

Elaboration and properties of renewable polyurethanes based on natural rubber and biodegradable poly(butylene succinate) soft segments

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ABSTRACT: Natural rubber (NR) is a renewable bio-based polymer, while poly(butylene succinate) (PBS) belongs to the family of biodegradable renewable polymers. In this article, novel polyurethanes (PUs) were prepared using hydroxyl telechelic natural rubber (HTNR) and hydroxyl telechelic poly(butylene succinate) (HTPBS) as soft segments, and using toluene-2,4-diisocyanate (TDI) and 1,4-butanediol (BDO) as hard segment. HTPBS oligomers of $\overline{M}_n = 2000$ and 3500 g mol^{-1} were synthesized by bulk polycondensation of succinic acid (SA) with BDO. The polyurethane materials were obtained by casting process after solvent evaporation. The influence of the hard segment content and the molecular weight of HTPBS on the materials' thermo-mechanical properties were investigated by means of tensile testing, DSC, TGA, and DMTA. The obtained polyurethanes were amorphous with phase separations between hard and soft segments as well as between HTNR and HTPBS segments, and they exhibited good physical properties. © 2015 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2016**, *133*, 42943.

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INTRODUCTION

Polyurethanes (PUs) are a class of very important polymeric materials thanks to their versatile and broad properties. They are employed in many applications including elastomers, plastics, adhesives and flexible or rigid foams, and their consumption is continuously growing over the world.¹ However, most of polyurethanes are nonbiodegradable polymers and are synthesized from petroleum based monomers.

The consumption of synthetic polymers is growing increasingly in every aspect of life and industries, resulting in the accumulation of waste, environmental pollution, and global warming.² In addition, nowadays the decrease of fossil resources and the high price of petrochemical have directly affected the plastic production. This occurrence activates the researcher to develop new products from renewable resources, which are biodegradable and nontoxic for the

environment, and exhibiting lower energy consumption.³ Indeed, renewable feedstock has been explored as raw materials for the development of sustainable alternatives for the plastic industry. During the last few years, the attentiveness in the biodegradable polymer and biopolymer was especially increasing.⁴ The use of bio-based polyols from renewable resources as a feedstock for the synthesis of polyurethane such as sunflower oil,⁵ castor oil,⁶ tannins,⁷ soybean oil,⁸ and Jatropha oil⁹ had been reported.

Natural rubber (NR), consisting of *cis*-1,4-polyisoprene, is an interesting renewable agricultural product. The major source for NR is the latex obtained from the *Hevea brasiliensis* tree, which is plentiful, especially, in Thailand. It has been used mostly as elastomeric products in tires, gloves and condoms etc. Because of the presence of a double bond in the polymeric backbone, NR is suitable for chain cleavage and chemical modification affording renewable monomers, such as hydroxyl telechelic

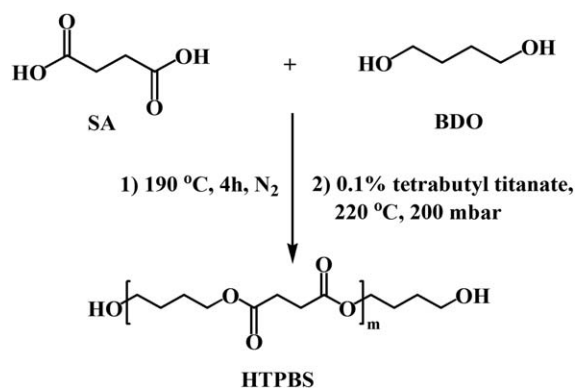


Figure 1. Chemical approach for synthesis of HTPBS.

natural rubber (HTNR).^{10–17} HTNR has been used as a starting material (Polyol) in the preparation of many kinds of polyurethanes.^{12–15,18–24} In addition, our group reported recently the preparation of bio-based polyurethane from HTNR and poly(ϵ -caprolactone) (PCL).^{25,26}

Polybutylene succinate (PBS) is a promising biodegradable and renewable aliphatic polyester which can be prepared from succinic acid and 1,4-butanediol. These monomers can be obtained from petroleum or biomass feedstock.^{27–29} Succinic acid can be derived from fermentation of sugars, which can easily be reduced to 1,4-butanediol.^{30,31} PBS has high flexibility, good impact strength, and thermal resistance. In addition, it can be processed at low temperature and displays mechanical properties close to polyolefin.^{32,33} The use of PBS in the synthesis of polyurethanes has been reported in recent works.^{30,34,35}

In this article, the goal is to synthesize new bio-based polyurethanes from hydroxyl telechelic natural rubber (HTNR) and hydroxyl telechelic poly(butylene succinate) (HTPBS) as polyols. 1,4-butanediol (BDO) was used as a chain extender and toluene diisocyanate (TDI) as an isocyanate agent. The influence of the composition and molecular weight of HTPBS on the physicochemical properties of the new polyurethanes is investigated.

