Journal of Macromolecular Science, Part A
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597274

Synthesis and Characterization of Poly(Copolyethers-*block*-Polyamides). I. Structural Study of Polyether Precursors

A. Boulares[a]; M. Tessier[a]; E. Maréchal[a]
[a] Laboratoire de Synthèse Macromoléculaire (CNRS, UMR 7610), Université Pierre et Marie Curie, Paris Cedex 05, FRANCE

To cite this Article Boulares, A. , Tessier, M. and Maréchal, E.(1998) 'Synthesis and Characterization of Poly(Copolyethers-*block*-Polyamides). I. Structural Study of Polyether Precursors', Journal of Macromolecular Science, Part A, 35: 6, 933 — 953

To link to this Article: DOI: 10.1080/10601329808002022
URL: http://dx.doi.org/10.1080/10601329808002022

J.M.S.—PURE APPL. CHEM., A35(6), pp. 933–953 (1998)

SYNTHESIS AND CHARACTERIZATION OF POLY(COPOLYETHERS-*block*-POLYAMIDES). I. STRUCTURAL STUDY OF POLYETHER PRECURSORS

Alya Boulares, Martine Tessier, and Ernest Maréchal*
Laboratoire de Synthèse Macromoléculaire
(CNRS, UMR 7610)
Université Pierre et Marie Curie
Case 184-4, Place Jussieu, 75252
Paris Cedex 05, FRANCE

Key Words: Polyoxyethylene, Polyoxytetramethylene, Polyoxypropylene, Copolyether, Hydroxy End Group, ^{1}H NMR, ^{13}C NMR, Mass Spectrometry

ABSTRACT

Structures of α,ω-dihydroxy polyethers and copolyethers were investigated extensively using ^{1}H and ^{13}C NMR spectroscopy and mass spectrometry (electrospray ionization technique).The ^{1}H NMR study was achieved from samples of which the hydroxy end groups were modified with trifluoroacetic anhydride. In particular, the nature of end groups (primary or secondary hydroxy end group), the accurate chemical structure and the molar mass of copolyethers were determined.

INTRODUCTION

Many block copolycondensates were described and part of our activity relates to this domain [1-16], particularly to poly(polyethers-*block*-polyamides) [1, 8, 14].

Poly(polyethers-*block*-polyamides) are often referred to as PEBA and some of them are commercialized: PEBAX® by Elf Atochem and VESTAMID® by Hüls; part of them are prepared from homopolyethers. This article and the following one [17] deal with new poly(copolyethers-*block*-polyamides) obtained by polycondensation of an α,ω-dicarboxy oligododecanamide (PA12dC) with various α,ω-dihydroxy triblock copolyethers, e.g. α,ω-dihydroxy (polyoxyethylene-*block*-polyoxypropylene-*block*-polyoxyethylene) (POE/POP/POE dOH).

In this present article, we analyze the structure of the functional oligoethers (homopolymers and copolyethers) used as precursors; the structure of PA12dC was previously described [18]· The second part of this series will be devoted to the block polycondensation, particularly its kinetics, and we will report on the characteristics and the properties of the resulting block copolycondensates [17].

Heatley *et al.* [19] published the preparation and the ^{13}C NMR analysis of block copolyethers of ethylene oxide and propylene oxide, and the corresponding homopolymers. In this work, the homopolyethers and the copolyethers we used are industrial products. The structural study by ^{13}C NMR of our various samples is carried out by referring to Heatley data. A complementary study by ^{1}H NMR is also achieved from oligoethers which previously reacted with trifluoroacetic anhydride (TFA) in order to confirm the nature of end groups and to determine the number-average molar mass of oligoethers. Moreover, these samples are analyzed by mass spectrometry (MS) which is a powerful method of characterizing the chemical structure.

The average molar masses determined by ^{1}H NMR and MS are compared with values obtained by size exclusion chromatography.

EXPERIMENTAL

Materials

α,ω-dihydroxy oligooxytetramethylene (POTMdOH), oligooxyethylene (POEdOH) and oligooxypropylene (POPdOH) were provided by BASF. Synperonic® and Pluronic® copolyethers were provided by ICI and by BASF, respectively.

Measurements

^{1}H NMR spectra were recorded in TFA/$CDCl_3$ (1/4 v/v) on a Bruker WM 250, a Bruker AM 500 or a Bruker DMX 500 spectrometers. ^{13}C NMR spectra were recorded in $CDCl_3$ on a Bruker AM 500 spectrometer. The ^{1}H and ^{13}C

chemical shifts were referenced to residual $CHCl_3$ at 7.26 ppm and to $CDCl_3$ at 76.9 ppm, respectively. In order to assign more completely the trifluoroacetylated POPdOH ^1H spectrum, 2D ^1H-^1H COSY-45 and 2D *J*-resolved spectra were recorded at a proton frequency of 500 MHz.

The positive-ion electrospray ionization (ESI) mass spectra were acquired by directly infusing the polymer solution into the Analytical of Brandford ESI ion source coupled to a R 10-10 Nermag quadrupole mass spectrometer. The m/z range of the mass spectrometer was 10 to 1500 Th. The polymers were dissolved (100ng/μL) in water/methanol (1/1 v/v) solution in the presence of sodium acetate (10^{-4} M). Number-average molar mass ($\overline{M_n}$) mass-average molar mass ($\overline{M_w}$) and polydispersity index ($\overline{M_w} / \overline{M_n}$) were calculated using Equations 1 and 2 where N_i is the relative peak intensities and M_i is the molar mass of each molecule identified.

$$\overline{M_n} = \Sigma N_iM_i / \Sigma N_i \quad \mathbf{1} \qquad\qquad \overline{M_w} = \Sigma N_iM_i^2 / \Sigma N_iM_i \quad \mathbf{2}$$

Size Exclusion Chromatography (SEC) was performed in tetrahydrofuran (0.5 mL/min) with Waters equipment: U6K injector, 510 pump, 410 Differential refractometer, Maxima 820 /Baseline 810 workstation and a PL-Gel column set (50, 100, 500 and 10^4 Å). The system was calibrated with polyoxyethylene standards.

Vapor pressure osmometry (VPO) measurements were performed with a Knauer osmometer in acetone at 25°C. The apparatus was calibrated with benzil.

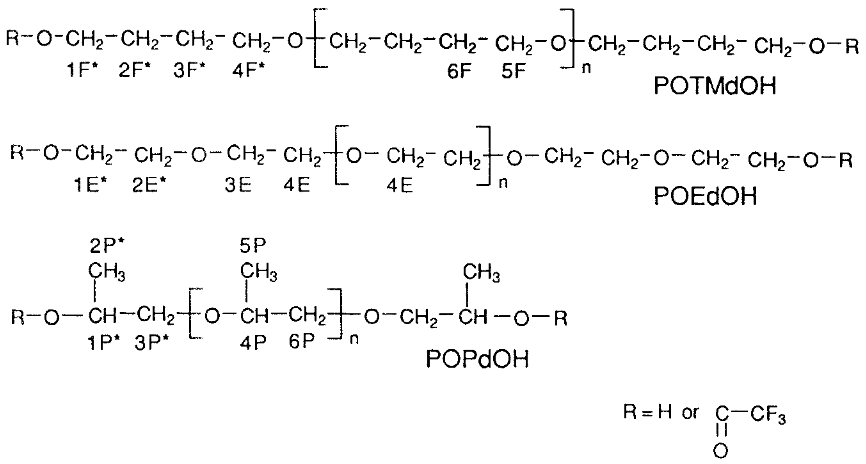
Titration of hydroxy end groups was carried out using a Mettler DL40RC automatic titrator. Samples reacted with an excess of acetic anhydride in pyridine at 90°C during 30 minutes. Then, the mixture was hydrolyzed with water during 10 minutes at 90°C. After cooling, a solution of KOH in ethanol was used as reactant.

