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The interaction of a phenolic anti-oxidant and an aromatic amine in a thermo-oxidative ageing process

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Abstract

An interaction of the sterically hindered phenolic anti-oxidant 1,3,5-trimethyl-2,4,6-Tris(3,5-di-*t*-butyl-4-hydroxybenzyl)-benzene, **1a** with the aromatic amine 4,4′-bis(α,α-dimethyl-benzyl)diphenylamine, **2a** in co-poly(ether esters) has been observed. This interaction is successfully analyzed by heating **1a** and/or **2a** in the polyether-mimicking solvent bis(2-methoxyethyl)ether using various analytical techniques, e.g. IR, HPLC–PDA, GC–FID, GC–MS and LC–MS. As well as a detailed insight of the action of the individual anti-oxidants, it has been shown that the quinone structure of the oxidized sterically hindered phenolic anti-oxidants are only stable in the absence of radical species, which results for the **1a**–**2a** system in the stabilisation of the oxidized **1a**.

Keywords: Interaction; Phenolic anti-oxidant; Aromatic amine

1. Introduction

Polymers have to be stabilized against thermo-oxidative degradation due to the susceptibility of organic materials towards oxygen, in combination with the use of these polymers in applications where severe requirements are demanded [1]. This also holds for co-poly(ether ester)s or TPE-Es which are used in, amongst others, automotive applications. TPE-Es consist in general of a crystalline poly(1,4-butylene terephthalate) or PBT "hard" phase and an amorphous polyether "soft" phase (mostly polytetramethyleneoxide or PTMO) [2–4]. It is generally accepted that the thermo-oxidatively labile phase in these TPE-Es is the amorphous PTMO segments [5–8]. Experimental studies including the analysis of the volatile compounds formed during thermo-oxidative ageing of TPE-Es, demonstrated the formation of formaldehyde, obviously from chain scission within the PTMO [5,6]. More detailed studies using low molecular weight model compounds suggest that the degradation starts with the oxidation of the α-CH_2 groups of the polyether [7,8]. In order to increase the thermo-oxidative stability of the PTMO, this phase is successfully stabilized towards thermo-oxidative degradation by using sterically hindered phenolic anti-oxidants like 1,3,5-trimethyl-2,4,6-Tris(3,5-di-*t*-butyl-4-hydroxy benzyl)benzene, **1a**, and/or aromatic amines like 4,4′-bis(α,α-dimethylbenzyl)diphenylamine, **2a** (Scheme 1) [5,6,9]. In the literature it is mentioned that a combination of **1a** and **2a** acts synergistically against the thermo-oxidative degradation of the above-mentioned TPE-Es [10,11]. For other systems the interaction of sterically hindered phenolic anti-oxidants and amines has been investigated and the observed synergism has been ascribed to the regeneration of the amine by the sterically hindered phenol [12].

Here, a detailed study is described dealing with the interaction of the sterically hindered phenolic anti-oxidant **1a** with the aromatic amine **2a** using several analytical techniques as, e.g. IR, HPLC-PDA, GC–FID, GC–MS and LC–MS. To enhance the analysis of the ageing process, bis(2-methoxyethyl)ether, a solvent mimicking the thermo-oxidative labile amorphous PTMO phase, has been used.

