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Determination of polyethylene glycols in water by reversed-phase high-performance liquid chromatography

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Abstract

This paper describes an RP-HPLC method to characterize the ozonation products of polyethylene glycols (PEGs) (general formula $\text{HO}(\text{CH}_2\text{CH}_2\text{O})_n\text{-H}$ with original mass 5000. Samples with different pH and ozonation times were studied. The amounts of individual products up to $n = 56$, the percentage of PEGs as a final product and the molecular distribution (M_w/M_n) were calculated. The samples were concentrated by liquid-liquid extraction.

Keywords: Ozonation; Polyethylene glycols

1. Introduction

An important purpose of water treatment is the removal of foreign substances by chemical or biological degradation. Polyethylene glycols (PEGs) are present in waste water as surfactant constituents [1-4] or catabolic products of these [5-8]. The PEGs are considered to be a refractory substratum for degradation [1,2,9-11]. PEGs with low molecular mass (less than 400) are biodegradable but those with high molecular mass cannot be completely degraded [1,2,12]. Therefore, preliminary chemical degradation is required to achieve substratum biodegradability.

Several methods for degrading chemical substances in an aqueous medium involve chemical treatment with ozone [13-15]. Ozonation has been used for compounds resistant to biological

degradation such as non-ionic surfactants [16,17] and PEGs [2].

The identification of final and intermediate products is very important for the optimization of ozonation processes aimed at obtaining biodegradable compounds. The great number of ozonolysis derivatives normally makes the analysis of the reaction products difficult. The characterization of these products has been performed for a limited number of compounds [16] only or by means of global chemical tests [2].

With the size-exclusion chromatographic method, the separation of PEGs is possible only in approximate groups [18,19] without the possibility of detecting the individual polymers or other types of molecules which could be in the same sample.

This paper is concerned with an RP-HPLC method for characterizing the compounds obtained by ozone treatment on PEG with high

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molecular mass [M_w 5000, $n(\text{average}) = 113$]. With this method, it is possible to observe the individual polymers of PEGs and other individual compounds.

2. Experimental

2.1. Instrumentation

A Gilson HPLC system was used (Gilson Medical Electronics, Middleton, WI, USA) equipped with a 20- μ l injector (Reodyne, Cotati, CA, USA).

A Dnamax UV-1 absorbance detector (Rainin Instrument, Woburn, MA, USA) set at 190 nm was used. The chromatograms were monitored with an Apple Macintosh Classic II computer.

The analyses were made using a 15 cm \times 4.6 mm I.D. Nucleosil C₁₈ (5 μ m, 120 Å) column at room temperature.

The mobile phase was prepared by mixing acetonitrile and 1.0 mM phosphoric acid according to the following gradient programme: $t = 0$ min, 2%; 10 min, 15%; 41 min, 36%; 60 min, 36%. The mobile phase flow-rate was 1.5 ml/min. Nitric acid (5 ppm) was used for absorbance equalization for water.

2.2. Sample concentration

The concentration method was as follows: (1) a 100-ml water sample mixed with 5.85 g of NaCl

and 100 ml of CHCl₃ was shaken with a magnetic stirrer for 6 h; (2) the separated organic layer was evaporated to dryness with a flow of air; (3) 1.0 ml of water was added to the residue and the solution was analysed by HPLC.

2.2. Ozonation runs

All the ozonated samples were withdrawn at different reaction times from a semi-batch ozonation reactor in which 800 ml of the polymer aqueous solution, buffered at the appropriate pH, were flowed with an ozonized oxygen stream.

3. Results and discussion

As reported in an earlier paper [20], it is possible to separate PEGs of molecular mass up to 1500 (polymers up to $n = 50$) by using a 15-cm Nucleosil column. By adopting a gradient programme (see Experimental) it is possible to detect and determine PEGs with a molecular mass higher than 1500 which are eluted as unresolved broad peaks. In Fig. 1, the separation of a mixture of PEG 200, 300, 400, 600, 1000, 1500, 2000, 3000 and 8000 is shown. As indicated under Experimental, the maximum concentration of acetonitrile in the mobile phase was 36% to avoid the presence of unknown peaks as reported by other workers [21,22].

