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# Functionalization of Soluble Polymers

## 4. Synthesis of Dichloro- and Di(4-Formylphenyloxyethyl) Poly(Oxyethylene)

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## Summary

Derivatives of poly(oxyethylene) with chlorine and aldehyde functions have been prepared by chemical modification in an one-step and two-step reaction respectively with thionyl chloride and 4-hydroxy benzaldehyde in excellent yields. The functionality of these important intermediates has been investigated spectroscopically and demonstrated by chemical conversion of the terminal groups.

## Introduction

Telechelic polymers represent important intermediates and have found great interest (KENNEDY et.al. 1979, GECKELER 1979, GECKELER and BAYER 1980). Their useful properties are the basis of various applications in organic chemistry and other fields (MUTTER 1978, GECKELER et al. 1982, ANZINGER and MUTTER 1982, BAYER et al. 1983).

Recently, we have reported the preparation of carboxyl derivatives of poly(oxyethylene) (GECKELER and BAYER 1980). The chlorine and aldehyde derivatives of soluble telechelic polymers are particularly attractive in view of their versatile application as basis polymers.

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The methods for the preparation of telechelic polymers presented here employ simple, high yield reactions applicable to commercially available poly(oxyethylene). We describe procedures for the transformation of hydroxyl groups of polymers into chlorine and aldehyde functions.

## Results and Discussion

The reaction scheme for the derivatives of poly(oxyethylene) (1) is outlined in Fig. 1. The dichloro product was prepared by a simple one-step reaction with thionyl chloride. For this reaction no solvents or other reagents were used and a substitution degree of practically 1.0 was obtained. In first attempts to prepare dihalides of (1) benzene as solvent and also molar quantities of pyridine were used (GALIN et.al. 1965) and the reaction was carried out under nitrogen (KOPPENHÖFER 1976). We have found that it is not neccessary to use these chemicals for this reaction, but it is more advantageous to use excess reagent as solvent. Thus we obtained product (2) with complete substitution which has been checked in three different experiments and elemental analyses. Additionally, we proved the functional availability of the telechelic groups by chemical reactions. In completion, we determined analytical and spectroscopic data of the compound and derivatives.

The procedure described avoids complex experimental techniques which are necessary for some other derivatives of (1) and results the polymer in over 95 % yield. Absence of excess reagent was tested with silver nitrate solution and no sulphur was found in compound (2) with the sodium nitroprusside test. This easily accessible derivative opens new possibilities of reac-

