ELSEVIER

Stabilisation of polyethylene and polypropylene glycol through inhibition of a β-positioned hydroxyl group relative to an ether group. A study of modified triethylene and tripropylene glycols

Jens Glastrup*

Department of Conservation, The National Museum of Denmark, Brede, Post box 260, DK 2800 Kongens Lyngby, Denmark

Abstract

Polyethers are subject to oxidative degradation. An examination of the possible degradation mechanisms suggests a protective substitution, which has been shown to be effective on short chain polyglycols. Inserting a methylene group at the end of triethylene and tripropylene glycols, between the hydroxyl and ether groups, has a stabilising effect on their degradation in air. At 70 °C, degradation is completely stopped in modified triethylene glycol, while modified tripropylene glycol shows diminished degradation. © 2003 Elsevier Science Ltd. All rights reserved.

1. Introduction

Poly(ethylene glycol), also known as PEG, and, at molecular weights greater than 35,000, poly(ethylene oxide) PEO, is generally regarded as a labile polymer at high temperatures and especially in oxidative conditions [1–9]. It has previously been demonstrated that tetraethylene as well as polyethylene glycols may also undergo disturbingly fast oxidative degradation in air under moderate heating (70–80 °C) [1,10–14]. This oxidation has been attributed to a central cleavage around the ether bonds [1,2,5,14,15]. The mechanism is considered to be analogous to peroxide-forming reactions in ethers, which have been thoroughly described by Riecke and co-workers [16,17]. Many reports show that formic acid and formaldehyde are always released during degradation of PEG, indicating that a C–C cleavage reaction is involved [1,4,9,13–15,18]. It has previously been shown that, during ageing in air at 70 °C in the dark, one oligomer of PEG, tetraethylene glycol is mainly decomposed to formic acid and its derivatives, and that the main degradation mechanism at this temperature is an oxidation of the terminal hydroxyl

group, rather than an attack on the central ether groups [12].

PEG is the main preservative used to treat historic waterlogged wood. When used in aqueous solutions with increasing concentration over time, the rôle of PEG is to replace water in the cells of waterlogged wood, thus imparting strength and structure to the material. In freeze-drying of waterlogged wood, PEG is used to modify the crystallisation behaviour of water. The treatment has been used on objects ranging from miniature wooden artefacts to large wooden hulls; Håfors [19] has discussed one of the earliest treatments, that of the Swedish warship Wasa.

PEG is susceptible to microbiolagal degradation [20,21]. During conservation treatment, where PEG is dissolved in water for extended periods of time, this degradation may be considerable, giving rise to massive growth especially on the edges of baths of PEG. During impregnation of waterlogged wood PEG is also heated, and this alone can, under unfortunate conditions, result in a complete decomposition of the polymer in as little as 16 h [10].

Such degradation damages the physical properties of PEG, resulting mainly in decreased stiffness of the pure polymer and lowering of the melting point. These physical parameters are necessary for successful conservation

---

* Fax: +45-33-47-33-27.
 E-mail address: jens.glastrup@natmus.dk (J. Glastrup).

of waterlogged wood. In a specific conservation treatment, the overall loss of PEG after impregnation, due to microbial activity, heating and probably other factors as well, was judged to be 20% [22].

In this article PEG oligomers, which still have the original chemical properties of PEG, are analysed, these are (see Fig. 1):

E: Triethylene glycol methyl ether, Cas. no. 112-35-6, this leaves one hydroxyl group free for oxidation.
E_x: The same molecule as E, with one extra methylene (–CH$_2$–) group inserted vicinal to the hydroxyl group, giving the structure 3-(2′-[2″-methoxyethoxy]ethoxy)-propan-1-ol.
P: Tripropylene glycol methyl ether, Cas. no. 20324-33-8. Note that tripropylene glycol methyl ether is a mixture of 8 isomers.
P_x: The same molecule as P, but with a 1-3 rearrangement at the terminal hydroxyl group relative to the ether group. This molecule is 3-(2′-[2″-methoxypropoxy]propoxy)-propan-1-ol, with four possible isomers.

