

Supplementary Information

Oxidative Degradation of Oligo(Ethylene Glycol)-terminated Monolayers

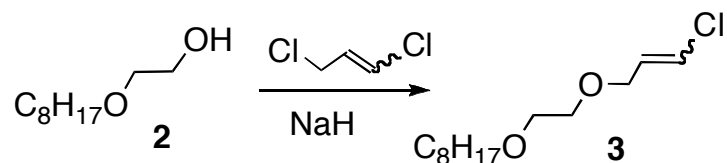
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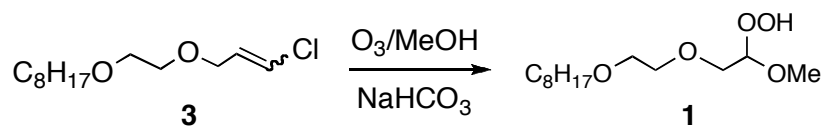
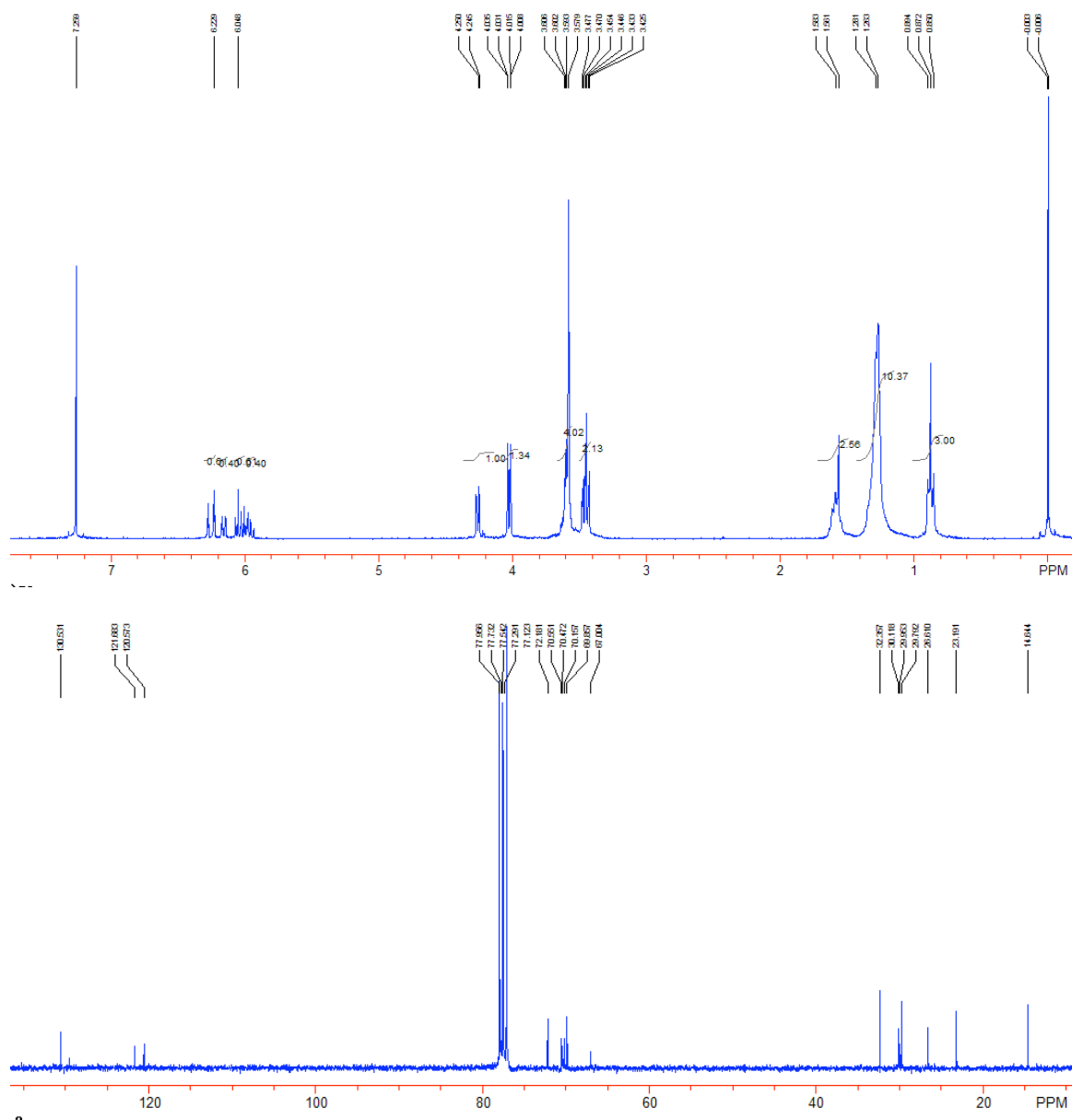
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1. Synthesis of the Hydroperoxide 1



1-Chloro-3-(2-octyloxy-ethoxy)-propene (3)