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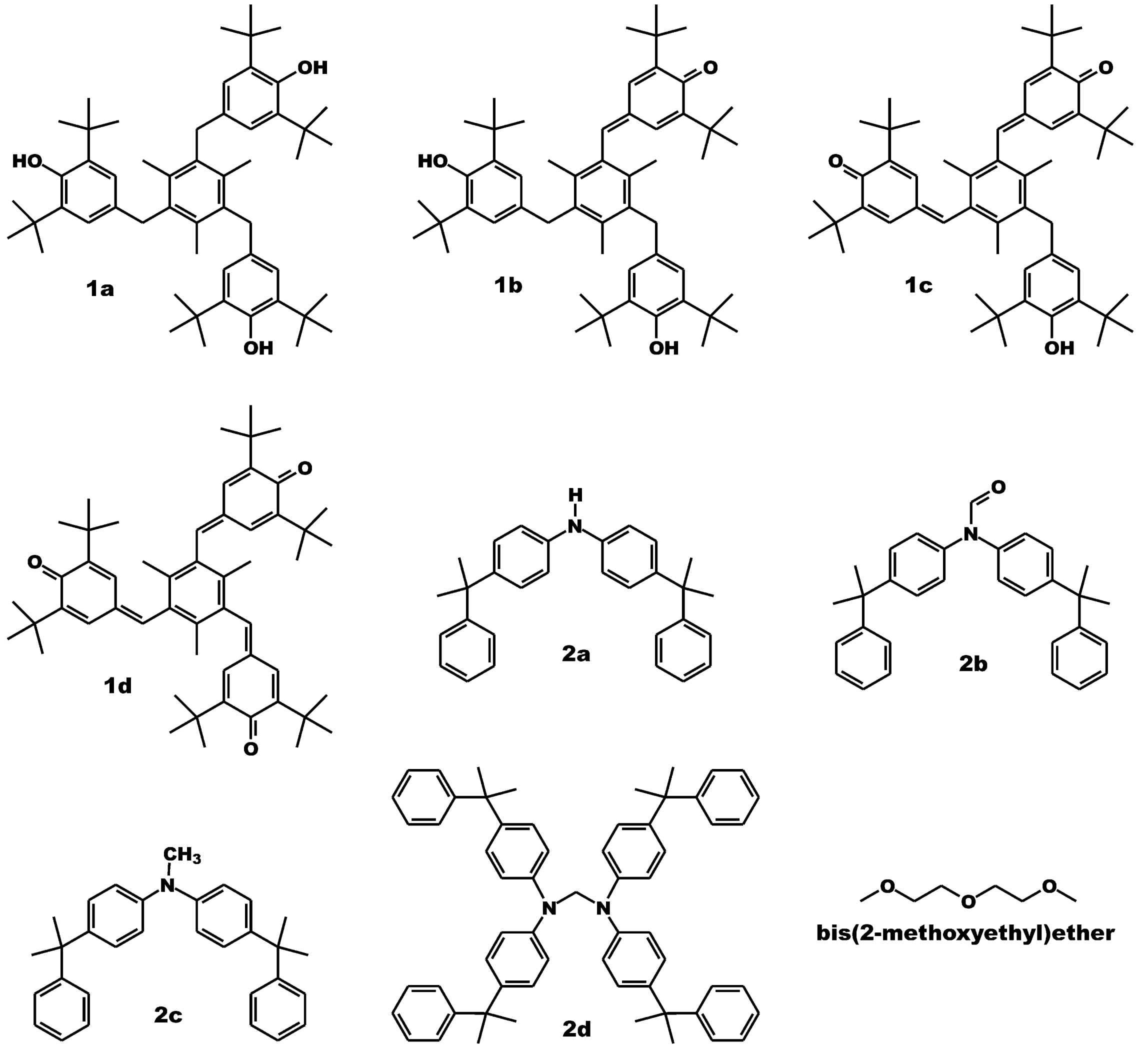


Scheme 1. Structural formulas of the sterically hindered phenolic anti-oxidant 1,3,5-trimethyl-2,4,6-Tris(3,5-di-*t*-butyl-4-hydroxybenzyl)benzene, **1a**, and its oxidation products **1b**, **1c**, and **1d**, together with the aromatic amine 4,4′-bis(α,α-dimethylbenzyl)diphenylamine, **2a**, its formaldehyde and methyl adduct, **2b** and **2c**, respectively, and its dimer **2d**. For completeness the structure of bis(2-methoxyethyl)ether is shown.

2. Experimental

The thermo-oxidative stabilizers 1,3,5-trimethyl-2,4,6-Tris(3,5-di-*t*-butyl-4-hydroxybenzyl)benzene, **1a**, and 4,4′-bis(α,α-dimethylbenzyl)diphenylamine, **2a**, where obtained from Ciba Specialty Chemicals and Uniroyal, respectively, and used as received. The bis(2-methoxyethyl) ether ($CH_3OCH_2CH_2OCH_2CH_2OCH_3$) was obtained from Aldrich. The ATR spectra were recorded on a Perkin-Elmer Spectrum One FT–IR spectrophotometer equipped with a Universal ATR. The crystal was a ZnSe/Diamond composite. Absorptions were corrected for baseline variations by using the non-varying ether absorption at 1453 cm^{-1} as reference for bis(2-methoxy ethyl)ether. The carbonyl index is defined as the absorption of the carbonyl at 1725 cm^{-1} divided by the absorption at 1453 cm^{-1}. The carbonyl intensity at 1755 cm^{-1}, which is less intense and omitted for clarity, shows the same behaviour as the depicted absorption at 1725 cm^{-1}.

