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CHEMICAL DEGRADATION AND ANALYSIS OF POLYOXYETHYLENE GLYCOLS AND ETHYLENE OXIDE–α-BUTYLENE OXIDE BLOCK COPOLYMERS

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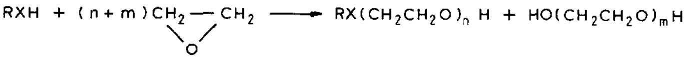
SUMMARY

The chemical degradation of polyoxyethylene glycols and block copolymers of ethylene oxide and α-butylene oxide by means of acetyl chloride in the presence of iron(III) chloride was investigated and used to determine with satisfactory precision and accuracy the content of polyoxyethylene groups in model and commercial products. The degradation products were identified by gas chromatography–mass spectrometry.

INTRODUCTION

Non-ionic surfactants having polyoxyethylene chains are complex mixtures containing homologues having different numbers of oxyethylene units, usually they also contain different homologues of polyoxyethylene glycols which are formed as by-products during the synthesis of surfactants:



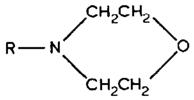
$$RXH + (n+m)\,CH_2\!-\!CH_2(O) \longrightarrow RX(CH_2CH_2O)_nH + HO(CH_2CH_2O)_mH$$

where X = O, C_6H_5O, S, COO, etc.

Gas–liquid chromatography of such polydisperse mixtures is limited to products containing less than 20 oxyethylene groups[1] in the least volatile homologue as a result of the too low volatility and thermal degradation of homologues having higher molecular masses. Hence direct analysis cannot be used for commercial products that contain more oxyalkylene units in some higher homologues present in polydisperse mixtures to be analysed. In such an event chemical or thermal degradation could be used to determine the average contents of polyoxyethylene chains and/or the average degree of ethoxylation. However, results published up to now are not satisfactory[2].

TABLE I

METHODS FOR DEGRADATION OF NON-IONIC SURFACTANTS HAVING POLYOXYETHYLENE CHAINS

Degradation agent	*Degradation conditions*	*Main degradation products*	*Chromatographic column filling*	*Ref.*
HCl	6 *M* HCl, 140–200°C, 10–20 h		PEG 4000 on Embacel-AW	3
HBr	40–50% HBr in CH_3COOH, 150°C, 2–3 h	$BrCH_2CH_2Br$, RBr	PEGA on G-Cel-AW Apiezon L on Chromosorb W Apiezon L on Universal Q OV-210 on silanized Chromosorb W OV-1 on Chromosorb W AW DMCS	4 5 6 7 8
HI	HI or HI–85% H_3PO_4, 150–160°C, 1 h	I_2*	–	9, 10
p-$CH_3C_6H_4SO_2OOCCH_3$	120°C, 0.5–2 h	Acetates	FFAP on Uniport Q	11, 12
H_3PO_4	85% H_3PO_4, 100°C	Aldehydes, olefins	–	13, 14
CH_3COCl	$CH_3COCl–FeCl_3$, 20–25°C	$ClCH_2CH_2Cl$, acetates	DC-550 on Chromosorb W	15
Thermal degradation	360–650°C, 0.5–2 h	Low-boiling hydrocarbons	DC-200 silicone oil	16
Thermal degradation –H_3PO_4	2% solution in H_3PO_4, 300–400°C, 0.5–1 h	Aldehydes, olefins	Citroflex on Chromosorb W	17
	500–600°C, few seconds	Aldehydes, olefins, Dioxane	Porapak Q	18–21

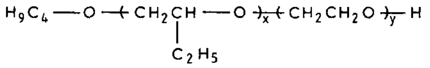
* Determined by titration with $Na_2S_2O_3$.

