



Reactivity of secondary amines for the synthesis of non-isocyanate polyurethanes



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ABSTRACT

The role of secondary amine, usually not taken into account in the case of polyhydroxyurethanes (PHUs) synthesis, was inspected. Butanediol bis carbonate **BBC**, trimethylolpropane tris carbonate **TMPTC** and resorcinol bis carbonate **RBC** were synthesized by carbonation of corresponding epoxides. The products, obtained with high yield, were characterized by NMR and mass spectrometry analysis. These carbonates were converted to biobased polyhydroxyurethanes by step growth polymerization with tetraethylene pentamine **TEPA**. The optimal carbonate–amine ratio was determined from the differential scanning calorimeter results. A maximum T_g value of 16 °C was found for the **BBC–TEPA** system considering three reactive amine group among five of **TEPA** hardener. These results were completed by model reactions. Firstly, the reaction between **BBC** and a secondary diamine (*N,N'*-dimethyl-1,6-hexanediamine) was highlighted by differential scanning calorimetry. Moreover, the products of reaction between a monocarbonate (i.e. propylene carbonate) and **TEPA** or *N,N'*-dimethyl-1,6-hexanediamine were characterized by FTIR, NMR and mass spectrometry, allowing the demonstration of the formation of hydroxyurethane groups. Contrary to most of the results found in the literature, this work clearly demonstrates that secondary amines can also react with cyclic carbonates. Further details, such as activation energy of 28 kJ mol⁻¹ (**BBC–TEPA** system), glass transition temperatures (from 16 to 67 °C) and good degradation temperature (Td 5% between 198 and 256 °C) completed this work.

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1. Introduction

The chemistry of polyurethanes (PUs) has been extensively developed for several decades, both in Industry and Academia. Their properties can be modulated to use them in many fields of applications (thermoplastics,

thermosets, elastomers, adhesives, coatings, sealants, fibers, foams and so on) and numerous researchers paid lot of attention to these versatile compounds [1]. Typically, PUs are obtained by the reaction of diisocyanate or polyisocyanate with compounds having at least two reactive hydrogen atoms such as hydroxyl terminated oligomer (polyol). As diisocyanates are harmful reactants for human health, the synthesis of non-isocyanate PUs has recently gained an increasing interest in chemical industry. Thus, step growth polymerization of dicyclocarbonates and diamines can be an alternative route for the synthesis of PUs. This reaction, already studied in the past by Whelan

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et al. [2] and Mikheev et al. [3], avoids the use of isocyanates and diamines and permits the formation of poly(hydroxyurethane)s (PHUs) with hydroxyl groups. This method was tremendously studied and has recently attracted much attention, particularly by Endo [4–8] and Figovsky et al. [9,10].

Cyclic carbonates were first described in the early 1930s by Carothers et al. [11–13]. From then on, useful synthons in organic synthesis were synthesized, for example, as starting compounds for polycarbonate derivatives [14]. Some five-membered cyclic carbonates are commercially available and various methods are used for their synthesis [15–20]. The most common and effective method remains the addition of carbon dioxide on cyclic ethers (epoxides or oxetanes) [21,22].

A wide range of CO₂ incorporation reactions for the synthesis of cyclic carbonates have been developed, including the use of alkali metal salts [21,23,24], onium salts [25–27], metal complexes [28–30], ionic liquids [31,32], silica-supported catalysts [33], polymer catalysts [34,35], chiral catalysts [36], and so on, under high pressure or mild conditions. This reaction is quite interesting since CO₂ is cheap, environmentally friendly and a biobased source of chemical carbon to substitute phosgene [36–38].