The HPLC measurements were performed with a Waters HPLC/PDA, equipped with a Chromsep ODS-2 column and a Photo Diode Area detector, using a gradient of acetonitrile and water as the eluent. The amounts of the thermo-oxidative stabilizers and their oxidation products were calculated using an internal standard. The response factors of **1a**, **1d**, and **2a** (Scheme 1) were determined with the help of the pure products in known concentrations. Product **1d** was isolated by crystallization of the oxidised **1a**–**2a** mixture at low temperatures. The response factors for the oxidation products **1b** and **1c** were calculated using the determined response factors of **1a** and **1d** in the formula $f_{1b} = f_{1a} + (f_{1d} - f_{1a})/3$ and $f_{1c} = f_{1a} + 2(f_{1d} - f_{1a})/3)$, respectively.

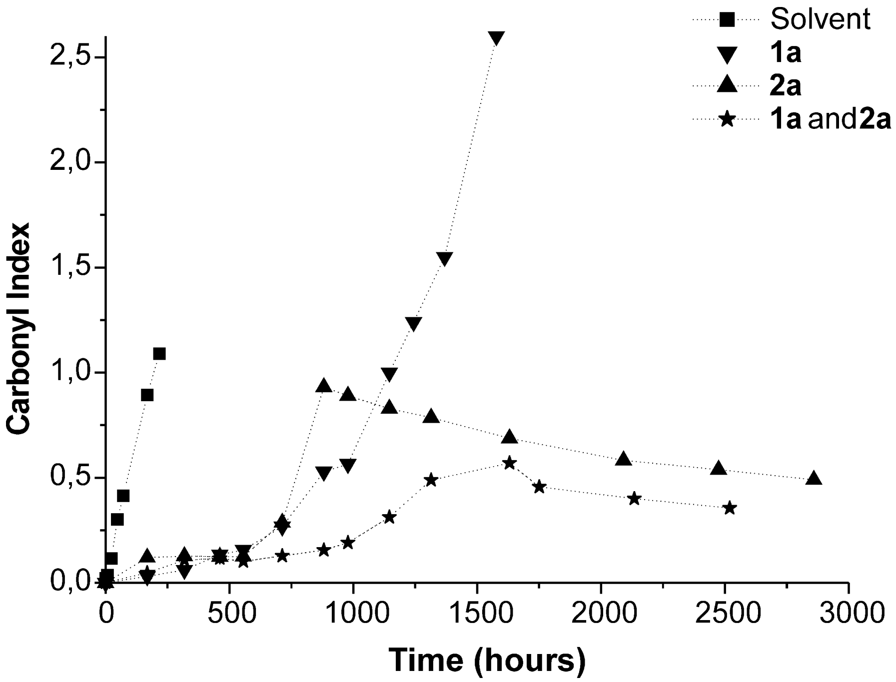


Fig. 1. The carbonyl intensities at 1725 cm^{-1}, as obtained by oxidation of bis(2-methoxyethyl)ether (■), bis(2-methoxyethyl)ether containing 5% (w/w) **1a** (▼), bis(2-methoxyethyl)ether containing 5% (w/w) **2a** (▲), and bis(2-methoxyethyl)ether containing a mixture of 5% (w/w) **1a** and 5% (w/w) **2a** (∗), versus ageing time.

