

SYNTHESIS OF NEW BIOBASED BUILDING BLOCKS FOR POLYMER SYNTHESIS

Sylvain Caillol, Rémi Auvergne, Bernard Boutevin

ICGM – IAM – UMR5253, ENSCM, 8 Rue Ecole Normale, 34296 Montpellier. Téléphone : 04 67 14 43 27, Télécopie : 04 67 14 72 20, Adresse(s) électronique(s) : sylvain.caillol@enscm.fr

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1. INTRODUCTION

In recent years, the sustainability is becoming increasingly important for the chemical industry; thus, the use of renewable resources has gained interest in polymer applications. Indeed, overall demand for chemical products will increase by 50% in volume by 2020 (Prudhon, 2010). Thus, American studies estimate that 90% of organic chemicals will come from renewable resources by 2090 (Eissen et al. 2002). However, it is not sufficient to synthesize exactly the same chemicals from renewable resources, even if they are harmful. Biobased chemicals could also be very dangerous. New processes have to be developed to replace hazardous reactives by harmless, biobased ones. Vegetable oils are extracted primarily from the seeds of oilseed plants. Their competitive cost, worldwide availability, and built-in functionality (ester functions and insaturations) make them attractive. The development of oleochemicals has been carried out from two distinct ways. The first one corresponds to the double-bond modification (Gunstone et al., 2001) of crude oils or fatty acid derivatives. The second one is the carboxylic acid group modification of vegetable oils (Corma et al., 2007). The chemical functionalizations of unsaturated oils to produce polyols have been widely developed to prepare new polyurethane structures, which depend on triglyceride and isocyanate reagents used (Zanetti-Ramos et al., 2006; Yeganeh et al., 2007; Guo et al., 2000). Demand for renewable resources is also increasing for polymers and composite applications. This demand is particularly strong for polyurethanes (PUs) and epoxy resins (ER) with a global production of respectively 14Mt and 2Mt per year (Shen et al., 2009). These polymers became among the most dynamic groups of polymers, exhibiting versatile properties suitable for use in practically all the fields of polymer applications—foams, elastomers, thermoplastics, thermosets, adhesives, coatings, sealants, fibers, and so on. In this context, our team synthesized new building-blocks from vegetable oils in order to synthesize biobased PUs and ER materials. Experimental conditions and characterizations of these works were previously reported and scale-up was performed by Specific Polymers Company, Av. de l'Europe, 34830 Clapiers France.

2. VEGETABLE OILS

2.1 Building blocks approach

We synthesized various reactants from vegetable oils in one or two step synthesis by thiol-ene coupling reaction, trans/esterification, ring opening addition or carbonatation of epoxidized vegetable oils (Figure 1). These reactants exhibit primary or secondary hydroxyl groups, primary amines, activated acid groups, five-, six-membered or dithio- cyclic carbonate groups. These reactants could be used as monomers for various polymer syntheses such as polyurethanes (PUs), non-isocyanate polyurethanes (NIPUs), epoxy resins, polyesters... We have also added some phosphorous group on vegetable oils and derivatives (Millet et al., 2013).