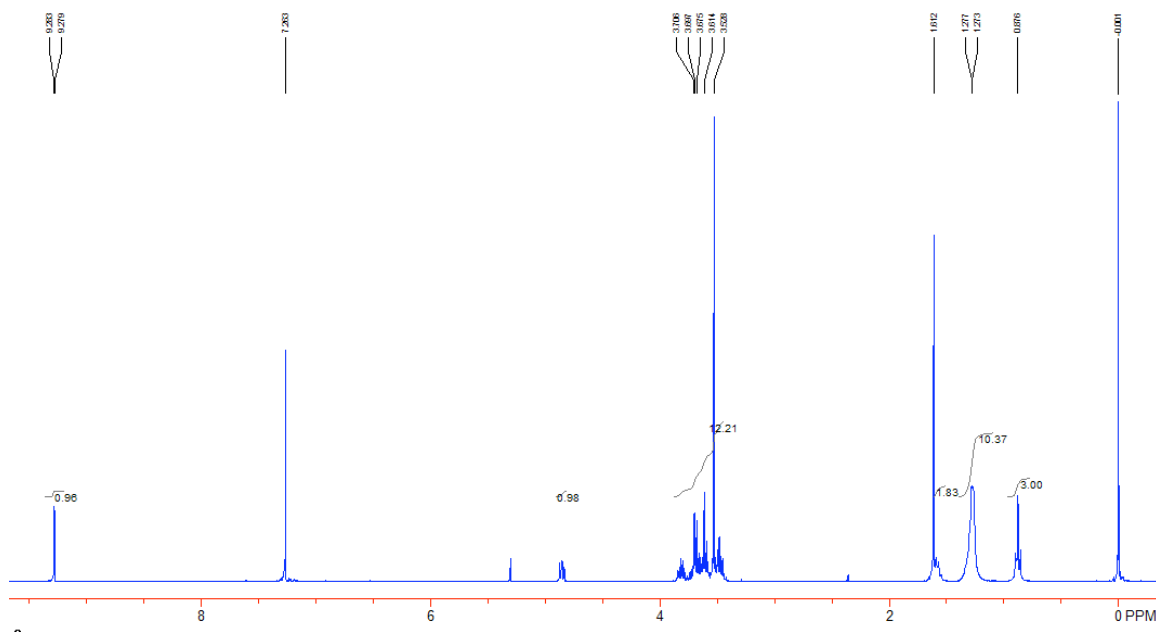
NaH (60% in mineral oil, 1.06 g, 26.5 mmol, Aldrich Co.) was added to a solution of **2** (4.30 g, 25.0 mmol, Aldrich Co.) in dried THF (10 ml). After the solution was stirred at 60 °C for 6 h, 1,3-dichloro-propene (8.32 g, 75.0 mmol) was added. The solution was stirred for 48 h at 65 °C. Hexane (30 mL) was added, and the organic solution was washed three times with water, dried over MgSO₄, and evaporated. Purification with flash chromatography (hexane/EtOAc 99:1) twice gave **3** as a pale yellow oil (2.03 g, 33% yield, as a mixture of trans- and cis-isomers with trans/cis = 3:2 based on the integration of ¹H-NMR signals of CH₂CH=CHCl). ¹H-NMR (300 MHz, CDCl₃): 6.28-6.22 (dt, trans-CHCl, *J* = 13.2, 1.5 Hz); 6.17-6.14 (dt, cis-CHCl, *J* = 7.5, 1.5 Hz, trans/cis = 3/2); 6.07-6.00 (m, trans-CH=CHCl); 5.98-5.93 (m, cis-CH=CHCl, cis/trans = 2/3); 4.27-4.25 (dd, cis-CH₂CH=CHCl, *J* = 5.4, 1.8 Hz); 4.04-4.01 (dd, trans-CH₂CH=CHCl, *J* = 6.4, 1.6 Hz, trans/cis = 3/2); 3.64-3.56 (m, 4H); 3.48-3.43 (m, 2H); 1.56-1.52 (m, 2H); 1.26-1.16 (m, 10H); 0.90-0.85 (t, 3H, *J* = 6.6 Hz). ¹³C-NMR (300 MHz, CDCl₃): δ 14.64; 23.19; 26.61; 29.79; 29.96; 30.12; 32.36; 67.00; 69.86; 70.16; 70.47; 70.55; 72.18; 120.57; 121.68; 130.53; MS (CI, *m/z*) [M+H⁺]: 249.77.

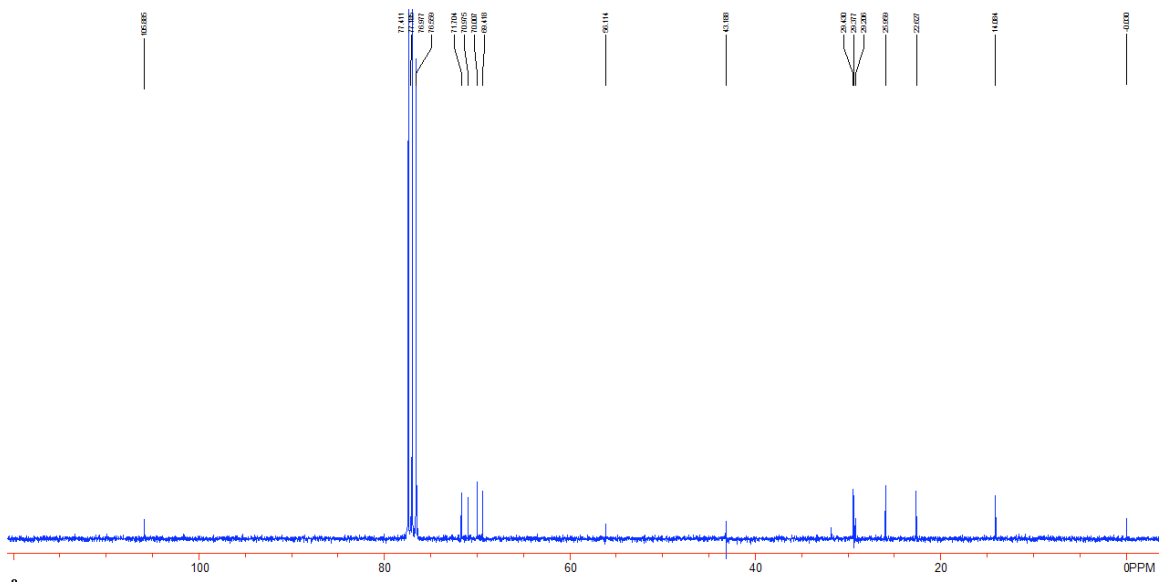


1-Methoxy-2-(2-octyloxy-ethoxy)-eth-1-yl-hydroperoxide (1)

Ozone was bubbled into a suspension of **3** (100 mg, 0.40 mmol) and NaHCO₃ (168 mg, 2.00 mmol) in MeOH (5 mL) cooled with a dry ice/acetone bath (−78 °C). After

the solution acquired a pale blue color, the addition of ozone was stopped, and the excess ozone in the solution was removed by passing oxygen through the solution until it became colorless. The mixture was allowed to warm to room temperature, filtered, and evaporated under reduce pressure to a volume of ca. 0.5 ml. Purification by flash chromatography (methanol/CH₂Cl₂ 1:99) gave **1** (82 mg, yield: 77%) as colorless oil. ¹H-NMR (300 MHz, CDCl₃): 9.25 (d, *J* = 0.9 Hz, 1H); 4.87-4.83 (ddd, 1H, *J* = 7.0, 4.5, 0.9 Hz); 3.86-3.44 (m, 11H); 1.61-1.57 (m, 2H); 1.24-1.28 (m, 10H); 0.89-0.85 (t, 3H, *J* = 6.6 Hz). ¹³C-NMR (300 MHz, CDCl₃): δ 14.08; 22.63; 25.96; 29.21; 29.38; 29.43; 31.79; 56.11; 69.42; 70.00; 70.97; 71.70; 105.89. MS (CI, *m/z*) [M+H⁺]: 265.18.