RESULTS AND DISCUSSION

Characteristics of the α,ω-Dihydroxy Homopolyethers

α,ω-dihydroxy oligooxytetramethylene (POTMdOH), oligooxyethylene (POEdOH) and oligooxypropylene (POPdOH) were provided by BASF and their structures were analyzed by ^1H and ^{13}C NMR, and mass spectrometry.

The proton and carbon numbering used for NMR analysis is described as follows :



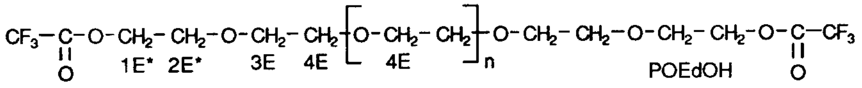
F, E and P symbolize oxytetramethylene, oxyethylene and oxypropylene units, respectively; the end units are asterisked (E*, F* and P*).

The ^1H NMR spectra of homopolyethers were recorded after the hydroxy end groups were reacted with trifluoroacetic anhydride (TFA). The chemical shifts and assignments of ^1H NMR signals are reported in Tables 1 and 2. This analytical technique was used by Yong and Wu [20] and by Goldwasser and Adolph [21]. It allows an easy determination of the number-average molar mass ($\overline{M_n}$) of the oligoethers as the protons in the end unit and those in the backbone give separated signals. Moreover, a difference may be noted between methylene end group ($\delta H^{1F*} = 4.35$ ppm and $\delta H^{1E*} = 4.47$ ppm) and methine end group ($\delta H^{1P*} = 5.22_5$ ppm) chemical shifts. The $\overline{M_n}$ values obtained from ^1H NMR analysis are tabulated in Table 3.

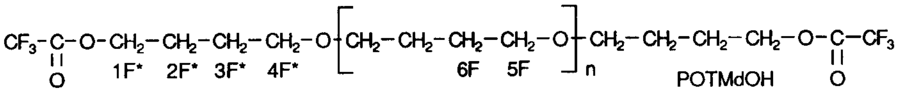
The oligooxypropylene sample hydroxy end groups are all secondary as the doublet at ~ 4.42 ppm relative to methylene protons in α position of trifluoroacetylated hydroxy group (i.e. CF_3-CO-O-C$\underline{H}_2$-CH(CH_3)-) is not observed. In order to characterize more completely the trifluoroacetylated POPdOH ^1H NMR spectrum, various ^1H NMR experiments were carried out.

The ^1H-^1H COSY spectrum (Figure 1) allows to assign the signals of the unit at the end of the chain, i.e. $\delta H^{3P*} = 3.67$ ppm and $\delta H^{2P*} = 1.32$ ppm, and those corresponding to the backbone unit, $\delta H^{4P} = 3.67_5$ ppm and $\delta H^{5P} = 1.15_5$ ppm. Moreover, it should be noted that the small peak at 3.81 ppm is typical of methine protons coupled to methyl and methylene protons, the chemical shifts of which are 1.15_5 and 3.45 ppm, respectively; these protons are probably specific of a

TABLE 1. Assignment of ^1H NMR Chemical Shifts Of Trifluoroacetylated α,ω-Dihydroxy Oligooxyethylene And Oligooxytetramethylene



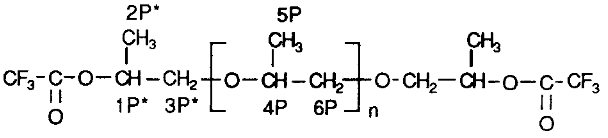
$CF_3-C(=O)-O-CH_2-CH_2-O-CH_2-CH_2-[O-CH_2-CH_2]_n-O-CH_2-CH_2-O-CH_2-CH_2-O-C(=O)-CF_3$



$CF_3-C(=O)-O-CH_2-CH_2-CH_2-CH_2-O-[CH_2-CH_2-CH_2-CH_2-O]_n-CH_2-CH_2-CH_2-CH_2-O-C(=O)-CF_3$

	POEdOH			POTMdOH			
n° H	1E*	2E*	4E, 3E	1F*	4F*, 5F	2F*	6F, 3F*
δ (ppm)	4.47	3.80	3.68	4.35	3.50	1.83	1.65

TABLE 2. Assignment of ^1H NMR Chemical Shifts Of Trifluoroacetylated α,ω-Dihydroxy Oligooxypropylene



$CF_3-C(=O)-O-CH(CH_3)-CH_2-[O-CH(CH_3)-CH_2]_n-O-CH_2-CH(CH_3)-O-C(=O)-CF_3$

n° H	1P*	4P	3P*	6P	2P*	5P
δ (ppm)	5.22_5	3.85 - 3.67	3.67	3.70 - 3.42	1.32	1.15_5

TABLE 3. Number-average Molar Mass ($\overline{M_n}$) of α,ω-Dihydroxy Oigoethers used in Block Polycondensation Determined from Different Analytical Methods (See Text and Experimental Part). The Polydispersity Index is Given Between Brackets.

	POTMdOH	POEdOH	POPdOH
End group titration	1075	1015	930
VPO	975	980	805
SEC	720 (1.90)	955 (1.10)	810 (1.05)
^1H NMR	1000	1050	880
ESI-MS	-	1070 (1.03)	925 (1.04)

