

Functionalization of Soluble Polymers

3. Preparation of Carboxy-Telechelic Polymers

Kurt Geckeler and Ernst Bayer

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

Summary

Two methods for the synthesis of bifunctional carboxy polymers are described. In a first example, poly(oxyethylene) was reacted with a bromoalkyl ester via the sodium salt to yield di(carboxyalkyl) poly(oxyethylene) after hydrolysis. As second method, an one-step procedure is reported in which polyglycols were converted to dicarboxy polymers by polymer-analogous reaction with anhydrides of dicarboxylic acids. Several examples of various chain extending molecules with latent carboxyl functionality for the synthesis of carboxy-telechelic polymers are summarized.

Introduction

Soluble polymers are used for various applications in scientific research and industry but they represent also important starting material for further syntheses. Preparation and application of functionalized soluble polymers have recently attracted great interest (GECKELER 1979a, GECKELER and MUTTER 1979c, GECKELER 1980a, ALDISSI et al. 1980, GECKELER et al. 1980b, BAYER et al. 1980, GECKELER et al. 1980c).

Special importance is due to telechelic polymers because of their particular structure and properties, of which some examples have been investigated exhaustively (MUTTER 1978, GECKELER and BAYER 1979b, KENNEDY et al. 1979). As part of our synthetic effort in this field we have already described examples of the substitution of the functional groups of poly(oxyethylene) by amino and carboxyl groups. This paper concerns two convenient methods of preparing bifunctional carboxy polymers by polymer-analogous functionalization of hydroxy-telechelic macromolecules.

Experimental

The solvents and reagents were purified and dried as described in the previous communications. Poly(oxyethylene) (1) ($M = 3000, 6000, 10\ 000\ \text{g}\cdot\text{mol}^{-1}$), 2-Bromopropionic acid ethyl ester (3), and succinic anhydride (6) were purchased from Fluka Feinchemikalien GmbH, Neu Ulm.

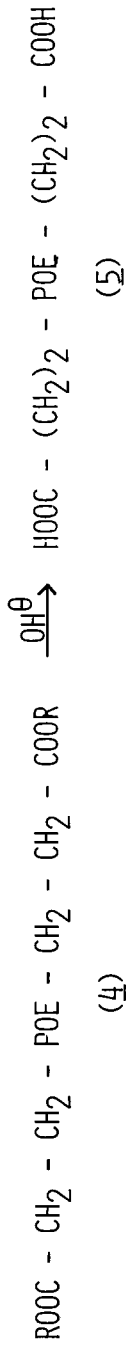
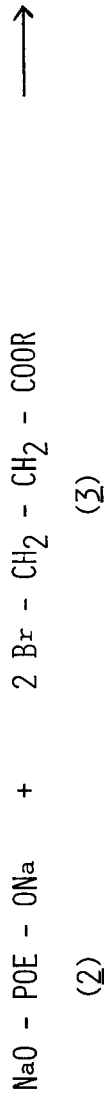
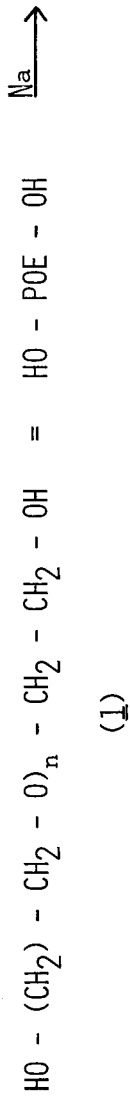
Di(carboxyethyl)poly(oxyethylene) (5).

At first, the disodium salt of poly(oxyethylene) (2) was prepared at room temperature in dry tetrahydrofuran with an excess of sodium dispersion (50% in paraffin) under nitrogen using a Schlenk apparatus (HENGEL 1979). To this solution, (3) (10 fold excess in tetrahydrofuran) was directly added and reacted in the same manner as reported previously (GECKELER 1979a). The polymer (4) thereby obtained was converted to the product (5) by hydrolysis with potassium hydroxide (GECKELER and BAYER 1979b).

Di(succinic acid) poly(oxyethylene) (7).

Poly(oxyethylene) (1) was dissolved in dry dichloromethane (approx. 10%) and then a solution of succinic anhydride (6) (4-fold molar excess referred to functional groups) and pyridine (5%) in dichloromethane (10%) was added under anhydrous conditions and heated under reflux for 24 h or stirred at room temperature for 3 days. Compound (6) can also be prepared in situ from succinic acid and dicyclohexylcarbodiimide (SHEEHAN and HESS 1955). Then, the polymer product (7) was precipitated by the addition of ether in small portions and cooled to 4°C, (7) was filtered off, washed with ether and dried in vacuo. For further purification the precipitation procedure was repeated or the polymer (7) was dissolved in water, the solution membranefiltrated and the solvent removed in vacuo.

Chemical analysis (coupling with an amino acid, cleavage and amino acid analysis) and determination of the acid number by titration showed for the polymers (5) and (7) an average content of carboxyl groups to be 75-85% of the theoretical value. The samples of amino acid analyses for the determination of functional groups (aliquot amount of polymer) were first hydrolysed (6 N HCl) in sealed evacuated tubes for 24 h at 110°C and then analyzed with the Biotronik amino acid analyzer (System LC 6 000 E).