Overall, the differences between E and E_x—and P and P_x—is the repositioning of the terminal hydroxyl group from the β- to the γ-position relative to the ether group. The oxidation of the terminal hydroxyl group of these analogues of PEG during accelerated thermal ageing tests, together with the oxidation of the ether groups, is the subject of this article.

2. Methods and materials

2.1. Ageing and analysis of samples

Ageing of the PEG and PPG oligomers in a chamber which excludes light and which imparts a maximum degradation rate, was done in the following way: 2 ml is placed in a borosilicate vial which is closed with a
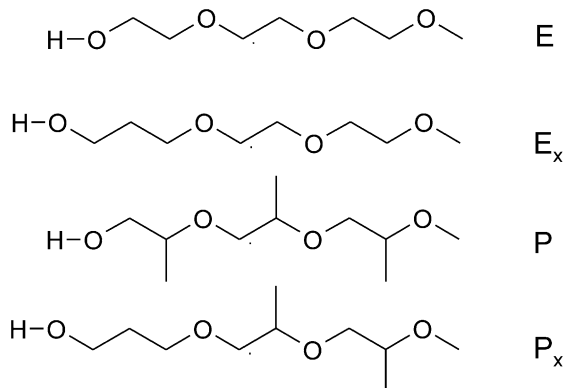

Fig. 1. The structure of triethylene glycol monomethyl ether, E, 3-(2′-[2″-methoxyethoxy]ethoxy)-propan-1-ol, E_x, tripropylene glycol monomethyl ether, P and 3-(2′-[2″-methoxypropoxy]propoxy)propan-1-ol P_x.

Teflon®/silicone septum. Teflon® tubing (1/16 inch) penetrates the septum to the bottom of the vial. Dried and purified air containing less than 5% relative humidity bubbles through the vial at a rate of 10 ml/min. The details are given in Ref. [11]. In the ageing experiment, care should be taken to exclude traces of metal ions as they tend to induce degradation of the ether bonds in the polymer structure, thereby disturbing the oxidation experiment by introducing a "false" oxidation of the oxidation resistant polymer. This can disturb the interpretation of the ageing experiment. After ageing, 2 μl of sample were taken at different time intervals and added to 1.00 ml of acetone. All samples were analysed on a gas chromatograph [12].

2.2. Chemicals

Triethylene glycol dimethyl ether 99% from Aldrich (T 5,980-3)
Triethylene glycol monomethyl ether (E) 95% from Aldrich (31,379-2).
3-(2′-[2″-methoxyethoxy]ethoxy)-propan-1-ol (E_x) was synthesised using the following method (Williamson ether synthesis):
A round bottomed, two-necked flask (100 ml), is equipped with a pressure equalising funnel and a double surface condenser. The condenser is equipped with a drying tube filled with CaCl$_2$. Nitrogen gas is supplied via the funnel at 100 ml/min. All solvents are dried over molecular sieve 0.4 nm before use. Diethylene glycol monomethyl ether (30 g, Aldrich 10,990-8) and 10 ml xylene (Fisher x/0250/17) is added to the flask and flushed for at least 12 h with N$_2$. Sodium (5.7 g) is added and under vigorous stirring the temperature is raised to 100 °C. After 2-h the stirring is stopped and the reaction mixture is cooled to room temperature. Residual sodium is removed from the reaction mixture and, after flushing with N$_2$ for 15 min; 3-chloro-1-propanol (20.8 ml, Aldrich C 4,640-3) is added slowly under vigorous stirring. After the addition is complete, 2.0 g of NaHCO$_3$ is added and the stirring continued for a further 10 min. The reaction mixture is now transferred to centrifuge tubes. After centrifugation, the supernatant is collected and kept in refrigerator. The content of the desired component in the supernatant is approximately 50% (based on GC peak area). Purification is done by vacuum distillation, twice. A two-necked 50 ml pear shaped flask is connected to a capillary tubing (5 m, 0.15 mm id, connected to a N$_2$ source) that extends down to the bottom of the flask, and to a 10 cm plain fractionating column with an internal diameter of 1.2 cm filled with fenske rings. Condensation of the distillate is done in a double surface condenser, which is connected to a desiccator containing 50 ml beakers. The different fractions are collected in the beakers by rotating the desiccator. The fraction of interest is collected at 66 Pascal

and 109.7-110.3 °C. Purity of the collected component is better than 96% (based on GC peak area).

