



# Peculiarities of complexation of sodium cations by star-shaped polymers with core formed from diepoxides and poly(ethylene oxide) arms



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## ABSTRACT

$^{23}\text{Na}$  NMR spectroscopy was used to study complexation of sodium cations ( $\text{NaClO}_4$ ) with a few of star-shaped polyethers. The bonding of sodium ions by these polymers having PEO arms and with model compounds has been studied in anhydrous methanol solutions. In this paper the preliminary studies are presented, indicating that star polymers built from PEO arms and core formed from diepoxides, containing cyclic structures, are good polydentate complexing agents of sodium cations. Core cyclic structures hinder exchange of the complexed sodium cation with free cations.

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## 1. Introduction

Sodium cations form complexes with poly(ethylene oxide) (PEO) and crown ethers. Complexes with crown ethers, studied in water and in non-aqueous solutions [1–4], are much more stable than that with PEO chains [5–7]. The strongest binding of cations was observed with 18-crown-6 (18C6), irrespective of cation size [8]. Various analytical methods (conductometric, calorimetric or potentiometric titration, spectroscopic) gave nearly identical values for the stability of 18C6 complexes with alkali ions in methanol solution [2,8–13]. Many papers devoting interaction of alkali salts (mainly picrates) with different ligands containing ether bonds (cyclic ethers, glymes) [12,14–17], linear PEO [18–22], and cross-linked PEO [16,23–25] in dioxane, toluene or THF were published previously. The coordination of sodium cations by PEO chains was discussed in many papers [1,26–28]. Polyethylene glycol (PEG) shows a strong ion-dipole binding affinity toward alkali metals even in methanol, exhibiting relatively high basicity. PEG–metal cation complex structures have been analyzed by a variety of methods, e.g., mass spectrometry [29],  $^1\text{H}$  NMR [28,30], IR and Raman spectroscopy [31]. Association complexes of monovalent

cations with some polyethylene glycol ethers were reported for  $\text{Na}^+$  and  $\text{K}^+$  by potentiometric and conductometric measurements [32] and by spectrophotometric titrations [15]. Smid also analyzed the role of solvent structure in alkali cation solvation [33].

$^{23}\text{Na}$  and  $^{13}\text{C}$  NMR are a very powerful techniques for studies of alkali cation complexes with macrocyclic ligands, particularly in non-aqueous solutions [3,4,34–37].

“Lariat ethers” built from a macrocyclic polyether ring and a flexible PEO arm extending from the cycle were also used to study the complexation of  $\text{Na}^+$  ions [38]. The complexation phenomena exhibited by lariat crown ethers are influenced by the hole-size relationship, ligand flexibility and conformation, total number of donor atoms, and solvation energies for the cation, macrocycle, and complex [3]. Some authors suggested that these flexible polyether systems do not abide by this “hole-size rule” [8,38].

In this paper the preliminary studies are presented, indicating that star polymers built from PEO arms and core formed from diepoxides are good polydentate complexing agents of sodium cations. The  $^{23}\text{Na}$  NMR method was applied for the study of  $\text{Na}^+$  complexation, because this method appeared to be efficient for the determination of the formation of complexes of polymers containing ethylene oxide (EO) units with alkali metal ions [19,20,22,39–42].

In this work we avoid comparing our results on complexation with ones obtained with different, mentioned above methods,

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because in our opinion they concern different levels of description of binding entities.

## 2. Experimental

### 2.1. Materials

Methanol was purified and dried conventionally. 18-crown-6 (18C6, Aldrich) was used after drying a few hours in vacuum at 70 °C. NaClO<sub>4</sub> (Aldrich) was dried under vacuum for 5 h at 80 °C before using. Monomethyl ether of poly(ethylene glycol) (MPEG 2000, Aldrich) was dried under vacuum for 5 h at 80 °C.

Star polymer with 15 arms and cross-linked core was prepared from monomethyl ether of poly(ethylene glycol) (MPEG 2000) and diglycidyl ether of neopentyl glycol as described previously [43–45]. Sodium derivatives exclusively were used in the synthesis procedures. Polymer had  $M_n = 37\,500$  (SEC) and the weight content of PEO arms in the star was equal to 81.6%. This star had cycles in the core.

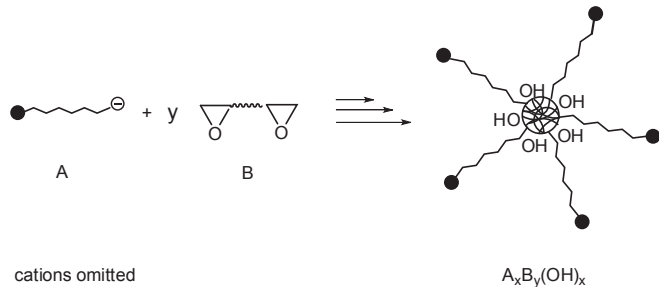
Star polymer with 4 arms (**1**), having no cyclic structures, unlike products with the core formed from diepoxides, was prepared in anionic polymerization of EO initiated with di(trimethylolpropane) in THF solvent, according to the known procedure [46]. Star had  $M_n = 7260$  (determined by SEC) and  $M_n$  of its arms was equal to 1750.