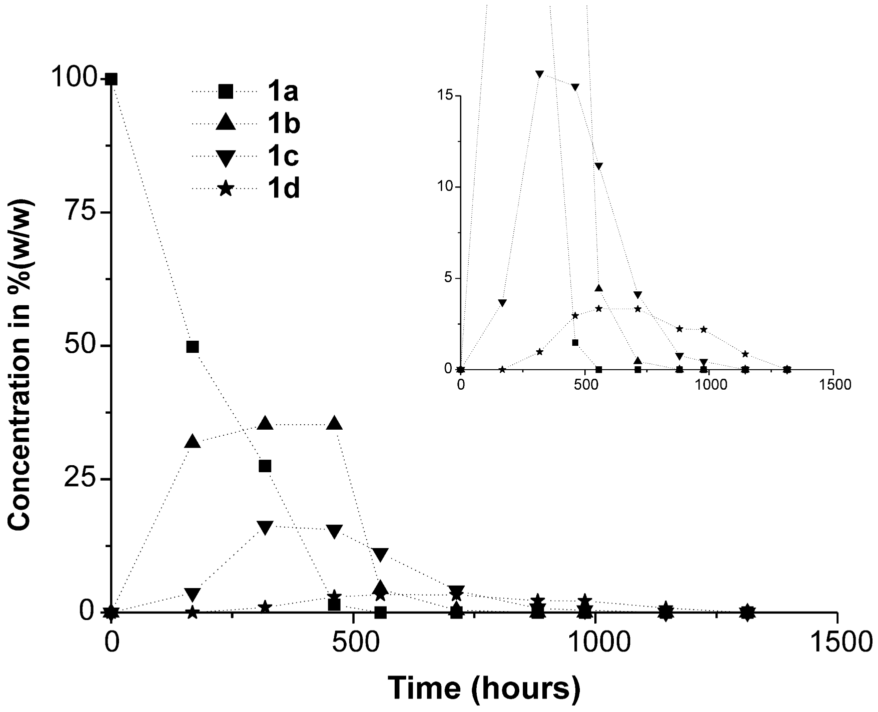


Fig. 2. Relative concentration of **1a–d** dissolved in bis(2-methoxyethyl)ether in time at 120 °C as determined using HPLC.

The response factors of the oxidation products **2b–2d** were assumed to be equal to the response factor of **2a**.

GC–MS analysis was performed on a MD800 bench top mass spectrometer (Fisons Instruments). Gas chromatographic separation was done on a 25 m×0.25 mm I.D. fused silica capillary column with 0.12 μm CP SIL5 CB stationary phase using He as the carrier gas at a constant flow of 1 ml min^{-1}. The following temperature program was used: 1 min 40 °C isothermal, followed by an increase of 10 °C min^{-1} to 180 °C and from there on

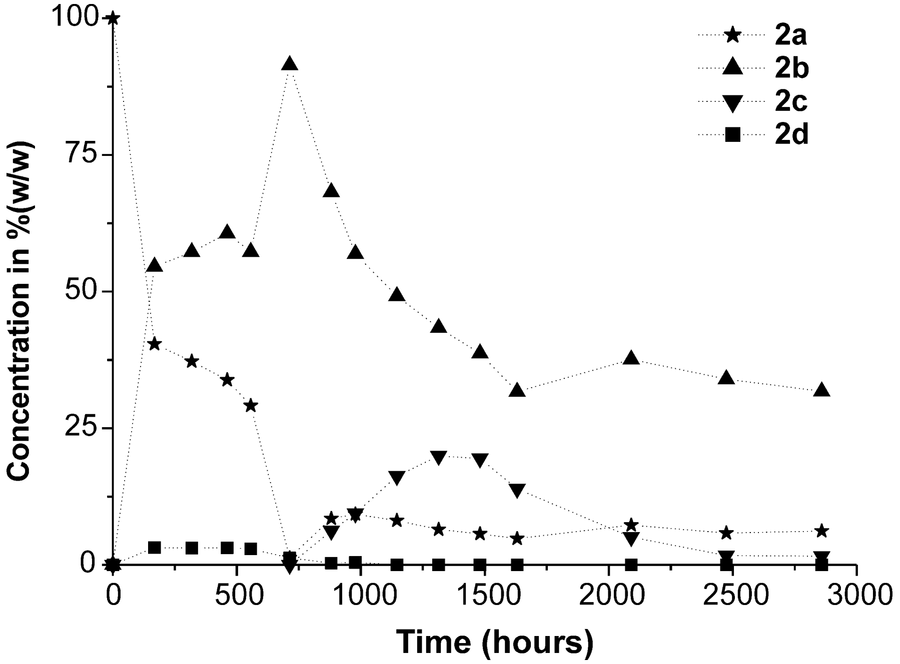


Fig. 3. Relative concentration of **2a–d** dissolved in bis(2-methoxyethyl)ether in time at 120 °C as determined using HPLC.

