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New kind of star-shaped polyethers prepared with cyclic oligo(potassium glycidoxide) as a macroinitiator

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Abstract

Cyclic oligo(potassium glycidoxide) activated 18-crown-6 is applied as a macroinitiator for the polymerization of propylene oxide, 1-butylene oxide and styrene oxide. This polymerization results in new star-shaped polyethers with a cyclic core. The size of the core and the number of its arms depends on the concentration of crown ether used for preparation of the macroinitiator.

Keywords: Potassium glycidoxide; Macroinitiator; Oxiranes; Polyethers; Star-shaped polymers; MALDI-TOF technique

1. Introduction

Linear polyethers and particularly polymers and copolymers of ethylene oxide and propylene oxide are important components for polyurethane synthesis. These polyethers are usually obtained via anionic polymerization. A lot of initiators have been used for this purpose. Their list started with potassium hydroxide [1] and closed down with potassium hydride [2,3] and bimetal cyanides [4,5]. The latter give poly(propylene oxide) with relatively high molar masses, i.e., about 10,000.

Potassium glycidoxide has been recently described as an inimer producing hyperbranched poly(propylene oxide) [6,7]. This alkoxide prepared in the reaction of glycidol with potassium hydride activated 18-crown-6 can also oligomerize spontaneously [8]. A cyclic oligomer with several alkoxide active centers is formed in this reaction. Its macromolecules are crown ethers containing three carbons between oxygen atoms. Their size depends on the initial concentration of the ligand. Hexamers and heptamers are mainly obtained at equimolar amounts of the reagents. This system is named 1:1. The trimer is almost exclusively formed at the 18-crown-6:potassium hydride:glycidol molar ratio equal to 3:1:1, respectively. Such system is called 3:1. Both the systems are for the first time described

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in this paper as new macroinitiators of the polymerization of propylene oxide, 1-butylene oxide and styrene oxide resulting in star-shaped polyethers with a cyclic core.

2. Experimental

2.1. Synthesis

Glycidol (Merck) was distilled at 61 °C/15 mm Hg. 18-Crown-6 (1,4,7,10,13,16-hexaoxacyclooctadecane) and potassium hydride were supplied from Aldrich and purified as described in Ref. [9]. Tetrahydrofuran (POCH) was purified by a standard method and finally dried over sodium–potassium alloy as in Ref. [10]. Propylene oxide, 1-butylene oxide and styrene oxide (all Aldrich) were dried over CaH_2 and distilled prior to use as in Ref. [11].

The reaction was performed in a 50 cm^3 reactor thermostatted at 20 °C containing a suspension of potassium hydride (0.09 g, 2.25 mmol) in tetrahydrofuran (10 cm^3) and 18-crown-6 (0.59 g, 2.25 mmol for 1:1 system or 0.178 g, 6.75 mmol for 3:1 system) in an argon atmosphere. A solution of glycidol (0.16 g, 2.25 mmol) in tetrahydrofuran (10 cm^3) was dropped into that suspension. The mixture was stirred for 40 min. Then, the monomer (22.5 mmol or 180 mmol for sample 1) was added to the reactor. Dowex 50WX2 ion exchanger as a protonation agent was introduced into the system at a minimum 95% conversion of the monomer. Methyl iodide was used instead of the ion exchanger to obtain methoxy end groups. The polymer was precipitated with hexane and dried under vacuum to a constant mass.

Table 1
Polymerization of oxirane monomers with cyclic oligo(potassium glycidoxide) obtained in the reaction of potassium hydride (8.0 g/dm^3, 0.2 mol/dm^3) with glycidol (0.2 mol/dm^3) in the presence of 18-crown-6

No	Monomer	$[Monomer]_0$ (mol/dm^3)	18-Crown-6/KH (mol/mol)	M_n (GPC)	M_w/M_n (GPC)
1	Propylene oxide	8.0	1:1	8000	1.50
2	Propylene oxide	2.0	1:1	2000	1.20
3	Propylene oxide	2.0	3:1	1200	1.30
4	1-Butylene oxide	2.0	3:1	4000	1.10
5	Styrene oxide	2.0	1:1	1500	1.50

Solvent: tetrahydrofuran. Temperature: 20 °C.

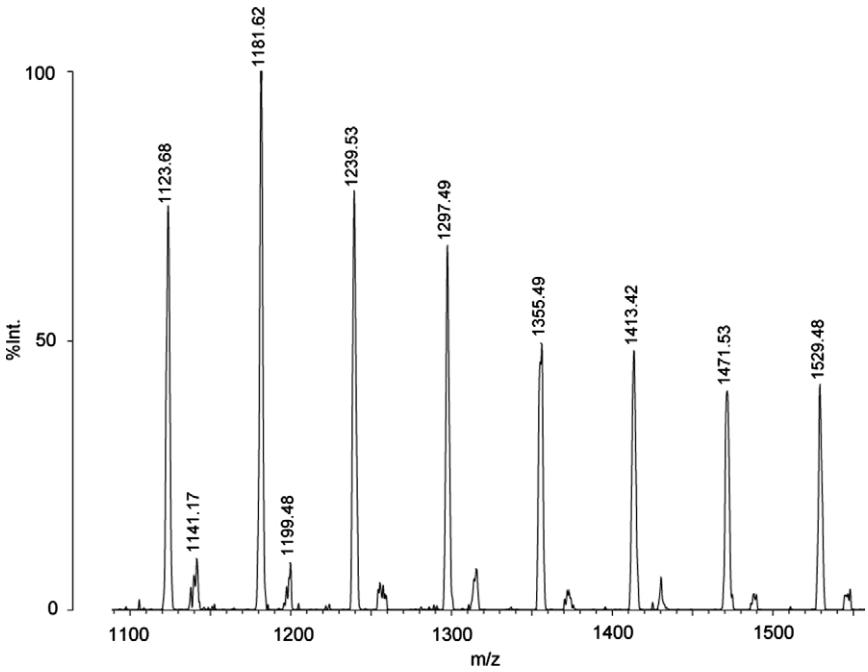

Fig. 1. A part of the MALDI-TOF spectrum of poly(propylene oxide) obtained with oligo(potassium glycidoxide) 1:1. Sample 1 in Table 1. The spectrum was acquired in the positive reflectron mode, using norharmane as the matrix.