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Highly-selective cationic co-polymerisation of bio-based 2-MeTHF to polyether polyols

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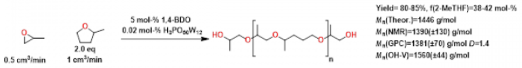
PURPOSE OF THE ABSTRACT

Polyethers with defined end group functionalities are indispensable building blocks to produce polyurethane based materials and high-performance adhesives. Currently polyether polyols are obtained by oligo- and polymerisation of cyclic ethers from petrochemical feedstocks, such as ethylene oxide, propylene oxide (PO) or THF. The lack of bio-based alternatives prompted us to investigate 2-methyl tetrahydrofuran (2-MeTHF), thus far mainly used as a solvent or fuel additive, as co-monomer. In contrast to THF, polymerisation of 2-MeTHF has never been descibed in the literature. However, we present the first reported methodology to co-polymerize 2-MeTHF with PO to hydroxy terminated polyethers (Scheme). The obtained materials are low in cyclic oligomers, which is otherwise difficult to achieve in cationic polymerisation.

Initial investigations showed that mostly cyclic oligomers were obtained in the presence of strong Lewis acidic catalysts. These cyclic oligomers presumably form via a backbiting reaction which is a common side reaction in cationic ring opening polymerization. On the other hand, when phosphotungstic acid was used as catalyst at only 0.02 mol-%, the incorporation of 2-MeTHF and the molecular weight of the polymer could be directly controlled by the ratio between the initiator and PO, which can be described as a living co-polymerisation (Figure). Some bifunctional alcohols were investigated as initiators from which 1,4-butanediol (1,4-BDO) had the best performance.

Combined NMR and ESI-MS studies proved the absence of cyclic oligomers as well as an average incorporation of (2-MeTHF) up to 43 mol%. The combination of all these findings allowed us to develop a process to synthesize the copolymer on a scale of up to 300g. Crosslinking experiments with 4,4-methyl phenyl isocyanate show promising applicability of these polyether polyols in two component adhesives.

FIGURES



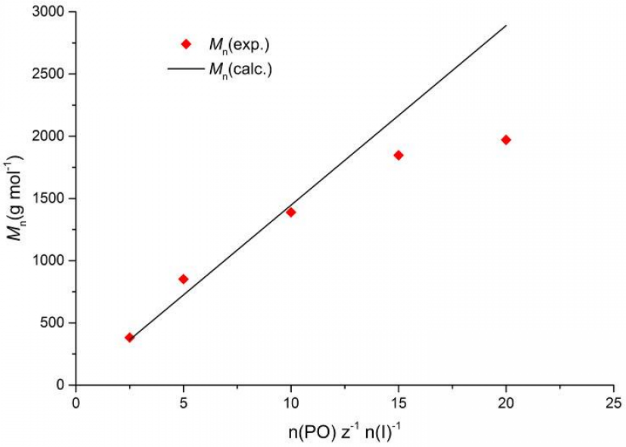


FIGURE 1

Co-polymerisation of 2-MeTHF and PO to -OH terminated polyether polyols

Scheme

FIGURE 2

Predicted vs. experimental Mn at different ratios of fed PO and 1,4-BDO

Figure

KEYWORDS

2-MeTHF | adhesives | oligomerisation | bio-based

BIBLIOGRAPHY