Different methods for the degradation of the polyoxyethylene chains in various types of non-ionic surfactants have been proposed[3–21] (Table I). Usually different acids or their derivatives were used, *e.g.*, HCl, HBr, HI, H_3PO_4, CH_3COCl and mixed anhydrides of carboxylic and sulphonic acids. Non-catalysed and catalysed thermal degradations have also been considered[16–21]. However, the degradation products are usually complex mixtures containing several different components and their compositions can vary with the degradation conditions, the type of surfactants degraded and the length of the polyoxyethylene chain. Moreover, high-boiling resins and tars are often formed, especially during the degradation of polyoxyethylene alkylphenols and alcohols by means of hydrobromic acid, which is very inconvenient for manual operations. With hydroiodic acid low-boiling products are formed which are inconvenient for chromatographic analysis. As a result, iodine is usually determined by titration with sodium thiosulphate. Non-catalysed and catalysed pyrolyses are very unselective methods and, as they give several very volatile degradation products, they are very inconvenient for quantitative analysis. Mixed anhydrides appear to be convenient degradation reagents but they must be prepared according to the methods described by Karger and Mazur[22–25]. Acetyl chloride is easily accessible and convenient to use. The degradation products obtained can be easily separated and determined.

The aim of this work was to identify the products of the degradation of polyoxyalkylene glycol and to use this chemical degradation to determine the contents of oxyethylene groups in model and commercial polyoxyethylene glycols and in block copolymers of ethylene oxide and α-butylene oxide. It was decided to continue the work of Waszeciak and Nadeau[15], who degraded polyoxyethylene glycols by means of acetyl chloride in the presence of different inorganic salts. It seemed to us that such a method could be used to degrade different types of non-ionic surfactants. The degradation products were identified by gas chromatography–mass spectrometry (GC–MS).

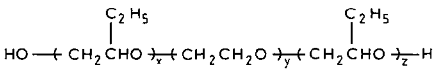
EXPERIMENTAL

Model trioxyethylene glycol, $HO(CH_2CH_2O)_3H$ (P.P.H. POCh, Gliwice, Poland), polyoxyethylene glycols PEG-200 (ICSO, "Blachownia", Kędzierzyn-Koźle, Poland) and Carbowax 1500 (LOBA-Chemie, Vienna, Austria), and block copolymers of ethylene oxide and α-butylene oxide, BE 1500-44[26] and BEB 2000-44[27], where 1500 and 2000 denote the average molecular weights and 44 the content of the polyoxyethylene chains calculated from the mass of reacted ethylene oxide, were used:



$$H_9C_4{-}O{-}(CH_2\underset{\displaystyle C_2H_5}{\underset{|}{C}}H{-}O)_x(CH_2CH_2O)_y{-}H$$

BE



$$HO{-}(CH_2\overset{\displaystyle C_2H_5}{\overset{|}{C}}HO)_x(CH_2CH_2O)_y(CH_2\overset{\displaystyle C_2H_5}{\overset{|}{C}}HO)_z{-}H$$

BEB

Samples of polyoxyethylene glycol or block copolymer (0.05 g) and *n*-hexadecane (0.01–0.02 g) used as an internal standard were weighed into reaction vials (Supelco, Bellefonte, PA, U.S.A.) of 5 cm^3 capacity and anhydrous iron(III) chloride (0.04–0.05 g) and acetyl chloride (0.7–1 cm^3) were added. The vials were shaken to obtain a clear solution and heated at 150°C for 0.5 h. After cooling, the degradation products were diluted with dichloromethane (1:1, v/v) and analysed.

A Perkin-Elmer Model 900 gas chromatograph with a flame ionization detector was used. The separation was carried out in a stainless-steel column (1.8 m × 2.7 mm I.D.) packed with Chromosorb W AW DMCS (80–100 mesh) coated with 12% Carbowax 20M–TPA. Argon was used as the carrier gas at a flow-rate of 30 cm^3/min. The temperatures of the injector and the detector were 250°C. The column temperature was 100°C for 1 min, then raised to 220°C at 5°C/min. The contents of the separated components were determinated from their peak areas and the peak area of the internal standard using appropriate correction factors, which were calculated according to the method proposed by Sternberg *et al*[28].

The identification of the separated components was carried out by means of a mass spectrometer coupled to a gas chromatograph (GC–MS 2091 LKB, Bromma, Sweden). The chromatographic column and the separation conditions were the same as in the GC analysis. The mass spectra were taken at the tops of the chromatographic peaks. An ionization energy of 70 eV and an ion-source temperature of 250°C were employed.

