Catalysis for biobased polycondensation materials

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Two different approaches can be taken in developing biobased polymers: (i) The production of conventional monomers by new pathways, starting from agricultural biomass. This approach requires a number of (bio)chemical steps before the monomers can be obtained and rely, therefore, on the economical and environmental benefits in using biomass for petrochemical feedstock replacement. (ii) The production of new monomers, easily available from biomass, for the development of innovative polymers, either in replacement of petrochemical ones, i.e. with similar properties and uses, or for new applications. This approach is more demanding in terms of polymer chemistry since catalysis and reaction conditions must be modified.

The most part of monomers or oligomers that can be obtained from biomass by straightforward routes contain carboxylic acid and/or alcohol functional groups. They are particularly suited to the synthesis of (new) polyesters or polyamides. The catalytic systems used for conventional polymers, i.e. protonic or Lewis acids and metal oxides or alkoxides (for polyesters) and phosphorus derivatives (for polyamides), should, therefore, carefully be studied.

In this presentation, the synthesis of potentially biodegradable furanic-aromatic copolyesters by the bulk transesterification of a furan-based polyester and PET in the presence of metal alkoxides is reported. The furan-based polyester was obtained by the bulk polycondensation of ethylene glycol with a difuranic diester derived from furfural, a biobased compound. The reaction mechanisms were investigated with the help of a model polymer system, showing the preponderant influence of hydroxy end groups on copolyester randomization.

The synthesis and properties of new unsaturated aliphatic and cycloaliphatic polyamides from Z-octadec-9-enedioic acid, a natural unsaturated fatty diacid produced by the fermentation of sunflower oil, will also be reported. The rigid semi-crystalline cycloaliphatic polyamides may find applications in the same domains as polyamide-6 and the amorphous ones as polymers with very good resistance to chemical agents and solvents.