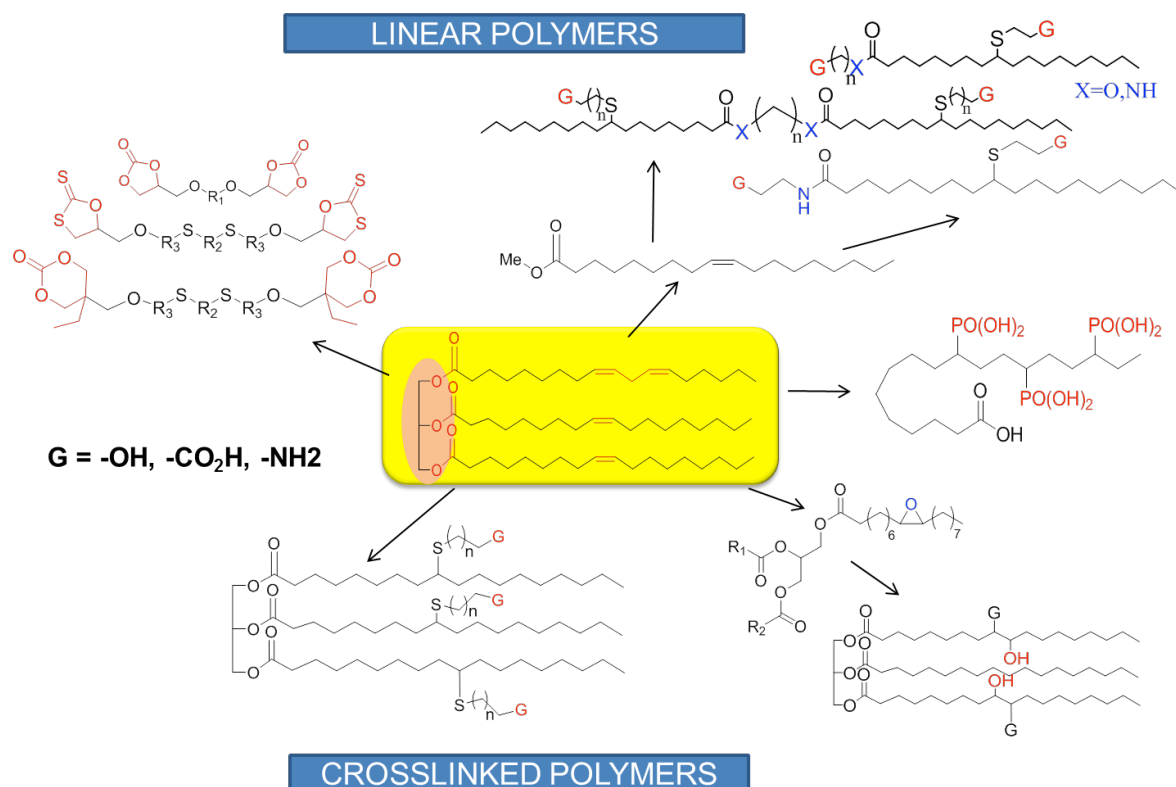


Figure 1. Synthesis of various building blocks from vegetable oils for polymer synthesis

2.2 Polyurethane precursors

PUs are obtained by the reaction of an oligomeric polyol (low molecular weight polymer with terminal hydroxyl groups) and a diisocyanate (or polyisocyanate). However, diisocyanates are not biobased and are generally very harmful reactants for human health. Thus, most used diisocyanates, methylene diphenyl diisocyanate (MDI) and toluene diisocyanate (TDI) are CMR products. Therefore the substitution of these compounds is crucial. To answer these questions, we proposed various solutions (Figure 1). In a first approach, since polyols correspond to 70% w/w of PU we synthesized new biobased polyols from vegetable oils by thiol-ene coupling or by ring opening of epoxidized vegetable oils. In a second approach, we used a reaction which is currently gaining much attention as an alternative route for the synthesis of PUs: step-growth polyaddition of dicyclocarbonates and diamines (Whelan et al., 1963; Mikheev et al., 1983). This method is quite interesting since no hazardous isocyanates are used and dicyclocarbonate reactants can be obtained from renewable resources such as glycerin. Moreover, this route allows the synthesis of NIPUs with hydrogen bonds, which have higher chemical resistance and better hydrolysis behavior.

2.3 Synthesis of di- and polyols by thiol ene coupling

On one hand, Soybean oil was reacted with mercaptoethanol in presence of an initiator. The study of the addition of mercaptoethanol on oleic acid allowed defining the experimental conditions (Desroches et al., 2011): synthesis was done in mass, with a ratio of thiol/double bonds of 3:1, at 80°C in the presence of AIBN with a ratio initiator/double bonds of 0.1/1.

Polyols were subsequently used to synthesize partially bio-based PUs materials. Formulations were performed with a MDI prepolymer with %NCO = 30.46 in the presence of functionalized triglycerides. Reaction mixtures exhibited a gel time of 170 min, monitored according to Winter

Chambon criterion. The obtained materials had a T_g around 0°C (determined by Differential Scanning Calorimetry), a shore hardness D of 20, and a Young Modulus of 7 N/mm^2 and tensile strengths at break of 1 MPa (Caillol et al., 2012). On the other hand, we have developed a synthetic strategy, which allows reaching a wide range of soft pseudo-telechelic diols from vegetable oils methyl esters. The soft segments of vegetable oils were comprised of either ester groups (one or two) or amide groups (one or two) with various spacer lengths between hydroxyl groups (Figure 2). Thus, the synthetic pathway was the following: 1) transesterification with a diol or amidification with hydroxylamine reactant; 2) thiol-ene radical coupling in presence of mercaptoethanol (Desroches et al., 2012). Two main parameters seemed to govern the physical properties of these pseudo-telechelic diols: the nature of ester/amide group and the spacer length. These parameters positively or negatively influenced the hydrogen bonding between pseudo-telechelic diols and thus modified their physical properties. For instance, the glass transition temperature decreased when the spacer length increased, whereas the melting temperature of amide containing pseudo-telechelic diols was much higher than that of ester containing pseudo-telechelic diols.