After the ozonation of PEG 5000 at pH or 8

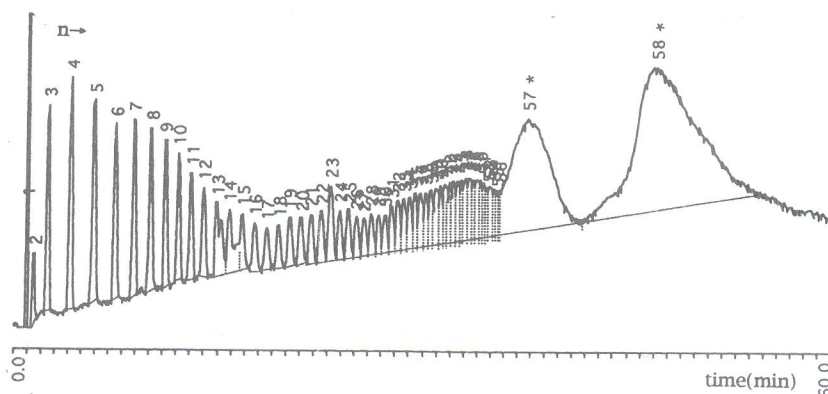


Fig. 1. Chromatogram of a mixture of PEGs: 0.4% (w/v) PEG 200, 300, 400 and 600, 0.65% PEG 1000, 1% PEG 1500, 1.3% PEG 2000, 2% PEG 3000 and 5.25% PEG 8000. For conditions, see Experimental.

for longer than 15 min, products with a molecular mass less than 3000 were observed. In this situation it is possible to monitor every polymer up $n = 56$ and the others as a peak.

We concentrated the samples by liquid–liquid extraction using chloroform as solvent [23] (for conditions see Experimental) before the HPLC analysis.

The recovery factor (R) obtained in the concentration experiment is shown in Table 1. In the range $n = 1–25$ (n is the degree of polymerization), R increases nearly linearly from 1% to 72.5% and for n higher than 25 R is constant at 73%. This can be explained by the behaviour of the equilibrium constant of the PEGs in chloroform–water as a function of their polarity.

The investigated samples were PEG 5000 as follows: (1) pH 4, $t = 0$ (non-ozonated); (2) pH 4, $t = 60$ min; (3) pH 4, $t = 120$ min; (4) pH 8, $t = 0$ (non-ozonated); (5) pH 8, $t = 15$ min; (6) pH 8, $t = 40$ min.

3.1. Ozonation products

The chromatograms obtained for the concentrated samples 1–6 are shown in Figs. 2 and 3 (for conditions see Experimental). In every chromatogram three peaks were present (around of 9.3, 16 and 24 min) which were due to impurities in the sample water (not from the chloroform). We think that this could be due to phthalates. The peaks with a capacity factor smaller than 1 (retention time less than 1.4 min) were not measured.

Table 1
Recovery factors (R) for PEG extraction from water in the range $n = 1–50$

n	R (%)	n	R (%)	n	R (%)
1	–	10	29.25	19	68.00
2	0.85	11	36.25	20	69.40
3	0.91	12	43.00	21	70.50
4	3.25	13	49.75	22	71.12
5	6.00	14	55.15	23	71.65
6	9.10	15	59.00	24	72.00
7	12.5	16	62.25	25	72.50
8	17.01	17	64.65	26	72.75
9	22.50	18	66.75	27–50	73.00

Individual polymers up to $n = 56$ were seen. After this value no separation could be made and in the chromatograms a sum of polymers appeared as a broad peak, marked as 57* and 58*.