2. Thermo Gravimetric Analysis & Differential Thermal Analysis (TGA-DTA) of 1

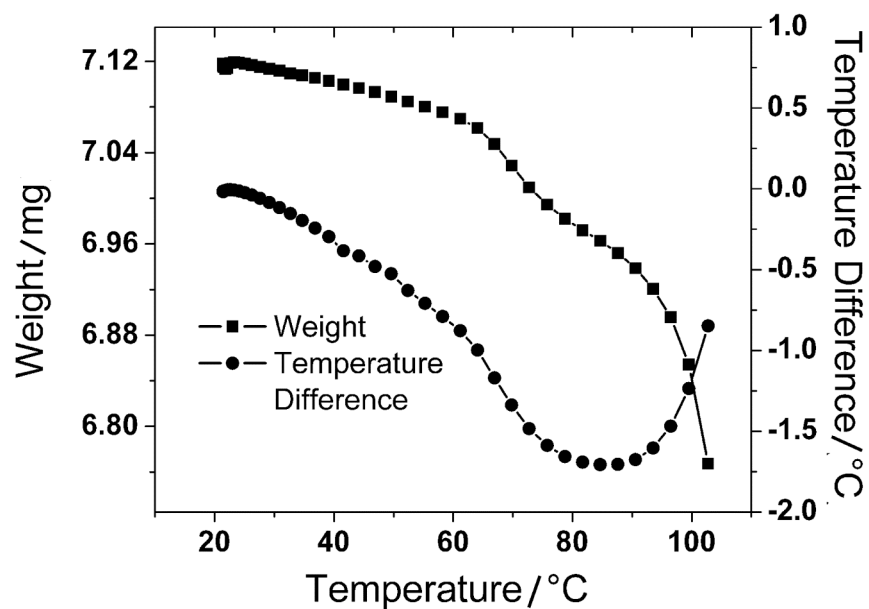
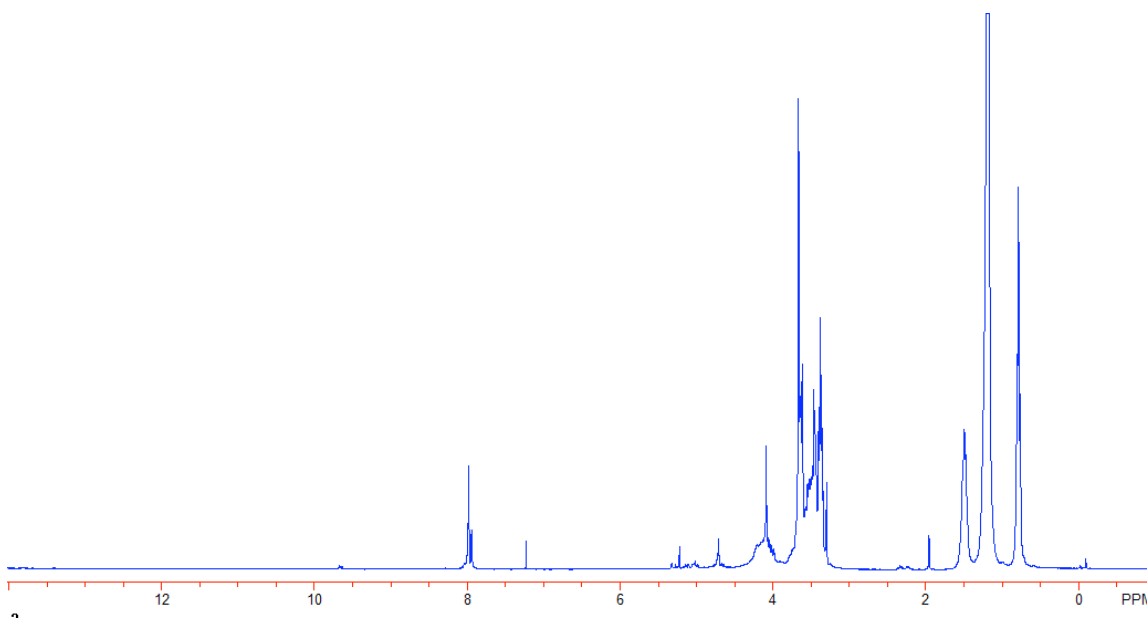


Figure S1. TGA-DTA diagram of the hydroperoxide **1**, obtained with a heating rate of 20 °C/min using a SDT 2960 Simultaneous DTA-TGA (TA Instruments).

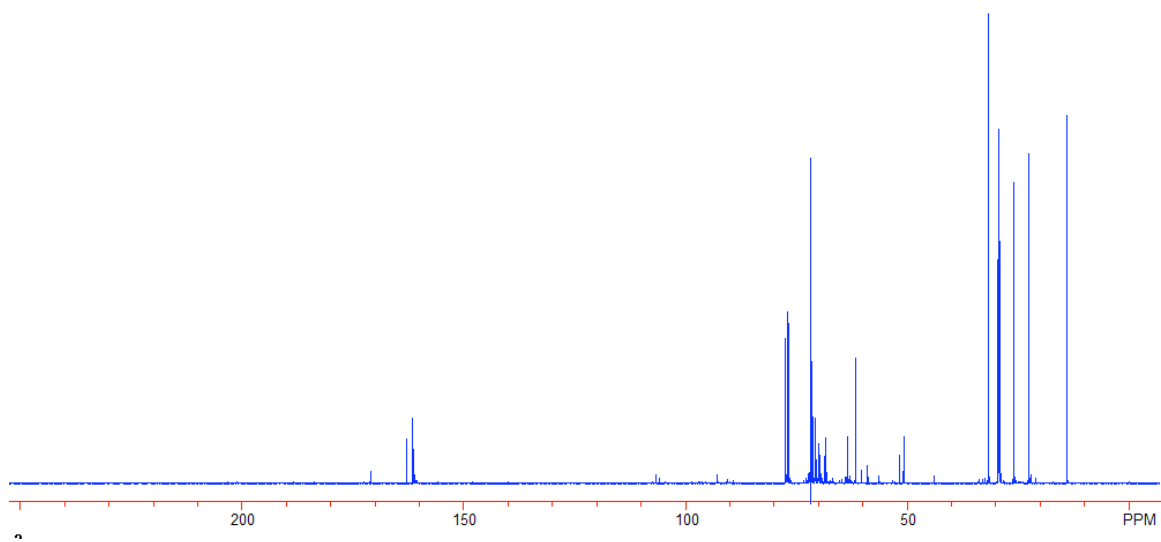
3. Thermal Decomposition of the Hydroperoxide **1**

Freshly prepared compound **1** (211 mg) in a 100 ml pear-shaped flask was heated in a water bath (bath temperature 80 °C) for 1 h. *Caution: Hydroperoxides are explosive, and should be handled in a small quantity and with shield protection.* After heating, the remaining materials weighted 184 mg, and was dried under vacuum (~1 torr) at room temperature for 3 h. The residue then weighted 139 mg. As shown by the ¹H- and ¹³C-NMR spectra below, the doublet peak at 9.25 ppm corresponding to the OOH group of **1** disappeared. The combined integration in the region of 0.9–2.0 ppm remained the same, indicating that alkyl chain was not affected during the decomposition of **1**. The singlet at 8.0 ppm in the ¹H-NMR spectrum and the peaks at 160 and 52 ppm in the ¹³C-NMR spectrum indicate the presence of methyl formate.¹ The peak at 162 ppm is assigned to formic acid.¹ These singlets disappeared after the sample was dried at 1 torr for 3 hrs.