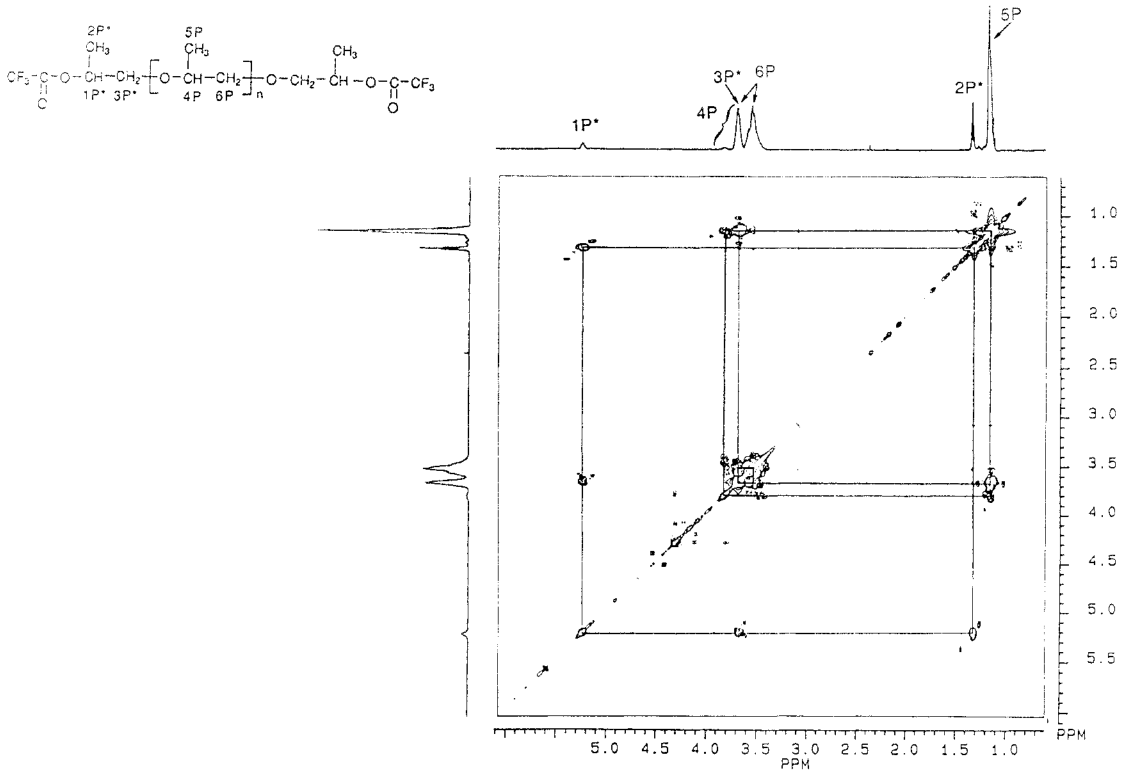


Figure 1. 2D ^1H-^1H COSY-45 spectrum of POPdOH ($CDCl_3$ / TFA)

particular enchainment not assigned at this time. On the other hand, from the COSY spectrum, it is difficult to assign precisely the signals of CH_2 protons H^{6P} in the backbone.

Bruch *et al.* [22] applied homonuclear two-dimensional *J*-resolved spectroscopy to the analysis of atactic polyoxypropylene, and showed that all the methylene protons are nonequivalent in different stereochemical environments; isotactic signals were unambiguously attributed. Comprehensive assignments of the ^1H NMR spectrum of poly((S)-(-)-oxypropylene) with irregular sequences have been reported by Miura *et al.* [23]. Nevertheless, these results do not directly apply to the low molar mass trifluoroacetylated POPdOH ^1H NMR spectrum.

Consequently, 2D *J*-resolved spectrum of the trifluoroacetylated sample was recorded. The 3.0-4.0 ppm range of the 2D *J*-resolved spectrum is shown in Figure 2. The upfield CH_2 proton region (3.48-3.60 ppm) is more complex than the one shown by Bruch *et al.* [22]. The multiplets centered at ~3.57 ppm correspond to nonequivalent methylene protons H_b^{6P} in different stereosequences with coupling constants JH_b^{6P}-H_a^{6P}(gem) = -10.4 Hz and JH_b^{6P}-H^{4P}(vic) = 6.5 Hz. The doublets centered at ~3.54 ppm correspond to equivalent methylene protons H^{6P} with JH^{6P}-H^{4P} = 5.1 Hz. The difference between our results and Bruch *et al.* data (i.e. presence of equivalent methylene protons in our oligomer structure) is probably due to the neighboring ester end group contribution. The other signals of the 2D *J*-resolved spectrum are too complex to be really interpreted. Nevertheless, the most downfield region (3.64-3.72 ppm) can be assigned to H^{4P}, H^{3P*} and nonequivalent methylene protons H_a^{6P}.

From this, we can only conclude that the chemical shifts of CH_2 protons in the backbone are in the 3.70-3.40 ppm range.

The methyl region of the 2D *J*-resolved spectrum is shown in Figure 3. Three main doublets are clearly visible at ~1.15_5 ppm (H^{5P}) and two at ~1.33 ppm (H^{2P*}) with, in all cases, the same coupling constant JCH_3-CH = 6.6 Hz. These components observed for H^{5P} and H^{2P*} are due to neighboring enchainment contributions.

The ^{13}C NMR study was directly achieved from α,ω-dihydroxy polymers. The assignments of the POEdOH ^{13}C NMR spectrum were consistent with those of Heatley *et al.* [19]. We observed the main chain resonance (C^{4E}) at 70.19 ppm and three resonances at 61.23, 72.27 and 69.77 ppm corresponding to C^{1E*}, C^{2E*} and C^{3E} terminal carbons, respectively.

In the same way, the assignments of POTMdOH ^{13}C NMR spectrum have been previously established [24]: Two main peaks at 26.32 and 70.33 ppm

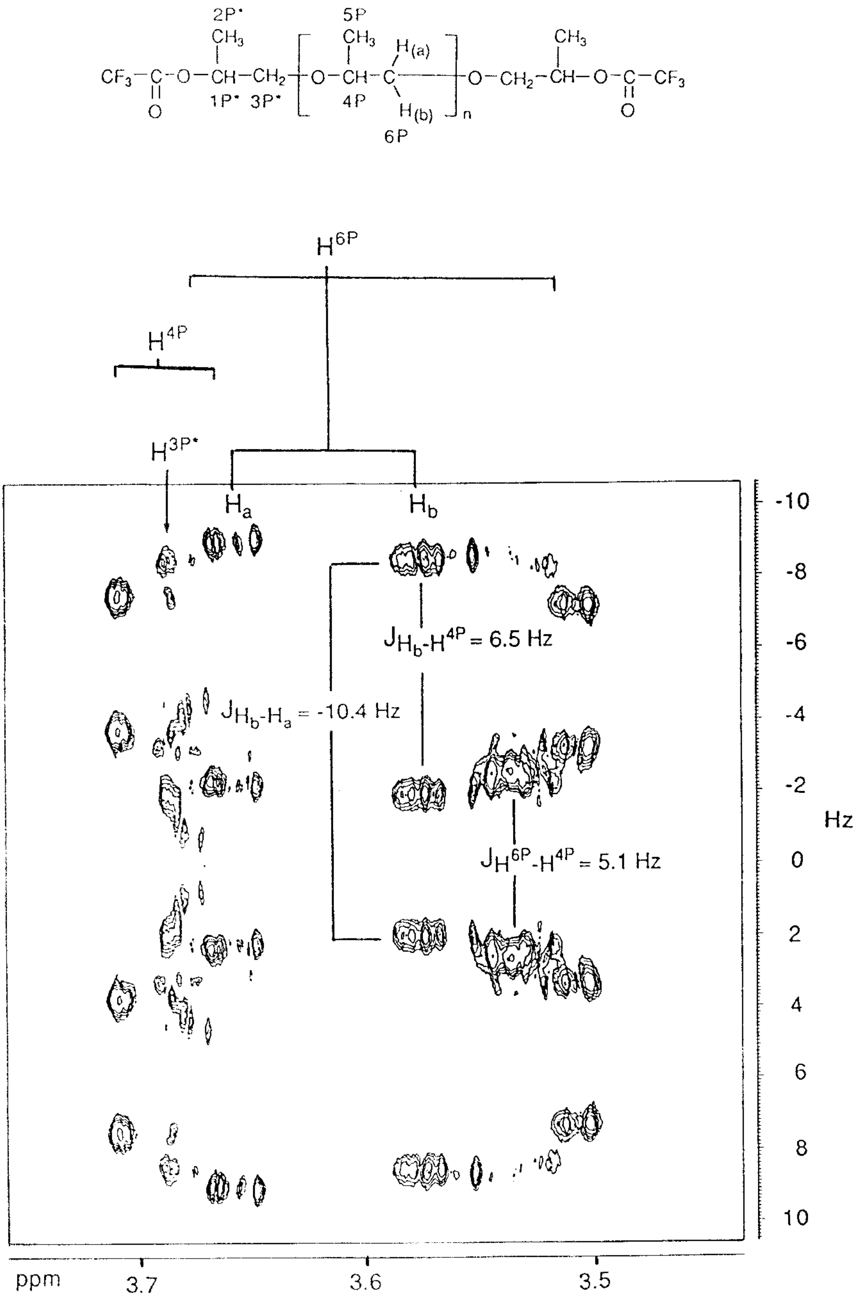


Figure 2. 2D *J*-resolved spectrum of POPdOH; 3.0-4.0 ppm range; ($CDCl_3$/TFA)