For the estimation of the number-average molecular mass (M_{n_i}) for the sum of PEGs eluting after $n = 56$, the chromatogram from Fig. 1 was used. By this method the M_{n_i} of the area eluting after $n = 56$, for samples 1–6, was identified as 5500 ($n = 124$), 3500 ($n = 79$), 2775 ($n = 63$), 5500 ($n = 124$), 3775 ($n = 85$) and 2775 ($n = 63$), respectively, shown in the chromatograms as 57*.

In Table 2 the quantitative results for groups of compounds eluting in different ranges of n in samples 1–6 are given. It can be observed that in samples 1 and 4 (non-ozonated), the highest concentration was around molecular mass 5500 ($n = 124$), but it was in the range $n = 11–15$ for samples 2, 3 and 5 and in the range $n = 1–6$ for sample 6.

Comparison of the chromatograms of ozonated samples with that of the standard mixture of PEGs (Fig. 1) shows the presence of additional peaks eluting between those of the n and $n + 1$ polymer molecules. The numbers shown on the chromatograms are marked only for the PEG polymers. The ozonation thus leads to the formation of degradation products with functional groups different from those of the starting polymer. According to the reaction mechanism proposed by Suzuki [2], the appearance of new functional groups can be ascribed to the formation of small polymers with aldehydic functions.

The satisfactory peak resolution in the range $n = 10–21$ allows the evaluation of the relative abundance of aldehydic polymers with respect to PEGs. ^{Q1} ~~is~~ one makes the likely assumptions that the same PEG calibration can be adopted for aldehydic polymers and that the relative product distribution in the entire n range remains constant at the same value as observed in this range. ⁵⁷ The results are given in Table 3.

3.2. Molecular mass distribution of the ozonation products

As reported [24], an important factor for the characterization of the polymers is the degree of

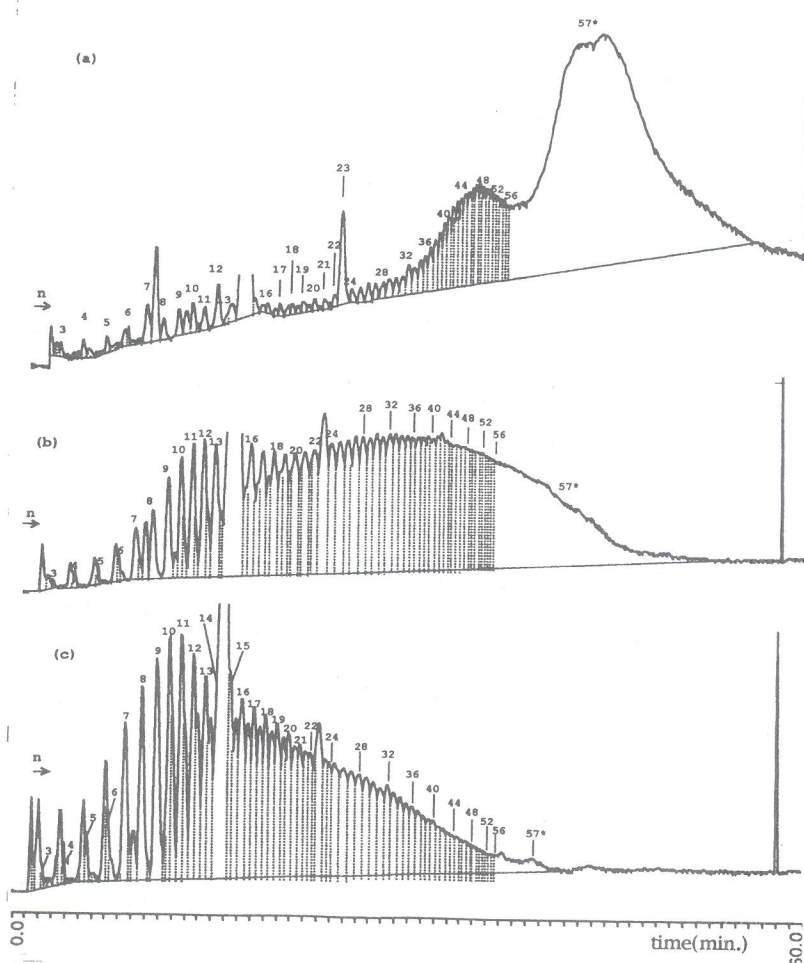


Fig. 2. Chromatograms for the ozonated samples in pH 4 medium. (a) $t = 0$ (sample 1); (b) $t = 1$ h (sample 2); (c) $t = 2$ h (sample 3).

polydispersity (molecular mass distribution), defined as the ratio M_w/M_n , where M_w is the weight-average molecular mass (centre of mass) and M_n the number-average molecular mass (the more probable molecular mass number).

