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Thermal degradation of poly(ethylene oxide–propylene oxide–ethylene oxide) triblock copolymer: comparative study by SEC/NMR, SEC/MALDI-TOF-MS and SPME/GC-MS

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Abstract

By comparing size exclusion chromatography/matrix assisted laser desorption ionisation (SEC/MALDI) and SEC/NMR spectra from virgin poly(ethylene oxide–propylene oxide–ethylene oxide) triblock copolymer, we were able to understand the bimodal distribution observed in poloxamer 407. Propylene oxide, isomerised to allyl alcohol during polymerisation, eventually forms a Poly(ethylene oxide–propylene oxide) diblock copolymer when EO is added to the feed. The oxidative thermal degradation of poloxamer 407 at 80°C in air was studied. We found by MALDI that degradation starts after 21 days in the PPO block of the copolymer. This result was confirmed by solid phase microextraction/gas chromatography-mass spectrometry (SPME/GC-MS): The first volatile degradation product to appear is 1,2-propanediol,1-acetate,2-formate. The structure of this molecule suggests that a six-ring intramolecular decomposition reaction of the PPO chain occurs at the very beginning of the polymer breakdown. Thus, the secondary hydroperoxide formed on the PPO chain plays a major role on the thermoxidation of poloxamer materials. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Poloxamer 407; Oxidation; Mass spectrometry

1. Introduction

Poloxamer materials are synthetic ABA type triblock copolymers of ethylene oxide and propylene oxide. A is made of hydrophilic poly(ethylene oxide) (PEO) chains and B of more hydrophobic poly(propylene oxide) (PPO) segments. Poloxamers were first synthesised in 1954 by Lundsted and Ile [1] when trying to develop new surface-active agents with new properties. There are several differences comparing poloxamers to classic surfactants. Firstly they exhibit a molar mass range 1000–15,000 whereas most other surfactant series have much lower mass. Then they have two hydrophilic groups, whereas most non-ionic surfactants have only one. The particular physical properties of poloxamers are used in pharmaceuticals, in drug delivery systems, and in other drug and medical studies as the following functions: emulsifying, thickening, coating, solubilising, dispersing and foaming.

Non-ionic surfactants composed of polyoxyalkene chains are very sensitive to autoxidation. The reaction occurs with the degradation of the hydrophilic chain resulting in the loss of tensile properties. Hydroperoxides and radicals formed in the autoxidation reaction are responsible for degradation and ageing in several kinds of commercial products in which the surfactants are added as minor components, for example in pharmaceutical or cosmetic products.

The mechanism of degradation of polyethylene oxide chain is quite similar to that of hydrocarbon chains, but the presence of oxygen in the molecules strongly activates the process by increasing the labile nature of protons on α-carbon atoms. Several autoxidative mechanisms of degradation of PEO (inert atmosphere) giving low molecular weight products have been presented. By pyrolysis Madorsky and Straus [2] observed the formation of oligomers of PEO as well as formaldehyde, ethanol, carbon dioxide and water. Grassie and Perdoma Mendoza [3] added methane, ethylene oxide and derivatives of acetaldehyde to this list. More recently attention was focused on the chain-ends of the polymer after pyrolysis [4–6]. It was concluded that at the lowest temperature (150°C) the dominant products result from the preferred cleavage of C–O bonds. At the highest temperature (550°C) C–C cleavage and dehydration become more favourable.

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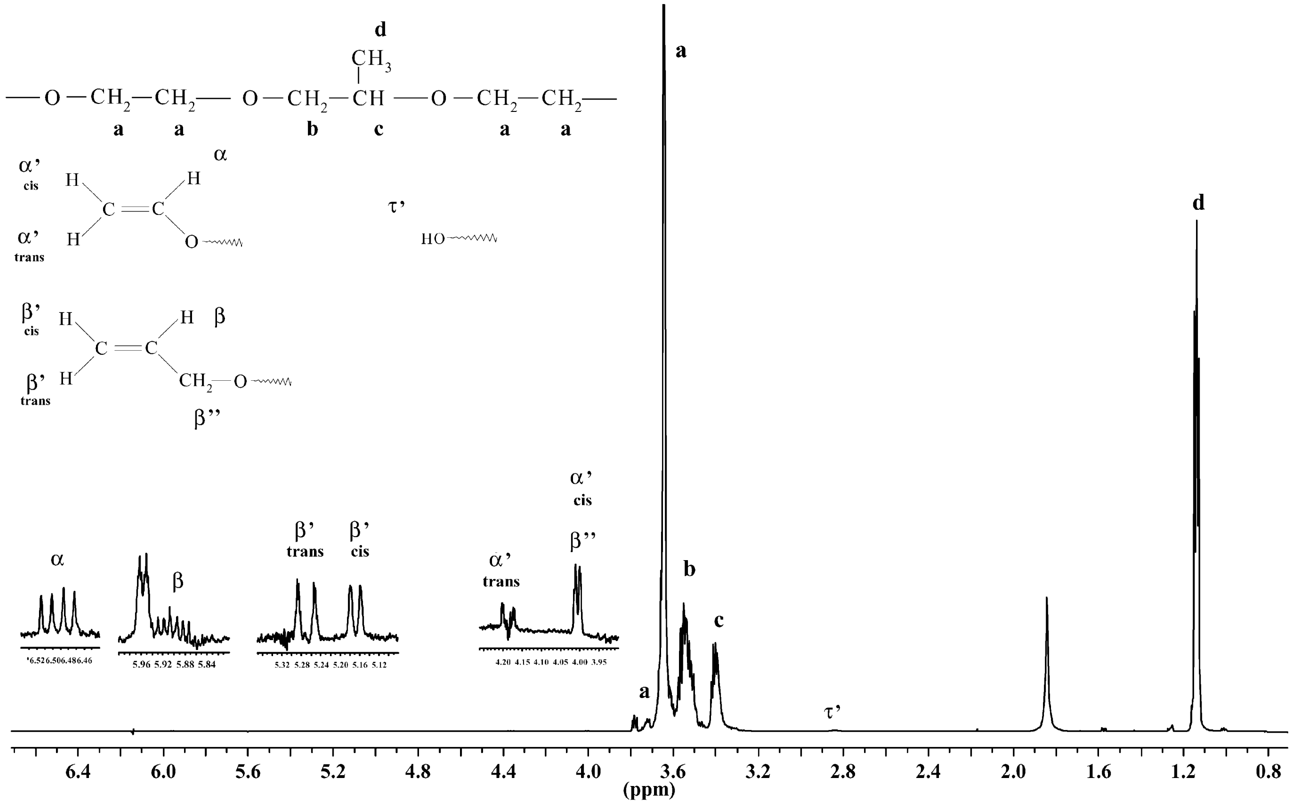


Fig. 1. ^{1}H NMR spectrum of virgin poloxamer 407.

In the presence of oxygen degradation of the polymer occurs in a very different manner as hydroperoxides are more readily formed on α-carbon atoms of the PEO chains. Progress of reaction is accompanied by decomposition of the hydroperoxides and by random chain scission at C–O and C–C bonds in a ratio depending on the temperature of oxidation. At 50°C Morlat and Gardette [7] found no evidence of homolysis of C–O bonds. C–C cleavage is the main mechanism of degradation. The same thing was previously observed by Yang et al. [8] at 150°C. It is only for higher temperatures that C–O cleavages do occur significantly.

PPO is less thermally stable than PEO because formation of a radical on a tertiary carbon of PPO is more probable than on a secondary carbon of PEO. However when studying the thermoxidation of PPO, authors have been arguing whether the secondary alkoxy radicals play a major role or not on the degradation of PPO. By NMR spectroscopy, Griffith et al. [9] monitored the end groups of PPO degraded at 125°C. Starting from dihydroxyl terminated PPO, they found after oxidation, acetate and formate end groups in a ratio of 2:3, as well as ketone chain-ends. These chain-ends were explained by taking into account the breakdown of both tertiary and less probable secondary hydroperoxide in some extent. Kemp and co-authors [10] used MALDI-TOF MS to monitor the thermoxidation of PPO at 155°C. They found that the degradation pathways implied a major role of the secondary alkoxy radical. These results support previous studies by Lemaire and co-authors [11]. By NMR spectroscopy Yang et al. [8] followed the thermal degradation of both PEO and PPO at 150°C. For oxidised PEO, formate end groups appear through intramolecular decomposition and esterification of hydroxyl chain-ends. For PPO they did show the importance of esterification of hydroxyl chain-ends during the oxidation, and suggested the predominance of the tertiary alkoxy radical at the beginning of the polymer breakdown.