A gas chromatograph (Model 400, MERA-ELWRO, Wrocław, Poland) with a thermal conductivity detector was used to determine the water contents of the polyoxyethylene glycols. A stainless-steel column (1.2 m × 4 mm I.D.) filled with Chromosorb 101 (80–100 mesh) was used. Hydrogen was used as the carrier gas at a flow-rate of 25 cm^3/min. The temperature of the injector and the detector were 250°C. The column temperature was 100°C for 1 min, then raised to 200°C at 4°C/min. Anhydrous acetone or ethyl methyl ketone were used as an internal standard and anhydrous ethanol as a solvent.

RESULTS AND DISCUSSION

The purity of model trioxyethylene glycol, as determined by direct analysis of its diacetate, was 94.95%. Small peaks of ethylene glycol, dioxyethylene glycol and tetraoxyethylene glycol were also observed but their contents were only 0.39, 3.09 and 1.57%, respectively. PEG 200 polyoxyethylene glycol contained successive homologues up to hexaoxyethylene glycol. Carbowax 1500 contained much higher homologues and hence it was impossible to analyse it directly.

Typical chromatograms of degradation products obtained without a catalyst and in the presence of iron(III) chloride are shown in Figs. 1 and 2 and the mass spectra of the main separated components obtained by polyoxyethylene glycol degradation are given in Fig. 3. The structures and retention indices of the separated compounds are presented in Tables II and III. Retention indices are also given on the chromatograms.

The chromatograms obtained demonstrate that much deeper degradation was achieved when iron(III) chloride was used as a catalyst, and the chromatograms obtained for the degradation of trioxyethylene glycol were similar to those obtained

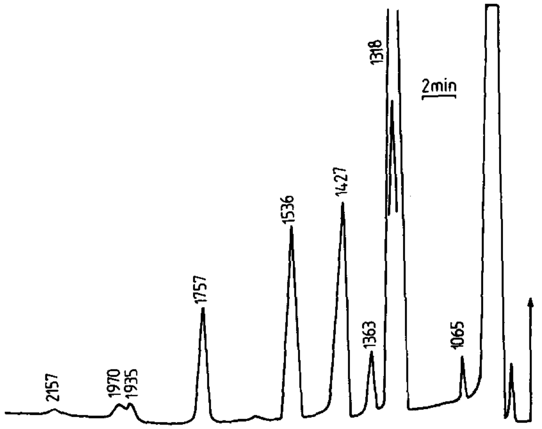


Fig. 1. Chromatogram of the degradation products of PEG-200 polyoxyethylene glycol (degradation without catalyst). Column and analytical conditions as in Experimental. For peak identification see Table II.

for Carbowax 1500. 2-Chloroethyl acetate was the main degradation product and its content was 96.33 and 96,68%, respectively, for trioxyethylene glycol and Carbowax 1500 degradation when acetic acid and γ-pyrone derivatives were not taken into consideration. Acetic acid is formed by the hydrolysis of acetyl chloride whereas γ-pyrones are formed by the reaction of acetyl chloride with acetic acid in the presence of a mineral acid[29]. Acetyl chloride and ion(III) chloride (15:1, m/m) were heated at 150°C for 0.5 h; a chromatogram of the reaction products is shown in Fig. 4 and mass spectra of the separated components together with their formulae are given in Fig. 5. Four different derivatives of γ-pyrone were identified by comparison of their mass spectra with those given in the literature[30]. Their retention indices were 2035, 2107,

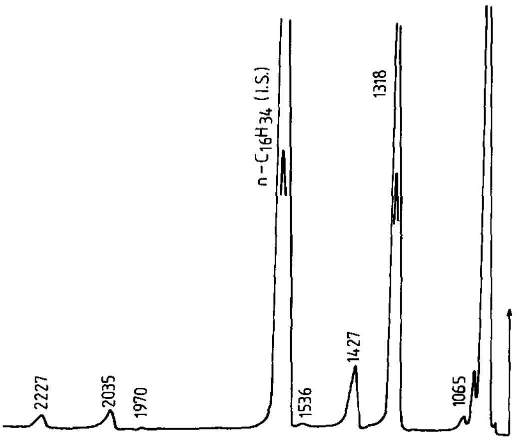


Fig. 2. Chromatogram of the degradation products of Carbowax 1500 [iron(III) chloride as a catalyst]. Column and analytical conditions as in Fig. 1. For peak identification see Table III.