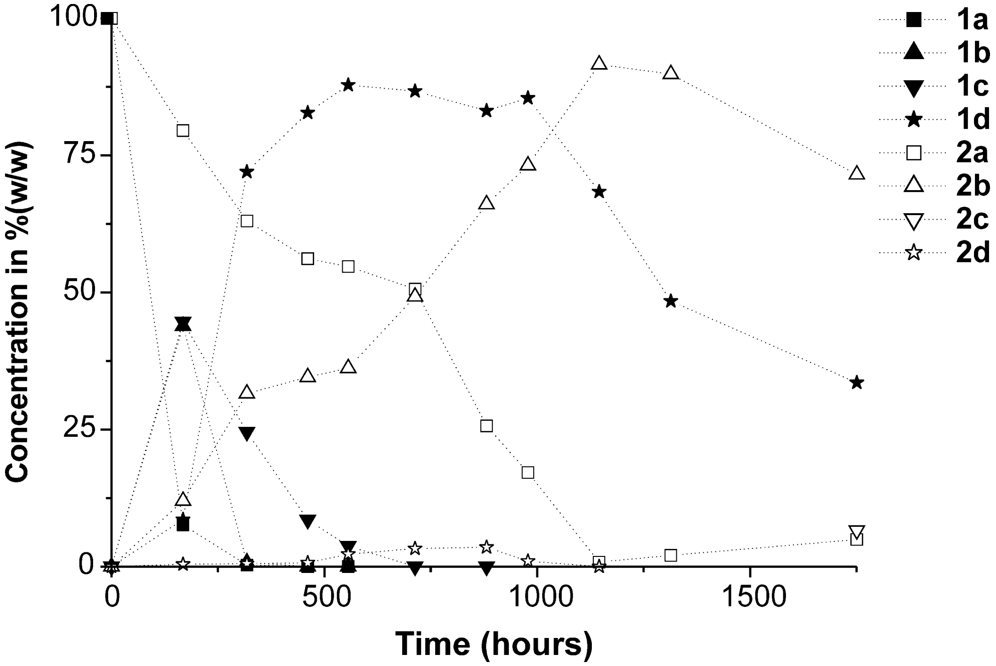


Fig. 4. Relative concentration of **1a–d** and **2a–d** dissolved in bis(2-methoxyethyl)ether in time at 120 °C as determined using HPLC.

with 4 °C min^{-1} up to 325 °C. The sample was injected on-column at a temperature of 60 °C. EI mass spectra were obtained in full scan mode, scanning from 20 to 600 amu. Data were processed using MassLab 1.3 software. GC–FID analysis was performed on a HP5890 instrument. Gas chromatographic separation was done on a 25 m×0.32 mm I.D. fused silica capillary column with 0.13 μm CP SIL5CB stationary phase using N_2 as carrier gas at a constant pressure of 8.7 psi. The same temperature program as described for the GC–MS analysis is used. For GC–FID, an on-column injection was performed at a temperature of 50 °C. The temperature of the FID was 350 °C. The amounts of the thermo-oxidative stabilizers and their oxidation products were calculated using an internal standard method. The response factors were determined with the help of the pure products in known concentrations or calculated as described for the HPLC method.

LC–APCI–MS data were obtained on a PE SCIEX API150 single quadrupole mass spectrometer (PE SCIEX, Toronto, Canada), coupled to an HP1100 liquid chromatograph. Unit resolution was used for all measurements. Positive as well as negative ion APCI–MS was used. The source temperature was 350 °C. Spectra were recorded over a mass range of 120–1500 amu at a fragmentor voltage of 50 V. Chromatographic separations were performed on a 150×4 mm Chromsep ODS-2 column (Chrompack, Middelburg, The Netherlands). The column was maintained at a temperature of 50 °C throughout the analysis, which was performed using a gradient elution starting with water/acetonitrile (40/60), going to 100% acetonitrile in 13.3 min. This condition was kept until 32 min. The flow rate was 1 ml min^{-1}. A UV detector was used in series with the MS. A UV signal was recorded at a wavelength of 220 nm.

The detailed chromatographic GC and HPLC data are available on request.

General ageing procedure. The thermo-oxidative stabilizers, 1 g (1.3 mmol **1a**, and hence 3.9 mmol phenolic units, and/or 2.5 mmol **2a**) were added to 19 g bis(2-methoxyethyl)ether in an open 100 ml erlenmeyer flask equipped with a water cooler and heated on an oil bath in an ambient atmosphere at 120 °C. At various times 0.5 g of samples were taken and analyzed by HPLC/PDA and IR.