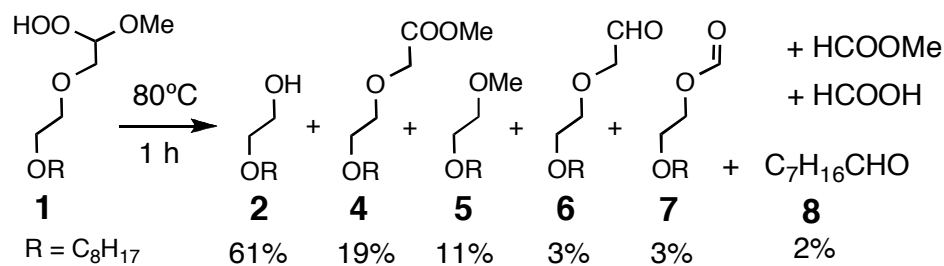
¹H-NMR spectrum after heating the hydroperoxide **1** at 80 °C in air for 1 h:



^{13}C -NMR spectrum after heating the hydroperoxide **1** at 80 °C in air for 1 h:



4. Analysis of the Decomposition Products by GC-MS

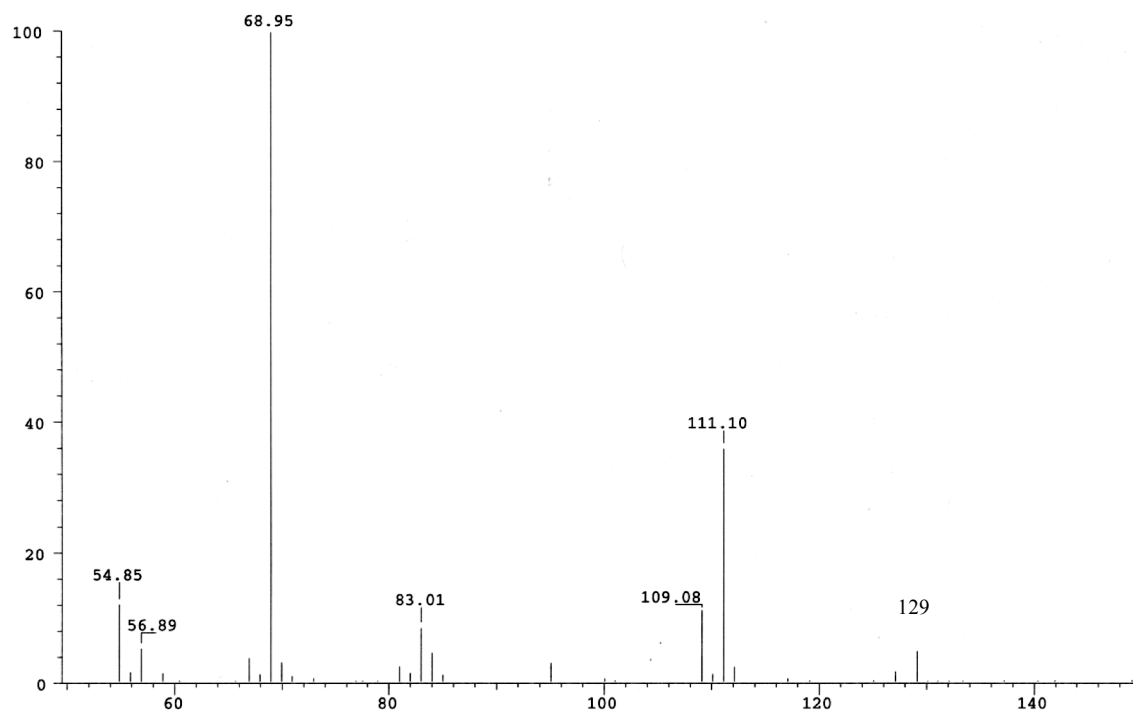


The initial identification of the non-volatile degradation products was performed by GC-MS (HP 5890 series II GC, Supelco MDN-5S capillary column, injector temperature 250°C, column temperature: 50 °C to 250 °C @ 20 °C/min, then 250 °C 10 min). The GC-MS diagram is depicted in Figure 1 (main text). Assignment of the peaks to the compounds as indicated in Figure 1 was based on the CI-MS showing the

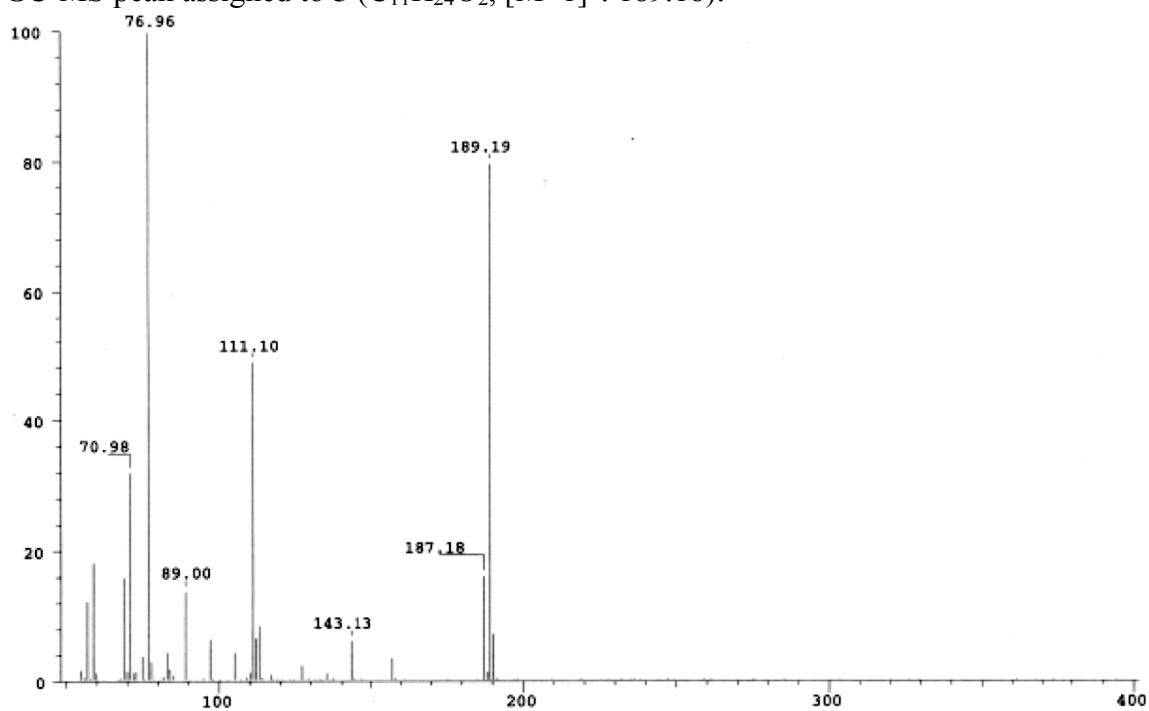
corresponding $[M+1]^+$ m/z . Except compound **6**, the assignment was confirmed by co-injection of the pure compounds **2**, **4**, **5**, **7** and **8**. Quantification of the yields of these products in the reaction mixture (without drying) was performed by GC (Shimadzu GC-2010, Restek RTX-5 column) using 2-(octyloxy)ethyl acetate as the internal standard and calibrated with the pure compounds **2**, **4**, **5**, **7** and **8**.

