



Renewable thermoplastic polyurethanes containing rigid spiroacetal moieties

Sophie Lingier^a, Pieter Espeel^a, Silvia Suarez Suarez^a, Oguz Türünç^a, Stefaan De Wildeman^{b,*}, Filip E. Du Prez^{a,*}

^a Department of Organic and Macromolecular Chemistry, Polymer Chemistry Research Group, Ghent University, Krijgslaan 281 S4bis, 9000 Ghent, Belgium

^b Biobased Materials, Faculty of Humanities and Sciences, Maastricht University, P.O. Box 616, 6200 MD Geleen, The Netherlands

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ABSTRACT

Unprecedented polyurethanes with rigid spiroacetal linkages in the backbone were synthesized from renewable resource compounds. First, the large-scale synthesis of a rigid diol monomer containing acetal bonds was established. Subsequently, this diol monomer was combined with seven different diisocyanates to vary the backbone of thermoplastic polyurethanes, leading to a spectrum of chemical and physical properties. The molar masses of the polymers ranged from 8 to 45 kDa and the corresponding polymers were obtained in high yields. DSC and DMTA analysis demonstrated glass transition temperatures up to 85 °C. Acid-mediated degradation of the materials was not noticed during hydrolytic stability tests.

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1. Introduction

In recent literature, there has been an increased interest for the synthesis of spiro polymers, i.e. polymers with spirocyclic units in the main chain [1–7]. This cyclic structure restricts conformational flexibility and hence results in an increased thermal stability of the polymers. Additionally, the mechanical strength of the corresponding polymers can be enhanced as a result of this rigidity. Among others, the synthetic approaches targeting spiro polymers, based on acetalization and analogous reactions, have been reported to be the most straightforward [1,3,4,7–14]. However, the solubility in common organic solvents and the processability of the reported polymers were found to be very poor. Therefore, an alternative synthesis method was applied to obtain spiro-containing polymers. Instead of forming the spirocyclic units upon polymerization, polymers can be built up via polyaddition or polycondensation [5,6,8,9,11,12,14,15] of monomers that already contain spirocyclic units [16–18]. For instance, polyurethanes, which constitute a large family of high-performance materials, show a wide variety of properties that are tuneable by a proper control of the molecular design [19]. While polyurethanes generally decompose around 200 °C, this degradation temperature can be elevated when rigid units are incorporated [20].

The incorporation of spiroacetal units into polyurethanes has been reported to obtain a new spectrum of properties because polymers with unique chemical and physical properties could be created [9,21]. It was shown that poor solubility and processability of the pure spiro polymers can be altered by introducing urethane groups in the polymer chain, whereas the rigidity of the polyurethanes can be enhanced by incorporating spirocyclic units. Furthermore, additional desired properties, such as transparency, were obtained by the introduction of amorphous regions, or suppressed crystallinity. High

* Corresponding authors.

E-mail addresses: s.dewildeman@maastrichtuniversity.nl (S. De Wildeman), Filip.DuPrez@ugent.be (F.E. Du Prez).

ductility was achieved by the introduction of spiro-centres along the polymer chain [22]. To date, a small number of patents have described the properties of polyurethanes containing rigid spiroacetal diols such as spiroglycol (Scheme 1, left) [17,23,24]. They focussed on fitting the synthesized polymers for the right application such as sheet-form articles [23]. In these reports, no studies were devoted to the specific features of these polyurethane structures.

The purpose of our research is to systematically investigate the chemical and physical properties of thermoplastic polyurethanes containing spiroacetal functionalities, which are partially created from renewable raw materials. Our primary goal was to overcome the common problems associated with the known spiroglycol containing polyurethanes, such as their bad solubility in common solvents, low molecular weight and limited processability.

Initially, a new and partially bio-based diol containing spiroacetal moieties was synthesized via a straightforward and large-scale synthesis. For its synthesis, the thiol-ene addition [25–28] was applied. This thiol-ene chemistry has been chosen because it enables to vary the functional groups attached to the spiroacetal structure. Apart from diols, also diamines, diester and diacids could be synthesized in a similar way.