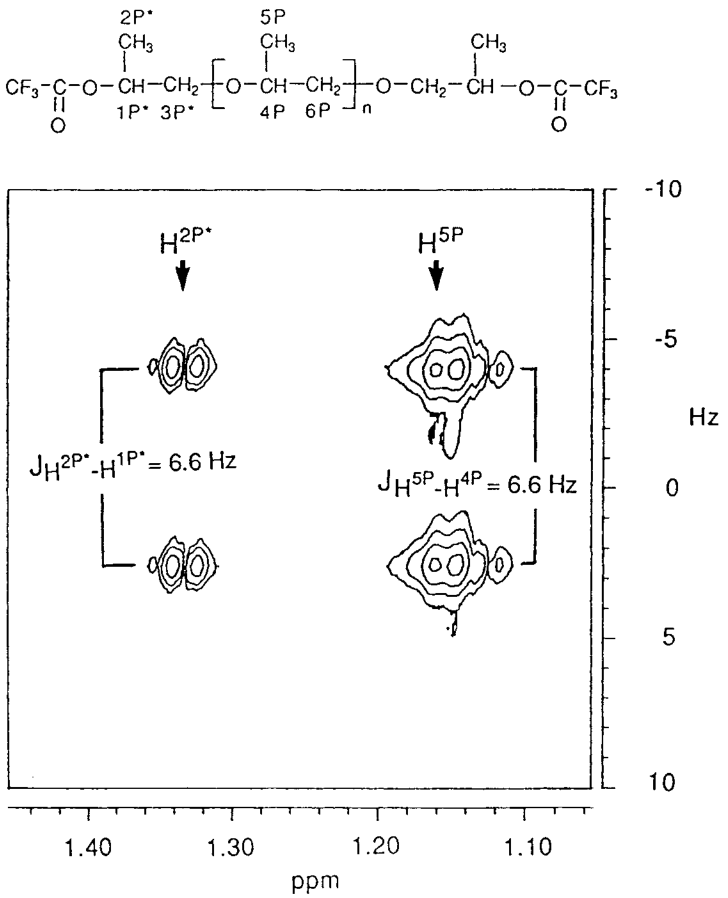


Figure 3. 2D *J*-resolved spectrum of POPdOH methyl region; ($CDCl_3$ / TFA)

corresponding to C^{6F} and C^{5F} chain carbons respectively, and four peaks at 62.19, 29.87, 26.49 and 70.47 ppm assigned to C^{1F*}, C^{2F*}, C^{3F*} and C^{4F*} end group carbons, respectively.

On the basis of the works of Heatley *et al.* [19], Campbell *et al.* [25] and Schilling *et al.* [26], we have easily assigned the different peaks of the POPdOH ^{13}C NMR spectrum (Figure 4a). A spectrum recorded with the "J-Modulated Spin Echo Technique (JMSET)" method confirms the assignments of CH_3, CH and CH_2 groups (Figure 4b). With respect to Heatley *et al.* [19] studies, in diad and triad sequence identification, we used the following notation: $\overrightarrow{P}$ symbolizes the oxypropylene unit from the CH_2 tail to the $-CH(CH_3)-$ head (i.e. $-OCH_2-CH(CH_3)-$) and consequently, $\overleftarrow{P}$ represents $-OCH(CH_3)-CH_2-$, $\underline{P}$ corresponds to the located

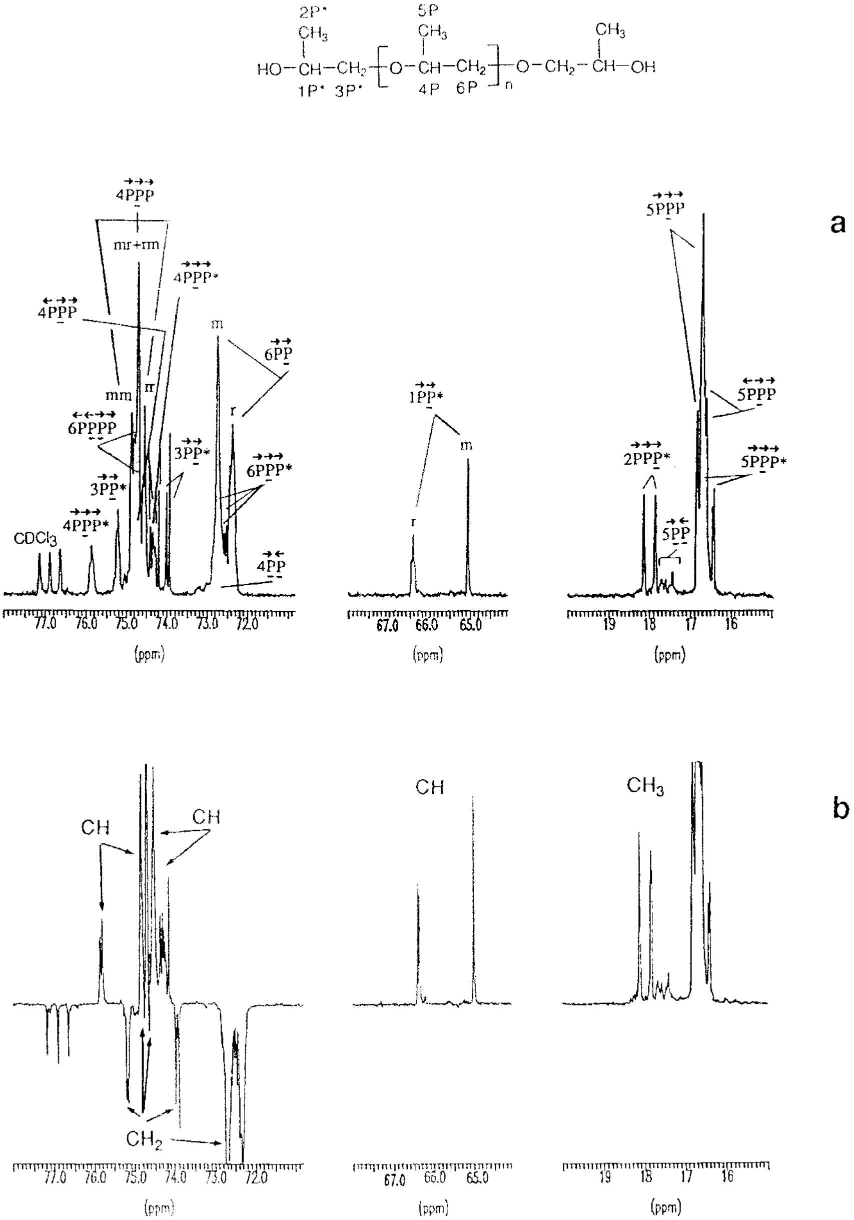


Figure 4. a) ^{13}C NMR spectrum of POPdOH ($CDCl_3$)
b) ^{13}C NMR "JMSET" spectrum of POPdOH ($CDCl_3$)

unit and the end unit is designated by P*, *m and r* are relative to isotactic and syndiotactic diads, respectively.