In order to solve the problem of the preferential degradation of PPO initiated on the secondary or the tertiary carbon of the polymer backbone we proposed to follow the thermoxidation of a poloxamer at a low temperature (80°C) slightly above the melting point of the material. This should also enable us to see what happens at the beginning of the degradation and confirm the preferential breakdown of the PPO block compare to the PEO block. To reach these goals we will have in a first step to study carefully the composition and structure of the commercial poloxamer utilised. One weakness of the previous studies was the high temperature usually chosen to oxidise the polymers (over 120°C) making difficult to observe the start of the degradation. Another weakness was the use of a single analytical technique at a time (usually NMR spectroscopy or MALDI-TOF mass spectrometry (MS)) to monitor the degradation. For this reason we compare in this paper results obtained by size exclusion chromatography (SEC), MALDI-TOF MS and NMR for the polymer matrix analysis, and solid phase microextraction–gas chromatography-mass

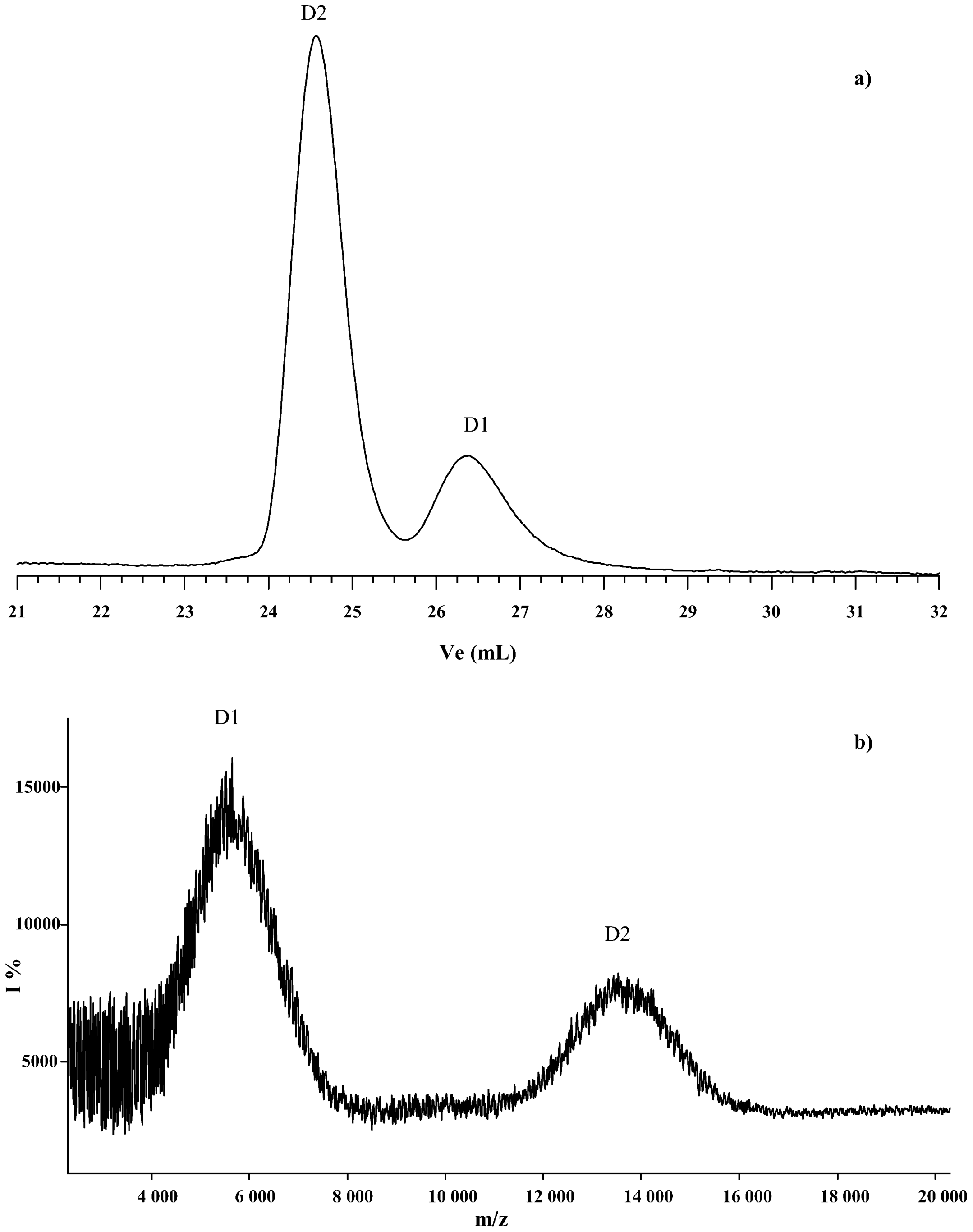


Fig. 2. Molecular weight distribution of virgin poloxamer as analysed by: (a) SEC and (b) MALDI-TOF-MS.

spectrometry (SPME–GC-MS) for the volatile products of degradation.

2. Experimental section

2.1. Material

The material used in this study is commercially available from BASF, known also under the name poloxamer 407 and trademark Pluronic® F127. According to the manufacturer this polymer has a molecular weight ranging from 9840 to 14,600 g mol^{-1} and the following structure: $H(O–CH_2–CH_2)_a–(O–CH_2–CH(CH_3)–)_b–(O–CH_2–CH_2)_a–OH$. At the maximum of the molecular weight distribution, $a = 101$ and $b = 56$.

Poloxamer 407 contains 100 ppm of the antioxidant butylated hydroxytoluene (BHT).

The melting point of the block copolymer is ranging from 53 to 57°C.

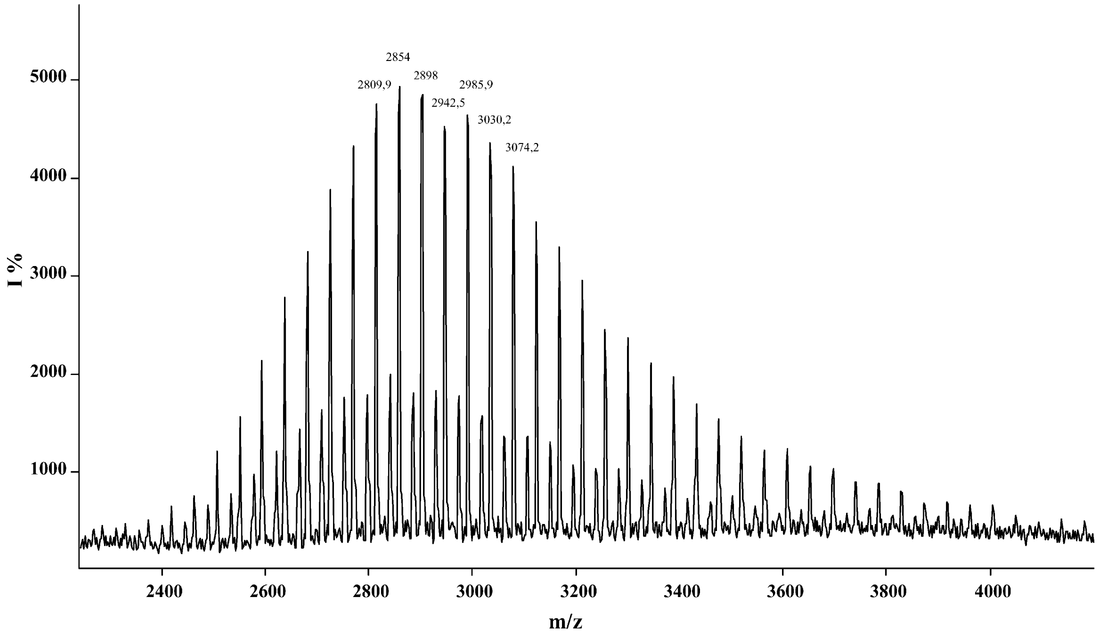


Fig. 3. MALDI spectrum of the SEC fraction of virgin poloxamer eluted at 27.9 ml. Possible assignments are shown in Table 2.

2.2. Thermal oxidation of poloxamer

The samples were submitted to thermal ageing at 80°C in air. Two hundred milligrams of poloxamer were placed in closed glass vials of 20 ml, and heated in an oven at 80°C for up to 53 days. A fresh sample was used for each degradation period. The choice to use closed vials was guided by the headspace analysis that had to be performed for each sample. As a result, oxidation takes place under oxygen starved conditions with approximately one molecule of oxygen for 24 repeat units.