Characterisation of the synthesised component: High resolution MS (FAB) of the collected component gave a MH^+ molecular weight of 179.1279, compared with a theoretical value of 179.1283 for the composition $C_8H_{19}O_4$. This suggests that the molecular formula of the analysed component is $C_8H_{18}O_4$.

C, H (and N) analysis of the collected component gave a content of C: 52.99% and H: 10.29%. Theoretical values of $C_8H_{18}O_4$ are: C: 53.91% and H: 10.18%.

Tripropylene glycol monomethyl ether (P) (mixture of eight isomers, Aldrich 30,286-4).

3-(2'-[2''-Methoxypropoxy]propoxy)propan-1-ol (P_x) (four possible isomers) was synthesised using the same experimental design as for the synthesis of E_x. The following amounts of reagents were used:

40.0 g dipropylene glycol monomethyl ether (Aldrich 28,328-2) and 10 ml xylene.
6.2 g sodium.
22.5 ml of 3-chloro-1-propanol.

Other parameters were the same, as was the approximate purity of the collected supernatant.

In the purification step the fraction of interest was collected at 65 Pascal and 97 °C. The purity of the product was better than 95% (GC peak area).

Characterisation of the synthesised components: High resolution MS (FAB + CI) of the collected component gave a MH^+ molecular weight of 207.1601, compared with a theoretical value of 207.1596 for the composition $C_{10}H_{23}O_4$. This suggests that the molecular formula of the analysed component is $C_{10}H_{22}O_4$.

Elemental (C, H and N) analysis of the collected components gave C: 56.59% and H: 10.66%. Theoretical values of $C_{10}H_{22}O_4$ are: C: 58.22 and H: 10.75.
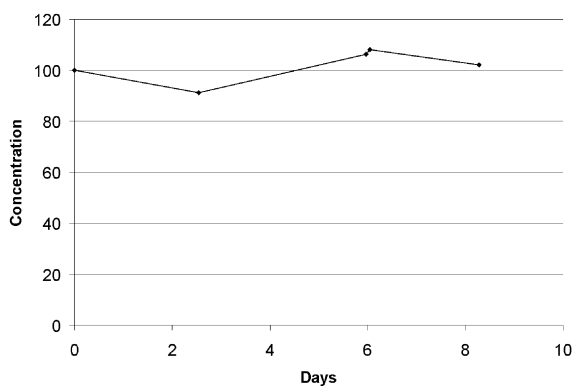
3. Results

To examine whether terminal methoxy groups protect against degradation during ageing, triethylene glycol dimethyl ether was exposed in the ageing chamber for 8 days at 70 °C. As seen in Fig. 2, no degradation occurred during this period.

E was examined under the same conditions and, as seen in Fig. 3, degradation does not occur during the first 3 days, after which degradation proceeds rapidly. The degradation process is a first order reaction, as can be seen when the residual amounts are plotted on a logarithmic scale (Fig. 4). The half-life of E is 3.1 days at 70 °C.

By contrast, the analogue E_x does not decompose under these conditions (Fig. 3). This indicates that the structure is stable under the given conditions, despite its free hydroxyl group.

P was also examined at 70 °C and, as seen in Fig. 5, the decomposition occurs rapidly: after 11 days nothing is left.

Ageing of P_x under the same conditions shows that decomposition of this structure does still occur, but at a lower rate. As seen in Fig. 6 the degradation reaction now proceeds as a first order reaction, with a half-life of 3.5 days.

