Polymer Bulletin 1, 691–695 (1979)

Polymer Bulletin

Functionalization of Soluble Polymers

2. Substitution of the Hydroxyl Groups of Poly(oxyethylene) by Carboxyl Groups

Kurt Geckeler and Ernst Bayer

Institut für Organische Chemie der Universität, Auf der Morgenstelle 18,
7400 Tübingen, Federal Republic of Germany

Summary

In a second example of the functionalization of soluble polymers the conversion of the hydroxyl groups of poly(oxyethylene) into carboxyl groups is reported. As protected carboxyl component, 4-toluenesulfonyl lactic acid ethyl ester was synthesized and was allowed to react with sodium salt of poly(oxyethylene). Polymer-analogous hydrolysis of the di(lactic acid ethyl ester) poly(oxyethylene) yielded the carboxyl derivative of poly(oxyethylene).

Introduction

The first communication in this series dealt with the replacement of the hydroxyl groups of poly(oxyethylene) by amino groups via reaction with 2-bromoethyl phthalimide and subsequent polymer-analogous hydrazinolysis (GECKELER 1979a). Synthesis and application of functionalized soluble polymers have recently attracted great attention (BATZ 1977, HUBERT et al. 1977, MUTTER 1978, DAS et al. 1979, GECKELER et al. 1979b, JOPPICH and LUISI 1979). In the course of our fundamental studies on the functionalization of soluble polymers we examined the introduction of other functional groups into macromolecules. In this paper we report the replacement of the terminal hydroxyl groups of bifunctional poly(oxyethylene) by carboxyl groups.

Experimental

The solvents were purified and dried by the usual manner. Thin layer chromatography (tlc) was carried out with silica gel plates (Merck 60 F_{245}). Solvent systems were chloroform/acetone (2:1, v.) (I) and acetic acid/n-butanol/water (3:1:1, v.) (II). Lactic acid ethyl ester (1) and 4-toluenesulfonyl chloride (2) were purchased from Merck-Schuchardt, Darmstadt, and purified by distillation and recrystallisation be-

0170-0839/79/0001/0691/$01.00

fore use.

2-(4-Toluenesulfonyl) lactic acid ethyl ester (3).

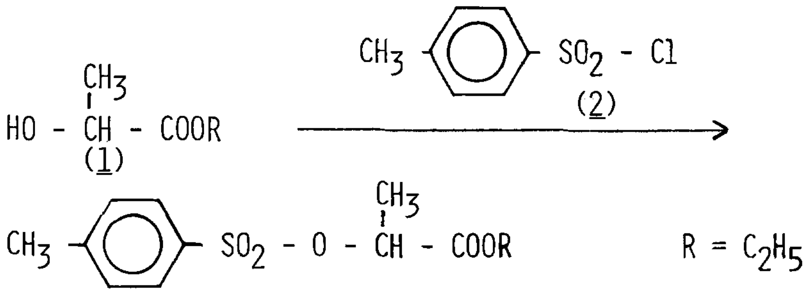
To a mixture of 4-toluenesulfonyl chloride (2) (81 g) in chloroform (170 ml) and lactic acid ethyl ester (1) (59 g, 0.5 mole), dry pyridine (68 ml) was dropwise added under anhydrous conditions and stirred for 3 h at room temperature. After addition of 350 g ice and concentrated hydrochloric acid (120 ml) the chloroform layer was separated, washed several times with water and dried over Na_2SO_4. Filtration and removal of the solvent on a rotary evaporator gave product (3) which was distilled in vacuo. Yield: 62 g (54 %), b.p. (0.6) 136-142°C, lit. b.p. (2) 158-160°C (FREUDENBERG and HUBER 1925), 164-166°C (KENYON et al. 1925), n_D (21) = 1.5014. Tlc: R_F = 0.68 (I).

Poly(oxyethylene) (4)

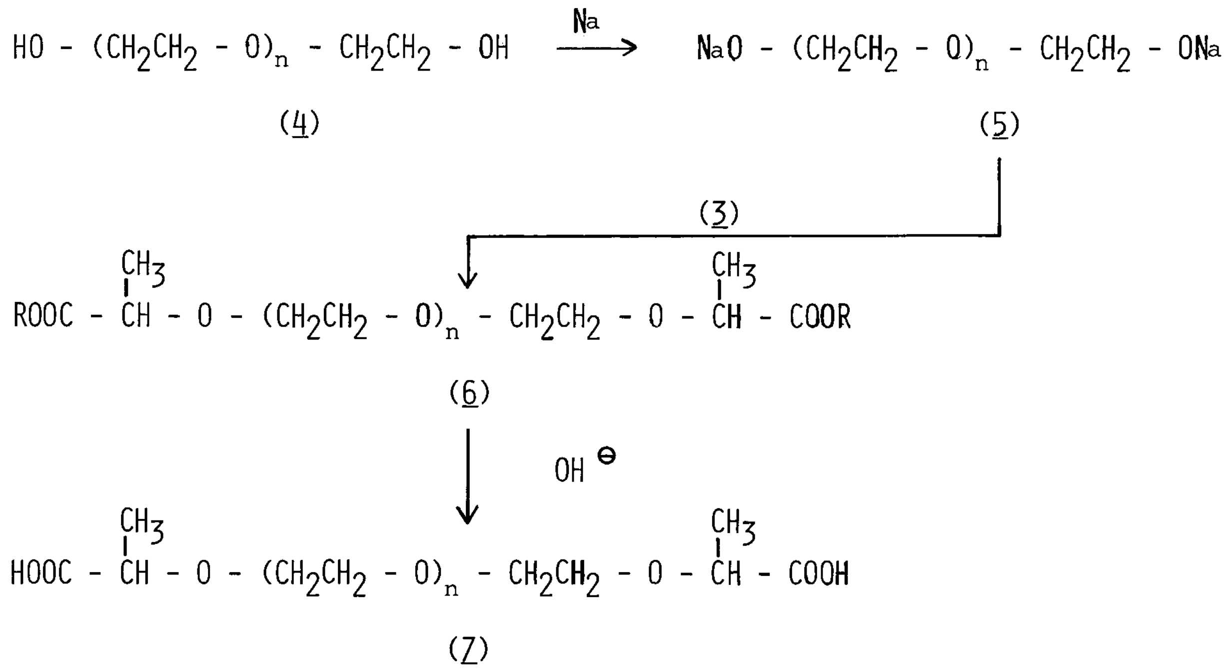
(m.w. 1500) was purchased from Fluka Feinchemikalien GmbH, Neu-Ulm. For purification it was precipitated twice from tetrahydrofuran/ether and dried over phosphorus pentoxide at the oil pump.