2.3. Size exclusion chromatography

The changes of molecular weight of poloxamer were followed by SEC. A Waters Associates Chromatography Pump 0-6000 with a LI-Chroma-Damp III column were used. Detection was realised by a differential refractometre. THF was the mobile phase with a flow rate of 0.1 ml min^{-1}. Calibration was performed with poly(ethylene glycol) standards (polydispersity = 1.02–1.03) ranging from 620 to 22,800 g mol^{-1}.

The preparative SEC analyses were performed in $CHCl_3$ with a Waters 6000A apparatus equipped with four ultrastyragel columns (in the order 10^4, 10^3, 500, 100 Å pore size) connected in series, using a Waters R401 differential refractometre. Sixty microlitres of a polymer solution (10 mg ml^{-1}) was injected and eluted at a flow rate of 1 ml min^{-1}. The fractionation of the Poloxamer 407 sample was performed collecting 12 drops for each fraction.

2.4. Solid phase microextraction

Volatile molecules were extracted through SPME. Two different fibres were used: Carbowax/Divinylbenzene (CW/DVB) 65 μm and Polydimethylsiloxane (PDMS) 100 μm. The fibres were exposed to the headspace over the solid during 30 min at 80°C.

The best extractions were obtained with the CW/DVB fibre, and the results presented in this paper refer to this fibre only.

2.5. Gas chromatography-mass spectrometry

The volatile products released during thermal degradation were analysed on a Finnigan GCQ with a CP-Sil 8CB (30 m × 0.25 mm ID) column. Helium was used as carrier gas. The SPME fibre was inserted into the injector for 5 min at 220°C. The temperature was programmed as followed: 3 min at 40°C then heating to 250°C at a rate of 10°C per minute and eventually 10 min at 250°C.

2.6. ^{1}H NMR analysis

The ^{1}H NMR analyses were performed at room temperature with a $^{\text{UNITY}}$INOVA Varian instrument operating at 500 MHz using deuterated chloroform as solvent and tetramethylsilane as standard.

2.7. MALDI-TOF mass spectrometry

The matrix-assisted laser desorption/ionisation time of flight mass spectra were recorded in linear and reflectron mode by using a Voyager-De STR (Perseptive Biosystem) mass spectrometer equipped with a nitrogen laser emitting at 337 nm with a 3 ns pulse width and working in positive mode. The accelerating voltage was 25 kV; the grid voltage and the delay time were optimised for each sample to achieve the higher molar mass values. The laser irradiance was maintained slightly above threshold.

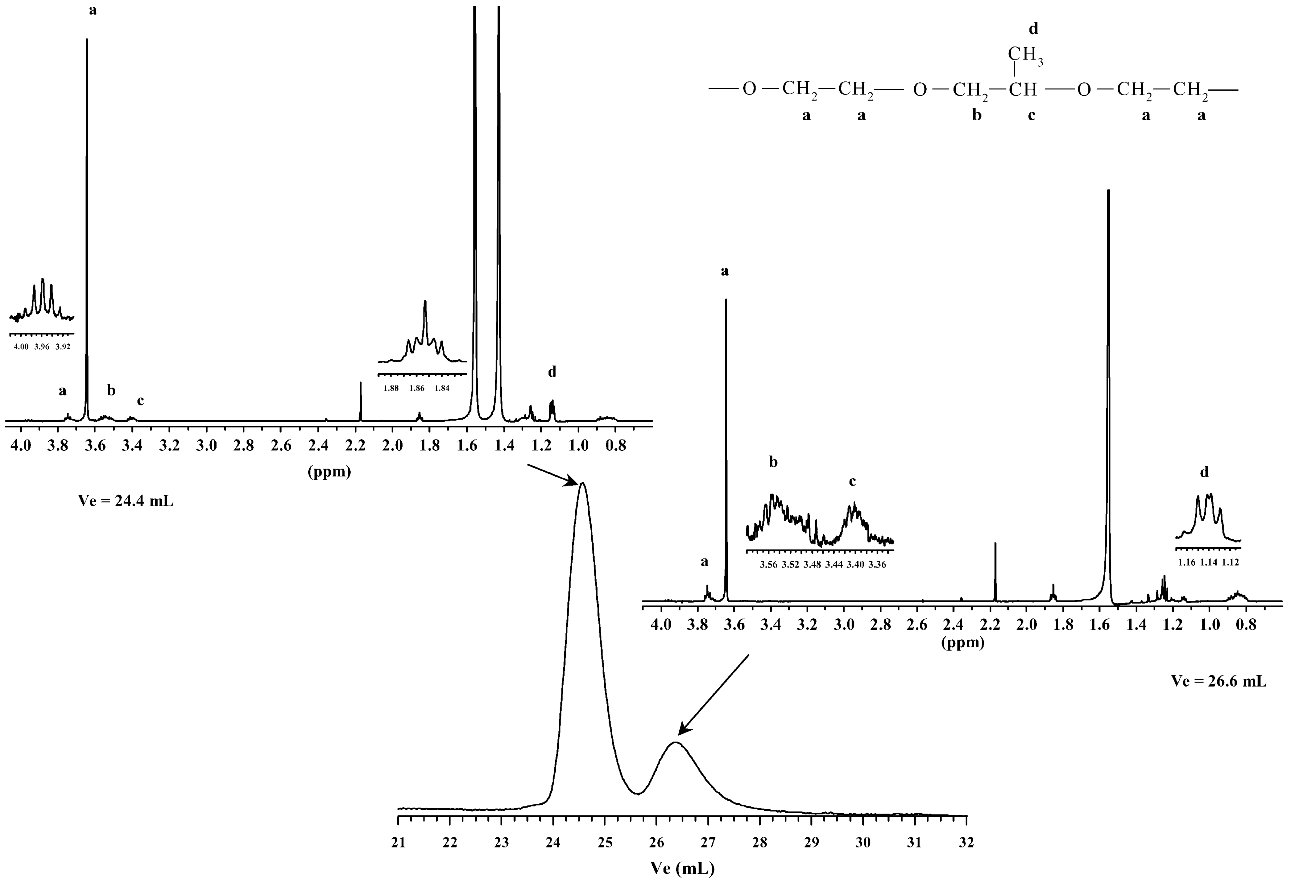


Fig. 4. SEC-^{1}H NMR of virgin poloxamer for two fractions eluted at the maximum of the two distributions.

2-(4-Hydroxyphenylazo)benzoic acid (HABA) (0.1 M in a THF/$CHCl_3$ mixture) was used as matrix.

The sample concentration of all unfractionated samples was 5 mg ml^{-1} in $CHCl_3$ whereas SEC fractions were dissolved in 20 μl of $CHCl_3$ after complete evaporation of the eluent. Equal volumes of sample solutions and matrix solution were mixed in order to obtain a 2:1, 1:1 and 1:2 ratio. One μl of a 0.1 M solution of sodium chloride (NaCl, in water) was added to aid cationisation. One microlitre of each sample/matrix mixture was spotted on the MALDI sample holder and slowly dried to allow matrix crystallisation.

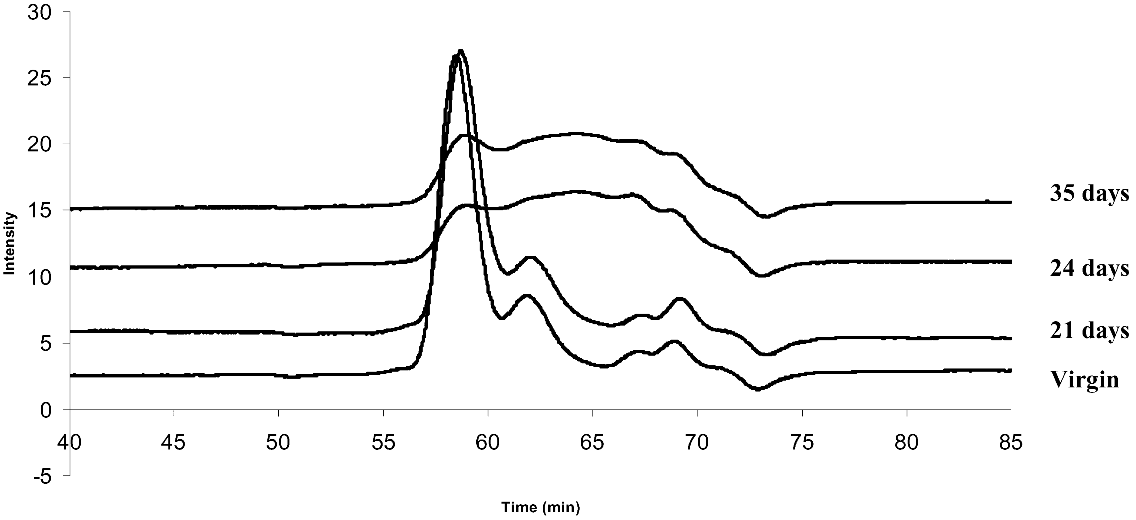


Fig. 5. Changes in molecular weight distribution of poloxamer 407 after 0, 21, 24 and 35 days of thermoxidation in air at 80°C.