4. Discussion and conclusion

The physical properties of polyethylene and polypropylene glycols depend on their terminal alcohol groups. Without these the water solubility and other physical properties change. This structure is therefore important for the many industrial uses of PEG and PPG [23].
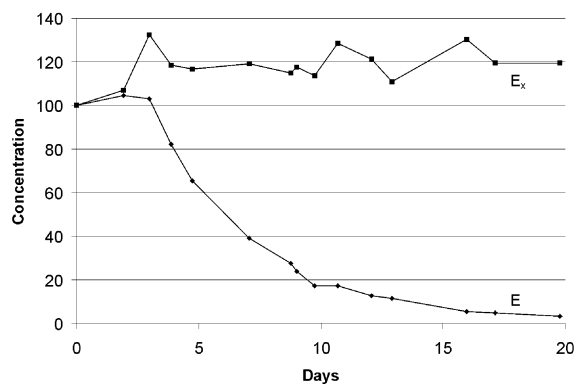
Fig. 2. The ageing of triethylene glycol dimethyl ether. The concentration found is given in % of the initial concentration.

Fig. 3. The ageing of E compared to the ageing of E_x. The reason for the apparent rise in concentration in E_x is the appearance of approximately 15% of 3-chloro-1-propanol in the sample (TriEG-m-A was only distilled once before use in the ageing experiment), which evaporated during the ageing experiment. The concentration found is given in % of the initial concentration.

To examine the ageing of polyether structures such as PEG, which has terminal alcohol groups and ethers in between, it is important to distinguish the reactions of the alcohol and the ether groups. The ageing of triethylene glycol dimethyl ether at 70 °C shows no degradation at all, and this suggests that at this temperature, in the dark, the ether bond can be considered stable as long as the ether oxygen atom is bound through a non-substituted carbon.

E has a terminal primary hydroxyl group in β-position to an ether group, and the fate of this structure during ageing can be seen in Fig. 3. It is clear that introduction of the alcohol group gives rise to oxidation which seems to be a first order reaction, as seen in Fig. 4. The reaction can therefore be expected to be of the type A → B + C. Glastrup [12] has previously described this reaction, and a degradation path to explain this reaction. However, inclusion of an extra methylene group between the terminal hydroxyl and the ether group, as in E_x, gives stability to the structure so that the molecule now resists oxidation in air. It therefore seems evident that the determining factor in the oxidation of the hydroxyl group is its β-position relative to the ether group. Introducing an extra methylene group and re-positioning the hydroxyl group to the γ-position relative to the ether group will add considerable stability to this structure.

P also has a terminating hydroxyl group in β-position to the ether group, as has E, and as seen in Fig. 5, the degradation of this structure proceeds even faster than does the degradation of E (Fig. 3). P is completely decomposed after 12 days and this reaction does not follow a first order reaction. Therefore, more than one degradation reaction may be involved. Fig. 5 shows that the inclusion of a methylene group to the terminal structure, as in E_x, adds stability to the P_x molecule. However, as seen from the graph, the result is only a lowering of the rate of degradation. This degradation now follows a first order reaction, see Fig. 6, and it is probable that the degradation is an oxidative cleavage of the secondary bound ether groups, as described by Molodovskii and Neiman [24]. This is also in accordance with previous results, which showed that the activation energies for the oxidation of polypropylene oxides are lower than those for polyethylene oxides [1].
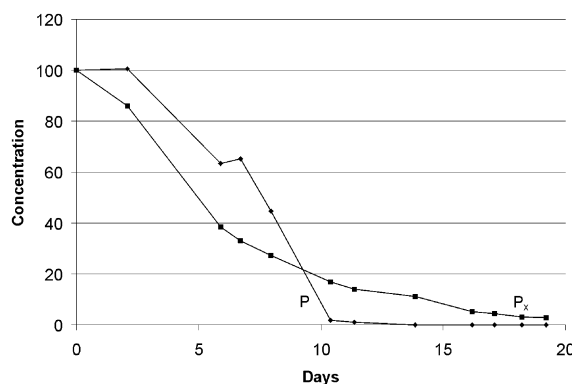

