropylene. The low efficiency of the hyperbranched antioxidants in PP was believed to be due to low mobility in combination with low solubility. The work with hyperbranched antioxidants continues with attempts to alter the polarity of the antioxidants to make them more compatible with polypropylene. The hyperbranched antioxidants may be effective as long-term stabilisers for polymers, where they are not required to diffuse quickly

to react with radicals. However, the hyperbranched hindered phenols were shown to be superior to commercial hindered phenols in stabilising a liquid substrate such as squalane. This would make them suitable as low volatile stabilisers for liquid systems such as oils and lubricants.

Acknowledgements

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