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# Syntheses of epoxyurethane polymers from isocyanate free oligo-polyhydroxyurethane



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#### ABSTRACT

Polyepoxyurethane polymers were synthesized from PolyHydroxyUrethane (PHU) prepolymers terminated amine and epoxy multifunctional. In order to ensure this, PHU prepolymers was synthesized from the reaction between  $\alpha$ ,  $\omega$ -bis-cyclic-carbonates (poly (propylene)oxide bis-carbonates) and different excess of diamines (ethylenediamine) to terminate these prepolymers by amine with differents chain length. Then, these aminotelechelic PHU oligomers were re-used in formulation with multifunctional epoxy compound (Bisphenol A Diglycidyl Ether, Di-epoxydized Cardanol or Phloroglucinol Tris Epoxy) to synthesize polyepoxyurethane polymers called also hybrid polymers. Firstly, the raw materials were analyzed in order to determine proportion stoichiometry for carbonate/amine and of hybrid materials formulations. Secondly, for the purpose to demonstrate that the reaction carbonate/amine form hydroxyurethane compound, a model study was realized. Then, syntheses and analyzes of prepolymers terminated amine by <sup>1</sup>H, <sup>13</sup>C NMR, TGA and DSC was conducted. Once these oligomers analyzed, the hybrid polymers were formulated from epoxy compounds at different temperatures to determine the best cross-linking proceed. Epoxyurethane polymers were characterized by ATG, DSC and measurement of their swelling index and gel content. These materials exhibited glass transition temperature between -5 °C and 42 °C and a thermal stability above 320 °C at 30% of weight loss.

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#### 1. Introduction

Since the discovery by Otto Bayer and coworkers in 1937 of the reaction between diisocyanates and polyols, the demand of polyurethane has continued to increase and it will attain in 2016 a production of 18 million tons [1,2]. These materials are used in a wide range of applications in everyday life: thermosets, thermoplastics, foams, elastomers, coatings, adhesives, sealants, fibers ... However, nowadays, a large quantity of materials and syntheses are suspected to be responsible of negative effects on environment and human health [3–5]. It is in this context that the European regulation REACH is seriously considering the effects of the synthesis of polyurethanes [6]. Indeed, the diisocyanates necessary for the preparation of polyurethanes are harmful reactants for human health, particularly for people exposed during polyurethanes synthesis and could

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entail adverse health effects such as asthma, dermatitis, conjunctives and acute poisoning [3]. Actually, the two isocyanates most widely used in PU industry, ethylene diphenyl 4,4'-diisocyanate (MDI) and toluene diisocyanate (TDI), are classified as CMR (Carcinogen, Mutagen and Reprotoxic) [7].

In order to design a PU materials without isocyanate (NIPU: Non Isocyanate PolyUrethane), an interesting alternative consists mainly to use the polymerization between dicyclocarbonates and diamines. The resulting materials are called polyhydroxyurethanes (PHUs), since they contain also hydroxyl groups throughout the macromolecular chain. These hydroxyl groups create thus inter and intramolecular hydrogen bonds with urethane group which confers higher chemical and physical strength to these PHUs [8,9]. Moreover, these PHUs exhibit also excellent thermal stability due to the absence of biurets and allophanates in the polymer chain. Additionally, studies have shown that PHUs were less sensitive to moisture than conventional polyurethanes [8,10]. In the 1960s, Whelan et al. [11] and Ried et al. [12] were the first researchers to pay attention to the reaction between five membered cyclic carbonates and amines. Since this date, this reaction has been tremendously studied and several methods of synthesis were described later [13–21], particularly by Endo et al. [22–26]. In 2015, Rokicki et al. [27] and Maisonneuve et al. [28] were published two reviews on NIPUs on their of synthesis, properties and applications. Moreover, recently Carré et al. [29] describes the syntheses of novel and fully biobased NIPU via a green chemistry process, without solvent and catalysts from vegetable oils.