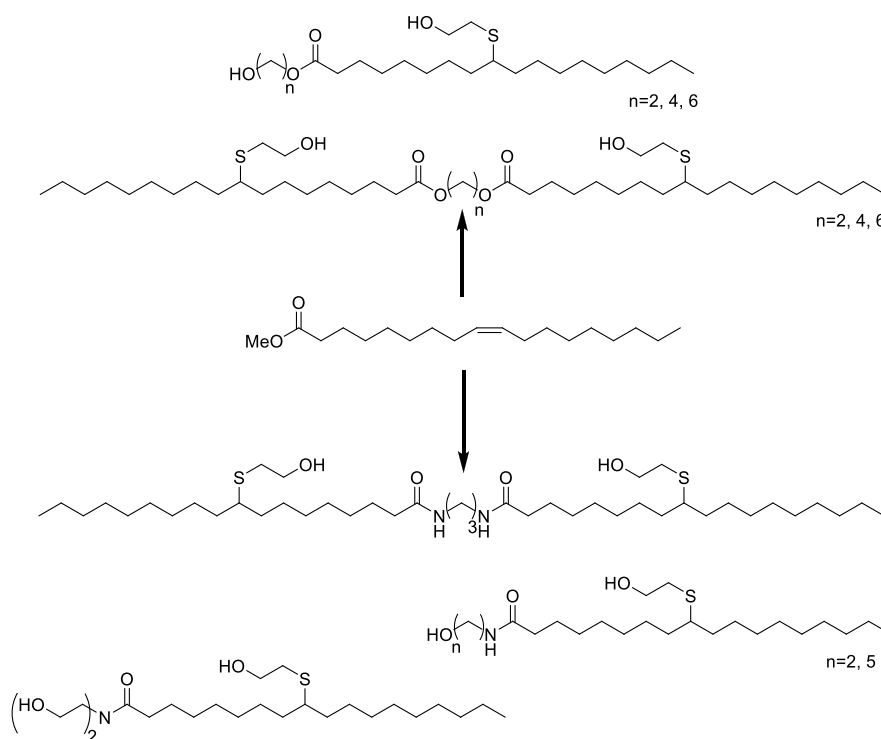


Figure 2. Ester/amide polyols from fatty acid esters.

These pseudo-telechelic diols were reacted with MDI to elaborate PUs. It is particularly interesting to note that the thermostability of these PUs was lowered in the presence of amide groups. In the other hand, PUs with amide groups exhibited the highest glass transition temperatures (around 60°C), due to hydrogen bonding enhancement. Furthermore, chain length between functional groups - ester and amide - modified the rigidity of corresponding PUs. Finally, we demonstrated that amide groups influence the curing behavior through a catalytic effect onto the isocyanate-alcohol reaction (gel times around 40 min for diols with amide groups and around 200 min for diols with ester groups).

2.4 Polyols by epoxide ring opening

We also worked on epoxidized vegetable oils which are interesting industrial biobased resources. We thus synthesized biobased polyols by epoxide ring opening of epoxidized vegetable oils, with three different acids: lactic and glycolic acids were selected since they are both biobased and present respectively a secondary and a primary hydroxyl group. Acetic acid, without hydroxyl group, was selected due to its low cost and widespread use in chemical industry. The polyol obtained from lactic acid is the most interesting in terms of renewable carbon content. It is noted that reactions occurred in mass, at relatively low temperatures, without initiator or purification, which meets the principles of green chemistry (Caillol et al., 2012).

2.5 Dicyclocarbonates for NIPUs

Isocyanate reactants are generally harmful for human health. Therefore the synthesis of PUs from step growth polyaddition of dicyclocarbonates and diamines should be favored. In that purpose, our team performed a new synthesis of 4-[(prop-2-en-1-yloxy)methyl]-1,3-dioxolan-2-one (AGC) by Williamson ether synthesis from 4-(hydroxymethyl)-1,3-dioxolan-2-one (glycerin carbonate) (Benyahya et al., 2011). Dicyclocarbonate was synthesized by UV thiol-ene coupling of AGC with a 2,20-oxydiethanethiol. This photochemical thiol-ene reaction was carried out under air, with neither solvent nor photoinitiator.

The synthesized dicyclocarbonate was used without purification to synthesize polyhydroxyurethanes without isocyanate by step growth polyaddition with 1,10-diaminodecane. The synthesized polyhydroxyurethane exhibited glass transition temperature of -31°C and a molecular weight of 9 000 g/mol. This value was comparable to those reported in the literature. For instance, the polyaddition of 4,4'-[ethane-1,2-diylbis(sulfanediylbutane-4,1-diyl)]bis(1,3-dioxolan-2-one) led to a NIPU with a yield of 67% and a molecular weight of 7500 g/mol (Tomita et al., 2001).

