



Polyether synthesis: From activated or metal-free anionic ring-opening polymerization of epoxides to functionalization

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ABSTRACT

Epoxide derivatives constitute a broad family of monomers which are able to be polymerized by anionic or related nucleophilic ring-opening mechanism. The main synthetic strategies developed are reviewed in terms of polymerization rates, side reactions, and possibilities for controlling such polymerizations. Ring-opening polymerization of ethylene oxide and substituted epoxides utilizing alkali metal derivatives or other initiating systems in conjunction or not with activating systems are discussed. Emphasis is also given on the use of organic initiators or catalysts to trigger the metal-free ring-opening polymerization of epoxides. Functionalization of polyethers is also described, which includes the use of functional initiators, post-chemical modification of reactive functions carried by the polyether backbone, or functional-monomer insertion. A focus is particularly given on the preparation of polyethers bearing hydroxy, amine, allyl, azide and other reactive groups, at the chain ends or in the chains.

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1. Introduction

In the last 40 years, efforts in polymer science were directed toward several aspects, from “tailor-made” macromolecular synthesis to materials manufacturing. Technological needs, often in tandem with an increasing demand of our modern society, force researchers to explore alternatives and solutions. Both the control of the selectivity of propagating reactive species, in order to induce the so-called “controlled/living” polymerization method, and the processes optimization, are necessary. A precise control of the structure, topology and functionality of polymeric chains enables the design of macromolecular scaffolds that may find applications in high added-value domains. Polyethers like poly(ethylene oxide) and poly(propylene oxide) – often referred to as poly(ethylene glycol) and poly(propylene glycol) respectively and obtained by polycondensation of alcohols – are produced worldwide in several million tons per year in commodity or high performance applications. These polymers are mainly used as precursors for polyurethanes, surfactants and lubricants, but also in biomedical or cosmetic domains.

The chemistry which enables their synthesis is mainly based on the ring-opening of epoxides by ionic or coordination mechanism. The focus will be given here on anionic polymerization due to its efficiency in terms of control of molecular features (molar mass, dispersity...). Initiation is a bimolecular nucleophilic substitution that forms alkoxide species the reactivity of which depends mainly on the nature of the counter-ion. The alkoxide acts as a nucleophile and attacks a new epoxide molecule enabling the propagation step. A preliminary complexation of the monomer by specific additives can be considered as an anionic-related mechanism. Epoxide reactivity and polymerization kinetics are predominantly influenced by their polymerization enthalpy and ring strain, but also by electronic and steric factors associated with the nature of the ring substituent as well as reaction conditions like temperature and solvent. The ability of epoxide monomers to be activated by complexation with an electrophile can also strongly facilitate nucleophilic ring-opening. Based on this chemistry as well as organic synthetic tools, many substituted epoxide monomers are able to be polymerized, opening pathways for well-defined polyether structures and functionalities and allowing for the preparation of materials with various properties.

After a brief overview of conventional anionic ring-opening polymerization, this review article highlights recent advances in the field of synthesis of aliphatic

polyethers utilizing monomer activation on one hand, and using metal-free initiating systems on the other hand, as well as the various ways to prepare functional polyethers.

2. Overview of conventional anionic polymerization of epoxides

Flory observed in the 1940s that propagation may proceed without side reaction in anionic polymerization of ethylene oxide [1]. Alkali metal derivatives like hydrides, alkyls, aryls, amides, and mainly alkoxides of sodium, potassium, and cesium, represent the most common initiators used for the anionic ring-opening polymerization of epoxides (AROP) [2,3]. By conventional anionic polymerization we mean that initiation is triggered by such alkali metal derivatives. Lithium alkoxides do not conduct the polymerization of such monomers due to strong aggregation between lithium species after insertion of the first epoxide unit. Polymerizations initiated by alkali metal alkoxides are generally carried out in aprotic and apolar media or in coordinative solvents like dimethylsulfoxide (DMSO) or dimethylformamide (DMF) in order to dissociate active species. The reaction temperature plays also an important role. The driving force for a ring-opening reaction is the relief of the strain energy of the epoxide ring. At low temperature, below -20°C , the most reactive epoxide named ethylene oxide is not reactive toward potassium-based initiators and can be used as solvent of the anionic polymerization of methyl methacrylate for instance [4]. High temperatures are usually needed for the AROP of long-chain alkylene oxides.

The different steps of conventional AROP of epoxides are shown in Scheme 1. The initiation step consists of a nucleophilic substitution $\text{-S}_{\text{N}}2$ type-of the alkoxide species leading to the formation of new alkoxide species able to further attack monomer molecules resulting in polyether chains with an atactic structure. The termination step is achieved by addition of an acidic compound with labile hydrogen. Alcohols and water are the most commonly used termination agents in order to obtain hydroxyl end-groups. Transfer to monomer is observed with most of the initiating systems when substituted epoxides are polymerized. It will be discussed in a following paragraph.

2.1. Ethylene oxide

Alkali metal derivatives are efficient initiators for the polymerization of ethylene oxide (EO). Anion radicals such as sodium naphthalene react by direct addition of the anion-radical to monomer [5]. It involves the addition of

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