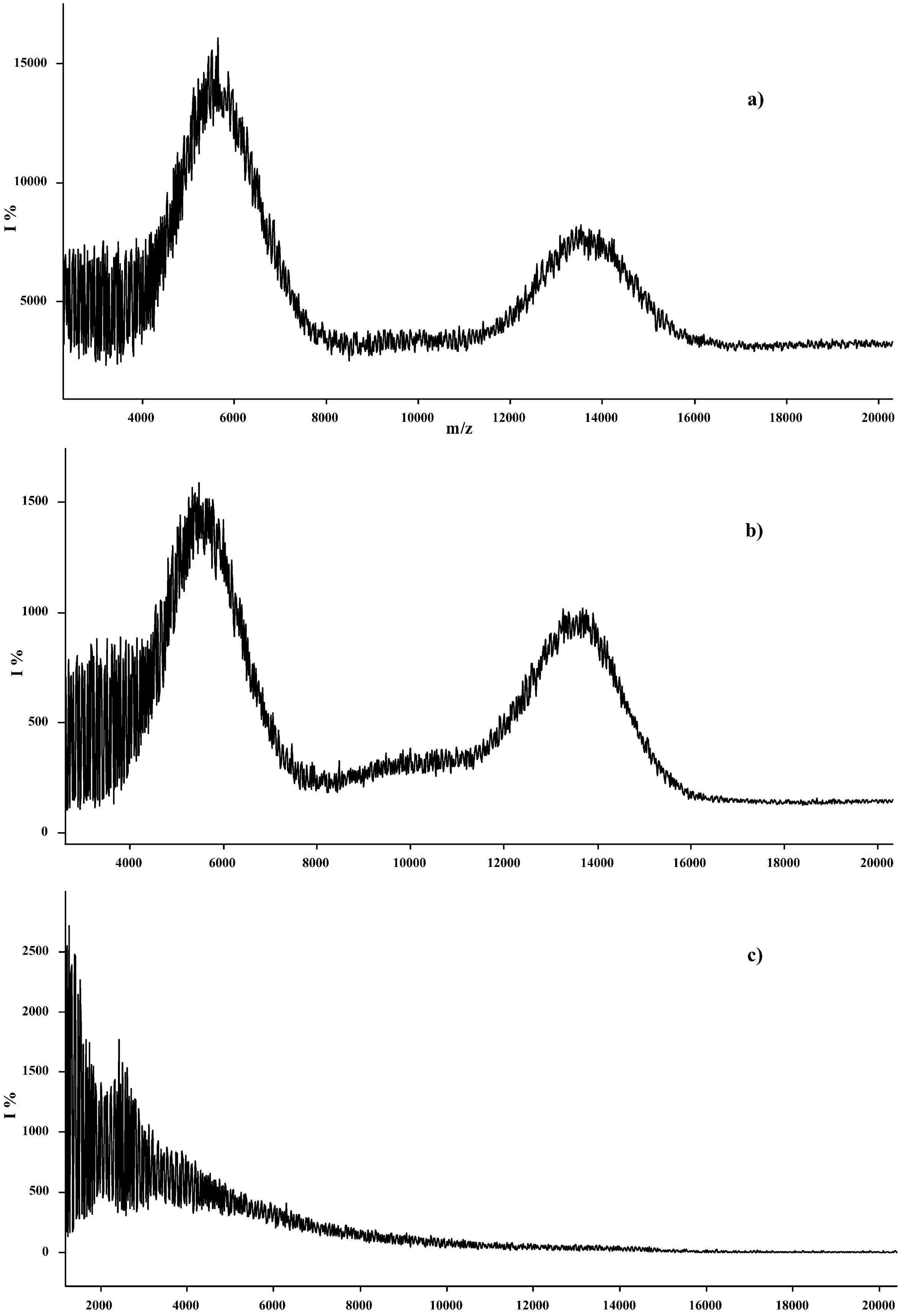


Fig. 6. MALDI-TOF-MS spectra of: (a) virgin poloxamer 407, (b) poloxamer thermoxidised 21 days, (c) poloxamer thermoxidised 24 days.

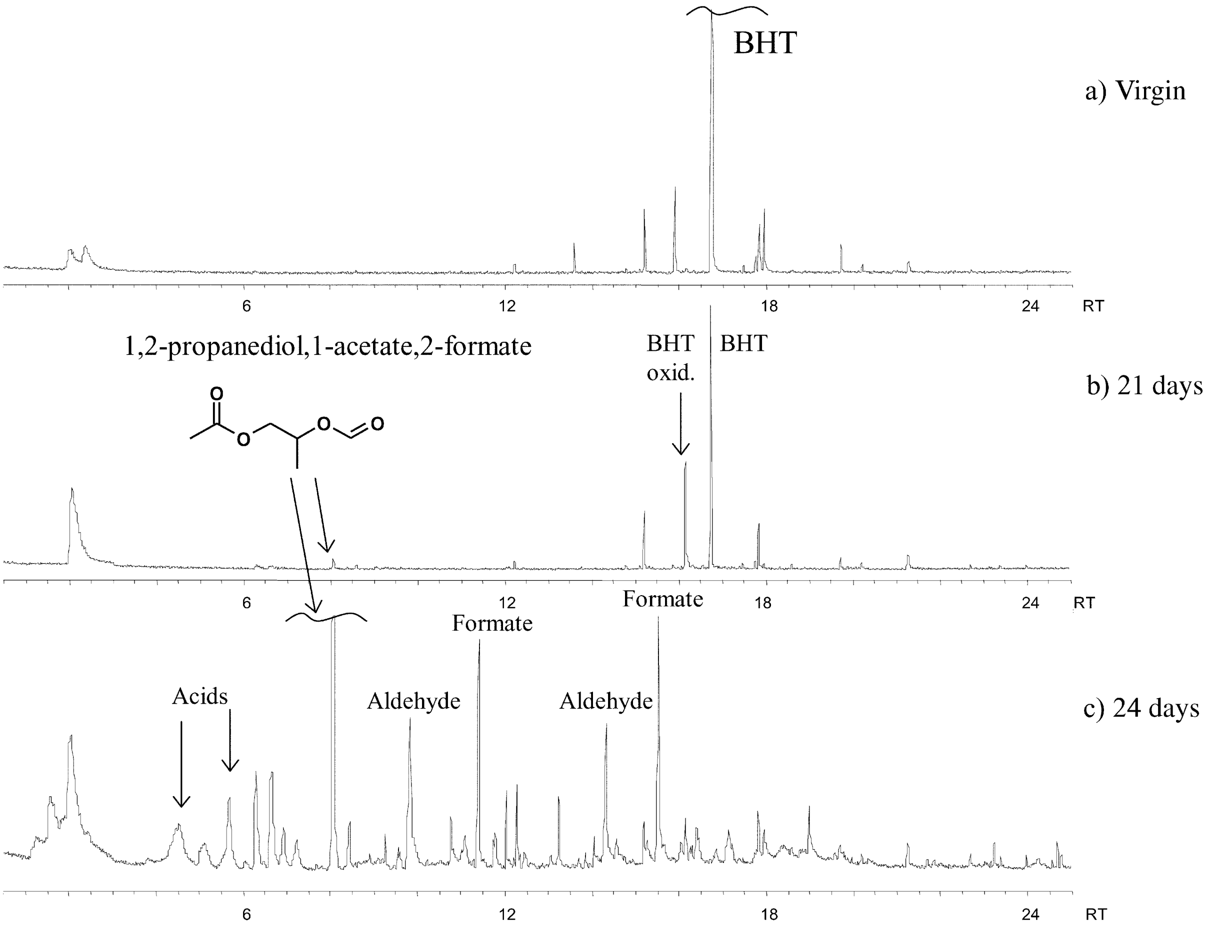


Fig. 7. GC-MS chromatograms of: (a) virgin poloxamer 407, (b) poloxamer thermoxidised 21 days, (c) poloxamer thermoxidised 24 days.