2.6 Polyurethane precursors

The synthesized polyols were reacted with MDI to yield PU materials with similar thermal and mechanical properties than conventional PUs. We report herein glass transition temperature of some of the PU polymers synthesized from our biobased polyols or the NIPUs synthesized from cyclic carbonate reactants.

Polyols from raw castor oil (Petrovic et al., 2008) (castor oil), or polymerized castor oil (Xu et al., 2008) (Es-pricin) led to low Tg PUs. Diesters synthesized by our team led also to low Tg PUs. PUs from our monoesters diols showed Tg around 20°C. Thiol grafting onto vegetable oil allowed obtaining PUs with Tg ranging from 0°C to 20°C. Finally, to ensure high Tg (>50 °C), it is recommended to use the epoxy ring opening of vegetable oils by hydroxyl acids. Amide diols synthesized by our team (MAD, DAD or MAT) led also to high Tg-PUs. Concerning the NIPUs, owing to the various structures or amine hardeners, polymers with various Tg were obtained.

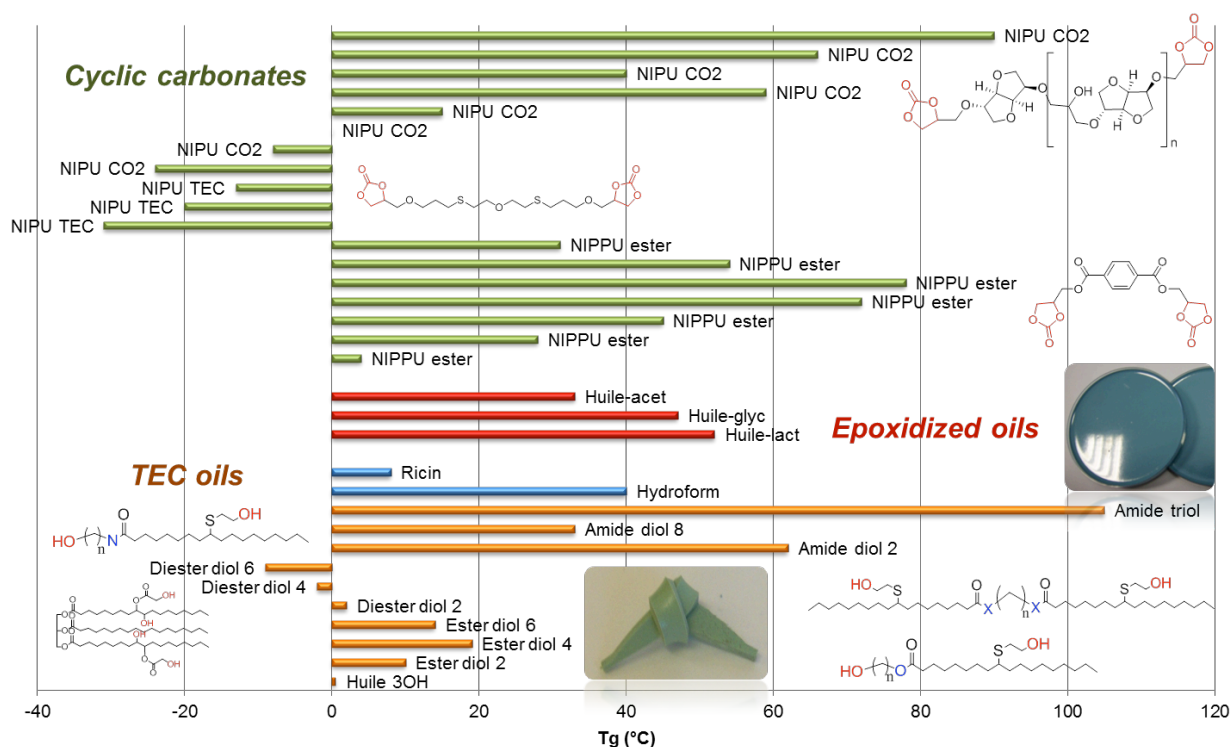


Figure 3. Glass transition temperatures of some of the synthesized PUs and NIPUs from our building blocks from vegetable oils.

3. CONCLUSION

We developed a real chemical toolbox based on thiol-ene coupling and amidification/esterification to synthesize a library of biobased building blocks with various functions and functionality from vegetable oils. The synthesized building blocks reported in this contribution are polyols, polyacids, polyamines and dicyclocarbonates from vegetable oils and from glycerine derivatives. They led to polymer synthesis such as polyurethanes, polyhydroxyurethanes and epoxy resins. These biobased building blocks led to polymers with various properties: low Tg polymers for coating or higher Tg polymers for composites.

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