

Synthesis of Monocarboxylic Polyoxyethylenes

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Summary

The various methods of synthesis which can be used to prepare ω -carboxy polyoxyethylenes are reviewed. The synthesis and the purification of α -methoxy ω -carboxy polyoxyethylenes ($\overline{M}_n \approx 1000$) are reported. The process consists of the reaction of halogenoacetic acids with an α -methoxy ω -sodium hydroxylate polyoxyethylene followed by a purification by extraction. α, ω -dimethoxy and α -methoxy ω -ethyl carboxylate polyoxyethylenes were synthesized.

Introduction

α -Methoxy ω -carboxy polyoxyethylenes and α -methoxy ω -hydroxy polyoxyethylenes are suitable models for the study of the kinetics of polyesterification in the melt. The use of these oligomers presents two advantages for kinetic studies. The first is that experimental conditions can be close to those used in industrial polyesterifications : high temperatures , low pressures, macromolecular medium. The second is that polyesterification can be carried out in conditions where kinetics studies have a meaning : concentrations of the reactive groups which are not too high and very small changes in the dielectric properties of the medium during the whole course of the reaction.

Synthesis of functional polyoxyethylenes

Bibliographic study

Monohydroxylic polyoxyethylenes can be obtained easily from ethylene oxide by initiating the polymerization with alcohols in the presence of anionic species.

In contrast to ω -hydroxy polyoxyethylenes , only very little information can be found, in literature, on the synthesis of carboxylic polyoxyethylenes, and nothing at all about their purification.

Two synthetic routes can be considered :

- Direct oxidation of hydroxyl groups to carboxyl. The resulting compounds contain α -alkoxyethanoic end groups : $-O-CH_2-COOH$.

- Addition of hydroxyl groups onto a carboxylic compound or one of its precursors. Such a synthesis can give any alkoxy-carboxylic end groups depending on the nature of the adduct.

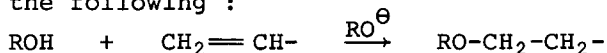
1- Direct oxidation :

Oxidisers such as CrO_3 or $K_2Cr_2O_7/H_2SO_4$ (Coleman 1959, Chem-Y Fabrik 1964) or HNO_3 in the presence of ammonium vanadate (Ash and Jackson 1953) can be used. Some references are relative to the first terms of the series ($\overline{DPn} < 5$) ; oxidisers can be the system $NaOCl / CoCl_2$ (Edwards et al. 1966) or O_2/Pt (Fuhrmann et al. 1967) .

Because polyoxyethylenes are very sensitive to oxidation, chain breaks cannot be avoided and, in our opinion, this method is not suitable for the synthesis of the well defined monocarboxylic compounds required by kinetic studies.

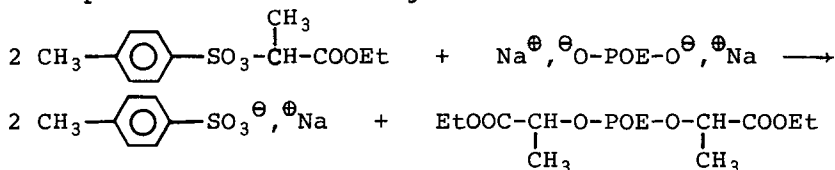
2- Reaction of the hydroxyl end groups of polyoxyethylenes :

- Addition on double bonds : This method was used with good yields to prepare alkyl β -alkoxypropanoates either from acrylates (Purdie 1891 ; Rehberg et al. 1946 1947, 1950 ; Dixon et al. 1948) or from acrylonitrile (Vogel et al. 1952 ; Andrews et al. 1966) . The reaction scheme is the following :



However yields decrease with increasing length of R- (Dixon et al. 1948) . We never obtained good yields by using this method.

- Interchange with ethyl 2-(4-toluenesulfonyloxy)propanoate (Geckeler and Bayer 1979) : This corresponds to the following reaction :

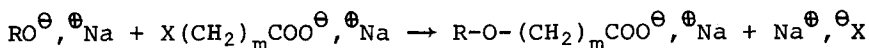


The carboxylic derivative was obtained by saponification of the oligomeric ester. However it was not separated from the residual hydroxy derivatives .

- Reactions with halogenated acids or esters:

This method is the most widely used for the

synthesis of alkoxyalkanoic acids :



In the case of polyoxyethylenes only limited information is available and the resulting compounds are never purified. Moreover references are relative to very low molecular weight polyoxyethylenes (Sandoz Ltd 1958) .

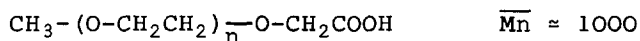
Palomaa's work (1909, 1911, 1917, 1930, 1931) relative to the synthesis and the purification of the following compounds:

$R-O-(CH_2CH_2O)_n-CH_2COOH$ $n = 1 \text{ or } 2$, $R = CH_3, C_2H_5$
is worth mentioning .

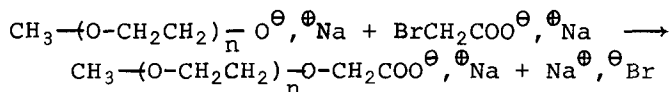
In principle this method allows synthesis of alkoxypropanoic acids. However the reactant must be an ester because the acid readily undergoes deshydrohalogenation (Palomaa 1912 ; Hamonet 1901 ; Jones and Powers 1924) . Unfortunately the yields are low and in some cases iodopropanoic esters are needed (Palomaa 1910) . Moreover the saponification which is necessary to obtain free carboxyl end groups considerably decreased our interest for this method.