Diads and triads were identified and comparison of the peaks relative to triads shows that POPdOH contains mainly atactic regular enchainments. Moreover, the spectrum reveals that all hydroxy end groups are secondary: The terminal methine carbon (i.e.-CH_2-$\underline{C}H(CH_3)$-OH) gives two peaks at 65.06 and 66.42 ppm corresponding to *m* and *r* diads $1\overrightarrow{P\underline{P}}^{*}$, respectively and the peaks corresponding to -$CH(CH_3)$-$\underline{C}H_2$-OH expected in the range 65.4-65.9 ppm [25, 27] are not observed, which fits ^1H NMR analysis.

However, the values of the chemical shifts of backbone carbons we obtained and those given in literature are somewhat different. In fact, we have observed that they depend on the solvent, the concentration, but also on the length of the oligomer: The carbon signals relative to the monomer unit are shifted towards the low fields as the molar mass increases; for instance $\delta C^{4\overrightarrow{P\underline{P}P}(mr+rm)}$ is 74.60, 74.73, 74.75 and 74.75 ppm when $\overline{M_n}$ is 600, 900, 1200 and 2000, respectively.

These oligomers were also characterized by mass spectrometry which was successfully used in the structural analysis of polyethers [28-35]. We used the electrospray ionization (ESI) technique which generates a distribution of multiply-charged molecular ions with minimal fragmentation. The positive-ion ESI mass spectra of polyether samples exhibited peaks corresponding to a majority of $[M_i+qNa]^{q+}$ species and some $[M_i+qK]^{q+}$ species. The number of charges q linked to each molecule increases with an increasing molecular mass; however, only singly-charged and doubly-charged molecular ions were observed since the number of monomer units is limited.

For instance, the spectrum of POEdOH (Figure 5) shows that each species in singly-charged series yields peaks at mass intervals of the monomer unit (m/z = 44 Th) while doubly-charged series displays peaks at mass intervals of one-half the monomer unit (m/z = 22 Th). Since all the peaks were identified, $\overline{M_n}$ and $\overline{M_w}$ could be obtained (Table 3).

The $\overline{M_n}$ values of homopolyethers obtained by ^1H NMR or MS are in accordance with those determined from other analytical methods such as size exclusion chromatography (SEC), vapor pressure osmometry (VPO) and hydroxy group chemical titration (Table 3).

Characteristics of α,ω-Dihydroxy Triblock Copolyethers

We used commercial copolyether samples provided by ICI (Synperonic®) and by BASF (Pluronic®). In principle they should obey the following formula :

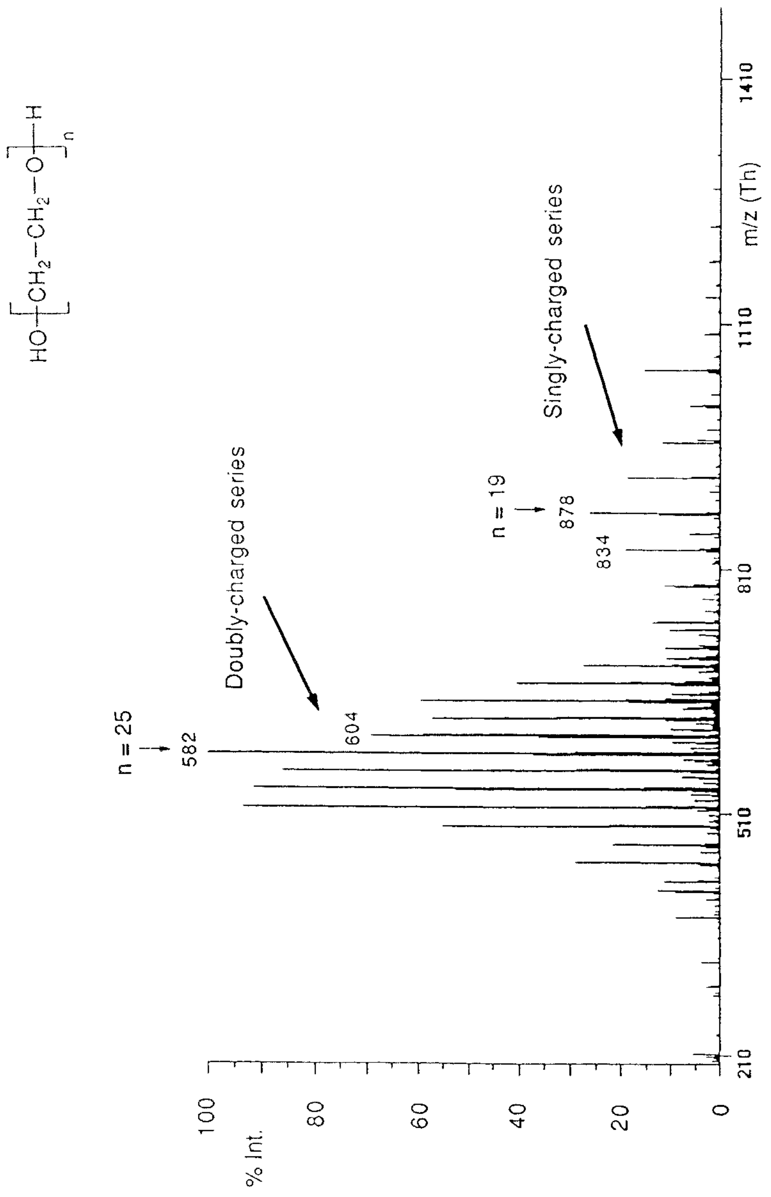
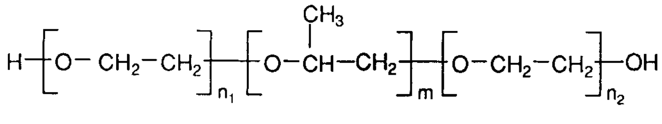


Figure 5: Positive-ion ESI mass spectrum of POEdOH

TABLE 4. Number-average Molar Mass ($\overline{M_n}$) of α,ω-Dhydroxy Triblock Copolyethers Determined from SEC, ^{1}H NMR and ESI-MS. The Polydispersity Index is Given Between Brackets. $\overline{M_n th}$ Corresponds to the Value Supplied by ICI or BASF.