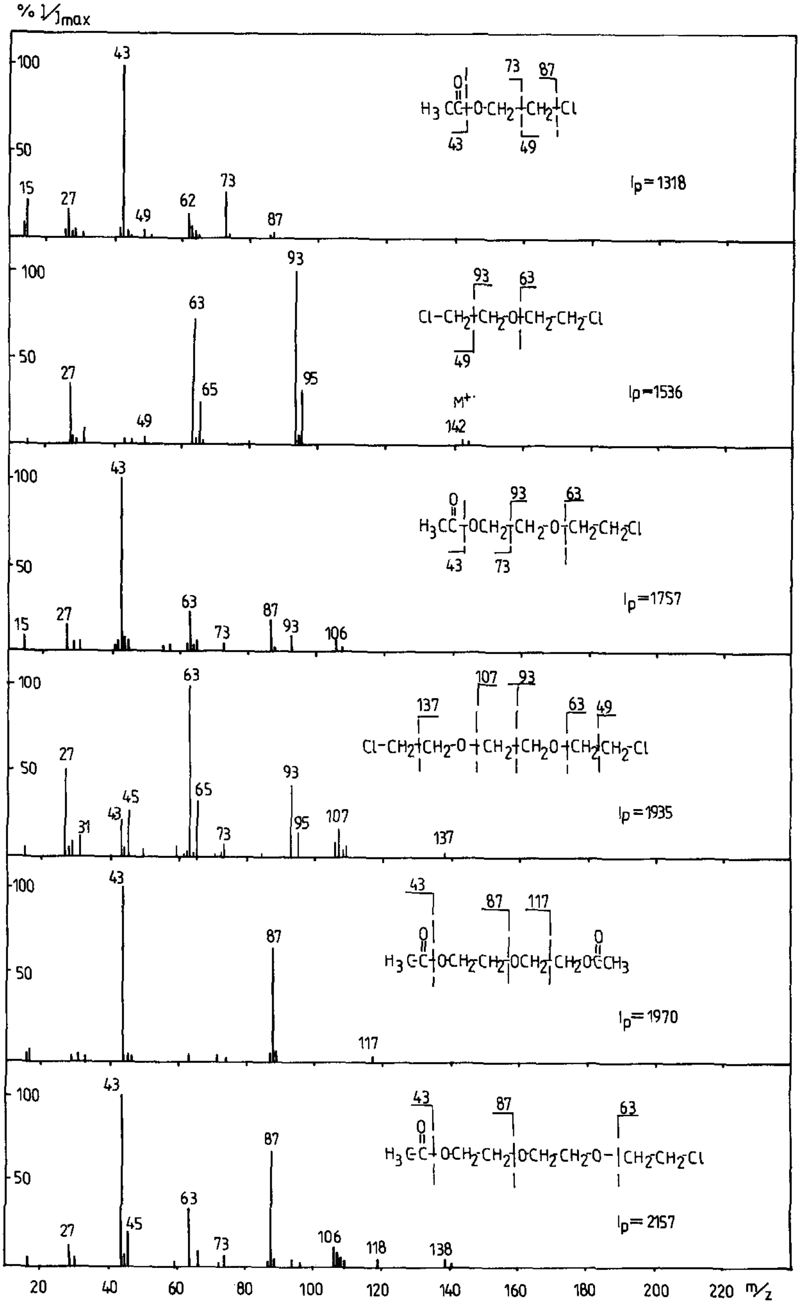


Fig. 3. Mass spectra of the separated components obtained by degradation of polyoxyethylene glycols.