Results and discussion

From bibliographic analysis and after preliminary studies we synthesized the following compounds:



by reaction of sodium chloracetate or bromacetate with ω -sodium hydroxylate polyoxyethylene according to :



ω -hydroxy polyoxyethylene was obtained by initiating ethylene oxide polymerization by 2-(2-methoxyethoxy)-2-ethoxyethanol and NaOH. After purification the polymer has an hydroxyl content of 1.09 eq.kg^{-1} and a functionality $f = 1$.

Because the classical method of conversion of hydroxyl groups to hydroxylates by action of sodium is slow and incomplete we used sodium naphthalene which reacts readily at room temperature (Stevens and Deans 1939) . This method has already been used by Galin et al. (1965) . The introduction of the green coloured solution of sodium naphthalene in dimethoxyethane is stopped when a permanent green colour develops in the solution of polyoxyethylene in dimethoxyethane. This indicates that

all hydroxyls have reacted and that there is a slight excess of sodium naphthalene.

Sodium chloracetate or bromacetate are insoluble in the reaction medium and react slowly with the alcoholate, even when they are finely powdered. The use of chloracetic or bromacetic acids is more appropriate since they are readily transformed into "colloidal" precipitates of sodium chloracetate or bromacetate. An excess of sodium naphthalene reconverts the hydroxyls released by the action of acid on hydroxylates into hydroxylates. The conversion of hydroxyl to carboxyl groups was never above 60%. On the other hand when ethyl chloracetate or methyl iodide are used the medium is homogeneous and the reaction takes place immediately and gives the corresponding products with a quantitative yield.

The only chemical difference between ω -hydroxy and ω -carboxy polyoxyethylenes is the nature of end groups. These have the same physical properties. However when ω -carboxy polyoxyethylenes are converted to ω -sodium carboxylate polyoxyethylenes the latter are no longer soluble in chloroform. In consequence the hydroxy polymer can be extracted by chloroform from an aqueous solution of the mixture (pH 10). By acidification of the residual aqueous layer ω -carboxy derivative is obtained.

The product is very hygroscopic, its hydroxyl content is very low (below experimental error) and its carboxyl content (1.03 eq.kg^{-1}) wholly fits the value calculated from the hydroxyl content of the initial ω -hydroxy polyoxyethylene. The functionality is close to 1 and the polydispersity index is 1.09 as for the initial polymer. Infrared spectrum exhibits a band near 1710 cm^{-1} . Methylene protons in α of the carboxyl group give a peak at 4.1 p.p.m. in ^1H NMR spectrum (CDCl_3 , ref TMS). All these properties fit the expected structure.

In conclusion the method described in this article is a simple way of preparing carboxylated derivatives of polyoxyethylenes. By using our purification process, very pure α -methoxy ω -carboxy polyoxyethylene ($M_n = 970$ from end group titration) was isolated.

Experimental

1- α -Methoxy ω -hydroxy polyoxyethylene

This compound (Produits Chimiques Uguine Kuhlmann) was crystallized at -10°C from its solution in a 90/10 (volume) mixture of Et_2O and CHCl_3 then dried in vacuo for at least a week. It must be stored in dry ni-

trogen in the dark.

$I_{OH} = 1.09 \text{ eq.kg}^{-1}$, $I_{COOH} < 10^{-3} \text{ eq.kg}^{-1}$, \overline{Mn} (vapour pressure osmometry, acetone 42°C): 980, m.p. (DTA)=40.5°C

2- α -Methoxy ω -sodium hydroxylate polyoxyethylene

A mixture of α -methoxy ω -hydroxy polyoxyethylene (100 g, $\approx 0.1 \text{ mol}$) and dimethoxyethane (150 cm³) was dried over 4 Å molecular sieve for 48 h and poured into a reaction vessel fitted with stirring device, condensor and thermometer. A 2 eq.l⁻¹ solution of sodium naphthalene in dimethoxyethane was dropped into the stirred medium until a persistent green colour appears in the polyoxyethylene solution. The hydroxylate was not isolated from its solution (A) which was used for the following synthesis.

3- α -Methoxy ω -carboxy polyoxyethylene

A dry solution of bromoacetic acid (16g, 0.11 mol) in dimethoxyethane (25 cm³) was dropped into solution A (see above) simultaneously with a volume of sodium naphthalene solution equal to that used in the preceding synthesis. A finely powdered white precipitate of sodium bromoacetate and sodium bromide appeared. Temperature increased and was allowed to remain at 50°C for 1 h. After cooling and acidification with concentrated hydrochloric acid dimethoxyethane was distilled off. The resulting crude product (130 g) was mixed with water (100 cm³) and washed several times with Et₂O to eliminate naphthalene and bromoacetic acid in excess. The pH of the resulting aqueous layer was adjusted to 8 with 1N sodium hydroxide and extracted with chloroform (30 to 60 cm³/min) on a column packed with Raschig rings. The extraction was carried out for 6 hours. The residual aqueous layer was acidified (pH 4) then washed twice with diethyloxide and extracted with chloroform (5 times 100 cm³). The chloroform layers were mixed, washed with water (twice 100 cm³) then dried and evaporated. The resulting polyoxyethylene was crystallized at -10°C from its diethyloxide solution, then dried for a week under vacuo. It must be stored under nitrogen in a dry place and in the dark.

$I_{COOH} = 1.03 \text{ eq.kg}^{-1}$; I_{OH} is too low to be titrated by acetic anhydrid-pyridin method ; m.p. (DTA) = 36°C ; \overline{Mn} (vapour pressure osmometry, acetone 42°C) : 890 .

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