Sample	$\overline{M_n th}$	$\overline{M_n}$		
		SEC	^{1}H NMR	ESI-MS
Synperonic® L-31	1100	1095 (1.10)	1090	1000 (1.07)
Synperonic® L-35	1900	1995 (1.05)	1920	2095 (1.07)
Synperonic® L-42	1650	1645 (1.05)	1570	1670 (1.01)
Synperonic® L-43	1900	1660 (1.10)	1840	1815(1.02)
Synperonic® L-44	2200	1975 (1.10)	2205	1750 (1.05)
Synperonic® L-61	2100	2050 (1.05)	1950	1915 (1.03)
Pluronic® 3100	1100	1055 (1.05)	1095	1025 (1.04)
Pluronic® 4300	1700	1700 (1.10)	1925	1920 (1.04)
Pluronic® 6100	2000	1560 (1.05)	1740	1840 (1.04)



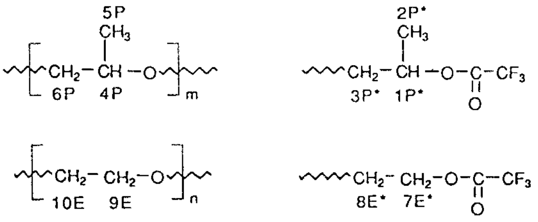
$$H\!\left[O-CH_2-CH_2\right]_{n_1}\!\left[O-\overset{CH_3}{\overset{|}{CH}}-CH_2\right]_m\!\left[O-CH_2-CH_2\right]_{n_2}\!OH$$

$n_1 + n_2 = n$

As for homopolyethers, these copolyethers were analyzed by SEC, NMR and MS. The $\overline{M_n}$ values determined from the three methods are similar (Table 4).

The proton and carbon numbering for NMR analysis is given in each spectrum.

The ^{1}H NMR spectra of trifluoroacetylated α,ω-dihydroxy copolyethers (i.e. after reaction with TFA) clearly showed the nature of the end groups. In the spectrum of Synperonic® L-31 (Figure 6) we observe, by comparison with the previous study of POEdOH and POPdOH homopolymers, the chemical shifts assigned to the presence of primary hydroxy end group (δH^{7E*} = 4.42 ppm, *triplet*)



n° H	1P*	7E*	8E*	4P	3P*	9E, 10E	6P	2P*	5P
δ (ppm)	5.16	4.42	3.74	3.83 - 3.52	3.60	3.62	3.65 - 3.34	1.26$_5$	1.09$_5$

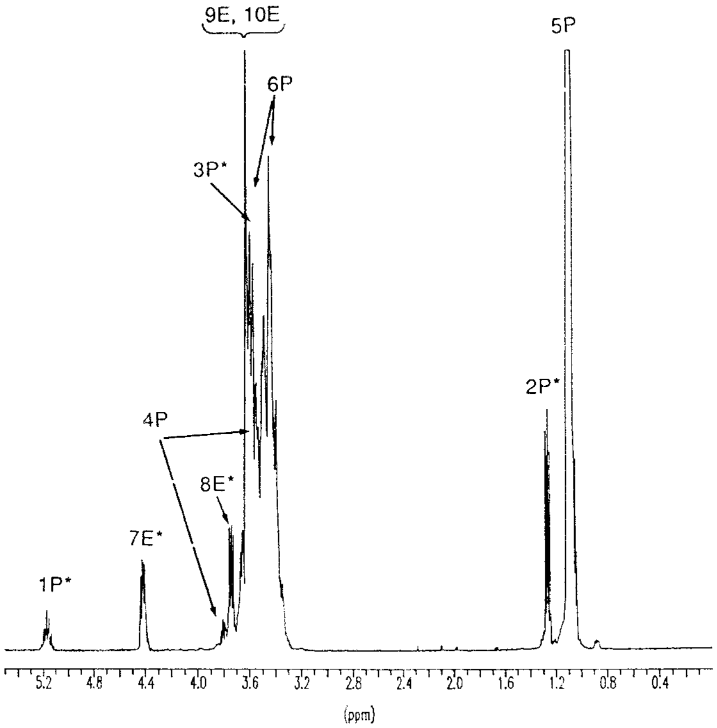


Figure 6: ^{1}H NMR spectrum of Synperonic® L-31 ($CDCl_3$ / TFA)

TABLE 5. Percentages of Primary (% pri-OH) and Secondary (% sec-OH) Hydroxy End Groups, OE/OP Ratio of Numbers of OE and OP Units in the Copolyethers Determined from ^{1}H NMR Analysis.

Sample	% pri-OH	% sec-OH	OE/OP
Synperonic® L-31	50	50	0.25
Synperonic® L-35	90	10	1.26
Synperonic® L-42	75	25	0.56
Synperonic® L-43	80	20	0.77
Synperonic® L-44	85	15	1.09
Synperonic® L-61	60	40	0.23
Pluronic® 3100	35	65	0.16
Pluronic® 4300	80	20	0.65
Pluronic® 6100	45	55	0.14

and secondary hydroxy end group (δH^{1P*} = 5.16 ppm, *sextuplet*). This means that the effective structure is somewhat different from the one proposed by the supplier i.e. a triblock copolyether. The percentages of primary and secondary hydroxy end groups and the ratio of the numbers of oxyethylene (OE) to oxypropylene (OP) units were determined from ^{1}H NMR analysis (Table 5).

The ^{13}C NMR spectra of the various copolyethers were easily analyzed using Heatley [19] data. For example, the spectrum of Synperonic® L-31 is reported in Figure 7. We observe that the peaks characteristic of POP block have the similar chemical shifts to those of atactic POPdOH homopolymer. In the range of 60-70 ppm, we note chemical shifts assigned to the presence of several kinds of sequences in end chain position (the same notation as previously has been adopted): $\delta C^{1P\underline{P}*}$ = 65.13 and 66.46 ppm (corresponding to *m* and *r* diads, respectively), $\delta C^{7EE\underline{E}*}$ = 60.98 ppm, $\delta C^{7PE\underline{E}*}$ = 61.05 ppm and $\delta C^{7PP\underline{E}*}$ = 61.27 and 61.37 ppm. Moreover, we do not observe peaks at about 65.5-66.0 ppm characteristic of -$CH(CH_3)$-$\underline{CH_2}$-OH end group.

The Synperonic® L-35 ^{13}C NMR spectrum (not shown) does not exhibit all these terminal resonances. The most intense peak is observed at 60.82 ppm