Fig. 5. The ageing of P compared to the ageing of P_x. In this experiment the degradation of P is seen to proceed faster than degradation of E, after 11 days nothing is left of the original components. By comparison, the degradation of P_x proceeds more slowly. After 19 days approximately 3% is left of the original amount. The concentration found is given in% of the initial concentration.
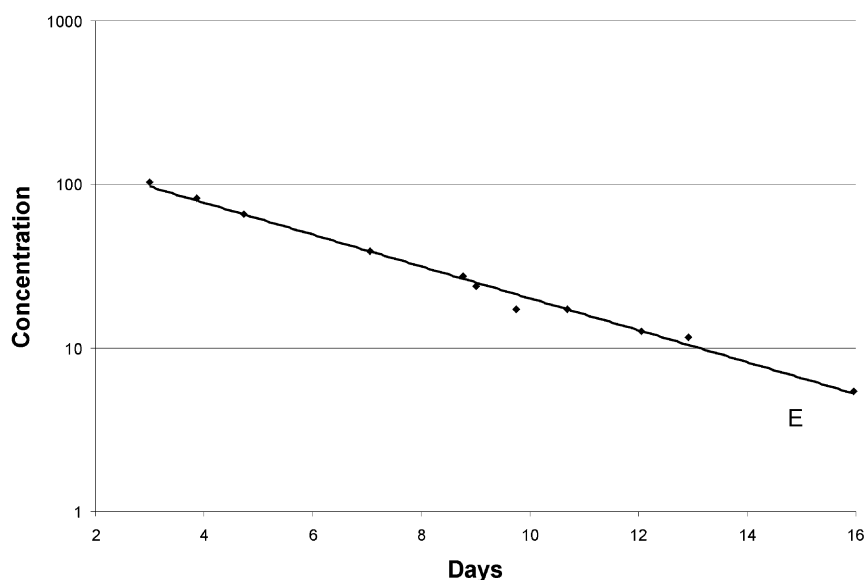

Fig. 4. Ageing of E plotted on a logarithmic scale. The data from Fig. 3, E, are plotted from day 3 to day 15, in order to exclude initial lag. Also included in the graph is an automatic trend line created by Excel© of an exponential plot. The plot shows a linear tendency, indicating a first order decay of the initial product. The calculated half-life of E under these circumstances is 3.1 days.

Results presented in this article show that the oxidation of the alcohol group, at least in short chain polyethylene glycols, is the rate-determining step. The results shown here and in a previous article [12] are in contrast to previous authors who conclude, that the oxidative degradation of polyethylene and polypropylene glycols always originate at the ether bonds, and that oxidation of PEG is always a result of chain scission of the C–O and C–C bonds due to addition of oxygen vicinal to the ether groups [1,2,5,8,9,14,15]. The results presented here are in accordance with authors [2,9,14,15] who specify the main degradation products as water and formic acid esters (seen in the IR spectrum in [2]). However, the oxidation reaction described here does not exclude other types of degradation of PEGs. In long-chain poly-glycols, with a low hydroxyl/ether ratio, oxidation of the ether groups may be important. Also other types of degradation, thermally induced [7] or light induced [9], give rise to series of homologous short chain poly-glycols.

In general, this re-positioning of terminal hydroxyl groups from β- to γ-positions would add more stability to polyglycols without fundamentally changing their solubilities in water and melting points. One can spec-ulate that introducing 1,3-propylene units in the back-bone of PEG polymers may inhibit total degradation of PEG by introducing "stop points" at intervals in the polymer structure. PPGs would probably decompose more rapidly because of the more labile $(CH_3)C-O$ and $(CH_3)C-C$ structure included in the polymer. Never-theless, 1,3-propylene units terminal and central in the structure may slow down the oxidative degradation.