2227 and 2405 and their contents in the products of the degradation of polyoxyethylene glycols did not exceed 5%. Hence γ-pyrone derivatives and acetic acid can be neglected. As a result, the content by weight of oxyethylene groups in the polyoxy-

TABLE II

DEGRADATION PRODUCTS: POLYOXYETHYLENE GLYCOL PEG 200, DEGRADATION WITHOUT A CATALYST

Component	*Formula*	*Retention index*
1,2-Dichloroethane	$ClCH_2CH_2Cl$	1065
2-Chloroethyl acetate	$ClCH_2CH_2OOCCH_3$	1318
Unknown	–	1363
Acetic acid	CH_3COOH	1427
Bis(2-chloroethyl) ether	$ClCH_2CH_2OCH_2CH_2Cl$	1536
5-Chloro-3-oxapentyl acetate	$ClCH_2CH_2OCH_2CH_2OOCCH_3$	1757
1,8-Dichloro-3,6-dioxaoctane	$ClCH_2CH_2OCH_2CH_2OCH_2CH_2Cl$	1935
Dioxyethylene glycol diacetate	$CH_2COOCH_2CH_2OCH_2CH_2OOCCH_3$	1970
8-Chloro-3,6-dioxaoctyl acetate	$ClCH_2CH_2OCH_2CH_2OCH_2CH_2OOCCH_3$	2157

TABLE III

DEGRADATION PRODUCTS: TRIOXYETHYLENE GLYCOL, CARBOWAX 1500, IRON(III) CHLORIDE AS CATALYST

Retention index (I_p)	*Component*
1065	1,2-Dichloroethane
1318	2-Chloroethyl acetate
14.27	Acetic acid
1536	Bis(2-chloroethyl) ether
1600	*n*-Hexadecane (I.S.)*
1970	Dioxyethylene glycol diacetate
2035	γ-Pyrone derivatives
2227	

* Internal standard.

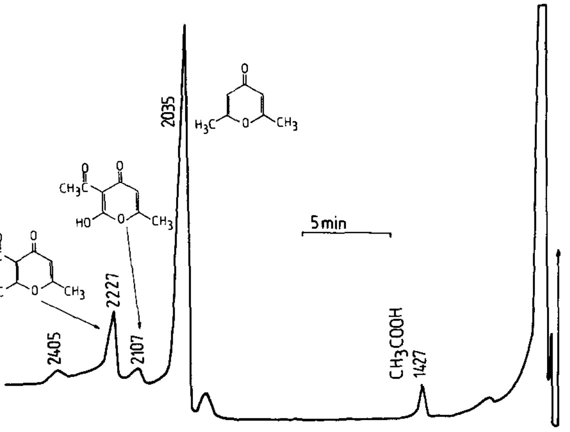


Fig. 4. Chromatogram of the products obtained by reaction of acetyl chloride with iron(III) chloride at 150°C.

