



Unexpected formation of a significant amount of polymer primary hydroxyl groups in synthesis of star-shaped polymer from linear alcoholate chains and diepoxides



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ABSTRACT

Following our previous paper on the course of the formation of star-polymers from oligo(oxyethylene) alcoholates as arms precursors and diglycidyl ethers as core building units [1], the nature of polymer alcoholate groups formed in this process has been studied. Primary alcoholate groups reacting with diepoxide or epoxide function in polymer give initially predominantly secondary alcoholate groups in the product. However, a small fraction of primary alcoholate groups of polymer is formed from the very beginning. When consumption of epoxide groups increases the contribution of polymer primary groups increases too, reaching eventually from 5 to 15% of total alcoholate groups, depending on reaction conditions. The increase of this proportion with the reaction progress is explained by intramolecular reaction of alcoholate groups with epoxide ones (cyclization) giving a large proportion of primary alcoholate groups. This explanation was supported by the quantum-mechanical calculations of the possible routes of cyclization.

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1. Introduction

Star shaped polymers due to their structure exhibit many solution, viscoelastic, and mechanical properties characteristic for nonlinear polymers, resembling in many of their features hyperbranched ones. In review by Hadjichristidis et al. [2] one can find information on their synthesis, properties, and applications. The synthesis, properties and some applications of star-shaped polymers having poly(ethylene oxide) (PEO) components are presented in several review papers [3–7]. Interest in star-shaped PEO polymers is mainly stimulated by their potential application in biomedical and pharmaceutical areas [8,9]. Nonionic and biocompatible PEO macromolecules have specific properties such as chemical stability, water solubility, non-toxicity, and resistance to recognition by the immune system. The introduction of the PEO chains into the star architecture may provide some additional advantages (for example multiple functional groups) as compared to linear PEO counterparts in these applications [8,9]. Functional star-shaped PEO polymers are also regarded as a particularly promising class of materials representing versatile building blocks for

structured polymer networks [10,11].

This paper is a continuation of our earlier papers [12–18] on the formation of star-polymers from oligo(oxyethylene)alcoholates as arm precursors and diglycidyl ethers as core building blocks. The course of reaction of monomethyl ethers of poly(ethylene glycol) (as alcoholate, MPEG-O[⊖]) and diglycidyl ether of neopentyl glycol (DGNG) was analyzed in detail in our recent paper [1].

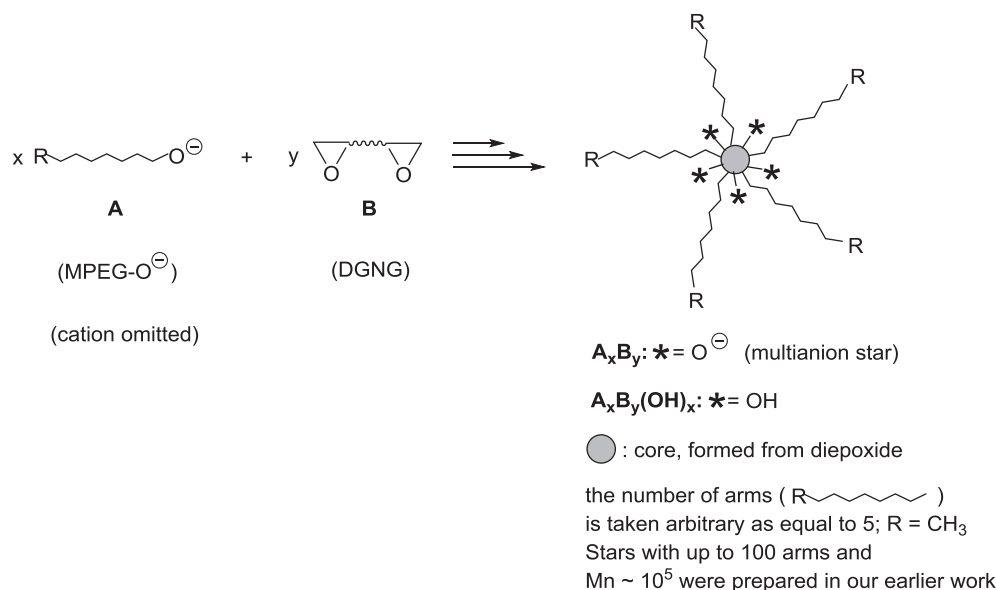
As it was shown, the overall process leading to the corresponding stars is illustrated on Scheme 1.

Precursor **A** reacts with diepoxide **B** and the first generation stars **A_xB_y** are formed. Reaction of **A** with epoxy groups is generating secondary –O[⊖] groups (*sec*-O[⊖]), able to react with epoxy groups either in the not yet reacted **B** or present in the core. Finally, after addition of terminating agent (“H[⊕]”, e.g., protons of weak acids), all active centers are transformed into hydroxyls (**A_xB_y(OH)_x**). We use the term “first generation stars” because these compounds were used by us to form stars with twice higher number of arms, after generating new ones growing from core anionic centers or directly attaching linear chains at these sites.

