

# Maximizing the utility of bio-based diisocyanate and chain extenders in crystalline segmented thermoplastic polyester urethanes: Effect of polymerization protocol



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## ABSTRACT

High molecular weight semi crystalline thermoplastic poly(ester urethanes), TPEUs, were prepared from a vegetable oil-based diisocyanate, aliphatic diol chain extenders and poly(ethylene adipate) macro diol using one-shot, pre-polymer and multi-stage polyaddition methods. The optimized polymerization reaction achieved ultra-high molecular weight TPEUs (>2 million as determined by GPC) in a short time, indicating a very high HPMDI – diol reactivity. TPEUs with very well controlled hard segment (HS) and soft segment (SS) blocks were prepared and characterized with DSC, TGA, tensile analysis, and WAXD in order to reveal structure–property relationships. A confinement effect that imparts elastomeric properties to otherwise thermoplastic TPEUs was revealed. The confinement extent was found to vary predictably with structure indicating that one can custom engineer tougher polyurethane elastomers by “tuning” soft segment crystallinity with suitable HS block structure. Generally, the HPMDI-based TPEUs exhibited thermal stability and mechanical properties comparable to entirely petroleum-based TPEUs.

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## 1. Introduction

Segmented thermoplastic polyester urethane (TPEU) elastomers have attracted significant interest because they generate a wide variety of industrial applications ranging from foams and coatings to medical devices, where the hydrolytically labile polyester functions provide controlled degradation [1,2]. TPEUs generally possess the structure  $(-X-Y-)_n$ , composed of a polyester macro diol “soft segment (SS) block” and urethane rich ‘hard segment (HS-block)’. Their remarkable versatility stems from the chemical compositions of X and Y units. In conventional TPEU elastomers the incompatible X and Y units phase separate into nano scale domains of amorphous HS that serve as the load bearing phase in the rubbery soft polyester phase which imparts extensibility.

Research interest on crystalline SS and HS block TPEUs has seen a surge recently, especially due to their potential shape memory properties [1]. Crystallinity of SS-block is observed for sufficiently long macro diols. A moderate soft segment crystallinity leads to

increased incompatibility between the hard and soft domains, and enhances the mechanical performance in TPEUs [3]. In this regard, numerous studies have been undertaken to tune the ordering of SS-blocks, includes varying the type of soft segment, their size [2–5], content [6], and introducing side chain liquid crystal soft segments [7]. Aliphatic hexamethylene diisocyanate (HMDI) have been shown to offer enhanced ordering of the hard segment and to prevent the hydrolytic degradation of ester groups in poly(ester urethane) elastomers [8]. However, the majority of commercial TPEUs do not exhibit hard segment crystallinity due to the lack of molecular symmetry for the industrially available diisocyanates and the low molecular weight of the chain extenders. As a consequence, a systematic conceptual understanding of the role of crystalline HS-blocks in controlling the SS-block crystallinity is limited.

TPEUs synthesized from renewable resources have been receiving increased attention due to a perceived need to reduce petroleum dependence and address negative impacts on the environment. A significant amount of that attention has focused on the use of vegetable oil derived feedstock due to their relative availability, flexibility with regards to chemical modification, low toxicity and inherent biodegradability. Numerous studies have been carried out to develop diols or polyols suitable for

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polyurethane production from vegetable oils, to entirely or partially replace conventional petroleum-based materials [7–19], with a certain degree of success realized. Efforts to synthesize diisocyanates from vegetable oils have been limited compared to those focused on polyols, but some progress has been made. The synthesis of fatty acid based diisocyanates were reported as early as the 1970s [20], and a C36 fatty acid based diisocyanate has been commercialized by Henkel Corporation Company. A soybean oil based polyisocyanate was prepared via a vinyl bromination of triglycerides followed by substitution with AgNCO [21]. More recently, diisocyanates were prepared at the laboratory scale from fatty acid derived diamines using a phosgene method, or directly from fatty acids using Curtius rearrangement [9]. Thermoplastic polyurethanes have been prepared from these fatty acid derived diisocyanates by combination with either petroleum-based or bio-based diols [10–12]. However, the resulting materials displayed low molecular weights due to the low chemical reactivity of these diisocyanates, particularly 1,7-heptamethylene diisocyanate (HPMDI), produced from Curtius rearrangement of fatty diacids [10,12]. The poor performance of HPMDI-based thermoplastics has motivated the current work. It is focused on the optimization of the polymerization reaction conditions, selection of suitable polyester macro diol and chain extenders in order to develop high molecular weight semi-crystalline TPEU elastomers with varying chemical compositions of HS and SS-blocks.