The following are the CI-MS for peaks in the GC-MS diagram (Figure 1) assigned to compounds **2**, **4**–**8**.

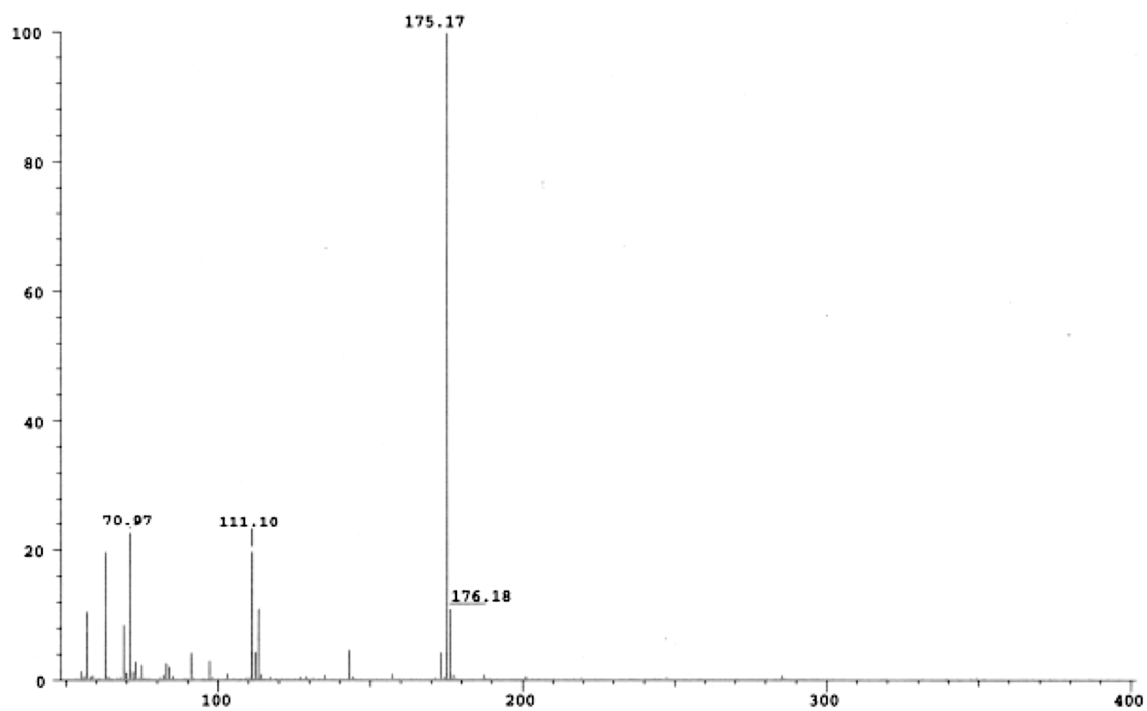
GC-MS peak assigned to **8** ($C_8H_{17}O$, M^+ : 129.13):



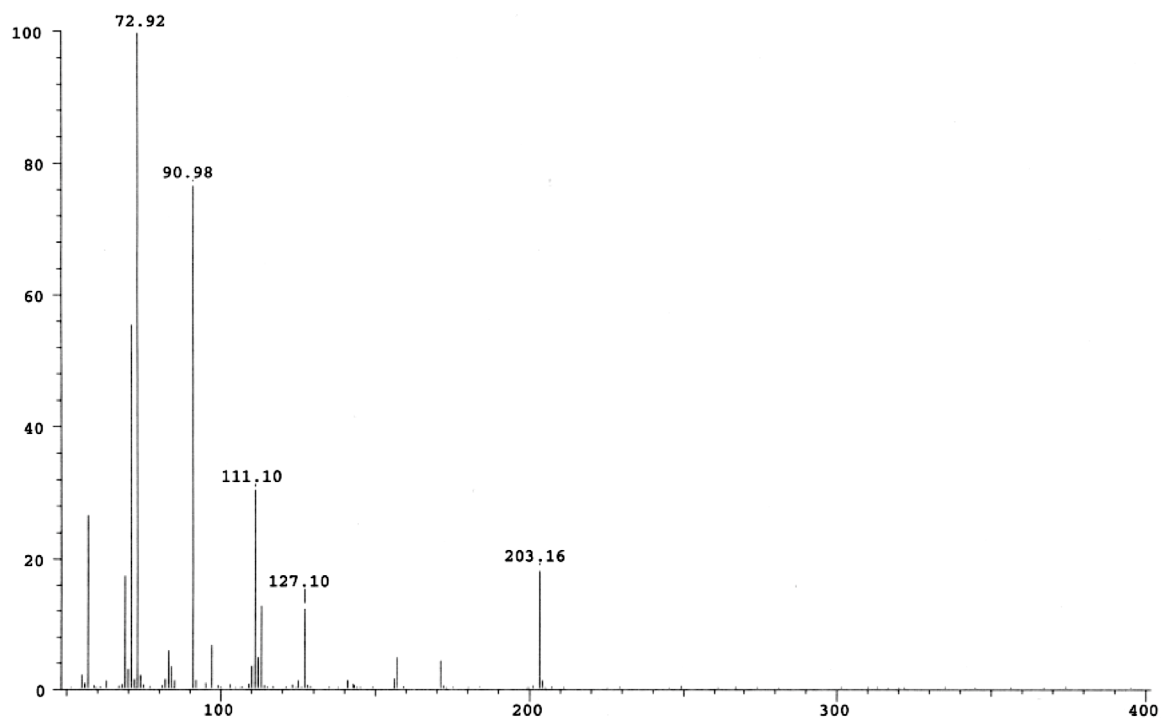
GC-MS peak assigned to **5** ($C_{11}H_{24}O_2$, $[M+1]^+$: 189.18):