We calculated M_w and M_n in accordance with Eqs. 1 and 2, respectively.

$$M_w = \frac{\sum (M_i A_i)}{\sum (A_i)} \quad (1)$$

$$M_n = \frac{\sum (A_i)}{\sum (A_i/M_i)} \quad (2)$$

where A_i is the peak area for $n = i$ and M_i is the molecular mass corresponding to A_i .

A_i was taken as the sum of the peak areas of PEGs with $n = i$ and all other compounds eluting between i and $i + 1$ and considering the molecular mass M_i in this range. The data for the samples 1–6 are given in Table 4. The variation of M_w and M_n with time are shown in Fig. 4.

The results show that the molecular mass decreased as a result of ozonation and the mass distribution is broad. The results are in agreement with those obtained by size-exclusion chromatography [2].

The experimental results reported in Table 4 indicate that the rate development for PEG degradation is markedly affected by the pH

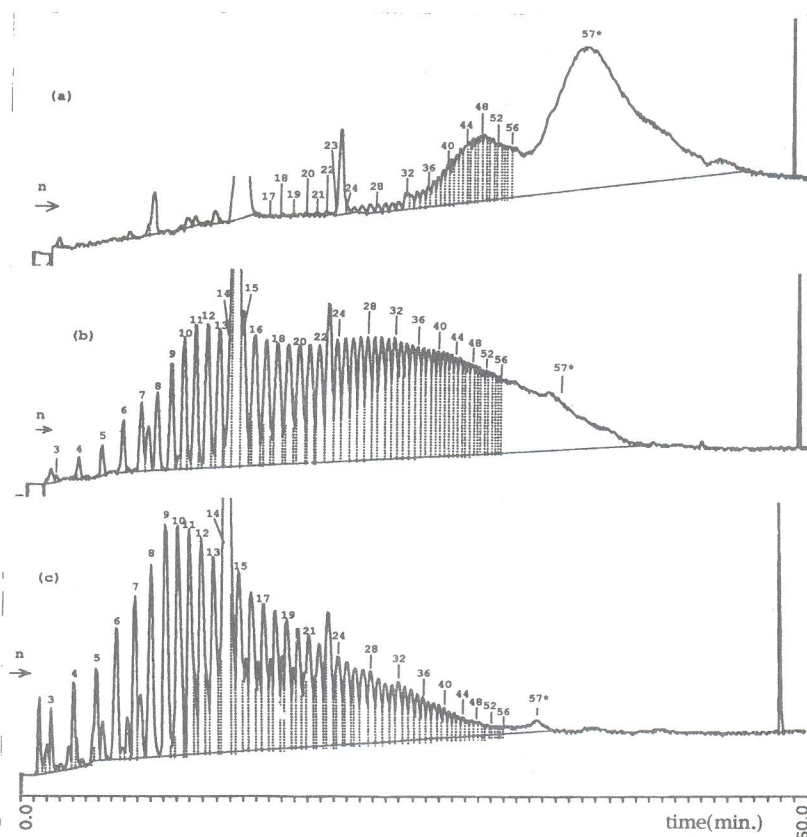


Fig. 3. Chromatograms for the ozonated samples in pH 8 medium. (a) $t = 0$ (sample 4); (b) $t = 0.25$ h (sample 5); (c) $t = 0.66$ h (sample 6).