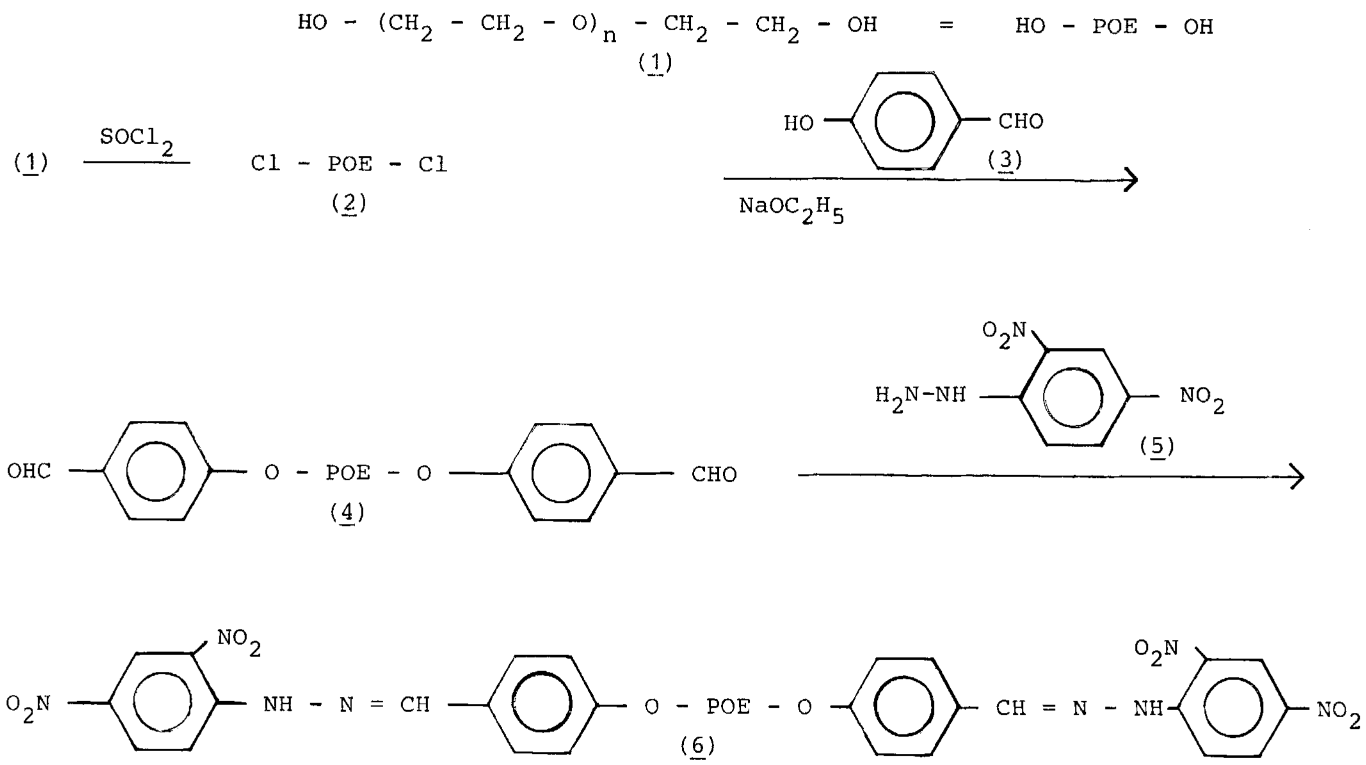

Fig. 1: REACTION SCHEME

tions in comparison to the hydroxyl group of (1). Several methods for the preparation of telechelic aldehydes have been tested. The most promising method seems to be the Williamson etherification by reaction with 4-hydroxy benzaldehyde (3). To this end, a sealed tube was used in a shaking apparatus with a thermostat in order to obtain good reaction conditions. Product (4) was isolated in 96 % yield and had a substitution degree of 0.91 referred to UV-spectroscopic analysis. Detailed studies on this reaction and their parameters will be reported in a separate paper (ZHENG et.al. 1983). The chemical identification of the terminal aldehyde groups of (4) is best done with 2,4-dinitro phenylhydrazine although we have also tested hydroxylamine and others. The main advantage of the use of (5) is the high nitrogen content of (6) what is essential for elemental analyses. These data of the orange polymer (6) correspond to spectroscopic investigations (see experimental part). The results show that (2) can be easily prepared with practically complete functionalization in an one-step reaction. Starting from (2) the aldehyde (4) is obtainable in excellent yields. It should be noted that all derivatives described are readily soluble in water as well as in most organic solvents.

## Experimental

The solvents and reagents were carefully purified and dried. Poly(oxyethylene) ($\bar{M} = 1500$) and 4-hydroxy benzaldehyde (both from Fluka Feinchemikalien GmbH, Neu-Ulm) were purified twice by precipitation with ether (1) or recrystallization from water (3). Thionyl chloride was distilled twice directly before use.

T.l.c. was performed with silica gel plates (Merck 60 $F_{245}$) and the solvent system acetic acid/n-butanol/ water (3:1:1, v.). Detection reagents were the Dragendorff-Bürger reagent and for the aldehyde (4) a solution of 2.4-dinitro phenylhydrazine (0.4 g in 3 ml water, 2 ml sulfuric acid and 10 ml ethanol).