3. Results and discussion

The thermo-oxidative stabilizers **1a** and/or **2a** were heated in the intrinsically thermo-oxidatively labile PTMO-mimicking solvent bis(2-methoxyethyl)ether in an ambient atmosphere at 120 °C. At various degradation times samples were taken and analyzed. To determine the stability of the bis(2-methoxyethyl)ether and the action of the stabilizers, IR measurements were recorded focusing on the formation of the α-CH_2 carbonyl absorptions found in general for polyethers. For bis(2-methoxyethyl)ether these carbonyl absorptions have been observed at 1725 and 1755 cm^{-1} [7,8]. As depicted in Fig. 1, an increase in the carbonyl absorption of the non-stabilized bis(2-methoxyethyl)ether is immediately observed after starting the experiment. In contrast, the solutions containing **1a** and/or **2a** show an increase of this carbonyl absorption after an induction time of about 700 h for the individual stabilizers and at about 1200 h for the mixture containing **1a**–**2a**. The course of the curve obtained for **2a** is remarkable. After the increase in the carbonyl intensity at about 700 h this increase stops and even turns to a decrease after about 800 h. The same, although less pronounced, holds for the mixture containing **1a–2a** at about 1000 and 1600 h, respectively. Obviously no significant additional oxidation of the bis(2-methoxyethyl)ether occurs. This effect will be addressed in more detail in the discussion dealing with the stabilization of bis(2-methoxyethyl)ether by **2a**.

To study the interaction of **1a** and **2a**, reference experiments have been performed using **1a** and **2a** separately, and the conversion products determined using HPLC–PDA, GC–FID and LC–MS. For sterically-hindered phenols like **1a** it is generally assumed that in the first stabilisation step the phenolic hydrogen is donated to a radical species. In a second step, an α- or benzylic-hydrogen is donated leading to a quinone structure [1,13–15]. Following this stabilization mechanism, and ignoring side reactions, **1a** is subsequently converted to **1b**, **1c** and finally to **1d** (Scheme 1). Looking at the highly conjugated structure of **1d** it is expected that further degradation reactions are possible leading to a variety of products. The oxidation sequence of **2a** is less clear. In the first step the amine hydrogen is donated. The resulting **2a**-radical is subsequently stabilized by the aromatic system leading to a large number of mesomeric structures, and hence to a variety of different degradation products [1,16]. Although not all degradation products could be determined here, the three major degradation compounds of **2a** in bis(2-methoxyethyl) ether, i.e. compounds **2b**–**2d**, could be identified by the combination of HPLC–PDA with LC–MS, GC–FID and GC-MS. Compounds **2b** and **2c** were identified as the (oxidized) formaldehyde and methyl adduct of **2a**, respectively, whereas compound **2d** is a methylene bridged dimer of **2a**.

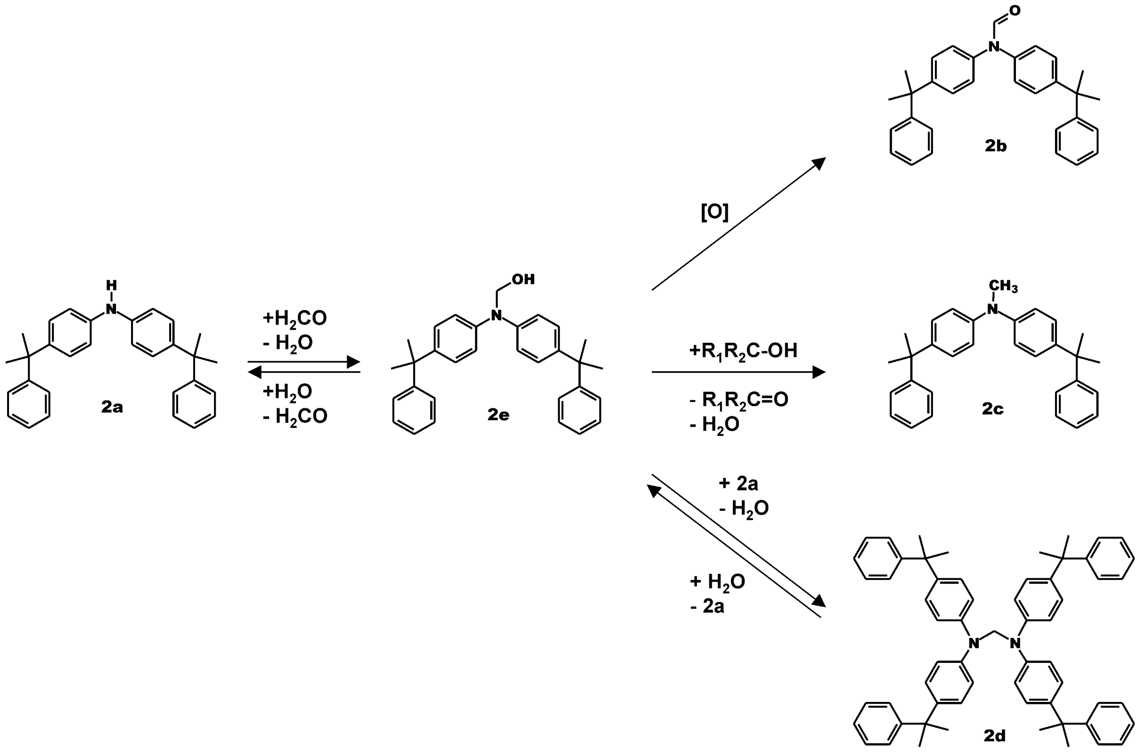
The analytical data obtained by HPLC of a heated mixture of **1a** dissolved in bis(2-methoxyethyl)ether in time are depicted in Fig. 2. As expected, a gradual decrease of **1a** is observed whereas almost from the start the concentration of the first oxidation product **1b** and at about 200 h the concentration of the second oxidation product **1c** increases and subsequently decreases. The third oxidation product **1d** is formed at about 400 hours and subsequently decreases in time, the latter indicating the oxidation and hence a (minor) stabilizing ability of **1d**. No attempts were performed to analyze the oxidation products of **1d** since, as mentioned above, a variety of products can be formed due to the highly conjugated structure of **1d**. The cumulative relative concentration of **1a**–**1d** in Fig. 2 does not equal 100% due to the fact that the response factors of the compounds **1b** and **1c** are unknown and are estimated, in combination with the instability of **1d**. The consumption of the compounds **1a**–**1c** fits almost perfectly with the increase in carbonyl intensity, originating from the oxidation of bis(2-methoxyethyl)ether, as depicted in Fig. 1. These results demonstrate that not only **1a** but also the phenol containing **1b** and **1c** are able to stabilize ether-containing species.

