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Synthesis and NMR study of some aliphatic block and branched α,ω-dihydroxy polyesterethers

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SUMMARY

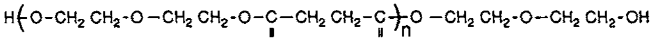
The following dihydroxy linear, branched and block polyesterethers: α,ω-dihydroxy-poly(di(oxyethylene)oxysuccinyl) (**1**), -poly(tri(oxy-ethylene)oxysuccinyl) (**2**), -poly(oxyethylene-oxysuccinyl)-block-poly(oxyethylene) (**3**), and -poly(oxy-3-(2-methoxyethoxy)propyleneoxysuccinyl) (**4**) have been synthetized using polytransesterification reactions. Their NMR spectra have been assigned and compared.

INTRODUCTION

In order to establish relations between the structure of some binders and their swelling properties in organic solvents, we studied the synthesis of several block or branched polyesterethers with hydroxy end groups. When reacted with diisocyanates these oligomers give networks whose properties were expected to depend on the oligomer structure. As all oligomers were reacted with the same diisocyanate, the swelling properties of the networks, determined for the same crosslinking density, are governed by the compatibility of the prepolymer with the solvent. This can be studied by reverse gas chromatography using the prepolymer as stationary phase; these studies will be reported in a forthcoming paper.

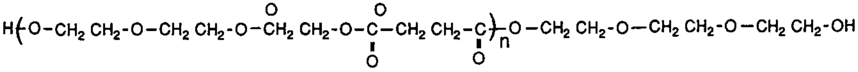
The present article describes the synthesis and the NMR study of α,ω-dihydroxy-poly(di(oxyethylene)oxysuccinyl) (**1**), -poly(tri(oxy-ethylene)oxysuccinyl) (**2**), -poly(oxyethyleneoxysuccinyl)-block-poly(oxyethylene) (**3**), and -poly(oxy-3-(2-methoxyethoxy)propyleneoxysuccinyl) (**4**):

1 :



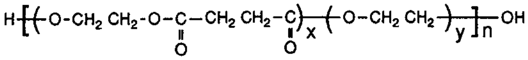
$$H\!\left(O-CH_2CH_2-O-CH_2CH_2-O-\underset{\underset{O}{\|}}{C}-CH_2CH_2-\underset{\underset{O}{\|}}{C}\right)_n O-CH_2CH_2-O-CH_2CH_2-OH$$

2 :



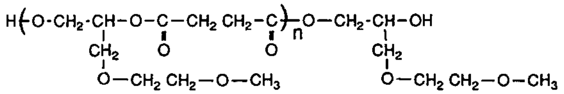
$$H\!\left(O-CH_2CH_2-O-CH_2CH_2-O-CH_2CH_2-O-\underset{\underset{O}{\|}}{C}-CH_2CH_2-\underset{\underset{O}{\|}}{C}\right)_n O-CH_2CH_2-O-CH_2CH_2-O-CH_2CH_2-OH$$

3 :



$$H\left[\left(O-CH_2CH_2-O-\underset{\underset{O}{\|}}{C}-CH_2CH_2-\underset{\underset{O}{\|}}{C}\right)_x\left(O-CH_2CH_2\right)_y\right]_n OH$$

4:



$$H\!\left(O-CH_2-\underset{\underset{O-CH_2CH_2-O-CH_3}{|}}{\underset{CH_2}{\underset{|}{CH}}}-O-\underset{\underset{O}{\|}}{C}-CH_2CH_2-\underset{\underset{O}{\|}}{C}\right)_n O-CH_2-\underset{\underset{O-CH_2CH_2-O-CH_3}{|}}{\underset{CH_2}{\underset{|}{CH}}}-OH$$

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RESULTS

α,ω-dihydroxy polyesterethers 1, 2 and block polyesterether 3.