4.1. Evidence from wood impregnated with PEG

PEG has been used for many years as impregnation material for conservation of waterlogged wood. Size exclusion chromatography of PEG 4000 from wooden logs that were impregnated 25 years ago, with internal standards of fresh PEG 4000 and 600, shows that the surface PEG now has an average molecular weight of around 3600 (results not shown). These logs (from the Skuldelev viking ships [25,26]) have since been exhibited in daylight and at room temperature. The analysis was performed without a sample of the original material, and conclusions must therefore rely on our belief that the PEG 4000 delivered at that time actually had a molecular weight of 4000. On that basis, we may assume that PEG over a 25-year period has decomposed only 10% and that there is therefore more than 150 years left before PEG liquifies, which happens at a molecular weight below 1000. This decomposition may well also be a combination of the oxidation reaction described here and photooxidation of the ether bonds as described by Morlat and Gardette [9]. We should not accept as adequate a material used to impregnate objects of our cultural heritage that decomposes significantly within about a century. We should make serious efforts to improve the material used for impregnation or find alternative conservation solutions.

Considering other applications, PEG is also used as coating material in gas chromatographic columns, and here the maximum temperature normally used is 250 °C. At this temperature the polymer is extremely sensitive to traces of oxygen and it is commonly known that even
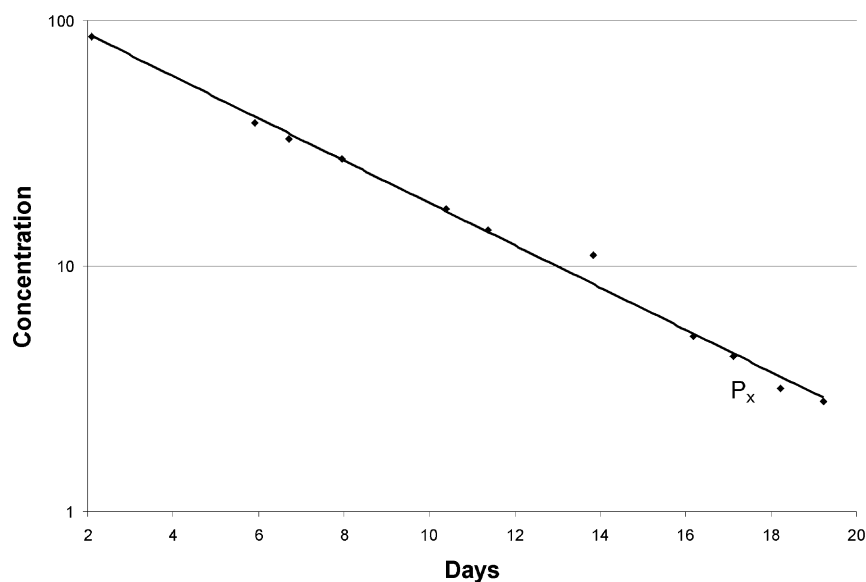

Fig. 6. Ageing of P_x plotted on a logarithmic scale. The data from Fig. 5, P_x, are plotted from day 3 to day 19, in order to exclude initial lag. Also included in the graph is an automatic trend line created by Excel® for an exponential plot. The plot shows a linear tendency, indicating a first order decay of the initial product under these conditions. The calculated half-life of P_x under these circumstances is 3.5 days.

minor leakages in the system may lead to the complete degradation of the column coating in minutes. Improvement of the stability of polyethylene glycol may lead to extended use in the future.

Acknowledgements

The author thanks Walther Batsberg Petersen for the SEC analysis and Gustav Bøjesen for the precise mass determination. Thanks also to Steen Hammerum for nomenclature suggestions, and to Yvonne Shashoua and Tim Padfield for proofreading and oxidising the manuscript.

References

[1] Goglev RS, Neiman MB. Thermal-oxidative degradation of the simpler polyalkyleneoxides. Vysokomol soyed A9 1967;10:2083–93.

[2] Dulog L, Storck G. Die Oxydation von Polyepoxiden mit molekularem Sauerstoff. Die Makromol Chem 1966;91:50–73.

[3] Dulog L. Oxidation von Polyepoxiden mit molekularem Sauerstoff. Farbe und Lack 1967;73(1):11–17.

[4] Conder JR, Fruitwala NA, Shingari MK. Thermal decomposition of polyethylene glycol 20M and essential oils in gas-liquid chromatography and the effect of traces of oxygen. J Chromatogr 1983;269:171–8.

[5] Grassie N, Mendoza GAP. Thermal degradation of polyetherurethanes: part 1—thermal degradation of poly(ethylene glycols) used in the preparation of polyurethanes. Polym Degrad Stab 1984;9:155–65.

