

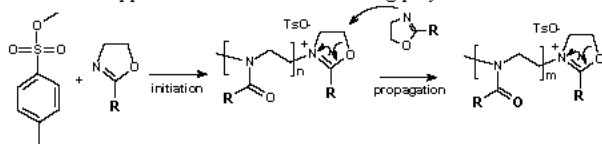
## Microwave-Assisted Cationic Ring-Opening Polymerization of Cyclic Imino Ethers

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### Introduction

The living cationic ring opening polymerization (CROP; see Scheme 1) of 2-oxazolines was discovered in 1966.<sup>[1-4]</sup> After this discovery, the resulting (biocompatible) poly(2-oxazoline)s have been used for a wide variety of applications from compatibilizers and emulsifiers to micellar catalysis and drug delivery.<sup>[5-7]</sup> Moreover, various (block) copolymer structures are easily accessible by the (sequential) copolymerization of differently substituted 2-oxazoline monomers. When the side-chain of the 2-oxazoline monomer is methyl or ethyl, water soluble polymers are obtained. Longer aliphatic or aromatic side chains will result in hydrophobic polymers allowing the preparation of amphiphilic structures by combining the different monomers. However, poly(2-oxazoline)s have never been applied in commercial applications because of their long polymerization times.

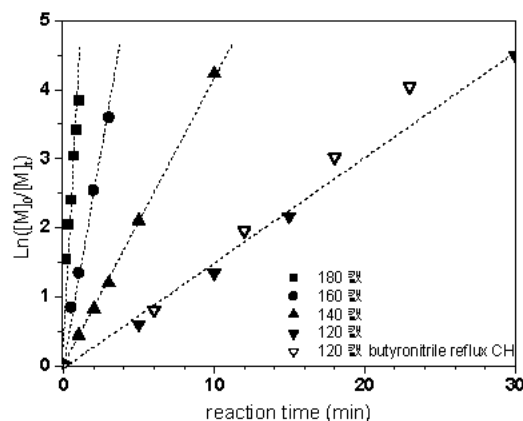


**Scheme 1.** Schematic representation of the cationic ring-opening polymerization of 2-oxazolines.

In this contribution, we report our investigations on the microwave-assisted cationic ring-opening polymerization of 2-oxazolines. The use of microwave irradiation as alternative heat source is gaining significant attention in organic and pharmaceutical chemistry.<sup>[8-10]</sup> However, the use of microwave heating in polymer science is still rather unexplored.<sup>[11]</sup> In addition, the microwave-assisted cationic ring-opening polymerization procedure was applied for the preparation of libraries of block copoly(2-oxazoline)s and statistical copoly(2-oxazoline)s. In addition, we have investigated the microwave-assisted cationic ring-opening polymerization of other cyclic imino ethers that have very low polymerization rates.

### Results and discussion

The polymerization of 2-ethyl-2-oxazoline is mostly performed in acetonitrile with conventional heating in open reaction vessels, which limits the polymerization temperature to the boiling point of acetonitrile (82 °C). However, the used microwave synthesizer (Emrys Liberator, Personal Chemistry) is operated with closed reaction vials and thus the polymerizations can be performed under pressurized conditions allowing superheating (heating beyond the boiling point of the solvent and reagents). The resulting first order kinetic plot for the polymerization of 2-ethyl-2-oxazoline under microwave-irradiation at 120, 140, 160 and 180 °C is depicted in Figure 1 demonstrating linear first order kinetics.<sup>[12,13]</sup> In addition, the number average molecular weights increased linearly with conversion (not shown) demonstrating the livingness of the polymerization. Using superheated conditions, the cationic ring-opening polymerization of 2-ethyl-2-oxazoline could be accelerated to several minutes, whereby the polymerizations at 140 °C revealed the best control over the polymerization. Nevertheless, control experiments in refluxing butyronitrile (Figure 1) and in autoclaves with conventional heating revealed similar accelerations demonstrating that the observed acceleration is a temperature effect and not a specific microwave effect.<sup>[14]</sup> Although the observed acceleration can be reproduced with conventional pressure conditions, the polymerizations under microwave irradiation resulted in narrower molecular weight distributions.<sup>[12,13]</sup> This improved control over the polymerizations is believed to result from the fast and homogenous non-contact heating that results in fast initiation and a continuous polymerization rate throughout the entire polymerization mixture.



**Figure 1.** First order kinetic plot for the cationic ring-opening polymerization of 2-ethyl-2-oxazoline under microwave irradiation in acetonitrile and in refluxing butyronitrile using conventional heating (CH).

The optimal polymerization temperature of 140 °C in acetonitrile was subsequently applied for the preparation of diblock<sup>[15]</sup> and triblock<sup>[16]</sup> copolymer libraries based on the 2-methyl-, 2-ethyl-, 2-nonyl- and 2-phenyl-2-oxazoline monomers. These libraries of copolymers were analyzed for their thermal and surface properties as well as their solubility and micellization behavior to determine structure-property relationships.

More recently, we have also investigated the microwave-assisted polymerization of other cyclic imino ethers including oxazines and 4- and 5-substituted oxazoline monomers. These results will also be discussed in this contribution.

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