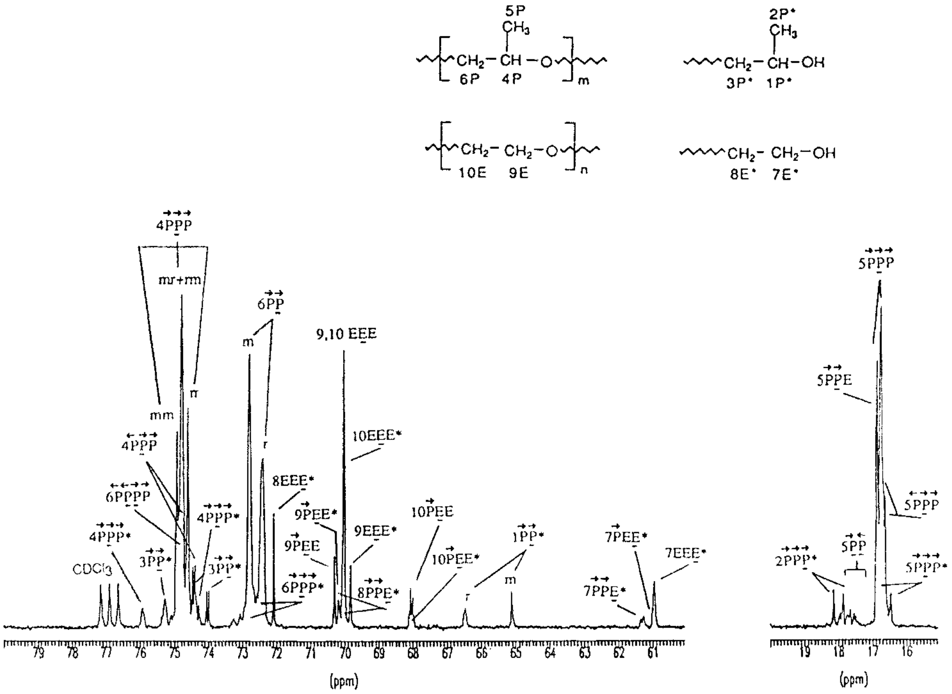


Figure 7: ^{13}C NMR spectrum of Synperonic® L-31 ($CDCl_3$)

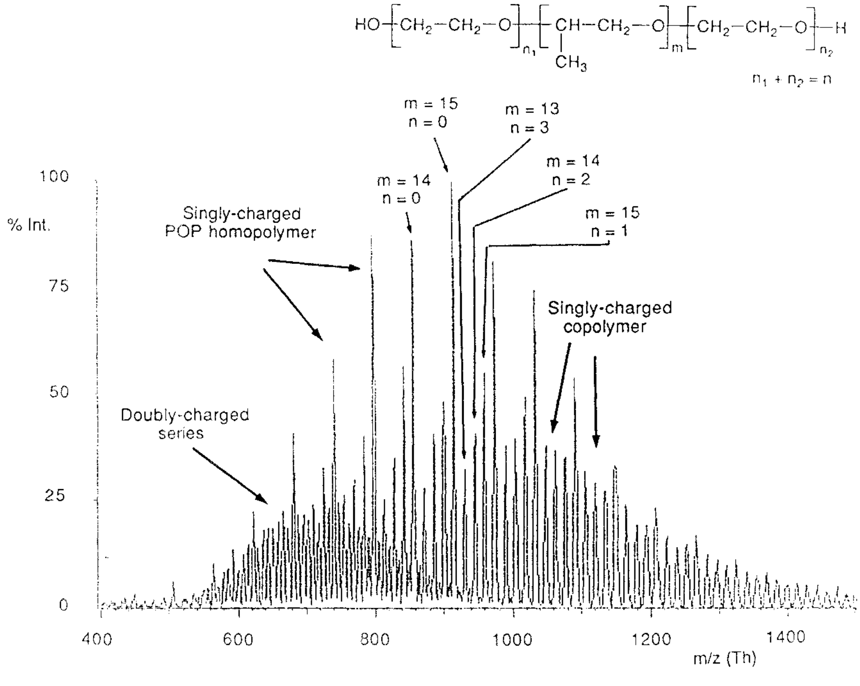


Figure 8: Positive-ion ESI mass spectrum of Synperonic® L-31

TABLE 6. Mass Spectrometry Study of Synperonic® L-31 . $\overline{M_n}$ and $\overline{M_w}/\overline{M_n}$ Determination o f POPdOH and Copolyether Fractions Constituting the Sample.

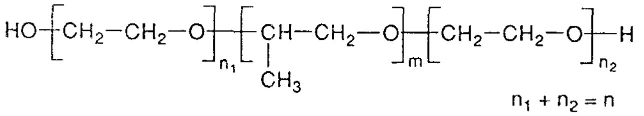
	POPdOH fraction (40 %)			copolyether fraction (60 %)			total sample
	singly-charged	doubly-charged	global	singly-charged	doubly-charged	global	
$\overline{M_n}$	900	1310	965	930	1460	1025	1000
$\overline{M_w}/\overline{M_n}$	1.04	1.01	1.05	1.04	1.02	1.07	1.07

relative to $C^{7EE\underline{E}*}$ indicating that this sample contains mainly POE-POP-POE triblock structure.

The analysis of copolyether ESI mass spectra perfected the structural study of these compounds. In the particular case of the Synperonic® L-31 mass spectrum (Figure 8), we observe three peak series. The most intense series has a separation between peaks of 58 m/z units and corresponds exactly to the singly-charged POPdOH homopolymer. The second series is characteristic of singly-charged ion species of block copolyethers. The third series whose peaks are smaller than those of the other two, is relative to doubly-charged species of POPdOH homopolymer and block copolyethers. So, each peak can be attributed to one well-defined macromolecule. The average molar masses of the homopolymer and of the copolymers constituting the Synperonic® L-31 sample were determined from mass spectrometry data and are given in Table 6. The total molar mass ($\overline{M_n}$) of this sample was calculated and this value is consistent with the one obtained by ^{1}H NMR and SEC (Table 4). Moreover, this study permitted us to determine the percentages (in number) of homopolyether and copolyether contained in the sample; they are 40 and 60%, respectively.

Nevertheless, the ^{1}H NMR analysis revealed that the ends of the chains of Synperonic® L-31 were formed of OE (50%) and OP (50%) units; these values and those obtained from mass spectrometry lead to the accurate molar composition of this sample: POP homopolymer (40%), POP-POE diblock copolymer (20%) and POE-POP-POE triblock copolymer (40%).

The Synperonic® L-35 mass spectrum (Figure 9) exhibits only one peak series assigned as doubly-charged ions (its molar mass is twice as high as



$HO-[CH_2-CH_2-O]_{n_1}-[CH(CH_3)-CH_2-O]_m-[CH_2-CH_2-O]_{n_2}-H$

$n_1 + n_2 = n$

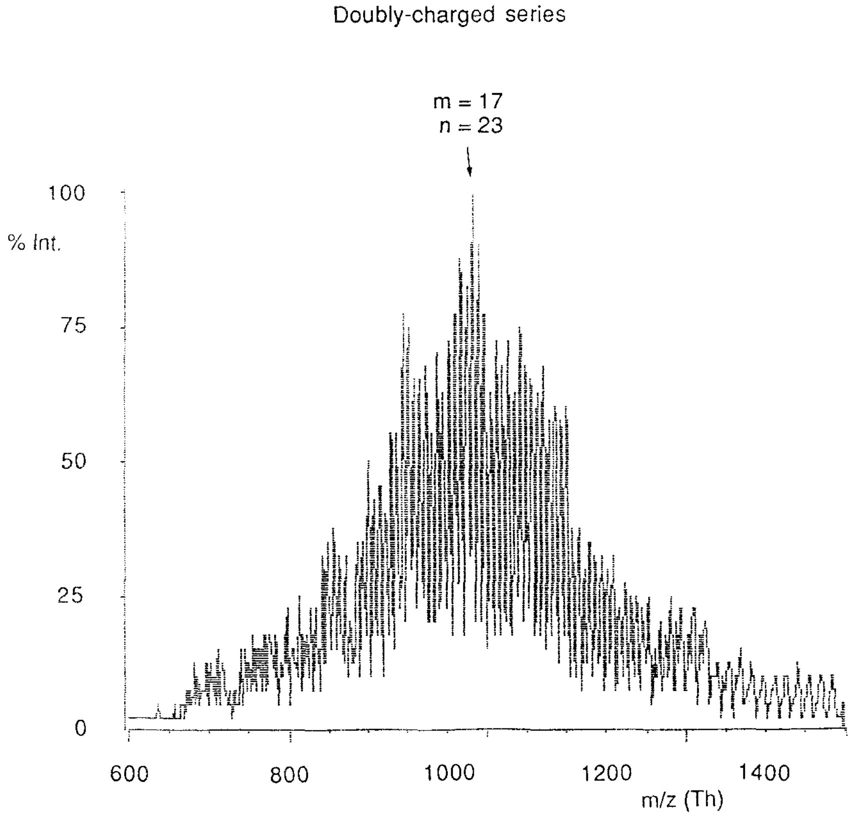


Figure 9: Positive-ion ESI mass spectrum of Synperonic® L-35

TABLE 7. Percentages (% in number) of POP, POP-POE and POE-POP-POE in Copolyethers.