However, this reaction has two major drawbacks: the low reactivity of carbonate/amine reaction at room temperature [26] when compared to iscocyanate/alcool and the low molar masses of PHUs obtained (Mn between 1.800 and 28.000 g mol<sup>-1</sup>) [15,22,30–33]. To solve these problems, many studies in the literature have been conducted to design PHUs from more reactive cyclic-carbonates, bearing electro-withdrawing substituent [15,17,22,24,30,31,34–39] or by using sixmembered, seven-membered or thio-cyclic carbonate [23,26,31,40,41]. But, the preparation of these compounds involves phosgene or its derivatives for six-membered carbonates or carbon disulfides for thiocarbonates, which remain harmful reactants [23,26,31,33,40,41].

Since the thermoplastic PHUs do not exhibit high molar masses from five membered carbonate and amine, cross-linking of PHUs by curing polyfunctional carbonate with di- and polyamines can be envisaged to afford PHU thermoset rubbers. In addition to PHU networks, Figovsky et al. have worked on PHU/epoxy hybrid materials. Indeed, this team partially carbonated polyepoxy compounds and reacted them with amines to obtain hybrid epoxy/PHU materials [42–46]. These hybrid coatings are actually commercialized under the trade name *Green Polyurethane*<sup>™</sup> and represent the first successful application of PHUs in everyday life. These hybrid polyurethanes offer several advantages with respect to conventional polyurethanes: zero volatile organic compounds, solvent-less, 30–50% more resistant to chemical degradation, 10–30% more adhesive (depending on substrate), 20% more wear resistant.

However, these hybrid materials do not solve the main issue of PHUs which is the low reactivity of reaction between cyclic carbonate and amine. This low reactivity entails uncomplete conversion which hurdles the development of PHUs.

In order to improve the kinetics of the carbonate/amine reaction, many researches have been devoted to the development of novel catalysts. Some of us and Lambeth et al. have shown that the 1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD) and cyclo-hexylphenyl thiourea are the best catalysts for promoting the carbonate/amine reaction [47,48].

We have developed another strategy to afford new hybrid PHUs with high conversion. This very innovative two-step approach consists in the first step in the synthesis of PHU prepolymers functionalized with primary amine functions that could easily react as co-monomers with various epoxy groups in a second step to yield a range of new PHUs.

These PHU prepolymers are synthesized by the reaction between bis-cyclic carbonate and diamines in excess. These amine functionalized telechelic PHU oligomers are then reacted with epoxide reactants used as chain extender to yield hybrid PHU networks. This approach provides a wide range oligomer of different molar masses in function of the amine excess in the reaction carbonate/amine. Then, owing to the epoxy reactants, we could yield hybrid PHUs with various properties. This articles present, for the first time, the synthesis of primary amine functionalized PHU prepolymers. These prepolymers are synthesized by from di-carbonate derive by carbonation of poly(propylene oxide) diglycidyl ether prior to the reaction with ethylenediamine. The chain extenders used in this work were bisphenol A diglycidyl ether (BADGE) and two biobased epoxide reactants: the di-epoxy cardanol (NC-514) from Cardolite Company and the tri-epoxy phloroglucinol (PGTE) from Specific Polymers Company. Thus, one of the objectives of our study is to demonstrate the interest of PHU oligomers for the formulation of new hybrid non-isocyanate polyurethane networks.

#### 2. Experimental

#### 2.1. Materials

Poly(propylene oxide) bis-carbonate (PPO-Bis-C<sub>5</sub>-640, SP-1P-0-004) and phloroglucinol tris-epoxy (PGTE, SP-9S-5-003) were purchased from Specific Polymers (Castrie, France). Propylene carbonate, poly(propylene glyclol) diglycidyl ether (Mn  $\approx$  380 g mol<sup>-1</sup>, PPO-DGE-380), lithium bromide (LiBr), ethylenediamine, bisphenol A diglycidyl ether (BADGE), dimethylformamide (DMF), ethyl acetate and toluene were purchased from Sigma Aldrich. Di-epoxydized cardanol (NC-514) was obtained from Cardolite. Deuterated solvents (CDCl<sub>3</sub> and DMSO-d<sub>6</sub>) were purchased from Eurisotop (Saint-Aubin, France).

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