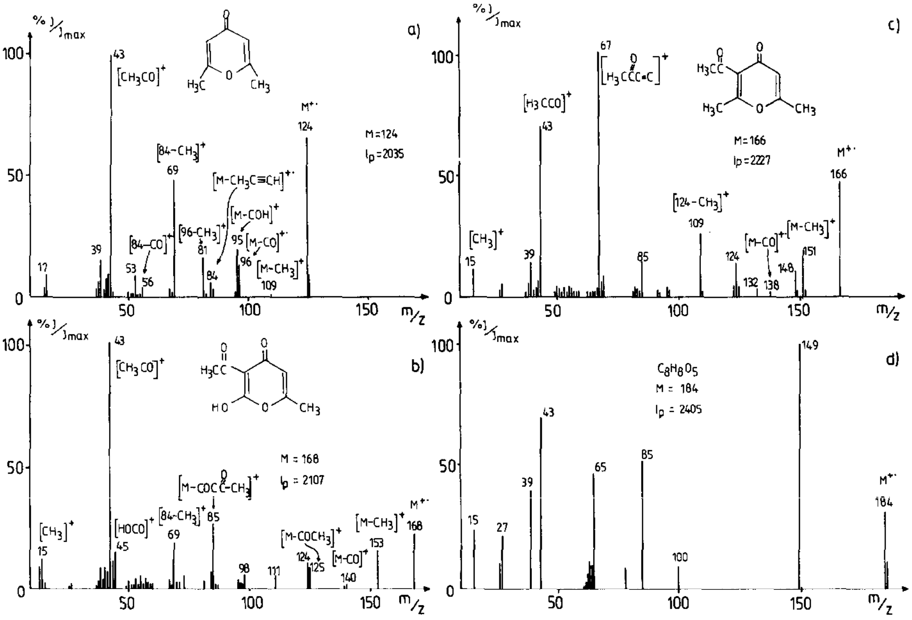


Fig. 5. Mass spectra of the separated γ-pyrone derivatives: (a) 2,6-dimethyl-γ-pyrone; (b) 2-hydroxy-3-acetyl-6-methyl-γ-pyrone; (c) 2,6-dimethyl-3-acetyl-γ-pyrone; (d) $C_8H_8O_5$.

ethylene glycols studied can be determined easily and precisely from the peak areas of the degradation products, mainly 2-chloroethyl acetate and *n*-hexadecane used as the internal standard. Such a determination is also possible when degradation is carried out without a catalyst. However, owing to incomplete degradation and the presence of products with higher molecular masses a larger number of separated components must be taken into consideration and the accuracy and precision of analysis are lower.

The data in Table IV demonstrate good agreement between the determined masses of polyoxyethylene glycols and those taken for analysis when the water contents (9.25% in trioxyethylene glycol and 1.65% in Carbowax 1500), determined separately by gas–solid chromatography were taken into consideration. The determined masses of polyoxyethylene glycols are only *ca.* 2.5–3.5% lower than the actual values. The confidence limits for a significance level of 0.05 are ±0.0017 g. Hence GC can be used to determine the contents of polyoxyethylene groups in commercial polyoxyethylene glycols.

TABLE IV

DETERMINED MASSES OF POLYOXYETHYLENE GLYCOLS

Glycol	*Glycol mass (g) (a)*	*Determined mass (g) (b)*	*Confidence limits (g) (α = 0.05)*	$\frac{b}{a} \cdot 100\,(\%)$
Trioxyethylene glycol	0.0412	0.0398	±0.0017	96.60
Carbowax 1500	0.1040	0.1013	±0.0017	97.40

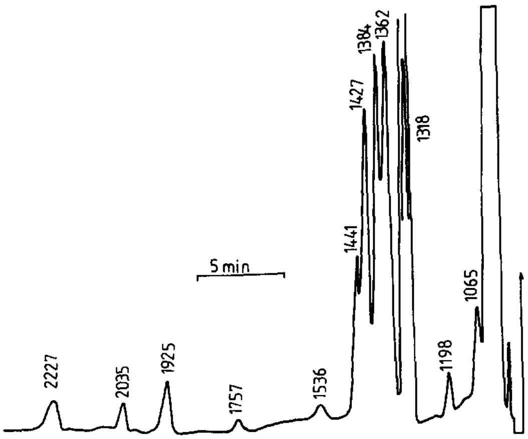


Fig. 6. Chromatogram of the degradation products of BEB 2000-44 block copolymer. Column and analytical conditions as in Fig. 1. For peak identification see Table VI.

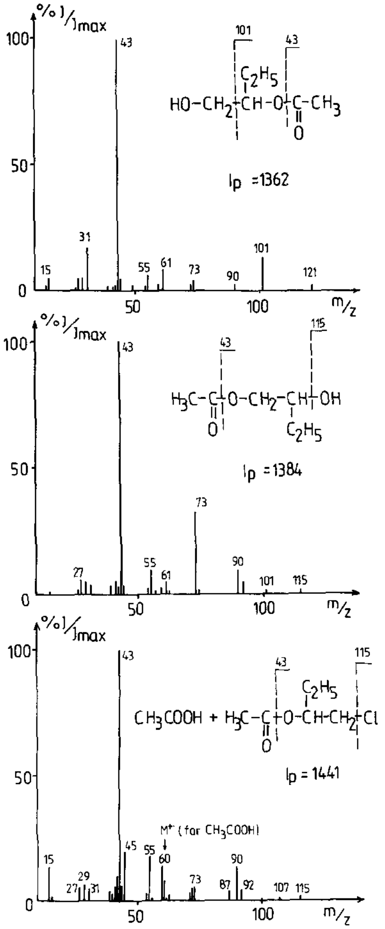


Fig. 7. Mass spectra of the degradation products obtained from polyoxybutylene chains.