3. Results and discussion

3.1. Characterisation of virgin copolymer

Poloxamer 407 is made by the addition of propylene oxide to a propylene glycol initiator to form a polyoxypropylene glycol having a molar mass of approximately 4000. This is performed at an elevated temperature and pressure in an anhydrous and inert atmosphere in the presence of an alkaline catalyst (in this case KOH). Once all propylene oxide has reacted, ethylene oxide is added in a controlled way to form two polyoxyethylene blocks. The product is then neutralised with an acid, typically phosphoric acid or acetic acid in such this case.

Fig. 1 shows the ^{1}H NMR spectrum of the virgin material. The total composition is obtained by integration of the signals at 3.65 ppm of EO and at 3.4 ppm of the methinic proton of PO. The copolymer consists of 77% EO units for 23% PO. This is in agreement with the data obtained from the manufacturer. Although the copolymer is mostly dihydroxyl terminated, small amounts of allyl ether end groups $CH_2{=}CH{-}CH_2{-}O{-}$ and vinyl ether end groups $CH_2{=}CH{-}O{-}$ are observed. These two end groups form during the polymerisation of the PPO (resp. PEO) block as a result of rearrangements i.e. propylene oxide rearranges to form allyl alcohol whereas the dehydration of the hydroxyethyl end group of the growing PEO chain produces vinyl ether end group.

Fig. 2(a) shows the SEC trace of the virgin sample and Fig. 2(b) the corresponding MALDI spectrum. An unexpected bimodal distribution is observed. The two distributions appear very narrow as expected for anionic polymerisation.

It is well known that for the analysis of polymers with narrow molar mass distribution, such in this case, the molar mass estimates provided by MALDI agree with the value obtained by conventional techniques [12]. Table 1 lists molar mass values and polydispersity indexes of the virgin sample (also shows bimodal distribution) obtained by SEC and by MALDI. The lower molar mass distribution presents a higher polydispersity index.

The technique of MALDI-TOF MS is also widely used with increasing success for the structural characterisation of synthetic polymers, particularly for end groups analyses. Nevertheless the MALDI spectra recorded for the triblock copolymer were not resolved. To overcome this failure, end

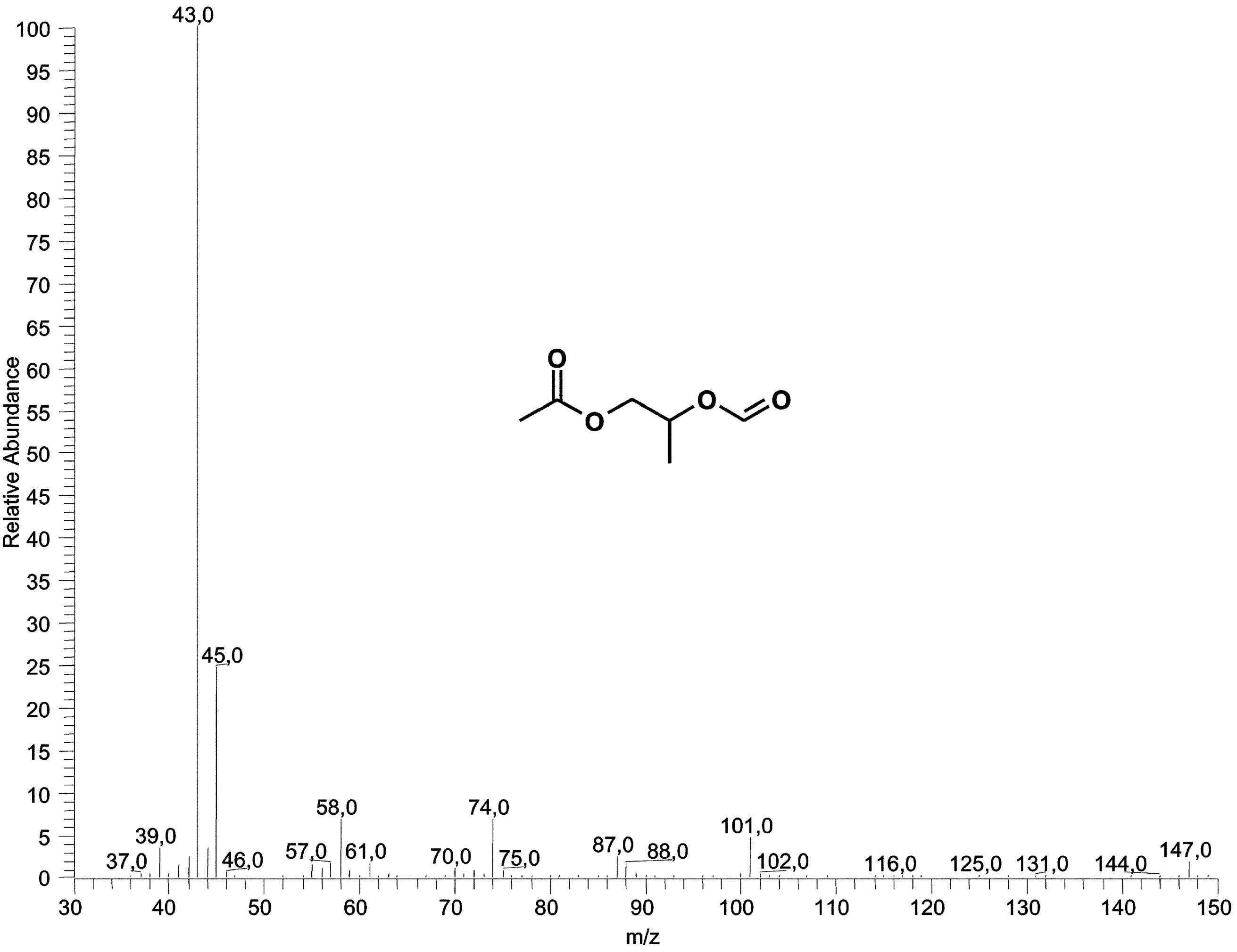


Fig. 8. Mass Spectrum of 1,2-propanediol,1-acetate,2-formate.

group analysis was performed by MALDI analysis of a lower molar mass SEC fraction. Fig. 3 shows the MALDI spectrum of the fraction of copolymer eluted at 27.9 ml. The MALDI spectrum is well resolved and this allows the characterisation of the end groups. Table 2 presents the assignment of the peaks. All the peaks were reasonably assigned to sodium alkoxide terminated oligomers of P(EO-*co*-PO) copolymers. Nevertheless vinyl/hydroxyl and allyl/hydroxyl terminated oligomers with different ratio EO/PO and more unlikely cyclic species are also possible.

Table 1
Molecular weight (M_p) and polydispersity index (PI) for the two distributions found in poloxamer 407