IR-spectra were measured on a Perkin-Elmer Model 281 B spectrometer, UV-measurement were performed with a Zeiss M4Q III and elemental analyses with a Elemental Analyzer Model 1104 (Carlo Erba). Elemental analyses were performed three times from different experiments with the same exact results for (2) (maximal deviation for chlorine 1.25 % from this value).

### Dichloro poly(oxyethylene) (2)[1)]

50.0 g (33.3 mmol) of poly(oxyethylene) (1) were dissolved in 100 ml thionylchloride at room temperature under stirring. After refluxing the solution in an oil bath over night, excessive thionylchloride was removed by distillation from the clear, slight yellow solution. Then, 50 ml of toluene and of dichloromethane were added and redistilled separately. For precipitation, the residue was dissolved in dichloromethane (200 ml) and 2 l of diethylether were added at room temperature and then stirred in an ice-bath. After storage at 4°C over night, the white solid was dissolved, reprecipitated and dried.

Yield: 48.3 g (96 %)

m.p.: 47-48°C

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[1)] Systematic name: Poly(oxy-1.2-ethanediyl)-$\alpha$-(2-chloroethyl)-$\omega$-(2-chloroethoxy)

$C_{66}H_{132}Cl_2O_{32}$ (1508)

| | | | | |
|---|---|---|---|---|
| Elemental analysis: | Calcd | C 52.54 | H 8.82 | Cl 4.71 |
| | Found | C 52.34 | H 8.78 | Cl 4.75 |

Conversion: 100 % (referred to Cl-analysis)

IR(KBr): 1465, 1340 (s;$CH_2$), 1110 (vs;C-O-C), 740, 660 (m;Cl) $cm^{-1}$.

## Di(4-formylphenyl oxyethyl) poly(oxyethylene) (4)

2.44 g (20 mmol) of 4-hydroxy benzaldehyde (3) were dissolved in a solution of sodium ethoxide (0.46 g; 20 mmol) in ethanol (4 ml). 6.0 g (4 mmol) of (2) were added under stirring in a tube which was cooled (liquid nitrogen) and sealed in vacuo. The reaction was carried out in a shaking apparatus with a thermostat at 130°C. After 15 h, the solution was cooled, filtered, adjusted to pH 5 with 6 N HCl, and 200 ml of ether added for precipitation. Then, after cooling, the product was filtered off, dissolved in dichloromethane (200 ml), reprecipitated with ether and dried.

Yield: 5.6 g (84 %)

m.p.: 37-39°C

Conversion: 91 % (UV)

UV(EtOH): $\varepsilon_{max}$ ($\lambda$ = 274 nm) = $1.57 \cdot 10^4$ $L \cdot cm^{-1} mol^{-1}$

IR(KBr): 1695 (m;CHO), 1600, 1506 (m;$C_6H_4$), 1460, 1350 (s;$CH_2$), 1100 (vs;C-O-C) $cm^{-1}$.

## 2.4 - Dinitrophenyl hydrazone of Di(4-formylphenyloxyethyl) poly(oxyethylene) (6)

To a solution of 0.80 g (0.5 mmol) of (4) in ethanol (2 ml), 2.4-dinitro phenylhydrazine reagent (8 ml) was added and stirred at 60°C overnight. By addition of ether (100 ml) to the red solution the product precipitated as a red oil. Adding sodium sulfate resulted a solid which was filtered off and dissolved in dichloromethane (5 ml). Reprecipitation, filtration and drying yielded the orange polymer.

Yield: 0.92 g (90 %)

m.p.: 31-32°C

| Elemental analysis: | Calcd | N 5.42 |
|---|---|---|
| | Found | N 5.00 |

Conversion: 91 % (referred to N-analysis)

IR(KBr): 1618 (s;C=N), 1505 (m;$NO_2$), 1465, 1340 (s;$CH_2$)
1100 (vs;C-O-C) $cm^{-1}$.

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