[6] Jones GK, McGhie AR, Farrington GC. Studies of the stability of poly(ethylene oxide) and PEO-based solid electrolytes using thermogravimetry-mass spectrometry. Macromolecules 1991;24:3285–90.

[7] Voorhees KJ, Baugh SF, Stevenson DN. An investigation of the thermal degradation of poly(ethylene glycol). J Anal Appl Pyrolysis 1994;30:47–57.

[8] Mikheev YA, Zaikov GE. Heterophase mechanisms of thermal oxidation of polymers. New horizons. Russian Chem Rev 2000;69(3):231–60.

[9] Morlat S, Gardette J-L. Phototransformation of water-soluble polymers. I: photo-and thermooxidation of poly(ethylene oxide) in solid state. Polymer 2001;42(14):6071–9.

[10] Padfield T, Glastrup J, Winsløw J, Pedersen WB. Decomposition of polyethylene glycol (PEG) on heating. 9th Triennial Meeting, Dresden, German Democratic Republic, 26–31 August 1990. ICOM Committee for Conservation, 1990. p. 243–245.

[11] Glastrup J, Padfield T. The thermal degradation of tetraethylene glycol, a model molecule for polyethylene glycol. 10th Triennial Meeting, Washington, DC, USA, 22–27 August 1993. ICOM Committee for Conservation, 1993. p. 251–256.

[12] Glastrup J. Degradation of polyethylene glycol. A study of the reaction mechanism in a model molecule: tetraethylene glycol. Polym Degrad Stab 1996;52:217–22.

[13] Han S, Kim C, Kwon D. Thermal degradation of poly-(ethyleneglycol). Polym Degrad Stab 1995;47:203–8.

[14] Han S, Kim C, Kwon D. Thermal/oxidative degradation and stabilization of polyethylene glycol. Polymer 1997;38(2):317–23.

[15] Stankoviak, Glass. Thermooxidativer abbau von Triethylenglycol. Internal report no.: 06-A30-0530-87. Hoechst, 1987.

[16] Riecke A. Über Peroxyde der Äther, der Carbonyl-Verbindungen und die Ozonide. Angew Chem 1958;70(9):251–78.

[17] Riecke A, Bischoff C. Über die Darstellung von Monoperoxyacetalen. Chem Ber 1961;94:2457–61.

[18] Decker C, Marchal C. Charactérisation des réactions primaires de dégradation oxydante au cours de l'autoxydation des poly oxyéthylènes à 25 °C: etude en solution aqueuse avec amorçage par radiolyse du solvant. V. Triéthylène glycol: Produits d'oxydation et schéma cinématique. Die Makromol Chem 1973;166:139–53.

[19] Håfors, B. Procedures in selecting and evaluating the conservation liquid for the Vasa wooden material. Proceedings of the 7th ICOM-CC Working Group on Wet Organic Archaeological Materials Conference, 1998. p. 87–94.

[20] Haines JR, Alexander M. Microbial degradation of polyethylene glycol. Appl Microbiol 1975;29(5):621–5.

[21] Kawai F. Microbial degradation of polyethers. Appl Microbiol Biotechnol 2001;58:30–8.

[22] De Witte E, Terfve A, Vynckier J. The consolidation of the waterlogged wood from the gallo-roman boats of Pommeroeul. Studies in Conservation 1984;29:77–83.

[23] Catalogue: Polyethylene glycols. Product Information. Clariant, 1998.

[24] Molodovskii VA, Neiman MB. The oxidation of diisopropyl ether in the liquid phase. Zhur Fiz Khim 1949;23:30–6.

[25] Olsen O, Crumlin-Pedersen O, editors. Five Viking Ships from Roskilde Fjord. Copenhagen: The National Museum of Denmark; 1978.

[26] Crumlin-Pedersen O. Skuldelev. Maritime archaeology, newsletter from Roskilde 2001. Available: http://www.mac-roskilde.dk/nyhedsbrev1.asp?pubid=158&Articleid=166.