EXPERIMENTAL

Materials

All chemicals were used as received. Succinic acid (SA, Acros[®]), tetrabutyl titanate (Acros[®]) and 1,4-butanediol (BDO, Merck[®]) were purchased from Acros and Merck, respectively (Merck Hohenbrunn, Germany). Block natural rubber (NR), STR5 CV60 grade, was produced by Jana Concentrated Latex, Thailand. Dibutyl tin dilaurate (Aldrich[®]), *m*-chloroperbenzoic acid (*m*-CPBA, Fluka[®]), and toluene-2,4-diisocyanate (TDI, Fluka[®]) were supplied by SIGMA-ALDRICH, MI. Periodic acid (Himedia[®]) and sodium borohydride (Rankem[®]) were manufactured by HiMedia Laboratories (Mumbai, India) and RFCL (New Delhi, India), respectively. Dichloromethane and tetrahydrofuran (THF) were supplied by Fisher Scientific UK Limited (Leicestershire, UK).

Synthesis of Hydroxyl Telechelic Natural Rubbe (HTNR)

Hydroxyl telechelic natural rubber (HTNR) was synthesized using previously described pathway.^{15,17,25,26} Briefly, in this procedure epoxidized natural rubber was cleaved in THF solution

Table I. Effect of Reaction Time on Molecular Weight of HTPBS in the First and Second Steps of the Polymerization Process

Step	Reaction time (min)	SEC		
		\overline{M}_n (g mol ⁻¹)	\overline{D}	NMR (g mol ⁻¹)
1st	60	360	2.52	580
	120	820	2.00	810
	180	990	2.03	930
	240	1070	2.12	1030
2nd	1	1980	1.47	1220
	5	3540	1.72	2780
	15	5030	1.89	5980
	30	5950	1.85	8730
	45	7480	1.76	11,480
	60	8140	1.97	20,000

using periodic acid at 30°C for 6 h to yield carbonyl telechelic natural rubber (CTNR), which was then reduced with sodium borohydride at 60°C for 6 h and then hydrolyzed to yield the desired HTNR. The chemical structure and molecular weight were investigated by using NMR, FTIR, and SEC.

Synthesis of Hydroxyl Telechelic Poly(butylene succinate) (HTPBS)

Hydroxyl telechelic poly(butylene succinate) (HTPBS) was synthesized through a two-step process as shown in Figure 1. First, a mixture of 1,4-butanediol (BDO) and succinic acid (SA) in 1.2:1^{2,30,35} initial molar ratio were added in a three-necked round bottom flask which was connected with Dean-Stark apparatus, gas inlet, and condenser. The stirred mixture was heated to 190°C for 4 h under nitrogen flow. Second, the reaction temperature was increased to 220°C and 0.1 wt % tetrabutyl titanate was added to reaction mixture. Then, the pressure was reduced to 200 mbar and the reaction was allowed to proceed for 60 min before cooling down to room temperature. During this time period, the viscosity and the polymer molecular weight increased as listed in Table I. The obtained product was dissolved in dichloromethane and then precipitated over methanol. The filtered white powder was washed with methanol and dried under vacuum at 40°C for 24 h.

Synthesis of Polyurethane (PU)

The new polyurethane (Figure 2) was synthesized by solution polymerization in a three-neck, round bottom flask equipped with a condenser and mechanical stirrer under nitrogen atmosphere. The solution of HTPBS, HTNR, and BDO in THF (20 w/v %) were put into the reaction flask and stirred until they were completely dissolved. Then, dibutyltin dilaurate (DBTL) followed by toluene-2,4-diisocyanate were added. The reaction was carried out at 70°C for 3 h and then the mixture was poured into a glass mold and kept overnight at 40°C in a ventilated oven to obtain polyurethane sheet after solvent evaporation. The molar ratios of TDI:HTPBS:HTNR:BDO were varied as presented in Table II.

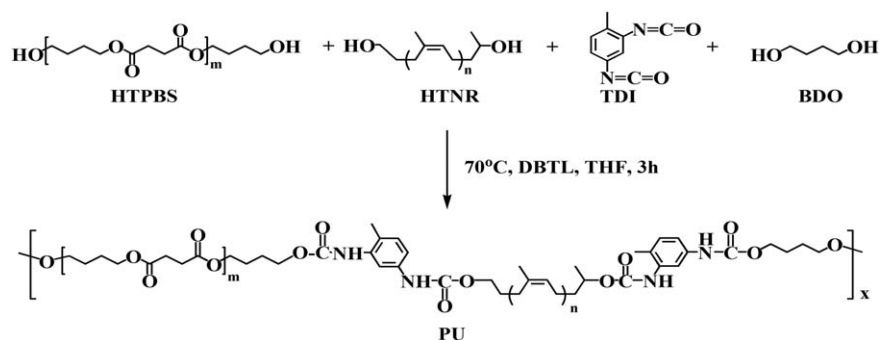


Figure 2. Chemical approach for synthesis of polyurethanes.