One of the renewability contributing compounds to obtain the novel spiroacetal diol is 3,9-divinyl-2,4,8,10-tetraoxaspiro[5.5]undecane (**1**, Scheme 1). This compound is readily available and is prepared through the reaction between pentaerythritol and acrolein, which are respectively made from methanol and formaldehyde [29] and the dehydration of glycerol [30]. A sustainable production pathway for pentaerythritol can be hypothesized once the feedstocks would be sourced from bio-methanol [29,31], which is already claimed by Perstorp [32].

Seven different diisocyanates with various chemical structures were combined with the prepared spiroacetal diol in the subsequent polyurethane synthesis. These endeavours allow for a systematic study in order to investigate structure–property relationships, relevant for potential industrial implementation of such class of polyurethanes. The molecular structure of the prepared polymers was characterized with NMR, FTIR and SEC analysis. Thermal characteristics were determined with TGA, DSC and DMTA measurements, while modulus, tensile strength and ductility were evaluated with tensile tests. The materials were also subjected to a visual test to check for transparency and crystallinity. The hydrolytic stability of the materials was evaluated over a wide pH range for a period of one month in order to assess potential degradation of the acetal units [33].

2. Experimental part

2.1. Materials

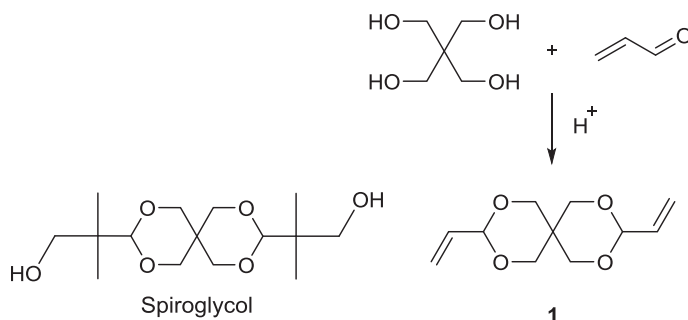
3,9-Divinyl-2,4,8,10-tetraoxaspiro[5.5]undecane (>98.0%), dibutyltin dilaurate (>95.0%, DBTL) hexamethylene diisocyanate (>98.0%, HDI), isophorone diisocyanate (>99.0%, IPDI) and toluene diisocyanate (>98.0%, TDI) were purchased from TCI. Mercaptoethanol ($\geq 99.0\%$), 2,2-dimethoxy-2-phenylacetophenone (99%, DMPA), 4,4'-methylenebis(cyclohexyl isocyanate) (90%, hMDI), 1,4-phenylene diisocyanate ($\geq 98\%$, PDI), methylene diphenyl diisocyanate (98%, MDI), dry ethyl acetate, hexane and diethyl ether were purchased from Sigma Aldrich. Trimethyl hexamethylene diisocyanate (TMDI) was obtained from Evonik. All substances were used as received without further purification.

2.2. Synthesis

2.2.1. Synthesis of spiroacetal diol

In a three-neck-flask, equipped with a mechanical stirrer, 25 g (0.118 mole) of dialkene (**1**) and 16.94 ml (0.241 mole) of 2-mercaptoethanol were added. The oxygen was removed via three cycles of vacuum-nitrogen flush. The mixture was stirred at 55 °C for 48 h after which the colourless mixture turned white. The obtained product was purified via two subsequent recrystallizations from hexane and diethyl ether, and dried in a vacuum oven with a yield of 80%.

$^1\text{H NMR}$ (300 MHz, DMSO- d_6 , ppm): 4.75 (*m*, 2 H), 4.56 (*app t*, 2 H), 4.26 (*app d*, 2 H), 3.62 → 3.46 (*m*, 8 H), 3.36 (*m*, 2 H), 2.56 → 2.45 (*m*, 8 H), 1.75 (*m*, 4 H).



Scheme 1. Chemical structure of spiroglycol and 3,9-divinyl-2,4,8,10-tetraoxaspiro[5.5]undecane (**1**). For the latter compound, the synthetic scheme starting from pentaerythritol and acrolein is shown.

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