However, the described picture of the formation of a star-shaped polymer is simplified because the detailed analysis of the products of a model reaction have shown that a small amount of primary alcoholate groups (*prim*-O[⊖]) was formed in the reaction of

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Scheme 1. Formation of the first generation of stars [1].

alcoholates (both primary and secondary) with epoxy groups. That is visualized on Scheme 2.

It is known from literature [19,20] that if oxirane ring is not activated, for example, with hydrogen bonding or Brønsted/Lewis acids, all nucleophiles predominantly attack less substituted atom β . The only exceptions are: (i) activation by the neighboring group and/or (ii) structurally intramolecular reactions, either these being real cyclizations or those involving unstable complexes of two or more molecules. In these reactions, proceeding with cyclic transition states, entropic effects can overcome enthalpic ones related with the steric hindrance and/or ring strain and the attack on more crowded α atom can be significant or even dominating [21–24].

In the paper by Gayral et al. [21] an example of the reaction involving diepoxide (1,2:5,6-dianhydro-3,4-dibenzyl-*L*-iditol bisepoxide) is given, where cyclization proceeds as the reaction of *sec*- O^- group, derived from one epoxy group after opening it with the Schöllkopf bislactim, a glycine anion equivalent. This *sec*- O^- group attacks next the more crowded α carbon atom of the second epoxy group. As the result of the cyclization *prim*-OH is formed.

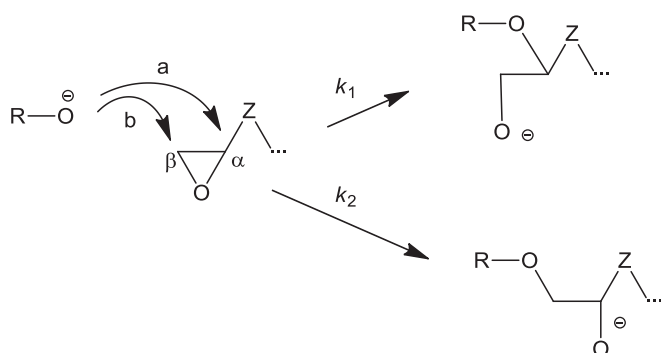
One can find here some analogy to our systems. This type of

reaction can proceed also intramolecularly in the course of synthesis of a star-shaped polymer, involving both reacting groups: alcoholate and epoxide, attached to the same polymer and/or oligomer molecule (cf. Scheme 3).

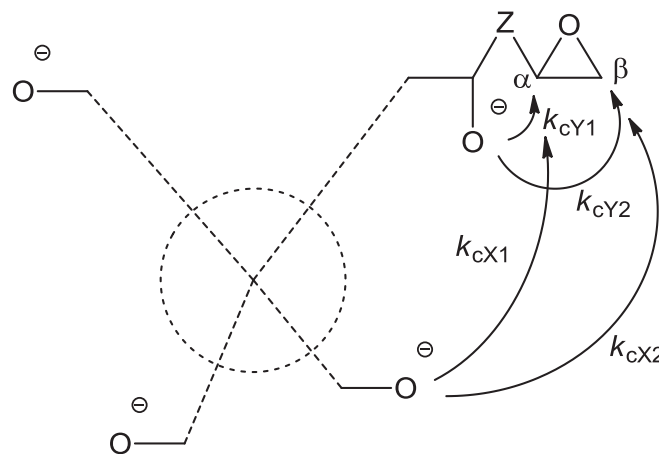
It is well known that cyclizations proceeding in polyaddition systems capable of network formation increase the gel-point conversion [25–27]. This phenomenon contributes also in our syntheses of star-shaped polymers. Therefore, in previous papers, we already discussed formation of cycles of different sizes in the cross-linked core of our products, although without analysis of the type of newly formed alcoholate groups [1,28].

Importance of cyclization route leading to primary alcoholate groups is presented in the present paper. Besides, this result is confirmed by the quantum-mechanical calculations, as discussed below.

The observed by us relatively high contribution of *prim*- O^- in synthesis of our star-shaped polymers is rather unexpected. In all reports on anionic polymerization of substituted epoxides *prim*- O^- are not observed. Besides, analysis of microstructure of the



Scheme 2. Two possible attacks of alcoholate groups on an epoxy group: mainly on less substituted carbon atom β (attack b) leading predominantly to secondary alcoholates (*sec*- O^-) (k_2) and less frequent on more substituted carbon atom α (attack a) giving primary alcoholates (*prim*- O^-) (k_1). Z denotes oxy-neopentoxy moiety - a chemical group joining two epoxide groups in diepoxide **B** or joining an epoxy group, or its open derivative, to polymer.



Scheme 3. Cyclization reactions in reaction systems involving epoxy groups and alcoholates attached to the same molecule. Formation of both primary (*prim*- O^-) and secondary (*sec*- O^-) alcoholate groups is possible.

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