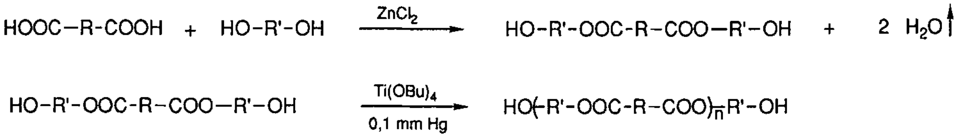
Synthesis

Low molecular weight (Mn ≈ 1000 to 2000) α,ω-dihydroxy-polyesters without residual carboxy end groups were prepared by a three step transesterification[1] including:

(I) The formation of the dihydroxy diester of starting diacid in the presence of an excess of diol, until all carboxyl groups are reacted,

(II) the distillation of diol.in excess,

(III) the polytransesterification of the diester:



$$HOOC{-}R{-}COOH + HO{-}R'{-}OH \xrightarrow{ZnCl_2} HO{-}R'{-}OOC{-}R{-}COO{-}R'{-}OH + 2\ H_2O\uparrow$$

$$HO{-}R'{-}OOC{-}R{-}COO{-}R'{-}OH \xrightarrow[0{,}1\ mm\ Hg]{Ti(OBu)_4} HO(R'{-}OOC{-}R{-}COO)_n R'{-}OH$$

The formation of diester is catalyzed by $ZnCl_2$ and the polytransesterification by $Ti(OBu)_4$. This catalyst cannot be used in the first step since the medium contains non-negligible amounts of reaction water which may lead to the formation of condensates (titanoxanes) of low catalytic activity[2,3]. This reaction path results in the formation of dihydroxy polyesters with a very low amount of residual carboxyl groups.

Block polyesterether **3** was obtained by reacting a mixture of α,ω-dihydroxy-polyoxyethylene (Mn ≈ 400) and of ethylene glycol with succinic acid. The relative amounts of reactants were chosen in order to obtain a product containing 50% (wt) of polyoxyethylene.

End groups concentration and molecular weight values obtained by different methods are reported in table 3.

NMR study

The spectra relative to linear polysuccinates **1**, **2** and **3** were easily assigned by comparison with those of known compounds; assignments are given by figs 1 and 2, and table 1. They fit the expected formulae.

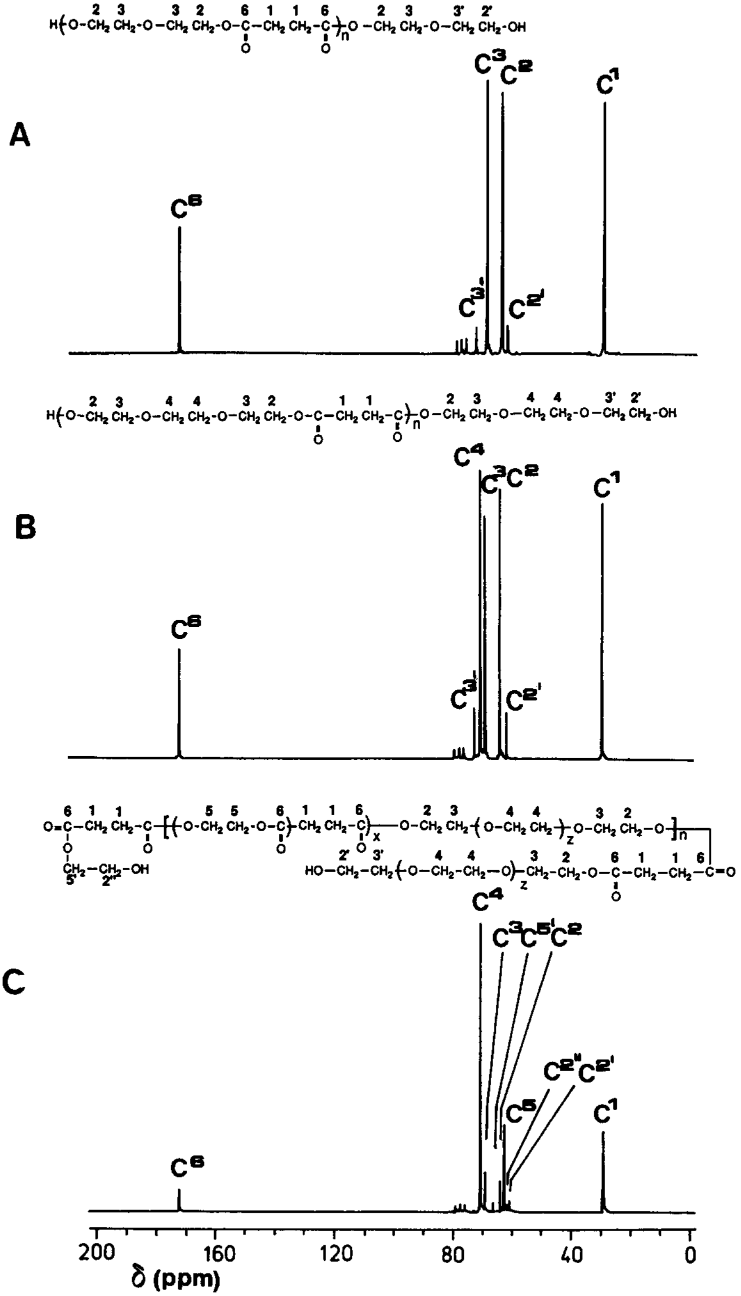


Figure 1: ^{13}C NMR spectra ($CDCl_3$, 20,15 MHz, ref. TMS) of : **1** (A), **2** (B) and **3** (C).