Sample Characterization

IR spectra were recorded on a FTIR spectrometer (BRUKER[®] EQUINOX 55) equipped with a diamond ATR device (attenuated total reflection). NMR spectra were recorded on a BRUKER[®] AC (400 MHz) Spectrometer. Deuterated chloroform was used as a solvent.

Polymer average molecular weights (\overline{M}_n and \overline{M}_w) and dispersity ($D = \overline{M}_w/\overline{M}_n$) were determined by size exclusion chromatography (SEC). Polymers were dissolved in CH_2Cl_2 , filtered (0.45 μm) and analyzed at 25°C using a Varian PL-GPC50 device equipped with two mixed packed columns (PL gel mixed type C). The mobile phase was CH_2Cl_2 and polystyrene standards (580 to 483,000 g mol^{-1}) were used for calibration.

Differential scanning calorimetry analysis was performed on a TA Instruments[®] DSC Q 100. The DSC thermograms were recorded with a scan rate of 10°C min^{-1} in the temperature range of -80 to 200°C, under nitrogen atmosphere. Thermogravimetric analysis was performed on a TA Instruments[®] TGA Q 500 under nitrogen atmosphere. A 30–600°C range was scanned at a heating rate of 10°C min^{-1} .

Dynamic mechanical thermal analysis was investigated by using a Rheometric Scientific[®] DMTA V. The experiment was carried out in the dual-cantilever bending mode at a frequency of 1 Hz with a strain control of 0.01%, a heating rate of 3°C min^{-1} , and a temperature range of -80 to 200°C.

Testing Mechanical Properties

The hardness Shore A (ASTM D2240) was investigated by a Shore Durometer[®] PTC 408. The tensile properties (ASTM D 412C) and tear strength (ASTM D 624 for the right-angle specimen) were determined by a universal testing machine (Lloyd[®] LR10K) at a crosshead speed of 500 mm min^{-1} . Testing was performed at 25°C \pm 2°C. At least four specimens were tested and the average values and standard deviations were reported. Young's modulus was determined from the slope of the linear portion of the stress–strain curves.

RESULTS AND DISCUSSION

Preparation of Hydroxyl Telechelic Oligomers

The general chemical approach for preparation of bio-based polyurethanes from hydroxyl telechelic natural rubber (HTNR) and hydroxyl telechelic poly(butylene succinate) (HTPBS) is depicted in Figure 2.

The preparation and characterization of HTNR has been described elsewhere by our research group.^{15,17,25,26} Briefly, controlled oxidative chain cleavage of natural rubber, using periodic acid afforded carbonyl telechelic natural rubber (CTNR). The reduction of CTNR by NaBH_4 led to HTNR with $\overline{M}_n \sim 1700$ g mol^{-1} . The FTIR analysis of HTNR showed mainly characteristics band of hydroxyl stretching vibration at 3365 cm^{-1} , C=C stretching vibration at 1664 cm^{-1} and C=C–H bending vibration at 834 cm^{-1} . The ¹H NMR showed the total disappearance

Table II. Composition and Physical Properties of Polyurethanes

Code	Molar ratio				HS ^a (%)	Appearances ^b
	TDI	HTPBS ₂₀₀₀	HTNR ₁₇₀₀	BDO		
PU1	1.05	0.1	0.9	-	9.6	VS, Y, T
PU2	2.05	0.1	0.9	1.0	20.5	S, Y, T
PU3	3.05	0.1	0.9	2.0	29.1	S, Y, T
PU4	3.05	0.2	0.8	2.0	28.8	S, Y, T
PU5	3.05	-	1.0	2.0	29.5	S, Y, T
PU6	3.05	0.1(3500)	0.9	2.0	19.2	S, Y, T

^a Hard segment (%) = 100 (weight of (isocyanate + chain extender))/total weight.

^b C: colorless; Y: yellowish; H: hard; S: soft; T: transparent.