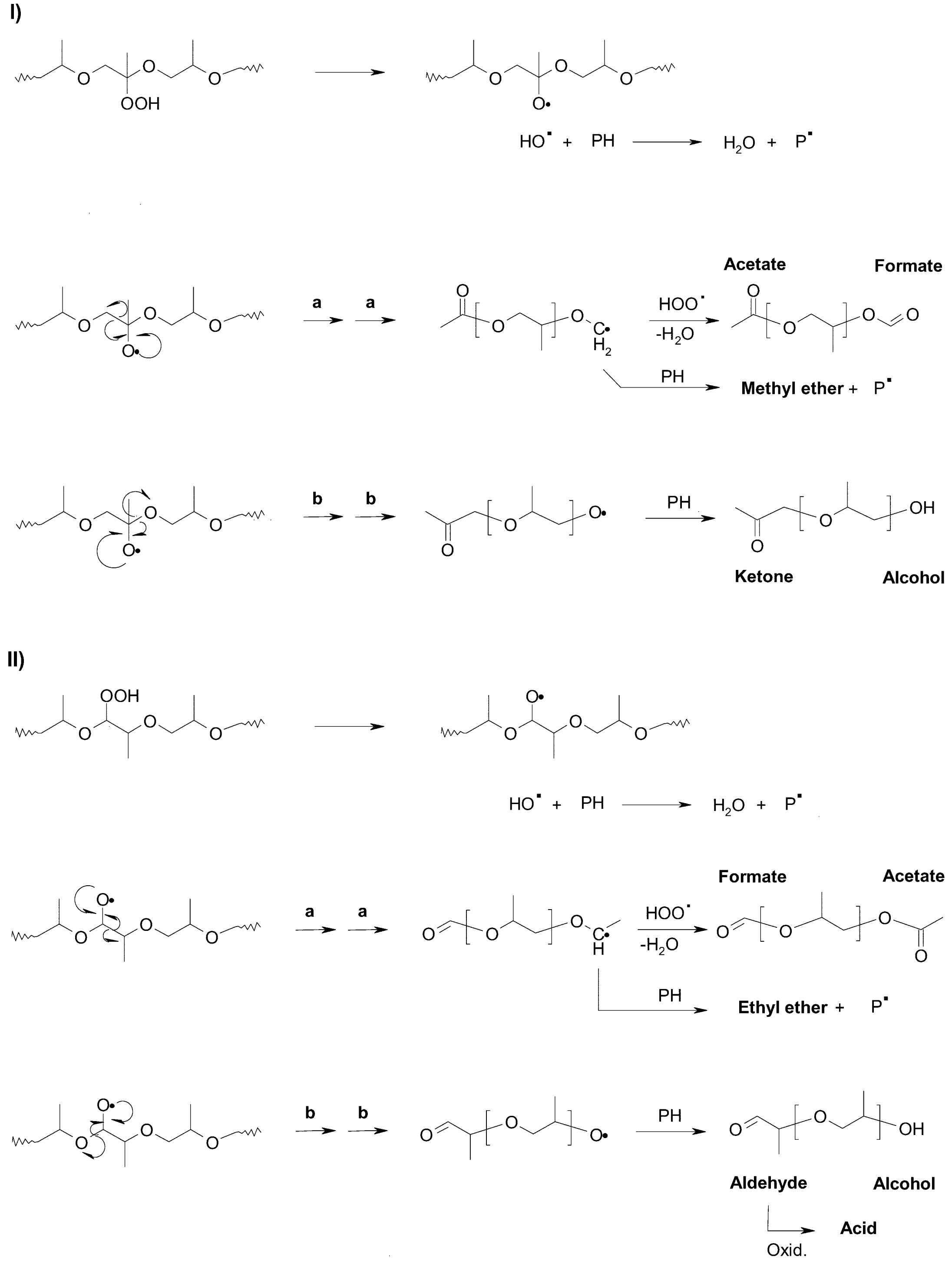
	M_p (Da)[a]	M_p (Da)[b]	PI[a]
Distribution 1 (D1)	5600	6600	1.022
Distribution 2 (D2)	13,600	15,500	1.007

[a] Determined by absolute calibration curve obtained by SEC/MALDI-TOF-MS.

[b] Determined by SEC, calibration obtained with PEG standards.

Table 2
Three possible assignments for the MALDI-TOF spectrum of SEC fraction of virgin poloxamer eluted at 27.9 ml

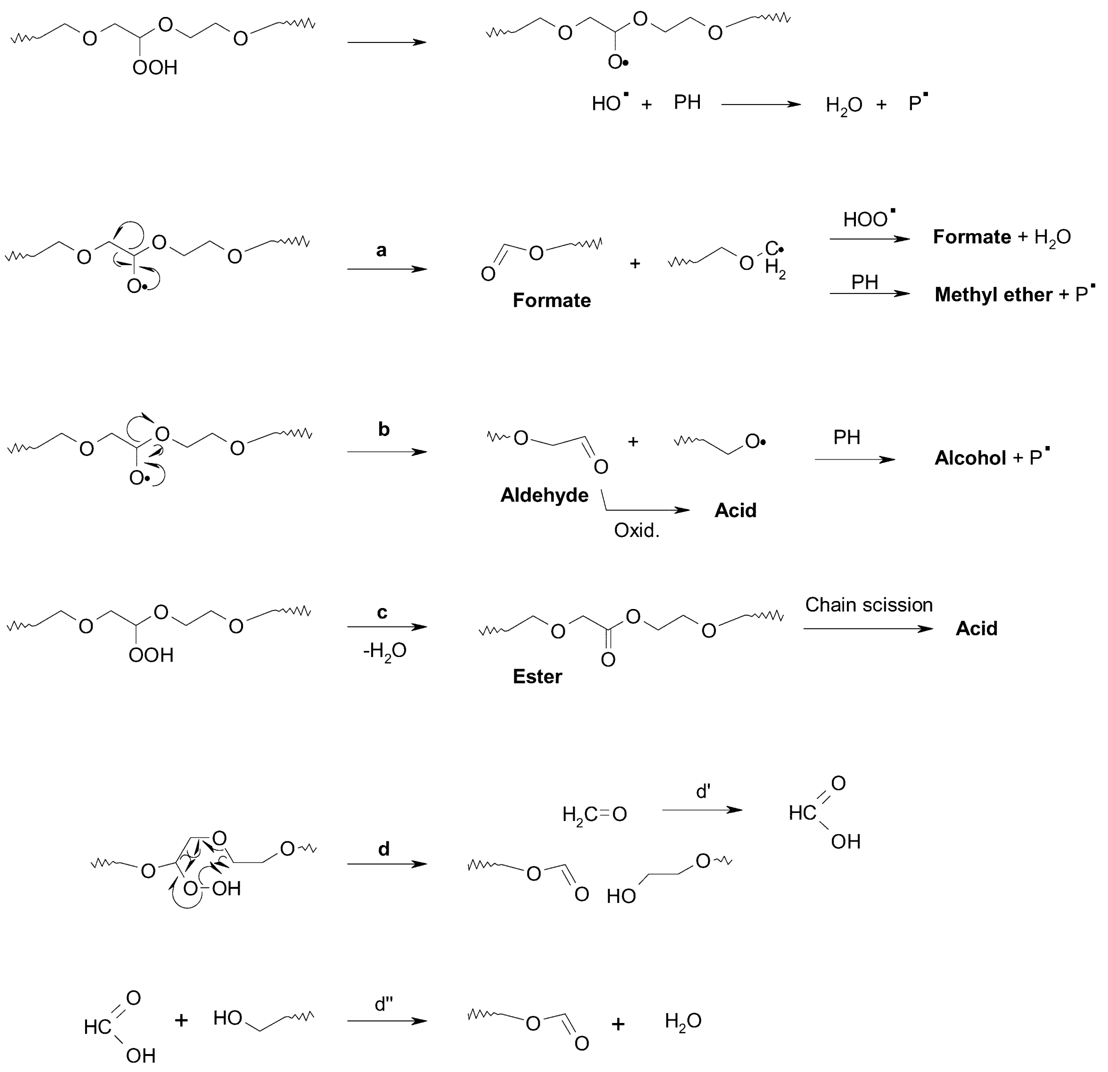
EO units/PO units			
Chain ends			
OH···OH	Allyl···OH	Vinyl···OH	M/z + Na (Da)
44/14	51/8	50/9	2792.4
51/9	58/3	57/4	2809.9
45/14	52/8	51/9	2836.4
52/9	59/3	58/4	2854.0
46/14	53/8	52/9	2880.1
53/9	60/3	59/4	2898.0
47/14	54/8	53/9	2924.8
54/9	61/3	60/4	2942.5
48/14	55/8	54/9	2968.7
55/9	62/3	61/4	2985.9
49/14	56/8	55/9	3012.3
56/9	63/3	62/4	3030.2
50/14	57/8	56/9	3056.6
57/9	64/3	63/4	3074.2
51/14	58/8	57/9	3100.6



Scheme 1.

In order to verify the composition of the two distributions we used SEC/NMR. Fig. 4 presents the SEC/NMR results. Composition is obtained by integration in the same way as for the original material. Although the composition of the narrower and main peak ($M_p = 13,600$ Da) is slightly different than the one expected with 75% EO and 25% PO units instead of 77:23, the broader distribution consists of 92% EO and 8% PO. The ratios for the latter are closer to the values found by MALDI (Table 2) for vinyl/hydroxyl or allyl/hydroxyl terminated oligomers than for dihydroxyl terminated chains.

The unexpected distribution around 5600 Da could be the result of the isomerisation of PO to allyl alcohol, which then reacts to form allyl ethers of PPO. This mechanism is well



Scheme 2.