Table 2
Concentrations (ppm) of compounds in samples 1–6

n range	Sample					
	1	2	3	4	5	6
1–6	0.00	244.28	1195.28	0.00	346.23	2845.5
7–10	0.00	380.78	924.80	0.00	389.99	884.03
11–15	1.36	546.53	1098.38	0.00	425.93	820.98
16–20	7.74	524.32	766.25	2.15	365.65	512.85
21–25	9.09	481.17	570.13	2.80	322.12	352.55
26–30	14.44	423.50	378.09	9.87	296.46	205.94
31–35	29.15	372.60	255.31	18.99	270.22	128.98
36–40	53.66	319.52	147.57	40.38	225.07	80.16
41–45	79.52	246.22	99.85	72.07	179.55	50.43
46–50	82.58	229.47	70.15	82.79	150.03	31.28
51–56	78.28	254.30	44.93	79.1	147.59	26.81
Other	$M_n = 5500$	$M_n = 3500$	$M_n = 2775$	$M_n = 5500$	$M_n = 3775$	$M_n = 2775$
	3356.52	1101.10	57.70	3014.19	639.60	74.74
Total	3713.68	5008.10	5226.51	3324.75	3704.60	4826.1

Table 3
Relative concentrations (%) of compounds in samples 1-6

Compounds	Sample					
	1	2	3	4	5	6
PEGs	100.0	66.6	54.94	100.0	89.3	70.2
Aldehydes	0.0	33.3	45.1	0.0	10.7	29.6

adopted. The higher reactivity observed at pH 8.0 can be reasonably ascribed to the intervention of a radical reaction mechanism initiated by OH radicals derived from ozone decomposition.

The relatively high concentration of PEGs produced by depolymerization, observed in the sample with pH 8, is sustained by a mechanism which implies a hydrogen abstraction at one of

the ethoxylated units followed by depolymerization, a process postulated for nonylphenol ethoxylate, at a high pH [16].

4. Conclusion

RP-HPLC is a suitable method for the characterization of compounds produced by ozonation of PEGs.

It is possible to obtain a separation of individual PEG polymers and a partial separation of other chemical products, with a similar polymer side, up to $n = 56$ ($M_n = 2482$) by gradient elution.

From the RP-HPLC trace it is possible to determine the molecular mass distribution of the

Table 4
Molecular mass distribution of the ozonation products in samples 1-6

Parameter	Sample					
	1	2	3	4	5	6
M_w	5155	1687	781	5171	1354	614
n	117	38	17	117	30	13
M_n	4595	1386	395	4715	765	266
n	104	31	8	106	17	6
M_w/M_n	1.12	1.22	1.97	1.10	1.76	2.31

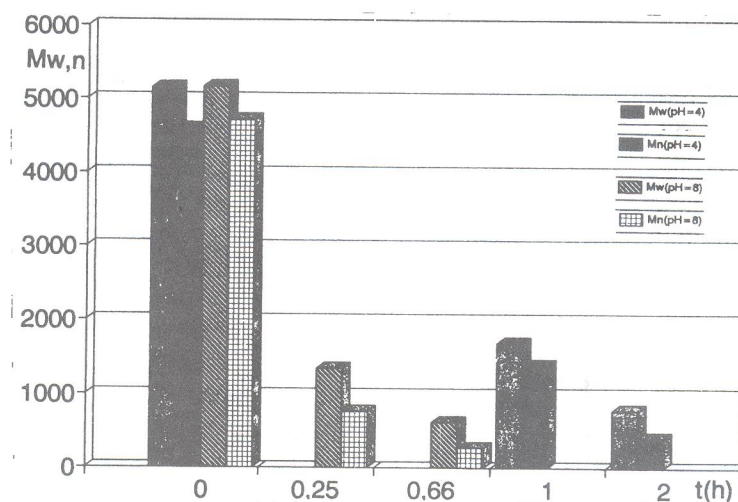


Fig. 4. Molecular mass distribution (M_w , M_n) versus ozonation time (samples 1-6).

polymers, as M_w and M_n , and therefore the polymer dispersity (M_w/M_n).

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