



The influence of macrocyclic ligands and water on propylene oxide polymerization initiated with anhydrous potassium hydroxide in tetrahydrofuran



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ABSTRACT

It was found that presence of macrocyclic ligands, such as coronand 18C6 and cryptand C222 influence unsaturation of polyethers obtained by the polymerization of propylene oxide (PO) initiated with highly dispersed anhydrous KOH in tetrahydrofuran at room temperature. Polymerization carried out at low initial concentration of PO and quenched with CH₃I resulted in the polymers without terminal –OH groups. In this case unsaturation is very high and is represented mainly by *cis*-propenyloxy starting groups due to isomerization of double bonds of allyloxy groups. The unsaturation increases in the presence of ligands. However, polymers synthesized at higher initial concentrations of PO possess OH terminal groups and addition of ligands diminishes unsaturation which is represented mainly by allyloxy starting groups. The highest molar mass of polymers obtained is $M_n = 9000$. KOH·H₂O/18C6 appeared to be also effective initiator giving the polymers which contain great amount of terminal –OH groups and very low unsaturation; their molar masses are rather low ($M_n = 2400$ – 2900).

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1. Introduction

Polymerization of propylene oxide (PO) was first reported by Levene in 1927 [1] and since then, research efforts have focused on poly(propylene oxide) (PPO) preparation due to its applications as functional oligomers, block co-oligomers, mainly as components for polyurethane synthesis [2–5]. PO is usually polymerized via anionic polymerization. Potassium hydroxide (KOH) is most frequently used catalyst for bulk propylene oxide (PO) anionic polymerization at 70–120 °C yielding oligoether-polyols for elastic polyurethanes [2–7]. This process needs to use polyfunctional starter which usually contains 2–3 hydroxyl groups per molecule. The most important starters

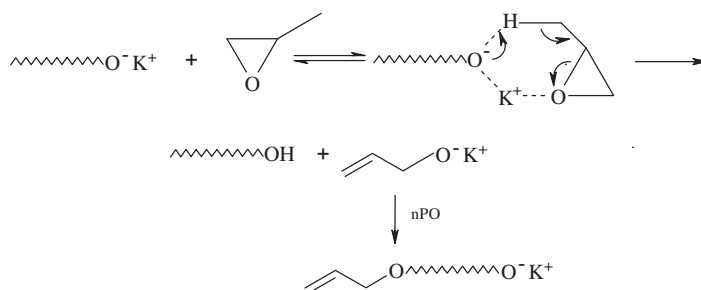
are ethylene glycol, dipropylene glycol and glycerol. Treating propylene oxide with propylene glycol in the presence of small amounts of KOH oligoether diols are formed [8]. In the case of glycerol monopotassium salt is formed which mediates PO polymerization resulting in star-like polyether triols [9]. Characteristic feature of PO polymerization is the side reaction of hydrogen abstraction from the methyl group of monomer which results in the formation of allyl double bonds (Scheme 1) [10,11].

In this reaction new chains are formed during the polymerization process. They take part in very fast cation exchange equilibrium reaction (Scheme 2).

All hydroxy chain-ends or alkoxy chain-ends propagate at similar rate. As a consequence of transfer reaction the number-average molar mass (M_n) of the polymer is limited to a relatively low value and the polymer dispersity is broadened [12].

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Scheme 1. Chain transfer reaction to the monomer leading to unsaturation of the polymer.



Scheme 2. Cation exchange reaction between macromolecules with hydroxyl and alkoxide end groups.

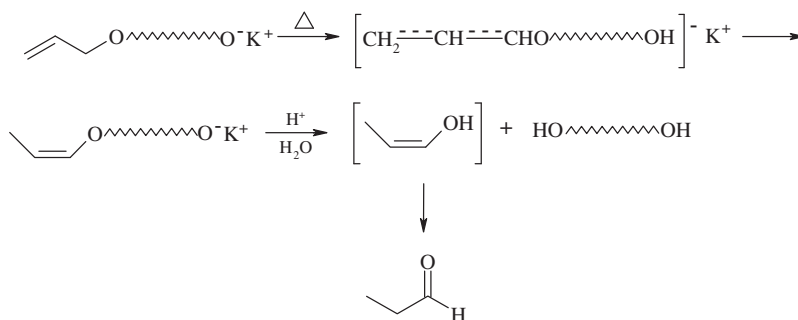
The reason for the side reaction called chain transfer to the monomer, is the relatively high acidity of the methyl protons of PO. This reaction is more significant at higher polymerization temperatures, with higher molecular masses polyethers and with reactors with metallic surface [6,13,14]. There is no literature data concerning the influence of the kind of polar solvents on chain transfer reaction, although some polymerizations of PO were performed in THF solution [15,16]. Allyl bonds are able to isomerize mainly to *cis*-propenyl ones at high temperatures under influence of alkoxide end group (Scheme 3) [17,18]. This transformation is very important in industrial practice because during the purification step the propenyl ether is hydrolyzed by the acids to propionaldehyde and polyether diol [6,19].

It is impossible to avoid the chain transfer reaction with the monomer, however it is possible to diminish it. In the presence of high concentration of alcohol hydroxyl groups the unsaturation is very low [20]. The explanation of this phenomenon is based on the strong affinity of the alkoxide for hydroxyl groups. As a consequence, hydroxyl groups being stronger ligands than PO are preferentially complexed and PO is eliminated from the alkoxide – PO complex (Scheme 4) [6]. Chain transfer reaction to the alcohol takes place in this case.

It is interesting to note, that the polymers obtained by potassium complexed catalysts have two to four times low-

er unsaturation than the polyethers synthesized by usual anionic PO polymerization with uncomplexed potassium cation. The minimum unsaturation of the polyether trials were found while using macrocyclic ligands, i.e. coronand 18-crown-6 (18C6) or cryptand C222 which appeared to be better than dibenzo-18C6 or poly(ethylene glycol)s [21]. Similar effect was observed by other authors in the bulk PO polymerization with potassium alkoxide/alcohol (1:3) mixtures and 18C6 [22,23]. One explanation of this effect is the acceleration of propagation and the deceleration of the transfer reaction. Ionescu [6] proposed that using a strong ligand (L) for potassium cation, PO is eliminated from the complex and thus the reaction is inhibited (Scheme 5).

Besides potassium alkoxides other compounds were also used for bulk PO polymerization, e.g. anhydrous KOH without hydroxylic initiators. Reaction proceeds readily at room temperature. However, the product consists largely of unsaturated, monohydroxy polyethers whose M_n is about 3000–5000 regardless of the monomer/initiator ratio [24]. The authors proposed that the reaction was initiated by the surface of the solid KOH. Contrary to that, Steiner et al. [25] reported that this reaction is not surface-initiated. It was established that the rate of polymerization and product characteristics are independent of the amount of solid KOH present as long as there is an excess of initiator. The real initiator is K^+OH^- being in solution (Scheme 6).



Scheme 3. Isomerization of allyl ether initial group to *cis*-propenylether one and hydrolysis of the latter leading to polyether diol.

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