The analytical data concerning the stabilization of bis(2-methoxyethyl)ether by **2a** are shown in Fig. 3. A decrease of the concentration of **2a** is observed together with an increase of **2b**, which is obviously the main oxidation product of **2a**. Compound **2b** is also detected by the formation and increase of a carbonyl absorption at 1690 cm^{-1} in IR. As depicted in Scheme 2, compound **2b** is probably formed by the condensation of **2a** with formaldehyde, which is a major oxidation product of ethers [5–8], subsequently followed by an oxidation of the intermediate **2e**. Next to compound **2b** a second oxidation product of **2a**, i.e. **2d**, could be identified. Compound **2d** is probably formed by the condensation of **2a** with **2e**. Although intermediate **2e** was not observed, the proposed formation of **2b** and **2d** presupposes the existence of **2e**. At about 700 h a dramatic increase of degradation products is detected by HPLC, whereas the concentration of **2a** is almost zero. This point coincides with the increase of the carbonyl absorbance of the oxidized bis(2-methoxyethyl)ether (Fig. 1), pointing in the direction that **2b** and **2d** do not have a significant stabilizing power. An interesting aspect occurring at about 700 h is the maximum observed for **2b** coinciding with the minimum in concentration for **2a**, the latter reflecting a regeneration of **2a**. This behaviour was also observed in a separate duplicating experiment. In addition, compound **2c** is formed at this point, probably by the reaction of **2a** with formaldehyde and an alcohol as shown in Scheme 2 [13–15]. A possible explanation of these observations is given below.

The regeneration of **2a** could be explained by the higher concentration in time of alcohols and water in the reaction mixture. As depicted in Scheme 2 compound **2d** is probably obtained by two condensation reactions, both involving **2a**. A higher concentration in time of water, and also alcohols, shifts the equilibrium of the condensation reactions from **2d** towards the starting product **2a**. The response factors, and hence the exact concentrations of **2b**–**2d** could not be determined. It is assumed that the concentration of **2d** is significantly higher as the line in Fig. 3 suggests. Due to the regeneration of **2a** it is, at first glance, expected that the concentration of **2b** should not decrease. However, due to the significantly higher concentration of the bis(2-methoxyethyl)ether degradation products formaldehyde, and more important (secondary) alcohols at 700 h compared to the situation at the start of the experiment, the formation of **2c** is obviously favored compared to the formation of **2b** (Scheme 2).

The stabilizers **1a** and **2a** are roughly equally effective in stabilizing the bis(2-methoxyethyl)ether towards oxidative degradation. Comparing the molar amounts of the individual stabilizers present in the reaction mixture, i.e. 1.3 mmol **1a** (and hence 3.9 mmol phenolic units) and 2.5 mmol **2a**, it is suggested that aromatic amines are more effective in the stabilization of ethers compared to sterically hindered phenols. The observed regeneration of **2a** will probably increase this effect.