TABLE V

COMPOSITION OF THE DEGRADATION PRODUCTS OF BE 1500-44 BLOCK COPOLYMER

*Group of products**	*Component*	*Retention index (I_p)*	*Average content (mol-%)*	*Confidence limits (α = 0.05)*	*Oxyethylene group content (wt.-%) (α = 0.05)*
I	1,2-Dichloroethane	1065	3.71	±2.35	44.13 ± 1.36
	2-Chloroethyl acetate	1318	51.53	±2.23	
	Bis(2-chloroethyl) ether	1536	0.08	±0.33	
	5-Chloro-3-oxapentyl acetate	1757	0.32	±0.29	
II	1,2-Dichlorobutane	1198	5.15	±1.36	
	2-(Hydroxymethyl)-propyl acetate	1362	12.36	±0.81	
	2-Hydroxybutyl acetate	1384	12.96	±0.97	
	2-(Chloromethyl)-propyl acetate	1441	9.78	±1.52	
	Bis(2-chlorobutyl) ether	1925	3.30	±0.73	

* I and II denote the products obtained from polyoxyethylene and polyoxybutylene chains, respectively.

A typical chromatogram of the products of the degradation of BEB block copolymer (Fig. 6) is more complex than the previous chromatograms as a result of degradation of the central polyoxyethylene chain and both terminal polyoxybutylene chains. Similar chromatograms were obtained for BE block copolymer. The mass spectra, although they do not contain molecular ions, give information about the structures of the separated components (Fig. 7). The retention indices of the separated components are in agreement with values obtained for commercially available

TABLE VI

COMPOSITION OF THE DEGRADATION PRODUCTS OF BEB 2000-44 BLOCK COPOLYMER

*Group of products**	*Component*	*Retention index (I_p)*	*Average content (mol-%)*	*Confidence limits (α = 0,05)*	*Oxyethylene group content (wt.-%) (α = 0.05)*
I	1,2-Dichloroethane	1065	6.68	±1.01	43.46 ± 2.14
	2-Chloroethyl acetate	1318	47.56	±1.64	
	Bis(2-chloroethyl) ether	1536	0.82	±0.45	
	5-Chloro-3-oxapentyl acetate	1757	0.64	±0.47	
II	1,2-Dichlorobutane	1198	2.73	±0.56	
	2-(Hydroxymethyl)-propyl acetate	1362	17.04	±0.61	
	2-Hydroxybutyl acetate	1384	15.34	±2.23	
	2-(Chloromethyl)propyl acetate	1441	7.07	±0.23	
	Bis(2-chlorobutyl) ether	1925	2.06	±0.87	

* I and II denote the products obtained from polyoxyethylene and polyoxybutylene chains, respectively.

standards. The separated components and their structures together with a statistical assessment of the results obtained, calculated from five independent analyses, are given in Tables V and VI. The results demonstrate a satisfactory precision. The calculated contents of polyoxyethylene chains (44.13 ± 1.36% and 43.46 ± 2.14% for BE and BEB block copolymers, respectively) are in agreement with the initial analytical data (44%).

CONCLUSIONS

Polyoxyethylene glycols and block copolymers of ethylene oxide and α-butylene oxide can be degraded to simple compounds by reaction with acetyl chloride at 150°C for 0.5 h in the presence of iron(III) chloride as catalyst. 2-Chloroethyl acetate is the main product (*ca.* 96%) of degradation of the polyoxyethylene chain. Degradation of polyoxybutylene chains is much more complex and several products are formed in similar amounts. The contents of successive degradation products can be determined by GC using an internal standard method. They can be further used to calculate with good precision and accuracy the mass and/or the content of polyoxyethylene groups.

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