Numerous studies [6,7,39–42] report step growth polymerization of 5-membered cyclic carbonates with various diamines leading to poly(hydroxyurethane)s having a M_n below 30,000 g mol⁻¹ and low Tgs. Recently, Fleischer et al. [43] reported the preparation of carbonated glycidyl ethers of glycerol, pentaerythritol and trimethylolpropane by carbonation. One of the most important problems chemists have to face to prepare a material is the reactivity of each reactive group since step growth polymerization is highly stoichiometry sensitive. For a long time, the reactivity of amines toward 5-membered cyclic carbonates is blurred and need a real clarification. Many authors postulate that only primary amines are reactive and few others considered that secondary amines may react at the same temperature (typically around 80 °C). This problematic was clarified in this article thanks to a deep investigation concerning the reactivity of both primary and secondary amines of **TEPA** toward **BBC**.

This original study is focused on the reactivity of secondary amines and their involvement concerning PHUs properties made of resorcinol, butanediol bicyclic carbonates (**RBC** and **BBC** respectively) as well as carbonated trimethylolpropane derivative (**TMPTC**) (Fig. 1). These carbonates were obtained by the reaction of the corresponding epoxides with carbon dioxide in the presence of LiBr

as catalyst. The functionality of the trimethylolpropane triglycidyl ether is of concern since the work made by Abuin et al. [44,45] demonstrated the formation of numerous side products during its synthesis. Among these products, halohydrins derivatives were formed and no tri functional carbonate was found. Thus, following Fleischer et al. [43] the determination of epoxide *per* molecule appears to be the best way to achieve a reliable formulation. Then the reaction of carbonates with linear tetraethylenepentamine **TEPA** is described. As a result, we were able to realize trustful formulations for each material with the aim of obtaining the best properties that are possible to reach. To further the study, we have performed the first characterizations of PHUs by TGA, DSC and DMTA. The materials obtained are candidates for coating applications because of their low Tgs, their good mechanical properties as well as their low expansion in water or solvents.

2. Experimental

2.1. Materials and methods

Butanediol diglycidyl ether (86%), resorcinol diglycidyl ether (purum), trimethylolpropane triglycidyl ether (technical grade), hexamethylene diamine (HMDA), *N,N*-dimethyl-1,6-hexanediamine, and propylene carbonate (PC) were purchased from Sigma Aldrich and used as received. Tetraethylenepentamine (**TEPA**) hardener was supplied by Huntsman Performance Products. *N,N*-dimethylformamide (DMF) was purchased from SDS Carlo Erba (Val de Reuil, France). Before use, DMF was dried according to current methods, distilled and stored under argon atmosphere. Deuterated solvents (CDCl₃ and DMSO-*d*₆) were purchased from Eurisotop (Saint-Aubin, France).

All Nuclear magnetic resonance (¹H NMR) measurements were recorded on a Bruker AC-400 MHz spectrometer at room temperature in deuterated chloroform (CDCl₃) or dimethylsulfoxide (DMSO). The chemical shifts were reported in parts *per* million relative to tetramethylsilane.

IR spectra were recorded with a Nicolet 210 FT-IR spectrometer. The characteristic IR absorptions mentioned in the text were strong bands and are reported in cm⁻¹.

Thermogravimetric analyses (TGA) were obtained on a TA Instruments Q50 apparatus. The initial weight of each sample tested was approximately 10 mg. Data were collected in Nitrogen atmosphere using a 10 °C min⁻¹ ramp from 20 °C to 580 °C. The temperatures of 5% and 30% weight loss (Td5) and (Td30) respectively, statistic heat-

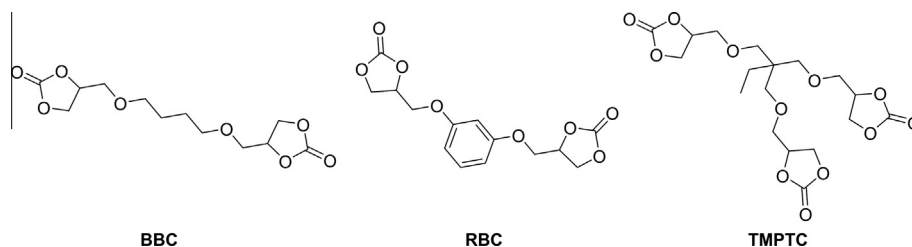


Fig. 1. Synthesized biobased cyclic carbonates.

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