### 2.2. NMR measurements

<sup>23</sup>Na NMR spectra (123 MHz) were recorded on a Bruker Avans III 500 MHz apparatus at 25 °C. 1 mol L<sup>-1</sup> solution of NaCl in D<sub>2</sub>O was used as an external reference ( $\delta = 0$  ppm) and the reported <sup>23</sup>Na chemical shifts were referred to this solution. Measurements were carried out in NaClO<sub>4</sub> solution ( $2 \times 10^{-2}$  mol L<sup>-1</sup>) in dry methanol.

## 3. Results and discussion

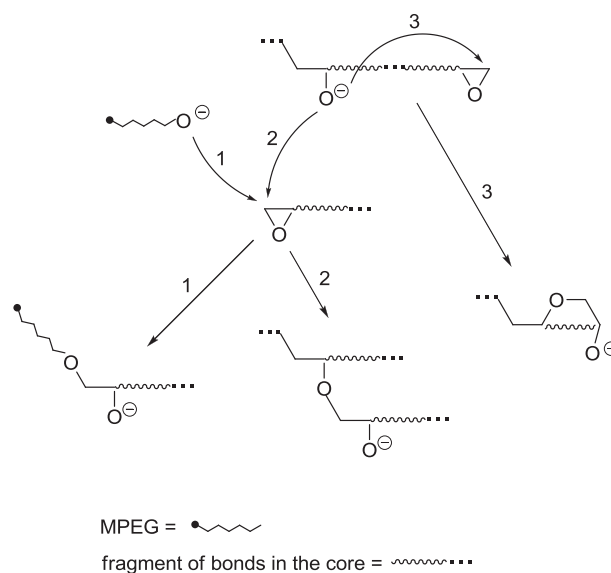
<sup>23</sup>Na NMR spectroscopy was used to study complexes of sodium cations with various donors. It enables to estimate the apparent complexation constants of sodium ions with EO units present in linear chains and in vicinity of branched points, following methods used for other polymeric systems [47,48]. The binding constants of sodium cations with PEG were measured in anhydrous methanol [12,17,26,32].



cations omitted

where: A denotes MPEG  
B denotes diglycidyl ether of neopentyl glycol

**Scheme 1.** Formation of star-shaped polymer with PEO arms.



**Scheme 2.** Formation of the ring structures in star-shaped polymer in competition with a macromolecule growth.

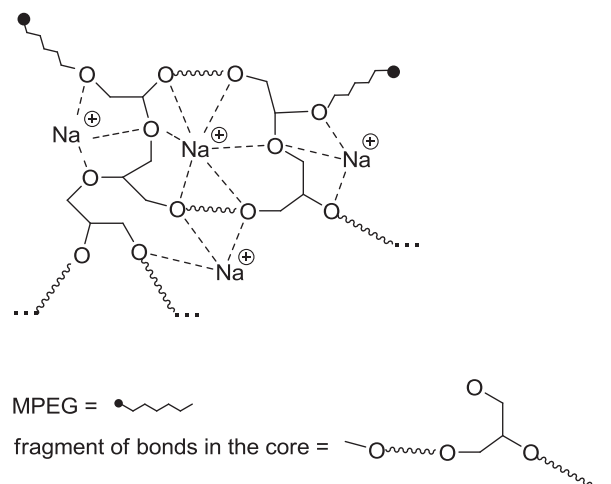
### 3.1. Synthesis of the star-shaped polymer

Nontoxic fully hydrophilic star PEO polymers were prepared, using anionic copolymerization of MPEG chains with diepoxides [43]. The synthesis is shown schematically in Scheme 1.

Star polymer A<sub>x</sub>B<sub>y</sub>(OH)<sub>x</sub> contains PEO arms and the core built of residues originating from diepoxide B used as branching/linking agent. Epoxide rings of B, or of its residue already incorporated into product, can be opened either by alkoxide group of precursor of PEO arms (MPEG, A) or by alkoxide group of diepoxide origin (formed while opening the epoxide cycle of B by alkoxide group of precursor or of a star, including the intermolecular cyclization reaction), as is shown in Scheme 2.

Consequently, three-dimensional branched core structure containing rings of various sizes and structures was formed. These ring structures, because of oxygen atom containing fragments originating from B, can complex metal cations, provided access to their inside or outside region (cf. Scheme 3).

The potential application of these PEO star-shaped polymers as solid polymer electrolytes is under investigation [49–51].



**Scheme 3.** Possible intra- and extra-cycle interactions of the star core moiety with Na<sup>+</sup> cations.

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