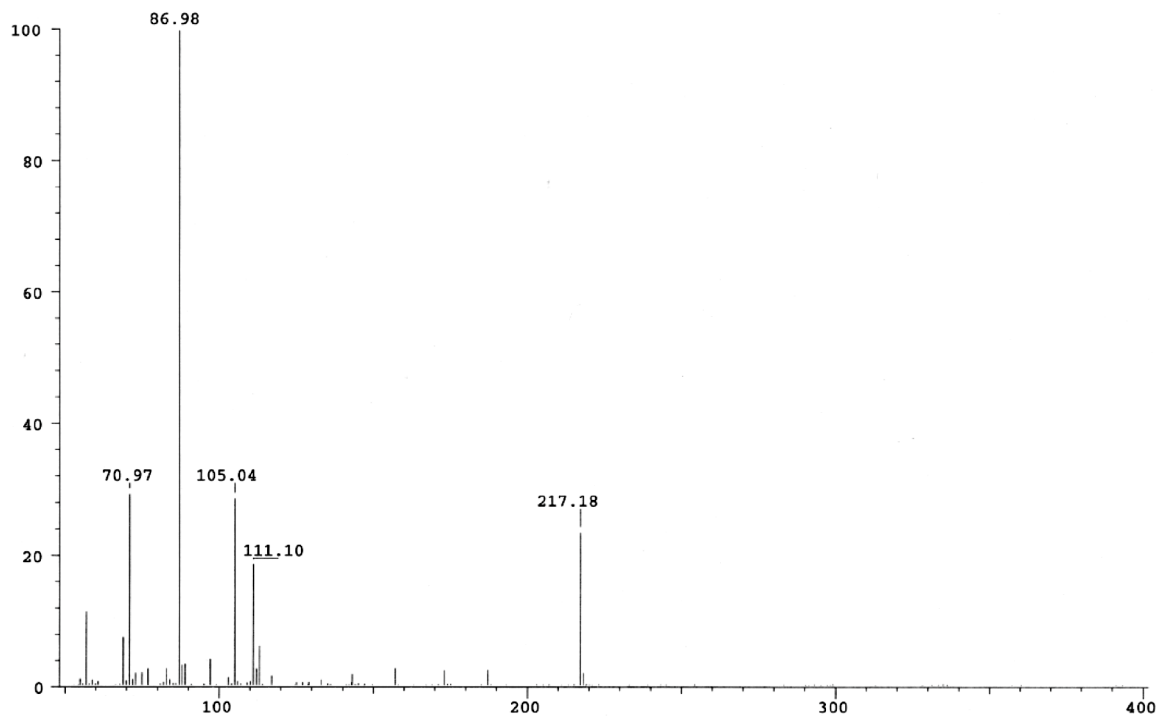
GC-MS peak assigned to **2** ($C_{10}H_{22}O_2$, $[M+1]^+$: 175.16):



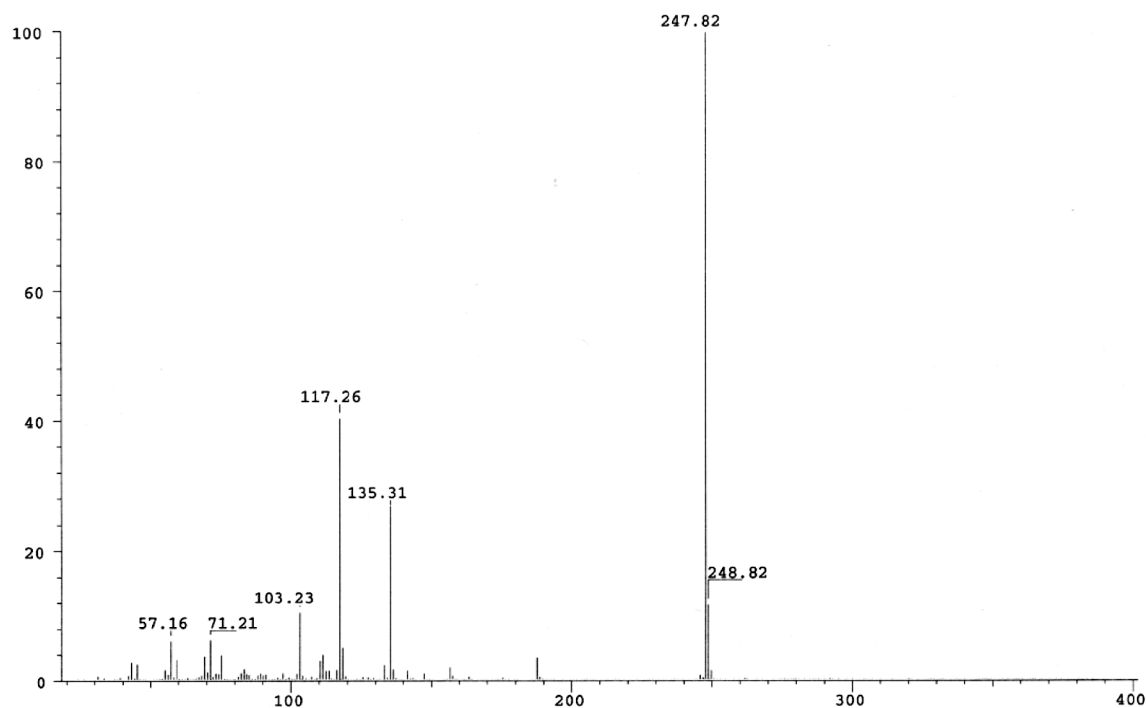
GC-MS peak assigned to **7** ($C_{11}H_{22}O_3$, $[M+1]^+$: 203.16):



GC-MS peak assigned to **6** ($C_{12}H_{24}O_3$, $[M+1]^+$: 217.17):



GC-MS peak assigned to **4** ($C_{13}H_{26}O_4$, $[M+1]^+$: 247.18):