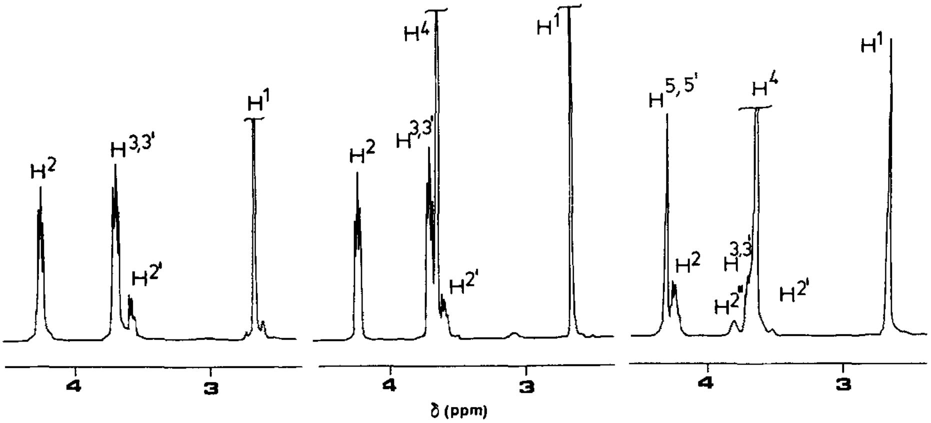


Figure 2: ^1H NMR spectra ($CDCl_3$, 250 MHz, ref. TMS) of : **1** (A), **2** (B) and **3** (C). Numbering: see Fig 1.

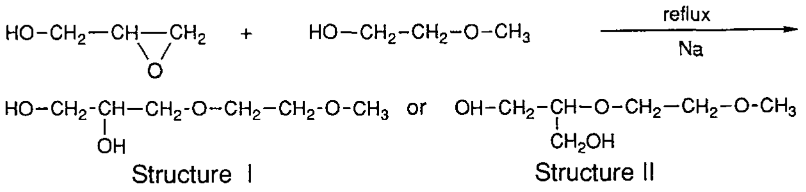
Table 1 : ^1H ($CDCl_3$, 250 MHz, ref TMS) and ^{13}C ($CDCl_3$, 20,15 MHz, ref TMS) NMR spectra of polyesterethers **1** to **3**. Chemical shifts δ (ppm) and assignments. Numbering of atoms is given in corresponding spectra.

Group Assignment	δ_H			δ_C		
	1	**2**	**3**	**1**	**2**	**3**
1	2,67	2,66	2,67	28,43	28,49	28,49
2	4,24	4,24	4,24	63,13	63,13	63,41
3	3,70	3,70	3,70	68,36	68,42	68,58
4		3,65	3,65		69,96	70,13
5			4,30			61,92
6				171,57	171,41	171,63
2'	3,57	3,59	3,59	60,98	60,98	61,20
2"			3,80			60,21
3'	3,70	3,70	3,70'	71,94	73,00	
5'			4,30			65,83

Poly(oxy-3-(2-methoxyethoxy)propyleneoxysuccinyl) 4.

Synthesis

3-(2-methoxyethoxy)propanediol (starting diol) was synthesized by reaction of 2,3-epoxypropanol with 2-methoxyethanol:



The GPC chromatogram of this compound exhibits only one peak showing that the epoxide did not polymerize. Depending on the orientation of the oxirane ring opening, the diol may be primary-secondary (structure I) or primary-primary (structure II). Its ^{13}C NMR spectrum (Fig 3) shows that only structure I has been obtained since only 6 resonances are observed, and since the peaks at 63,8 and 70,9 ppm can be assigned to the carbons of $-CH_2-OH$ and of $-\underset{|}{C}H-OH$ respectively. This is confirmed by the esterification of the product by succinic acid which leads to the quantitative formation of secondary ester $-COO-\underset{|}{C}H^3-$, whose H^3 resonance can be easily identified in the ^{1}H NMR spectrum. The resonances of the $-CH_2-O-$ carbons in the side diether chain are well separated, but cannot be unambiguously assigned.