A series of TPEUs were prepared from a vegetable-oil based diisocyanate (HPMDI), chain extenders and a petroleum-based polyester macro diol (Poly(ethylene adipate) diol, DESMOPHEN 2000), using varying polymerization protocols. The TPEUs were chemically and physically characterized. The effects of HS-block content, distribution and type on crystal structure, thermal stability, melting and crystallization behavior, and mechanical properties were investigated with XRD, TGA, DSC and tensile analysis, respectively.

## 2. Experimental

### 2.1. Materials

DESMOPHEN<sup>®</sup> 2000 (molecular weight 2000 g/mol), a petroleum based poly(ethylene adipate) diol (PEAD) was procured from Bayer Materials Science, Canada. 1,7-heptamethylene diisocyanate (HPMDI) was synthesized in our laboratories according to a previously reported procedure [10]. The petroleum-based Stannous octoate (Sn(Oct)<sub>2</sub>) catalyst, 1,4-butanediol (BD), 1,6-hexanediol (HD), 1,9-nonanediol (ND) and 1,3-propanediol (PD) were purchased from Sigma Aldrich, Canada. Note that all these diols, namely, BD [13], HD [14], ND [15], and PD [16] are also obtainable from bio-based sources. Chloroform, methanol, and DMF were obtained from ACP chemical Int. (Montreal, Quebec, Canada). All reagents except DMF was used as obtained. DMF was purified by drying overnight using 4A molecular sieves followed by a vacuum distillation (~20 mm Hg).

### 2.2. TPEU synthesis

A series of HPMDI based TPEUs were prepared by reaction of a bio-based diisocyanate, HPMDI, with poly(ethylene adipate) diol (PEAD) and/or aliphatic diol chain extenders (PD, BD, HD and ND) using the industrially used one-shot (Method 1 and 2), pre-polymer (Method 3 and 4) and multistage polyaddition (Method 5) polymerization methods. The NCO: OH ratio for all TPEU samples was fixed at 1.1:1.

Table 1 provides the nomenclature and the chemical composition of the TPEUs. The samples are labeled based on the chemical

**Table 1**

Sample designation and chemical composition of TPEUs. The aliphatic diol chain extenders ( $C_m$ ) are  $m = 3$  (PD), 4 (BD), 6 (HD) and 9 (ND).

Series	TPEUs	Method	$m$	HS-block [ $C_mI$ ] <sub>x</sub>		SS-block [ $P(C_mI)_y$ ] <sub>z</sub>		
				HS (wt %)	$x$	P (wt %)	$y$	$z$
S1	PU1-100x-0y <sub>0</sub> /z <sub>0</sub> -9	1	9	100	–	–	–	–
	PU3-74x <sub>5</sub> -24y <sub>0</sub> /z <sub>1</sub> -9	3	9	74	5	24	0 = 1	1
	PU3-56x <sub>4</sub> -40y <sub>0</sub> /z <sub>1</sub> -9	3	9	56	4	40	0 = 1	1
	PU3-46x <sub>3</sub> -49y <sub>0</sub> /z <sub>1</sub> -9	3	9	46	3	49	0 = 1	1
	PU3-36x <sub>2</sub> -58y <sub>0</sub> /z <sub>1</sub> -9	3	9	36	2	58	0 = 1	1
	PU3-16x <sub>1</sub> -76y <sub>0</sub> /z <sub>1</sub> -9	3	9	16	1	76	0 = 1	1
	PU4-3x <sub>1</sub> -88y <sub>0</sub> /z <sub>3</sub> -9	4	9	3	1	88	0 = 1	3
S2	PU2-0x <sub>0</sub> -92y <sub>0</sub> /z <sub>74</sub>	2	–	–	–	92	0 = 1	74
	PU3-46x <sub>3</sub> -49y <sub>0</sub> /z <sub>1</sub> -9	3	9	46	3	49	0 = 1	1
	PU5-46x <sub>0-1</sub> -49y <sub>2</sub> /z <sub>1</sub> -9	5	9	46	0–1	49	2	1
	PU5-46x <sub>0-2</sub> -49y <sub>1</sub> /z <sub>1</sub> -9	5	9	46	0–2	49	1	1
	PU4-46x <sub>0-3</sub> -49y <sub>0</sub> /z <sub>1</sub> -9	4	9	46	0–3	49	0 = 1	1
	PU3-16x <sub>1</sub> -76y <sub>0</sub> /z <sub>1</sub> -9	3	9	16	1	76	0 = 1	1
	PU4-16x <sub>0-2</sub> -76y <sub>0</sub> /z <sub>1</sub> -9	4	9	16	0–2	76	0 = 1	1
S3	PU5-46x <sub>0-2</sub> -49y <sub>1</sub> /z <sub>1</sub> -9	5	9	46	0–2	49	1	1
	PU5-46x <sub>0-2</sub> -49y <sub>1</sub> /z <sub>1</sub> -6	5	6	46	0–2	49	1	1
	PU5-46x <sub>0-2</sub> -49y <sub>1</sub> /z <sub>1</sub> -4	5	4	46	0–2	49	1	1
	PU5-46x <sub>0-2</sub> -49y <sub>1</sub> /z <sub>1</sub> -3	5	3	46	0–2	49	1	1