The analytical data obtained by HPLC concerning the stabilization of bis(2-methoxyethyl)ether by a mixture of **1a** and **2a** are shown in Fig. 4. An interaction of **1a**



Scheme 2. Suggested formation of the oxidation products **2b**, **2c** and **2d**.

and **2a** is clearly observed. The course of the decrease and formation of the different products is comparable to that discussed for the individual **1a** and **2a** alone. However, the rate of decrease and formation, together with the amounts formed, is significantly different. Focusing on compound **2a** a longer lifetime is observed in the **1a**–**2a** mixture. The concentration of **2a** becomes zero at about 1200 h, which is an increase in lifetime of about 500 h. Combined with this the formation of **2b**–**d** is also delayed. The further decrease and formation of compounds **2a**–**d** after about 1200 h is analogous to the behaviour of **2a** in bis(2-methoxyethyl)ether alone (Fig. 3). In contrast to **2a** an accelerated decrease of **1a** is observed in the **1a**–**2a** mixture. The concentration of **1a** becomes zero at about 300 hours compared to about 500 hours for **1a** alone. Linked to this, the formation and decrease of **1b**–**d** is accelerated too. Compounds **1b** and **1c** are both formed from the beginning and the concentrations become already zero at about 300 and 700 h, respectively. The largest effect is obtained for compound **1d**. As illustrated in Fig. 2, the formation of **1d** is hardly noticed in the absence of **2a** and the relative concentration does not exceed 3% (w/w). In the **1a**–**2a** mixture however, the formation of **1d** is clearly visible (Fig. 4) and a relative concentration of about 85% (w/w) is obtained. This high concentration of **1d** decreases together with the decrease of **2a**. Also for the **1a**–**2a** system, the increase of the carbonyl intensity of the oxidized bis(2-methoxyethyl)ether at about 1200 h (Fig. 1) coincides with the point that the concentration of the last active stabilizer **2a** is zero.

The observed accelerated consumption of **1a** and the increased lifetime of **2a** could be explained by an activation of **1a** by **2a** or by a regeneration of **2a** by **1a**. Results described in the literature suggest the regeneration of **2a** by **1a** [12], based on the reaction kinetics of aromatic amine and phenolic radicals. The combination of the high concentration of **1d** in the presence of **2a** together with the simultaneous decrease of **1d** and **2a** suggest that **1d** is stable in the absence of radicals. The instability of **1d** in the presence of radicals is also expected from the highly conjugated structure of **1d**. This highly conjugated structure, obtained by the conversion of the sp^3 carbons present in **1a** to sp^2 carbons in **1d**, dramatically decreases the solubility and enhances the crystallization of compound **1d**. In summary it is concluded that the quinone structures of the oxidized sterically hindered phenolic anti-oxidants are not stable in the presence of radical species. In the situation of combining **1a** with a compound that neutralizes the radical species formed at the time that **1a** is oxidized to **1d**, in this case compound **2a**, compound **1d** is stabilized. Studies dealing with the combination of a variety of different stabilizers as, e.g. sterically hindered phenols, aromatic amines or HALS will be described elsewhere.

4. Conclusions

The observed interaction of the sterically hindered phenolic anti-oxidant **1a** with the aromatic amine **2a** in co-poly(ether esters) is successfully analyzed by heating **1a** and/or **2a** in the polyether-mimicking solvent bis(2-methoxyethyl)ether using various analytical techniques as, e.g. IR, HPLC–PDA, GC–FID, GC–MS and LC-MS. The determined time at which the stabilizing species are consumed fits in all cases with the observed increase of the carbonyl intensity of the oxidized bis(2-methoxyethyl)ether. It is shown that not only **1a** but also its phenol containing oxidation products **1b** and **1c** are able to stabilize ether-containing species whereas **2b**, which is the main degradation product of **2a**, has no stabilizing activity. However, the mono-amine containing compound **2a** is roughly equally effective in stabilizing the bis(2-methoxyethyl)ether compared to the Tris-phenolic compound **1a**, suggesting that aromatic amines are more effective compared to sterically hindered phenols in the stabilization of ethers. The observed regeneration of **2a** will probably increase this effect. The main deactivation of **2a** occurs by the addition of formaldehyde, one of the main degradation products of ethers. The quinone structure of the oxidized sterically hindered phenolic anti-oxidants are not stable in the presence of radical species. In the situation of combining **1a** with a compound that neutralizes the radical species formed at the time that **1a** is oxidized to **1d**, in this case compound **2a**, compound **1d** is stabilized.

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