Some characteristic features of the ^{1}H NMR spectrum were identified: (I) the methoxy group at 3,39 ppm, (II) between 3,5 and 3,7 ppm, the superposition of the A_2B_2 system of $-CH_2{}^5-CH_2{}^6-$ and of the AB system of $-CH_2{}^4-O-$ whose the two protons are not equivalent due to the neighbourhood of asymetric carbon 3, (III) the AB system of non-equivalent protons of $-CH_2{}^2-OH$ near 4,3 ppm, and (IV) at 3,9 ppm the complex resonance of $-\underset{|}{C}H^3-$ which is coupled with H^2 and H^4.

The polymer is obtained by polytransesterification of bis(3-(2-methoxyethoxy)propanediyl succinate in the same way as above. End group analysis and molecular weights are reported in table 3.

The ^{1}H NMR spectrum of **4** can be assigned more easily than the spectrum of the starting diol since the resonances of $-COO-\underset{|}{C}H-$ and $-COO-CH_2-$ are are not superimposed to those of ether groups (Fig 4, table 2).

Table 2: ^{1}H NMR spectrum ($CDCl_3$, 250 MHz, ref. TMS) of branched polyesterether **4**. Chemical shifts δ_H (ppm) and assignments. For the numbering of atoms, see the corresponding spectrum (Fig.4).

Assignment	H^1	H^2	H^3	H^4	H^5	H^6	H^7	$H^{2'}$	$H^{3'}$	$H^{3''}$
δ_H	2,65	4,22	5,21	3,62	3,64	3,51	3,37	4,05	5,09	3,79

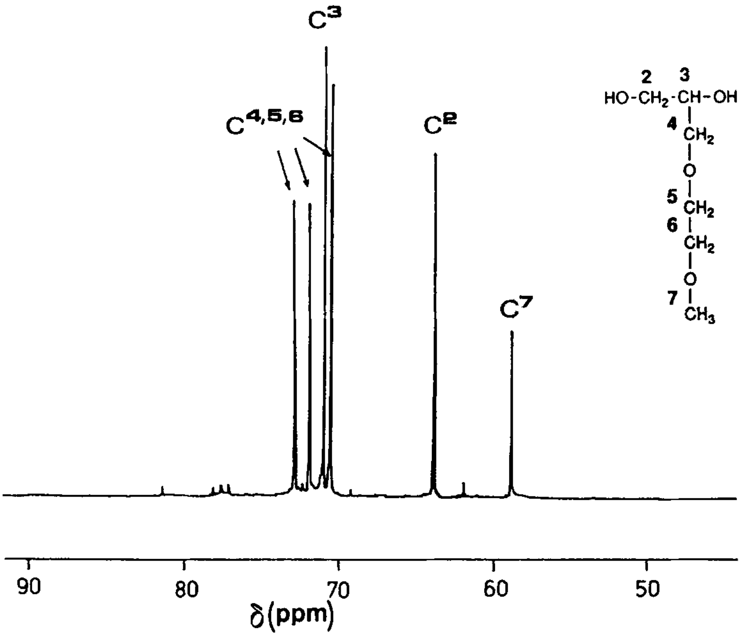


Figure 3: ^{13}C NMR spectra ($CDCl_3$, 20,15 MHz, ref. TMS) of 3-(2-methoxyethoxy)-1,2-propanediol.

