



Novel fatty acid based di-isocyanates towards the synthesis of thermoplastic polyurethanes



Arvind S. More^{a,b}, Thomas Lebarbé^{a,b,c}, Lise Maisonneuve^{a,b}, Benoit Gadenne^d, Carine Alfos^d, Henri Cramail^{a,b,*}

^a Univ. Bordeaux, LCPO, UMR 5629, F-33600 Pessac, France

^b CNRS, LCPO, UMR 5629, F-33600 Pessac, France

^c French Environment and Energy Management Agency, 20 Avenue du Grésillé-BP 90406, F-49004 Angers Cedex 01, France

^d ITERG, 11, rue Gaspard Monge, F-33600 Pessac, France

ARTICLE INFO

Article history:

Received 1 September 2012

Received in revised form 9 December 2012

Accepted 17 December 2012

Available online 9 January 2013

Keywords:

Bio-based

Polyurethanes

Phosgene-free

Hydrazine

Fatty acids

Di-isocyanates

ABSTRACT

Fatty acid derivatives have been successfully transformed into diisocyanates via a non-phosgene and green method. The structure of these novel diisocyanates was confirmed through FTIR and ¹H NMR spectroscopies. These diisocyanates were reacted with commercially available and fatty acid based diols to obtain partially and fully bio-based polyurethanes respectively. The selected diols were of various structural features: with linear methylene spacers from 3 to 12 units, with sulfur-containing unit, ester linkages or cyclo-aliphatic units. The polyurethanes obtained were thoroughly characterized by FTIR, ¹H NMR spectroscopy, SEC studies, DSC and TGA experiments. Most of the polyurethanes were semi-crystalline in nature with well-identified melting transitions. However, due to plasticization and/or conformational issues, insertion of methylene dangling chains or cyclic moieties imparted amorphous feature to the polyurethanes. The polyurethanes displayed fair thermal stability with no significant weight loss below 235 °C.

© 2013 Elsevier Ltd. All rights reserved.

1. Introduction

Polyurethanes (PU) constitute a versatile class of polymeric materials and represent about 6% of the world production of plastics [1]. In general, PU result from the reaction of a diisocyanate (or a polyisocyanate) with a polyol, both obtained from petroleum-based resources. However, the finite fossil resources will be arguably diminishing within few generations, generating numerous initiatives to replace fossil resources by renewable counterparts [2–26]. In this light, vegetable or plant oils represent a renewable resource that can be used as reliable starting material to access new products with a wide array of structural and functional variations. The abundant availability

and the relative low cost make plant oils industrially attractive raw material for the plastic industry.

Vegetable oils are mostly triglycerides and contain several reactive sites, such as double bonds and ester groups, opening up various possibilities to tailor new structures. Most of the scientific literature available today has been centered on modifying vegetable oils to obtain polyols to prepare 3D networks, or well-defined linear PU structures [3,6–12,15–24].

The other building blocks in PU synthesis are diisocyanates; the latter can be prepared in many ways. The reaction of gaseous phosgene with amines or their corresponding salts has been the most viable and industrially used method [27–30]. However, the high toxicity of the phosgene coupled with the urge for sustainable chemistry has led to the development of new phosgene-free methods to isocyanates. In addition to some well-known laboratory procedures, such as Curtius [31], Hofmann

* Corresponding author. Tel.: +33 05 40 00 62 54; fax: +33 05 40 00 84 87.

E-mail address: cramail@enscbp.fr (H. Cramail).

[32] and Lossen rearrangements [33], several new syntheses are available [27–30]. The use of phosgene equivalents, like diphosgene, triphosgene is a preferred mean to produce isocyanate [34–37]. The use of oligomeric *t*-butylcarbonates is reported as an efficient mean to achieve direct conversion of diamines into diisocyanates [38]. One of the important pathways to isocyanate is the carbonylation of nitro compounds, followed by the thermal cleavage of so-formed carbamate [27–30]. This two-step method is favored due to the simple process and the good yields. Various carbonylating reagents such as carbon dioxide, carbon monoxide, dimethyl carbonate, etc. have been successfully employed for the synthesis of carbamates [27–30]. For instance, in a BASF proprietary method, isophorone diisocyanate is synthesized from isophorone diamine by reaction with urea and butanol, followed by pyrolysis of the carbamate [39]. The use of halosilanes has also been of interest owing to the milder reaction conditions and high yields of isocyanates [40–43].