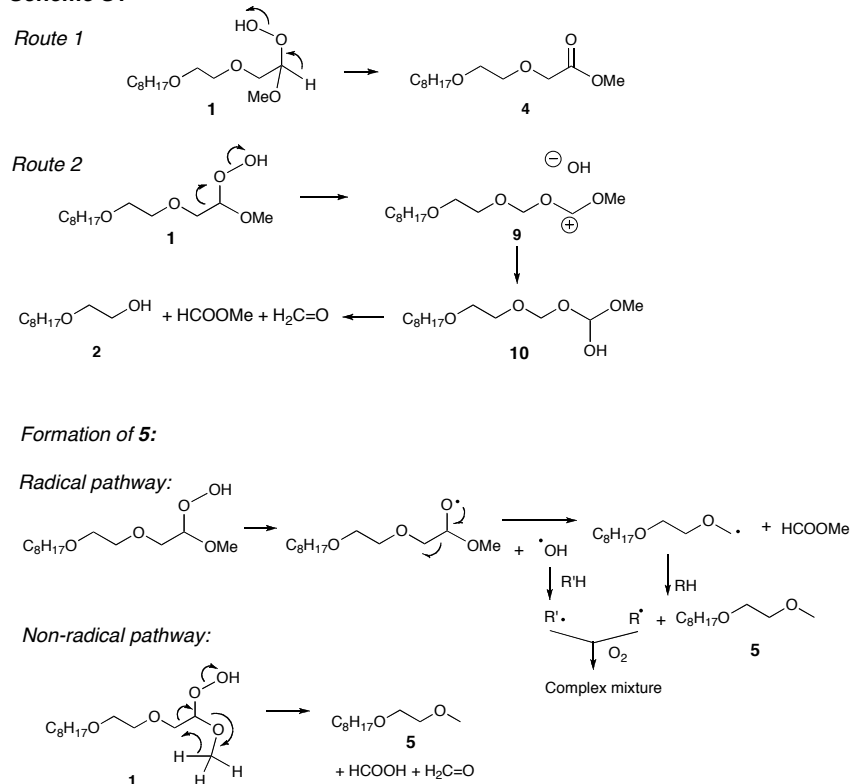
5. Discussion of Mechanism for Oxidative Degradation of OEG Monolayers

Mechanism of decomposition of **1**

The decomposition of **1** is likely to proceed mostly via *route 2* (Scheme 1) through the previously proposed mechanism³ outlined in Scheme S1, involving a concerted O–O heterolysis and alkyl shift leading to the carbon cation **9** stabilized by the ketal, which combines with the hydroxyl anion to the hemiformate **10** that readily decomposes to the alcohol **2**, methyl formate and formaldehyde.¹ To a lesser extent, **1** may also decompose by dehydration (*Route 1*). Both routes may be promoted by activating the hydroperoxy group with formic acid generated by air oxidation of formaldehyde produced by *route 2*. The methylether **5** is unlikely generated from the radical pathway since it would also

produce active radicals leading to a complex mixture, although the non-radical pathway proposed in Scheme S1 is highly speculative.