Results and Discussion

The first procedure reported here is based on the reaction of telechelic sodium salt of poly(oxyethylene) (2), which was prepared under nitrogen in absolute tetrahydrofuran with 2-bromopropionic acid ethyl ester (3). As shown in the previous communications, the disodium salts of polyglycols can be used as convenient starting materials for the synthesis of functionalized telechelic polymers. The latent carboxyl function in the diester (4) was deblocked by polymer-analogous hydrolysis to yield di(carboxyethyl) poly(oxyethylene) (5). The sequence of reactions representing this method of preparation of carboxy polymers is depicted in Fig. 1.

As an example of a secondary functionalization method for the preparation of α, ω -difunctional oligomers and polymers, some results with the reactions of intramolecular anhydrides of dicarboxylic acids are presented. In this procedure, polyglycols, e.g. poly(oxyethylene)s, were reacted with succinic anhydride (6) in dichloromethane-pyridine solution and yielded the carboxy-telechelic poly(oxyethylene) (7) in an one-step reaction. Principally, other anhydrides of dicarboxylic acids, such as glutaric acid and substituted compounds, can also serve for the synthesis of α, ω -dicarboxy polymers. They are commercially available or by reaction of the dicarboxylic acid and acetic anhydride or acetyl chloride.

The application of intermolecular anhydrides of dicarboxylic acid monoesters, which can be easily prepared by the use of the coupling reagent dicyclohexyl carbodiimide (SHEEHAN and HESS 1955) from the suitable compounds, opens a great variety of possibilities for the preparation of such polymers.

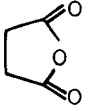
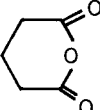
Carboxy-telechelic condensation polymers from succinic acid and glycol, which are synthesized by heating the two compounds at 200°C for some hours, have been reported (CAROTHERS and DOROUGH 1930). However, these types of telechelic polymers involve great instability for basic and acid conditions because of the labile ester group in the constitutional repeating unit of the polymer.

As representatives of the great variety of chain lengths in the case of poly(oxyethylene) average molecular masses from 3 000 to 10 000 have been investigated for the procedures described here. The excellent solubility properties of (1) were not influenced remarkably by the chain extension molecules as terminal groups contribute little to the physico-chemical properties of long-chain macromolecules. Evidently, an alteration of the hydrophilic character of (1) can only be caused by the application of hydrophobic derivatives or higher homologues

of chain-extending molecules. General studies on the chain extension parameters have been published recently (IVAN and KENNEDY 1980).

Both quantitative amino acid analysis (MOORE and STEIN 1965) and determination of the acid number by titration, showed experimental values of the terminal functionality between 1.5 and 1.7. Spectroscopic characterization methods confirmed the analytical results and indicated therein no remarkable difference to the data already reported.

Table 1

Some Examples of Functionalization for the Preparation of Carboxy Polymers from Hydroxy Polymers			
Chain Extender with Latent Carboxyl Functionality	Chain Extension Number (C-Atoms)	Catalyst	Deblocking Reaction
$\text{Br-CH}_2\text{-CH}_2\text{-COOR}$	3	-	Hydrolysis
Br-CH-COOR CH_3	2	-	Hydrolysis
	4	Pyridine	-
	5	Pyridine	-
$\text{TOS-O-CH}_2\text{-CH}_2\text{-CN}$	3	-	Hydrolysis
$\text{CH}_2\text{=CH-CN}$	3	RONa	Hydrolysis
TOS-O-CH-COOR CH_3	2	-	Hydrolysis

R = CH_3 , C_2H_5

TOS = 4-Toluene sulfonyl

Also, on the same line, we have prepared functionalized carboxy derivatives of poly(oxyethylene) by the use of other carboxy chain-extending units. Some examples of these results are summarized in Table 1. The extension of these functionalization concepts to multifunctional polymers opens the accessibility of many new functional soluble polymers. The applicability of functionalized soluble polymers as polymeric supports and chelating agents is specified in the references cited.

References

- ALDISSI, M., SCHUE, F., GECKELER, K., and ABADIE, M.: Makromol. Chem. 181, 1425 (1980)
- BAYER, E., WEINGAERTNER, K., and GECKELER, K.: in preparation (1980)
- CAROTHERS, W.H. and DOROUGH, G.L.: J. Am. Chem. Soc. 52, 711 (1930)
- GECKELER, K.: Polym. Bull. 1, 427 (1979a)
- GECKELER, K. and BAYER, E.: Polym. Bull. 1, 691 (1979b)
- GECKELER, K. and MUTTER, M.: Z. Naturforsch. 34b, 1024 (1979c)
- GECKELER, K.: Int. Symp. Polym. Sci. Appl. (IUPAC), Madras (1980a)
- GECKELER, K., LANGE, G., EBERHARDT, H., and BAYER, E.: Pure Appl. Chem. 52, 1883 (1980b)
- GECKELER, K., WEINGAERTNER, K., and BAYER, E.: in Polymeric Amines and Ammonium Salts, E. Goethals, ed., Pergamon Press, Oxford, 1980c
- HENGEL, R.: Dissertation, University of Tuebingen, 1979
- IVAN, B. and KENNEDY, J.P.: Polym. Bull. 2, 351 (1980)
- KENNEDY, J.P., CHANG, V.S.C., SMITH, R.A., and IVAN, B.: Polym. Bull. 1, 575 (1979)
- MOORE, S. and STEIN, W.H.: Meth. Enzymol. 6, 819 (1965)
- MUTTER, M.: Tetrahed. Lett. 31, 2839 (1978)
- SHEEHAN, J.C. and HESS, G.P.: J. Am. Chem. Soc. 77, 1067 (1955)

Received October 16, 1980