

A Fatty Acid Based 2-Oxazoline Monomer: More then Renewable

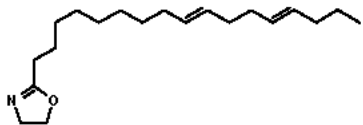
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Introduction

The use of renewable feedstock is becoming a more and more important issue in chemistry due to the increasing oil-prices and the concerns about future oil-supplies.^[1] In polymer chemistry, the use of renewable resources has attracted significant attention in the last couple of years as well. The renewable resources that were used in polymer chemistry include, e.g., starch,^[2,3] saccharides^[4,5] and fatty acids.^[6,7] Besides being a green alternative, the use of fatty acids provides new opportunities for polymer science due to the present unsaturated bonds that can be used for crosslinking of the polymers upon UV-irradiation.^[8,9] Although the use of fatty-acid based monomers has been exploited by many groups, we are only aware of one example in which an unsaturated fatty acid based monomer (cardanyl acrylate) was used in a living/controlled polymerization technique (atom transfer radical polymerization) to prepare well defined polymers with unsaturated side chains.^[9]

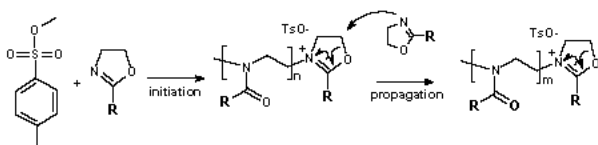
In this contribution, we report the cationic ring-opening polymerization of a 2-oxazoline monomer with soybean fatty acid side chains (SoyOx) under microwave irradiation. Kinetic experiments were performed to investigate the livingness of the polymerization in both acetonitrile and in the absence of solvent. In addition, both block and statistical copolymers were prepared using the SoyOx monomer.



Scheme 1. The soy-base 2-oxazoline monomer (SoyOx) that was used in this study.

Results and discussion

The cationic ring-opening polymerization of 2-oxazolines is an established method for the preparation of well-defined (block) copolymers.^[10,11] The polymerization mechanism is schematically depicted in Scheme 1 with methyl tosylate as electrophilic initiator.



Scheme 1. Schematic representation of the cationic ring-opening polymerization of 2-oxazolines. In this work, R stands for soybean fatty acid side chains.

The polymerization kinetics in both acetonitrile and in bulk were investigated at 140 °C in closed microwave vials using methyl tosylate as initiator.^[12] SoyOx polymerizations were performed for different reaction times and the resulting mixtures were analyzed with gas chromatography and ¹H-NMR spectroscopy to determine the monomer conversion and with size exclusion chromatography to measure the molecular weight (distribution). The ¹H-NMR spectra of the bulk polymerization are depicted in Figure 1 demonstrating almost complete conversion after only 7.5 minutes polymerization time as is indicated by the disappearance of the triplets at 3.8 and 4.2 ppm and the appearance of the broad polymer backbone signal at 3.4 ppm. Furthermore, the resonances of the protons next to the unsaturated sites (5.3 ppm) remain constant demonstrating that they are not affected by the cationic ring-opening polymerization. Linear first order kinetics as well as a linear increase of number average molecular weight with conversion was obtained demonstrating that the SoyOx polymerizations were performed in a living manner.

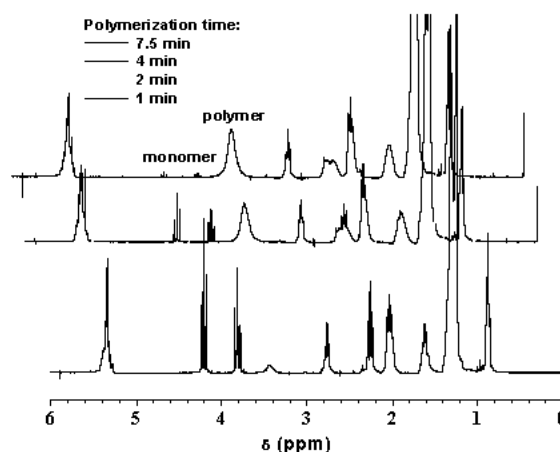


Figure 1. ¹H-NMR spectra taken after different reaction times for the polymerization of SoyOx in bulk at 140 °C using methyl tosylate as initiator. The spectra were recorded in CDCl₃.

As a result, pSoyOx was obtained with polydispersity indices of 1.20 or lower. After UV-irradiation of the polymer, it was insoluble in dichloromethane proving successful cross-linking of the polymer by exploiting the unsaturated fatty acid side chains.

Subsequently, amphiphilic diblock copolymers were prepared with poly(2-ethyl-2-oxazoline) (pEtOx) as hydrophilic part and pSoyOx as hydrophobic part.^[13,14] Micelles could be formed from these block copolymers and UV-irradiation resulted in the formation of core-crosslinked micelles that reversibly changed into rice-like micelles when they were transferred from water to the non-selective solvent acetone.

In addition, statistical copolymers were prepared covering the complete composition range from EtOx to SoyOx in steps of 10%.¹⁵ The effect of copolymer composition on the thermal and surface properties was investigated as well as the effect of UV-crosslinking on these properties.

Acknowledgement

The authors would like to thank the Dutch Scientific Organisation (NWO) and the Fonds der Chemischen Industrie for financial support. The 2-soy-2-oxazoline monomer was kindly provided by Henkel.

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