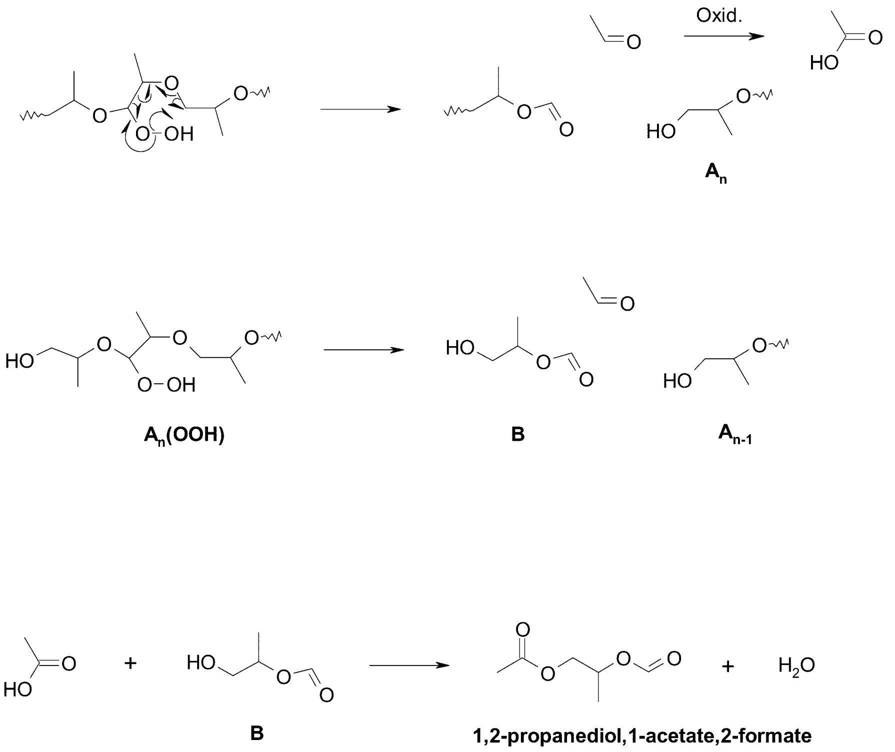
described in the literature [13,14] and is known as being a factor that limits the maximum molecular weight of PPO produced by basic catalysis. When introducing EO in the reactor, chains of diblock copolymer would then be produced with an allyl ether end group on the side of the PO chain and a hydroxyl end group on the EO chain, to form the unexpected distribution.

3.2. Thermal oxidation of poloxamer copolymer

Fig. 5 shows the changes in the molecular weight distribution of poloxamer 407 when exposed to thermal ageing at 80°C. The degradation of the block copolymer starts after an induction period of between 21 and 24 days. This period is likely to vary for different materials depending on the quantity of antioxidant present in the copolymer (in this case 100 ppm BHT).

Fig. 6 shows the MALDI-TOF-MS of thermoxidised triblock copolymer. The same induction time is found also in the MALDI results. The appearance of new masses in the range 8000–12,000 Da for the sample degraded for 21 days suggests, however, an induction period closer to 21 days. For the copolymer degraded for 24 days the MALDI-TOF-MS detector is saturated by low molar mass products and is unable to give information about the overall molecular weight distribution. Nevertheless, a study of the masses in the range 1200–4000 Da shows that no formation of oligomers arising from homopolymer PEO after 24 days of thermal ageing had occurred. This is a clear indication that the first chain cleavages occur near the centre of the copolymer i.e. in the PPO block. After 27 days molar mass is strongly reduced but the many isomers do not allow the univocal assignment of peaks.

In order to clarify the role of the secondary and tertiary alkoxy radical formed during thermal degradation of PPO, we need to detect and identify by GC-MS the low molecular weight products released at the start of the chain breakdown (i.e. between 21 and 24 days of ageing). Fig. 7 displays the GC-MS chromatograms of the virgin copolymer and the samples oxidised 21 and 24 days. Prior to GC-MS analysis,



Scheme 3.

the volatile products are extracted by SPME. This method is very useful in this case because the sample has to be as less disturbed as possible in order to observe the beginning of the degradation. A more common liquid–liquid extraction would not have provided the same ideal conditions [15,16].

BHT is the main volatile product extracted from the polymer matrix of the virgin material. The other peaks observed are impurities and ghost molecules coming from the SPME fibre. After 21 days the BHT concentration decreased significantly and another BHT derivative, which actually is degradation product of BHT (oxidised product) appeared. At this stage, when radicals are no longer trapped by the antioxidant, the degradation of the polymer starts. Thus, the induction period of 21 days found by SEC and MALDI-TOF-MS is confirmed also by GC-MS. Two peaks retain our attention in the second chromatogram. The peak with a retention time of 2 min is a result of chloroform contamination. More interesting, with a retention time of 8.1 min, 1,2-propanediol,1-acetate,2-formate is the first volatile product to appear that is a direct result of polymer degradation. Fig. 8 shows the mass spectrum of this product. The molecule, never reported before, is of crucial importance when trying to understand the mechanisms involved at the very beginning of the polymer cleavage. As explained before, the PPO block is more sensitive to thermoxidation than the PEO block, and the structure of this molecule further confirms this.

Scheme 1 (oxidation of PPO through hydroperoxide intermediate: (I) tertiary hydroperoxide, (II) secondary hydroperoxide) shows the different mechanisms that are involved in the oxidation of PPO [8–10]. Even though both mechanisms (I) and (II) would explain the formation of 1,2-propanediol,1-acetate,2-formate, they fail to explain why it is the first volatile product to appear if a random chain scission proceeds along the PPO chain. Decker and Marchal [17] studied in detail the thermoxidation of PEO. They found that a peroxy radical undergoes a six-ring intramolecular decomposition reaction. Scheme 2(d) (oxidation of PEO through hydroperoxide intermediate: (a) C–C scission, (b) C–O scission, (c) C–H scission, (d) six-ring intramolecular decomposition) shows this mechanism for the hydroperoxide intermediate. Yang et al. [8] extended this mechanism by suggesting that the formaldehyde formed is rapidly converted to formic acid (d') that can further react with alcohol terminated chains to form formate terminated molecules (d'').

Scheme 3 (six-ring intramolecular decomposition of secondary hydroperoxidised PPO) shows the mechanism we now propose to apply for the thermoxidation of PPO in poloxamer triblock copolymer. The mechanism shows that acetaldehyde is formed as well as 1,2-propanediol,2-formate (Scheme 3(B)). Acetaldehyde is oxidised to acetic acid, which esterifies 1,2-propanediol,2-formate into 1,2-propanediol,1-acetate,2-formate. This reaction emphasises the major role of the secondary radical in the polymer chain — giving rise to a secondary hydroperoxide — when the thermoxidation of the PPO block starts. The cyclic chain scission is the only mechanism that can justify the appearance of the acetate-formate molecule at the very beginning of the degradation, before any significant changes in