Scheme S1

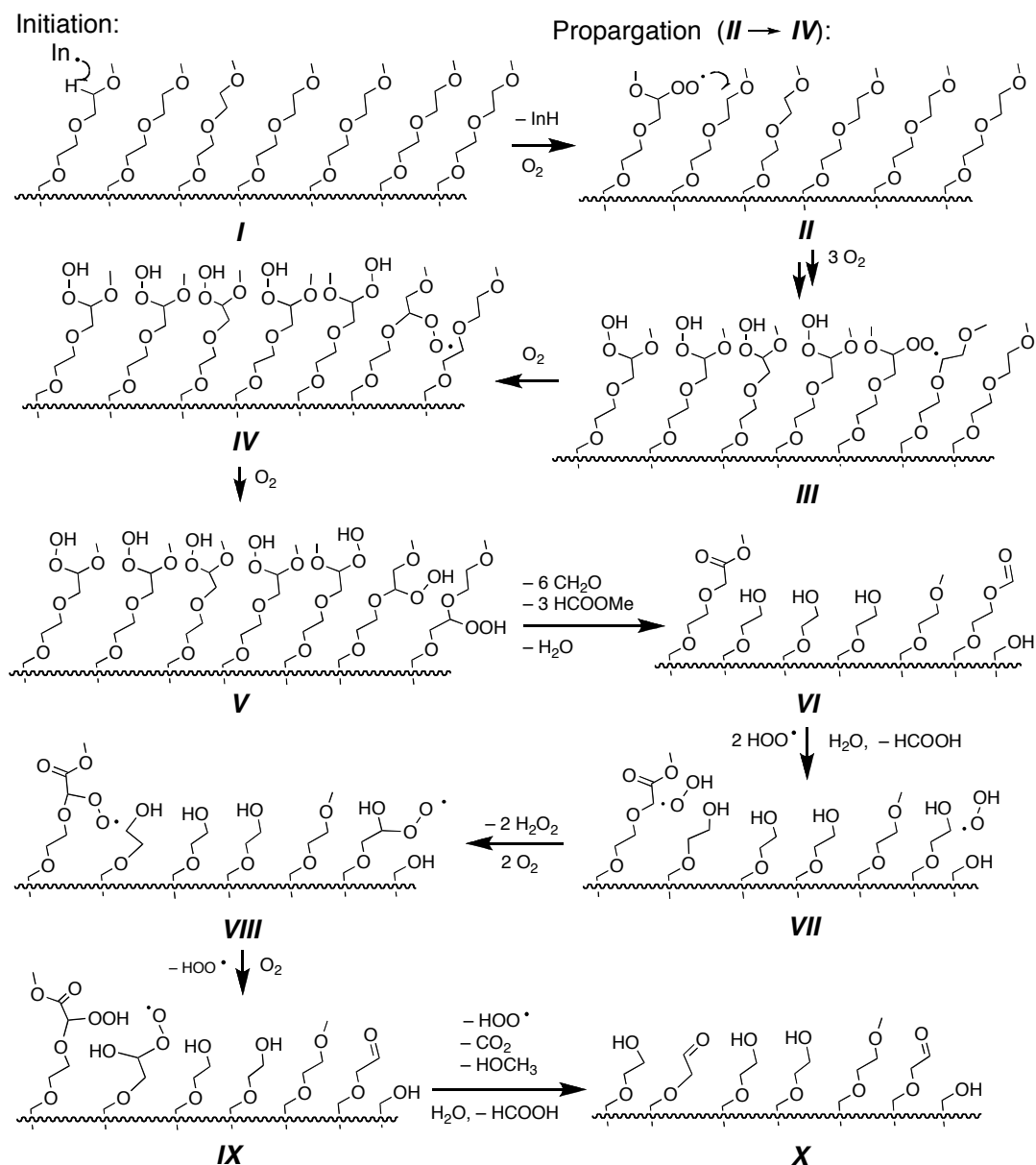


Mechanism for oxidative degradation of OEG monolayers

A radical chain reaction is proposed for the formation of hydroperoxides by autoxidation. It starts by hydride abstraction with a radical initiator ($In\cdot$). If the radical initiator is highly active, such as $\cdot OH$ radicals, this step is diffusion-controlled, and the hydride at the outmost layer, i.e., the methyl group should be abstracted. On the other hand, for hydroperoxy radicals that are likely the predominate radicals involved in the reaction due to their constant regeneration in the subsequent steps (see below), the hydride abstraction is selective, favoring the formation of the secondary radicals as shown in **I** (Scheme S2). Hence, the methylene hydrides near the film surface should be preferentially abstracted. The radical chain propagation consists of two steps: rapid trapping of the carbon radicals

by triplet state oxygen to form peroxy radicals as in **II**, and hydrogen abstraction from an adjacent methylene hydride to generate a new radical that can continue the chain reaction (**II** to **IV**). It is expected that the propagation steps preferentially occur in the outmost CH₂ layer due to the closer proximity of the adjacent peroxy radicals in the same layer, especially for the closely packed OEG films. However, due to the fluctuation of the OEG chains, a small portion of the hydride abstractions may move to the deeper layer as shown

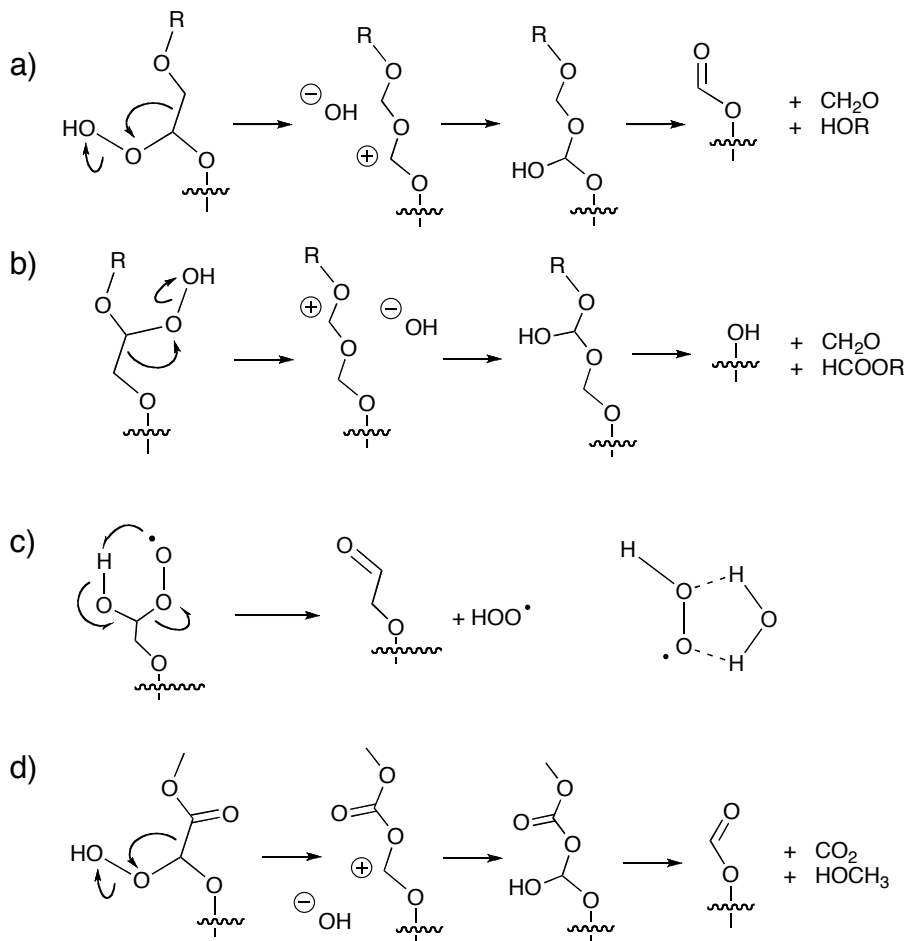
Scheme S2



especially for the closely packed OEG films. However, due to the fluctuation of the OEG chains, a small portion of the hydride abstractions may move to the deeper layer as shown by the right molecule in *IV* and *V*. The decomposition of the hydroperoxides in *V* may proceed via the mechanism outlined in Scheme S1 and discussed above, generating mostly alcohols together with a small portion of esters and ethers. Decomposition of the hydroperoxides in the deeper layer is expected to follow a similar mechanism as proposed in Scheme S3a,b, again generating mostly alcohols or formate esters in *VI*. The formates are readily hydrolyzed to alcohols. The mechanism proposed for the oxidation of the OEG films terminated mostly with hydroxyl groups is different from the general mechanism for the autoxidation of OEG/PEG in the bulk. The key difference is that the peroxy radicals are predominately located on the OEG/PEG chain in the bulk, while the radicals on the OH-terminated OEG films are mostly small, diffusible radicals, such as $\text{HOO}\cdot$, that kinetically prefer to abstract the hydride from the surface CH_2OH groups. Upon addition of O_2 to the $-\text{CHOH}$ radical, rather than undergoing hydride abstraction, the resultant peroxy radical (such as the one generated by interacting of $\text{HOO}\cdot$ on the right side of *VII* and *VIII* in Scheme S2) spontaneously decomposes to an aldehyde and hydroperoxy radical⁴ that may diffuse out to the bulk solution after forming two hydrogen bonds with a water molecule⁵ (Scheme S3c). Therefore, the degradation might be slowed down, and the propagation of peroxy radicals to the adjacent OEG chains is limited to the peroxy radicals located not at the CH_2OH group, such as the one generated from the ester above the film (left *VII* to *VIII*), which may abstract hydride from the adjacent CH_2OH group leading to the peroxy radical that spontaneously decomposes to an aldehyde and hydroperoxy radical (*IX* to *X*). Therefore, after the degradation of the

first CH₃O-terminated EG layer, further oxidative degradation leads to a surface composed of mostly alcohols and aldehydes as illustrated by **X**. More aldehydes are formed with higher concentrations of reactive oxy radicals on the surface, which can further oxidize aldehydes to carboxylic acids.

Scheme S3



References

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