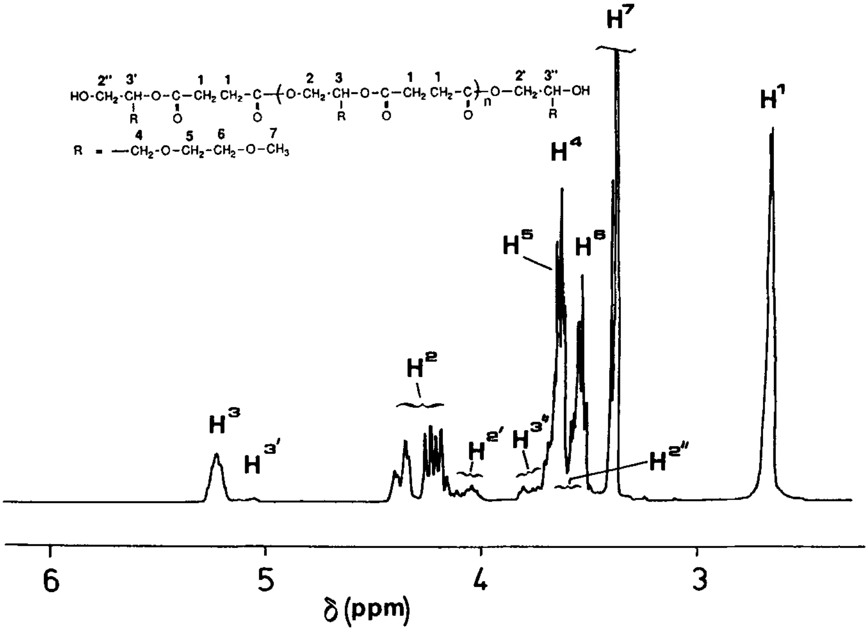


Figure 4: ^{1}H NMR spectra ($CDCl_3$, 250 MHz, ref. TMS) of **4**.

The compatibility of polymers **1-4** with triacetin has been studied by reverse gas chromatography. The corresponding interaction parameters were determined and used to compare their properties with those of linear polyesters, polyethers or polycarbonates. This study will be soon reported.

EXPERIMENTAL

*Synthesis of polyesterethers **1** and **2** .*

Succinic acid (118 g, 1 mol) and 4 mol of diol (diethylene or triethylene glycol) are reacted under nitrogen in the presence of 0,1% of $ZnCl_2$ (wt) at 170°C for 24 h. Water is formed in amount corresponding to the theory and the residual carboxyl group concentration becomes lower than 0,02 $mol \cdot kg^{-1}$. The diol in excess is distillated off under vacuum, then $Ti(OBu)_4$ (150 ppm) is added and the mixture is heated to 140 - 180°C under 0,1 mm Hg. The extent of reaction is monitored by GPC . End group titrations and molecular weights are reported in table 3.

*Synthesis of block polyesterether **3**.*

Succinic acid (118 g, 1 mol), dihydroxy polyoxyethylene (Mn ≈ 400; 0,3 mol) and ethylene glycol (248 g, 4 mol) are reacted under nitrogen in the same experimental conditions as above. End group concentrations and molecular weights are reported in table 3.

Synthesis of 3-(2-methoxyethoxy)-1,2-propanediol.

2-methoxyethanol (482,5 g, 6 mol) are refluxed over sodium (6,9 g, 0,3 mol) for 0,5 h. 2,3-epoxypropanol (93,9 g, 1,25 mol) is introduced dropwise in the medium and the reflux maintained for 3 h. The excess of 2-methoxyethanol is distilled off and the 3-(2-methoxyethoxy)-1,2-propanediol is distilled under vacuum (2,5 mbar, 120°C). End group concentrations and molecular weights are reported in table 3.

*Synthesis of branched polyesterether **4**.*

3-(2-methoxyethoxy)-1,2-propanediol (90 g, 0,6 mol) and succinic acid (23,6 g, 0,2 mol) are reacted in the experimental conditions used for **1-3**. End group concentrations and molecular weights are reported in table 3.

End group titrations:

Carboxy end groups were titrated in acetone solution with alcoholic potassium hydroxide (0,1N). Hydroxy end groups were titrated by acetylation with acetic anhydride in pyridine followed by a back titration of carboxyl groups in excess.

Vapour pressure osmometry was carried out on a Knauer apparatus.

Table 3: End group titrations and molecular weight determinations for polymers **1-4**.

	[COOH] mol·kg^{-1}	[OH] mol·kg^{-1}	$\overline{Mn}$ (end groups)	M_{peak} GPC	$\overline{Mn}$ (vapour pressure osmometry)	$\overline{Mn}$ ^1H NMR
1	0,06	2,20	890	1750	890	950
2	0,03	1,50	1250	1850	1000	1300
3	0,05	1,10	1810	2200	1000	
4	0,08	1,10	1820	2000		

^1H and ^{13}C NMR spectra were recorded on 250 FT and 80 FT Bruker spectrometers respectively.

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1) D. Judas, A. Fradet and E. Maréchal, Makromol. Chem **184,** 1129 (1983).
2) A. Fradet and E. Maréchal, J. Macromol. Sci. Chem. **A17,** 881 (1982).
3) F. Leverd, A. Fradet and E. Maréchal, Eur. Polym. J. in press.

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