sample	%		
	POP	POP-POE	POE-POP-POE
Synperonic® L-31	40	20	40
Pluronic® 3100	40	50	10
Pluronic® 6100	35	40	25

Synperonic® L-31). No POP homopolymer peaks are detected. So, this sample contains 80% POE-POE-POE triblock copolyether and 20% POP-POE diblock copolyether.

All the studied samples contain less than 10% of POP homopolymer with the exception of Synperonic® L-31, Pluronic® 3100 and 6100 (Table 7).

CONCLUSION

The two analytical methods, ^{1}H NMR and MS, are complementary to one another to provide comprehensive structural informations of the copolyethers such as the nature of end groups, the percentage of POP homopolymer in the samples, the OE/OP ratio and the molar mass. These results are essential to analyze the block polycondensation kinetics.

The nature of the different stereochemical enchainments present in the POP block can be easily identified from ^{13}C NMR analysis.

ACKNOWLEDGEMENTS

The authors thank Professor J.C. Tabet and Doctor B. Duretz, Laboratoire de Chimie Structurale Organique et Biologique, Université Pierre et Marie Curie, for ESI mass spectrometry measurements. They also acknowledge ICI and BASF for providing Synperonic® and Pluronic® samples, respectively.
Alya Boulares gratefully acknowledges the "Société des Amis des Sciences" for financial support.

REFERENCES

[1] G. Deleens, P. Foy, and E. Maréchal, *Eur. Polym. J.*, *13*, 337, 343, 353 (1977).
[2] C. Leriche, C. Michaud, and E. Maréchal, *Bull. Soc. Chim. (Chim. Mol.)*, *717* (1977).
[3] A. Fradet and E. Maréchal, *Eur. Polym. J.*, *14*, 749, 755, 761 (1978).
[4] P. J. Madec and E. Maréchal, *J. Polym. Sci.*, *16*, 3157, 3165 (1978).
[5] M. Tessier and E. Maréchal, *Eur. Polym. J.*, *20*, 281 (1983).
[6] A. Pourjavadi, P. J. Madec, and E. Maréchal, *Eur. Polym. J.*, *20*, 305, 311 (1984).

[7] D. Gagnebien, P. J. Madec, and E. Maréchal, *Eur. Polym. J.*, *21*, 273, 289, 301 (1985).

[8] P. Laporte, A. Fradet, and E. Maréchal, *J. Macrom. Sci.*, *A24*, 1289 (1987).

[9] G. Torres, P. J. Madec, and E. Maréchal, *Makromol. Chem.*, *190*, 203, 2789 (1989).

[10] M. Tessier and E. Maréchal, *J. Polym. Sci. Polym.Chem. Ed.*, *27*, 539 (1989).

[11] P. J. Madec, R. Pérès, and E. Maréchal, *Makromol. Chem., Macromol. Symp.*, *47*, 35 (1991).

[12] T. Nykolyszak, A. Fradet, and E. Maréchal, *Makromol. Chem.*, *193*, 2231 (1992).

[13] T. Galcera, A. Fradet, and E. Maréchal, *Makromol. Chem. Macrom. Symp.*, *47*, 35 (1991).

[14] M. Acevedo and A. Fradet, *J. Polym. Sci. Polym. Chem. Ed.*, *31*, 1579 (1993).

[15] P. Thuillier, M. Tessier, and E. Maréchal, *Makromol. Chem. Makromol. Symp.*, *70/71*, 37 (1993); *Molecular Crystals and Liquid Crystals Science and Technology*, Section *A254*, 1 (1994).

[16] T. Galcera, A. Fradet, and E. Maréchal, *Eur. Polym. J.*, *31*, 733 (1995).

[17] A. Boulares, M. Tessier, and E. Maréchal, Part II, to be published.

[18] V. Girardon, M. Tessier, and E. Maréchal, *Eur. Polym. J.*, in press.

[19] F. Heatley, Y. Z. Luo, J. F. Ding, R. H. Mobbs, and C. Booth, *Macromolecules*, *21*, 2713 (1988).

[20] Z. Yong and M. Wu, *Gaofenzi Xuebao*, *6*, 401 (1988).

[21] J. M. Goldwasser, and H. G. Adolph, *Polym. Eng. Sci.*, *26*, 1510 (1986).

[22] M. D. Bruch, F. A. Bovey, R. E. Cais, and J. H. Noggle, *Macromolecules*, *18*, 1253 (1985).

[23] K. Miura, T. Kitayama, K. Hatada, and T. Nakata, *Polym. J.*, *25*, 697 (1993).

[24] P. Thuillier, *Ph. D. Thesis*, University P. et M. Curie, Paris 1992.

[25] C. Campbell, F. Heatley, G. Holcroft, and C. Booth, *Eur. Polym. J.*, *25*, 831 (1989).

[26] F. C. Schilling and A. E. Tonelli, *Macromolecules*, *19*, 1337 (1986).

[27] J. Kriz and J. Stehlicek, *Macromol. Chem. Phys.*, *195*, 3877 (1994).

[28] R. J. Cotter, J. P. Honovich, J. K. Olthoff, and R. P. Lattimer, *Macromolecules*, *19*, 2996 (1986).

[29] G. Montaudo, M.S. Montaudo, C. Puglisi, and F. Samperi, *Macromolecules*, *28*, 4562 (1995).

[30] R. M. Whittal, L. Li, S. Lee, and M. A. Winnik, *Macromol. Rapid Commun.*, *17*, 59 (1996).

[31] U. Bahr, A. Deppe, M. Karas, F. Hillenkam, and U. Giessmann, *Anal. Chem.*, *64*, 2866 (1992).

[32] K. B. Sherrard, P. J. Marriott, M. J. McCormick, R. Colton, and G. Smith, *Anal. Chem.*, *66*, 3394 (1994).

[33] R. B. Cody, J. Tamura, and B. D. Musselman, *Anal. Chem.*, *64*, 1561 (1992).

[34] Z. Barton, T. J. Kemp, A. Buzy, and K. R. Jennings, *Polymer*, *36*, 4927 (1995).

[35] B. Duretz, *Ph.D. Thesis*, University P. et M. Curie, Paris 1995.

Received November 10, 1998
Revision received February 10, 1998