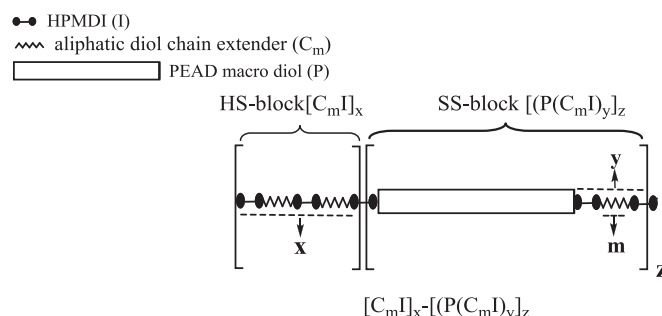
composition of the repeating units represented as  $[C_mI]_x-[P(C_mI)_y]_z$ , where  $[C_mI]_x$  is the hard segment block (HS-block) with  $x$  number of repeating HPMDI-chain extender units. The soft segment block  $[P(C_mI)_y]_z$  consists of polyester diol (P with a molecular weight of 2000 g/mol) linked to either HPMDI (I) ( $(C_mI)_{y=0} = 1$  when  $y = 0$ ) or  $(C_mI)_y$  units and has a length given by  $z$  number of repeating units. A schematic representation of the TPEU repeating unit structure is shown in Scheme 1. TPEUs were designated according to the following structure:

PU[method #] – [HS-block content] [ $x$ (no. of repeating HS-block units)] – [PEAD content] [ $y$ (no. of repeating  $C_mI$  units in SS-block)]/[ $z$ (no. of repeating SS block units)] – [ $m$ ], where PU denotes TPEUs and  $m$  represents the number of methylene groups in the aliphatic diol chain extender ( $C_m$ ).

The molar ratios as well as the sequence of addition of various reagents are summarized in Table 2. For a fixed polyester diol (P) chain length (2000 g/mol) TPEUs with varying combinations of HS-block type ( $m$ ), content ( $x, y$ ) and distribution ( $x$ ) of HS-blocks were investigated.

#### 2.2.1. One-shot method (methods 1 and 2)

An excess amount of HPMDI (5.5 mmol) was dissolved initially in 16 mL of anhydrous DMF under a N<sub>2</sub> atmosphere in a three-neck flask, and stirred. In Method 1, the 1,9-nonanediol and Sn(Oct)<sub>2</sub> dissolved in anhydrous DMF (20 mg/5 mL) was added through an addition funnel fitted to the three-neck flask. The reaction mixture was then stirred at 80 °C for 3 h (step 1). The 1,9-nonane diol was



**Scheme 1.** Schematic representation of  $[C_mI]_x-[P(C_mI)_y]_z$  TPEUs.

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