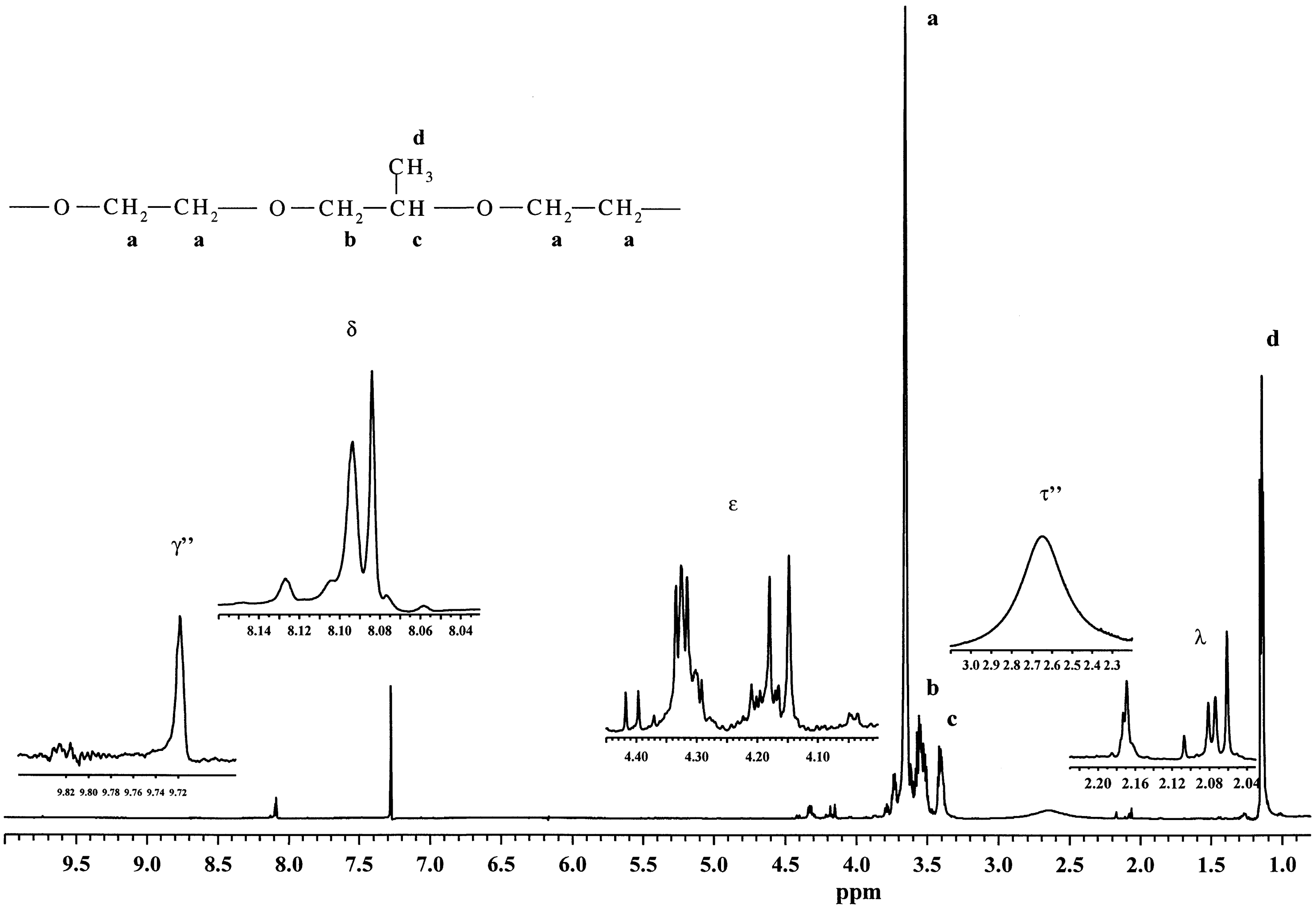


Fig. 9. ^{1}H NMR spectrum of poloxamer 407 thermoxidised 24 days in air at 80°C.

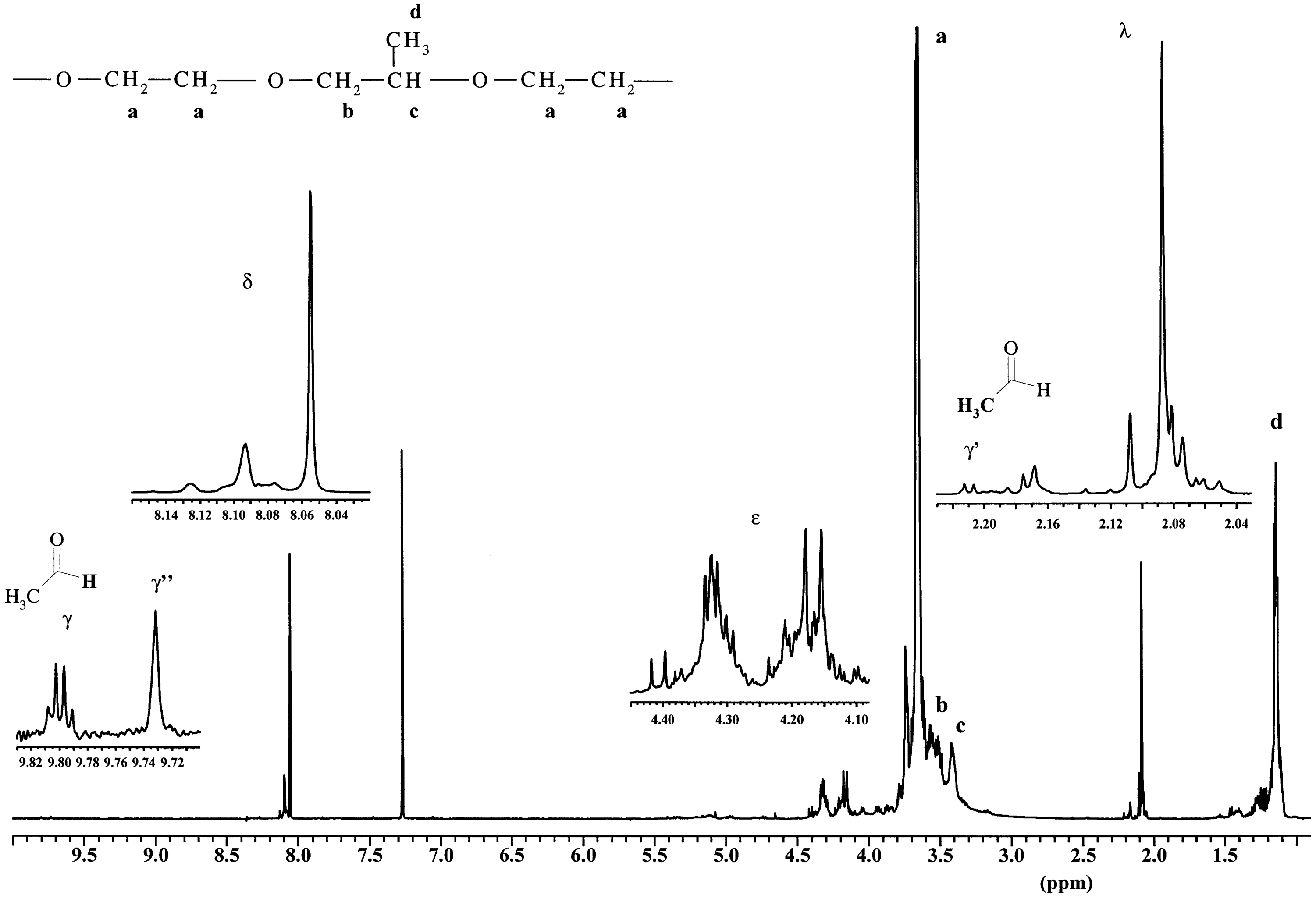


Fig. 10. ^{1}H NMR spectrum of poloxamer 407 thermoxidised 27 days in air at 80°C.

molecular weight distribution can be observed. It is noteworthy that this molecule can be produced by three different mechanisms (Scheme 1(I)a and (II)a, Scheme 3) and that as a result, after 24 days exposure to thermoxidation at 80°C 1,2-propanediol,1-acetate,2-formate is the major volatile degradation product. Other products formed are difficult to identify because of isomerism problems. In fact, all reactions displayed in Schemes 1–3 can take place at the same time, and once the oxidation is initiated the pattern of degradation of poly(EO–PO–EO) triblock copolymers becomes very complicated. We were, however, able to identify functional groups such as formates, aldehydes and acids in the chromatograms of oxidised poloxamer. C–O homolysis (Scheme 1(I)b and (II)b) is not favoured as no ketones are observed among the degradation products. This is due to the rather oxygen starved conditions used for this experiment. In fact, when submitting the polymer to continuous oxygen flow at 125°C, Griffiths et al. [9] observed the formation of ketones and C–O homolysis.

To confirm the proposed degradation mechanisms, ^{1}H NMR spectra were recorded for samples thermoxidised 24 and 27 days (Figs. 9 and 10). The main differences between Figs. 9 and 1 (virgin material) are the appearance of formate (δ,ϵ) and acetate (λ) signals after 24 days. The signal τ'' shows that hydroxyl end groups are still present after 24 days. However, after 27 days (Fig. 10) this signal disappears to the profit of acetate and formate end groups. At the same time acetaldehyde starts accumulating in the matrix (γ, γ') as it is produced from both PPO and PEO blocks. This is further confirming the mechanism that we propose (Scheme 3) for the start of the thermoxidation of PPO in poloxamers.

4. Conclusions

The combination of MALDI-TOF-MS for the analysis of oligomers, SPME/GC-MS for the analysis of low molecular weight compounds and ^{1}H NMR for chain-end determination is very successful. The thermal oxidation of poloxamer 407 at 80°C in air proceeds in three steps: After an induction period depending on the quantity of antioxidant present in the polymer (21 days for 100 ppm BHT), the degradation starts through a six-ring intramolecular decomposition reaction of the PPO block of the copolymer. This result was confirmed by SPME/GC-MS: The first volatile degradation product to appear is 1,2-propanediol,1-acetate,2-formate and it shows that the secondary hydroperoxide formed on the PPO chain plays a major role on the thermoxidation of poloxamer materials. Finally, more chain scissions occur both in the PPO and PEO block of the copolymer, leading to dramatic decrease of the molecular weight and the appearance of formates, acetates, aldehydes and acids.

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