Di(2-lactic acid ethyl ester) poly(oxyethylene) (6).

To a solution of dried (4) (15 g) in benzene (150 ml), sodium (920 mg) was added in small portions under nitrogen atmosphere and stirred for 2 h. The excess of sodium was removed by filtration, 5.8 g of (3) was slowly dropped to the solution of (5) and refluxed for 3 h. After stirring overnight at room temperature the precipitated 4-toluenesulfonic acid sodium salt was filtered off and the solvent evaporated in vacuo. Yield: 15.9 g (78 %).



(3)



$$HO-(CH_2CH_2-O)_n-CH_2CH_2-OH \xrightarrow{Na} NaO-(CH_2CH_2-O)_n-CH_2CH_2-ONa$$

(4) (5)

(3)

$$ROOC-\overset{CH_3}{CH}-O-(CH_2CH_2-O)_n-CH_2CH_2-O-\overset{CH_3}{CH}-COOR$$

(6)

$OH^{\ominus}$

$$HOOC-\overset{CH_3}{CH}-O-(CH_2CH_2-O)_n-CH_2CH_2-O-\overset{CH_3}{CH}-COOH$$

(7)

FIG. 1: REACTION SCHEME

Di(2-lactic acid) poly(oxyethylene) (7).

Polymer (6) (15 g) was dissolved in 100 ml potassium hydroxide solution (5 %) and stirred for 4 h at room temperature. Then, the solution was adjusted to pH 4 and extracted four times with dichloromethane (50 ml). On removal of the organic solvent, the product thereby obtained (11.5 g) was dissolved in benzene (65 ml) and precipitated with ether (400 ml). After filtration the polymer (7) was washed twice with ether (100 ml) and dried over phosphorus pentoxide in vacuo. Yield: 10.5 g (67 %), m.p. 41-42°C. IR (CCl_4): 2860 (ν_{C-H}), 1710 ($\nu_{C=O}$) cm^{-1}. Tlc was used for reaction control and product identification with bromocresol purple as detecting reagent for carboxyl groups and Dragendorff reagent for poly(oxyethylene). The functional reagent (3) (R_F = 0.68) could be easily separated from the polymeric products with R_F-values less than 0.22 (I) and 0.40 (II).

Results and Discussion

The synthesis started with the preparation of compound (3) which was fixed to the polymer by polymer-analogous reaction and contained a protected carboxyl group. In this study we chose 4-toluenesulfonyl lactic acid ethyl ester (3) which can be easily obtained by tosylation of lactic acid ethyl ester (1). For the protection of the carboxyl group we used the ethyl group but other esters are also suitable. This compound (3) was allowed to react with disodium poly(oxyethylene) (5) which was prepared by conversion of (4) with metallic sodium in benzene at room temperature. For a good yield we used two folds excess of sodium. The product di(lactic acid ethyl ester) poly(oxyethylene) (6) was converted to the free carboxylic acid (7) by simple hydrolysis. There are no stability problems in this polymer-analogous reaction because the functional unit is linked by a stable ether bond to the polymer chain.

The best method for the purification of the polymer was the precipitation with ether. Attempts to separate low molecular excesses from the polymer by dialysis were not satisfactory because of the high loss of polymeric product. There are no suitable semi-permeable membranes for this range of molecular masses. Polymer (7) showed no significant alteration of the known solubility properties of polymer (4). Steps of the synthesis were controlled by infrared spectroscopy and thin layer chromatography. As detecting reagents for tlc, bromocresol purple for carboxyl groups (KNAPPE et al. 1962) and Dragendorff reagent for poly(oxyethylene) (THOMA et al. 1964), were used, which both gave a positive colour test for polymer (7).

The average yield of carboxyl groups was 70-80 %, determined by the indirect method of coupling a protected amino acid derivative with following amino acid analysis (GECKELER and BAYER 1974).

This synthetic path allows an easy modification of the terminal functional group by variation of the carboxyl component. Depending on the chain length of the polymer the functional capacity can be varied over the broad range of molecular weight fractions of commercially available poly(oxyethylene). Principally, the concept can be applied to multifunctional hydroxy polymers.

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Received July 26, 1979