Vegetable-based building-blocks for the synthesis of renewable polyurethanes and polyesters made thereof

T. Lebarbé[1,2], L. Maisonneuve[1,2], E. Cloutet[1,2], B. Gadenne[3], C. Alfos[3] ,H. Cramail[1,2]

1 Université de Bordeaux, Laboratoire de Chimie des Polymères Organiques, IPB-ENSCBP, Pessac, France

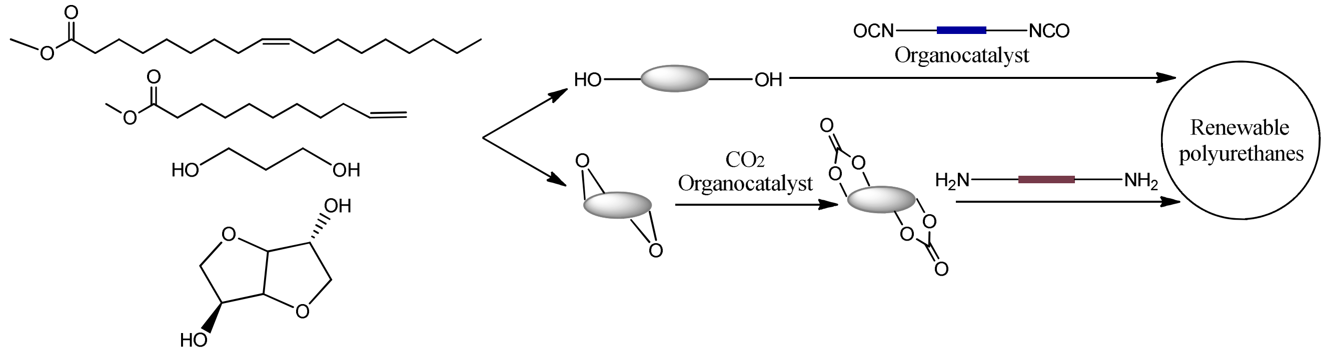
2 CNRS, Laboratoire de Chimie des Polymères Organiques, UMR 5629, Pessac, France

3 ITERG, Pessac, France

World-wide potential demands for replacing petroleum-derived raw materials with renewable ones are quite significant from the societal and environmental points of view. Among the various polymeric systems derived from renewable resources, polyesters gained a widespread interest over the last decades since new semi-crystalline thermoplastics are needed. Poly(lactic acid) is commonly considered as one of the best candidates to replace polymers from petroleum. However, since few decades, vegetable oils are also gaining widespread interest thanks to their availability, sustainability and biodegradability. Vegetable oils are triglycerides composed of different fatty acids which can be isolated by transesterification or saponification. The latter bring different functional groups (ester functions, double bonds, hydroxyl groups…) that can be derivatized to design new functional building blocks for the synthesis of novel polymers.

In this present work, monomers with various functionalities were synthesized. Thus new building block diols from ricin and sunflower oils were designed for step-growth polymerization with bio-based diacids or diesters. Hydroxyesters and AB2 type monomers were also studied in order to vary the macromolecular architecture of the polyesters made thereof. These building-blocks were obtained by transesterification, aminolysis, metathesis, epoxidation and thiol-ene reactions.1.2.3.4. Depending on the monomer structure, a large range of polyesters with various thermomechanical properties were obtained. The structure-properties relationship of the so-formed polyesters will be discussed in the presentation.

Moreover, new ester diols and bis-epoxides from ricin and sunflower oils obtained by transesterification, thiol-ene reaction and epoxidation are presented. [1][2][3][4][5][6] The starting bio-soured materials used are methyl undecenoate and oleate, propanediol and isosorbide. The latter two can be obtained from glycerol and starch respectively. A large range of polyurethanes with various thermomechanical properties can be obtained by varying the diol structure. Glass transitions from -27℃ to 66℃ but also crystallizations were obtained wit h these linear polyurethanes. The relationship between the diol structure and properties of the so-formed polyurethanes will be discussed in the presentation. One non-isocyanate route to PUs that consists of the reaction between diamines and biscarbonates, obtained by reaction of the fatty ester bis-epoxides, was also explored.[4]



Typical route to bio-based polyurethanes

1. A. Boyer, PhD Thesis. University Bordeaux 1. 2010.

2. D. V. Palaskar; A. Boyer; E. Cloutet; C. Alfos; H. Cramail Biomacromolecules. 2010, 11, 1202- 1211.

3. WO patent 030075 (2011), H. Cramail, A. Boyer, E. Cloutet, C. Alfos.

4. WO patent 030076 (2011), H. Cramail, A. Boyer, E. Cloutet, R. Bakhiyi, C. Alfos.

5. A. Boyer; E. Cloutet; T. Tassaing; B. Gadenne; C. Alfos; H. Cramail Green Chem. 2010, 12, 2 205-2213.

6. Manuscript under writing