Despite the large amount of literature data available on the synthesis of isocyanates, vegetable oil based isocyanates have not been fully explored until now. The inherent aliphatic nature coupled with the low reactivity of these vegetable oil based isocyanates make them not suitable to replace most commonly used diisocyanates in industry, typically 2,4-toluene diisocyanate and 4,4'-diphenylmethane diisocyanate. Nevertheless, the synthesis of fatty acid based diisocyanates has been described [44]. The fatty diamines obtained from dinitrile precursors of fatty acids were treated with phosgene. C36 fatty acid diisocyanate, typically used in coating applications, has been commercialized by Henkel Corporation Company [45–47]. In another example, Soybean oil based polyisocyanates have been prepared via allylic bromination of triglycerides followed by substitution with AgNCO [48]. More recently, two diisocyanates have been synthesized starting from azelaic and oleic acid via Curtius rearrangement and used for the preparation of fully bio-based thermoplastic polyurethanes (TPU) with comparable properties to those derived from commercially available 1,6-hexamethylene diisocyanate [49,50].

Since last few years, we have been actively engaged in developing novel fatty acids based macromolecular structures, including PU, polycarbonates and polyesters [51–59]. In the present article, we would like to put our efforts on the preparation of new vegetable oil based diisocyanates using simple organic modifications for PU syntheses. Precisely, we have efficiently used castor oil derivatives to synthesize two new diisocyanates via diacyl hydrazide intermediate with high yield and purity. The diisocyanates thus synthesized have been used as efficient comonomers in PU synthesis. We will be focusing our discussions on the synthesis and preliminary thermo-mechanical properties of the PU obtained.

2. Experimental

2.1. Materials and Instrumentations

Butanol ricinoleate (BuRicin, Purity by GC: 97.8%) and Ripol 2033 (Croda, France) were kindly supplied by ITERG,

Pessac, France. Dimethyl sebacate, acetic acid, dibutyltin dilaurate (DBTDL), anhydrous N,N-dimethyl formamide (DMF), 1,3-propanediol, 1,4-butanediol, 1,6-hexanediol, 1,12-dodecanediol, 2-mercaptoethanol were purchased from Sigma–Aldrich and purified wherever necessary. 10-Undecen-1-ol, sodium azide (NaN₃) and hydrazine hydrate (99%) were received from Alfa Aesar and used as received. Methyl 10-undecenoate (MUD), methyl thioglycolate and dianhydro-*D*-glucitol (Isosorbide) were purchased from TCI, Europe. The solvents were of reagent grade quality and were purified wherever necessary according to the methods reported in literature [60].

Infrared spectra were obtained on a Bruker-Tensor 27 spectrometer using the attenuated total reflection (ATR) mode. ¹H NMR spectra were recorded using a Bruker AC-400 NMR at room temperature by dissolving the samples in CDCl₃ or DMSO-*d*₆. Size exclusion chromatography (SEC) analyses were performed in THF (40 °C) on a PL-GPC 50 plus Integrated GPC from Polymer laboratories-Varian with a series of four columns from TOSOH (TSKgel TOSOH: HXL-L (guard column 6.0 mm ID × 4.0 cm L); G4000HXL (7.8 mm ID × 30.0 cm L) ; G3000HXL (7.8 mm ID × 30.0 cm L) and G2000HXL (7.8 mm ID × 30.0 cm L)). SEC analyses of PU were performed in DMF (80 °C) on a PL-GPC 50 plus Integrated GPC from Polymer laboratories-Varian with a series of three columns from Polymer Laboratories (PLgel: PLgel 5 μm Guard (guard column 7.5 mm ID × 5.0 cm L); PLgel 5 μm MIXED-D (7.5 mm ID × 30.0 cm L) and PLgel 5 μm MIXED-D (7.5 mm ID × 30.0 cm L)). In both cases, the elution of the filtered samples was monitored using simultaneous UV and RI detectors. The elution times were then converted to molar masses using a calibration curve based on low dispersity (*M_w/M_n*) polystyrene standards. Differential scanning calorimetry (DSC) thermograms were measured using a DSC Q100 apparatus from TA Instruments. Polymer samples were first heated from –100 to 200 °C and then *T_g* and *T_m* values were calculated from a second heating run. All runs were performed at a rate of 10 °C min⁻¹. Thermogravimetric analysis (TGA) was performed on TGA-Q50 system from TA instruments at a heating rate of 10 °C min⁻¹ under nitrogen atmosphere.

3. Syntheses

3.1. Synthesis of fatty acid based diisocyanates

3.1.1. 1-Isocyanato-10-[(isocyanatomethyl)thio]decane (DITD, 5)

(a) Methyl-11-[(2-methoxy-2-oxoethyl)thio]undecanoate (**2**)

The thiol-ene addition of methyl thioglycolate to the MUD was carried out in two ways:

(i) MUD (**1**: 38 g, 191.62 mmol) and methyl thioglycolate (50.84 g, 479.07 mmol) were weighed into the flask. The reaction mixture was further stirred at 35 °C for 48 h. After confirming the completion of the reaction with ¹H NMR spectroscopy, excess

Download English Version:

<https://daneshyari.com/en/article/10608519>

Download Persian Version:

<https://daneshyari.com/article/10608519>

[Daneshyari.com](https://daneshyari.com)