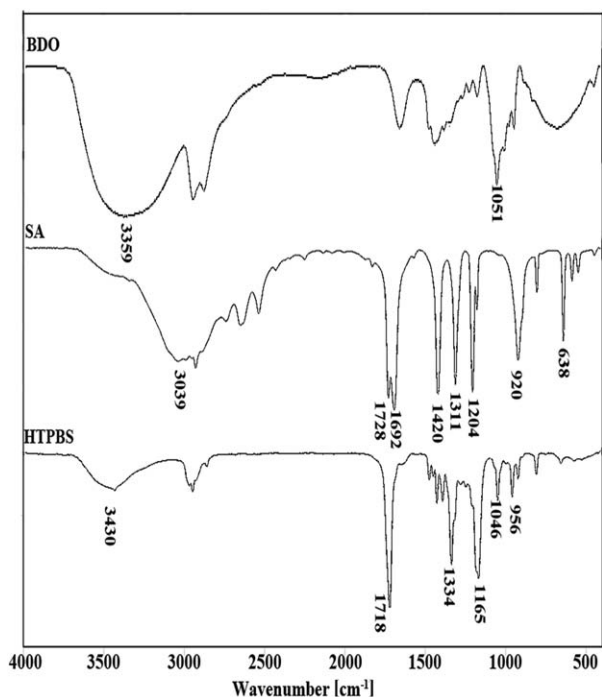


Figure 3. FTIR spectra of 1,4-butanediol (BDO), succinic acid (SA) and hydroxyl telechelic poly(butylene succinate) (HTPBS).

of the signals of protons in α and β positions of the carbonyl groups and the appearance of signals the protons in α positions of primary and secondary alcohols at 3.65 and 3.80 ppm, respectively.

HTPBS was prepared by reacting 1,4-butanediol and succinic acid in 1.2:1 initial molar ratio. The chemical structure and molecular weight of HTPBS were characterized by FTIR, ^1H NMR, and SEC. The FTIR spectrum of HTPBS (Figure 3) showed mainly a characteristic strong absorption band of O—H stretching vibration at 3430 cm^{-1} , C—H stretching band of methylene groups at $2857\text{--}2966\text{ cm}^{-1}$, C=O stretching band of ester groups at 1718 cm^{-1} , CH_2 scissors vibration band in aliphatic compound in the range of $1425\text{--}1475\text{ cm}^{-1}$, a very shape C—O—C asymmetric stretching band at 1165 cm^{-1} , C—O stretching band in primary alcohol at 1046 cm^{-1} and C—O—H bending band in alcohols at 653 cm^{-1} . Furthermore, the succinic acid bands at 3039 (O—H stretching), 1692 (C=O stretching), and 638 (—C—C=O bending) cm^{-1} , had totally disappeared.

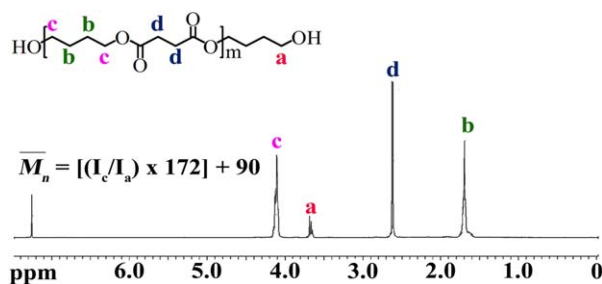


Figure 4. ^1H NMR spectrum of HTPBS. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

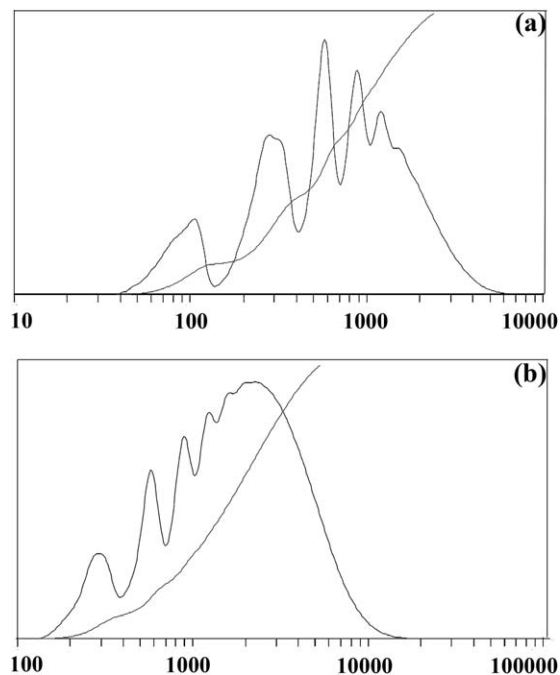


Figure 5. Effect of reaction time on SEC distribution of synthesized HTPBS before adding catalyst: (a) 1 h and (b) 4 h.

A representative ^1H NMR spectrum of HTPBS is depicted in Figure 4. One can observe that the signal of carboxylic proton (COOH) at 2.5 ppm, corresponding to the methylene protons of the succinic acid end-group,² has totally disappeared. In addition, the intensity of the signal at 3.65 ppm (H_a), corresponding to methylene groups in α position of hydroxyl groups, decreased with reaction time. This suggests the total conversion

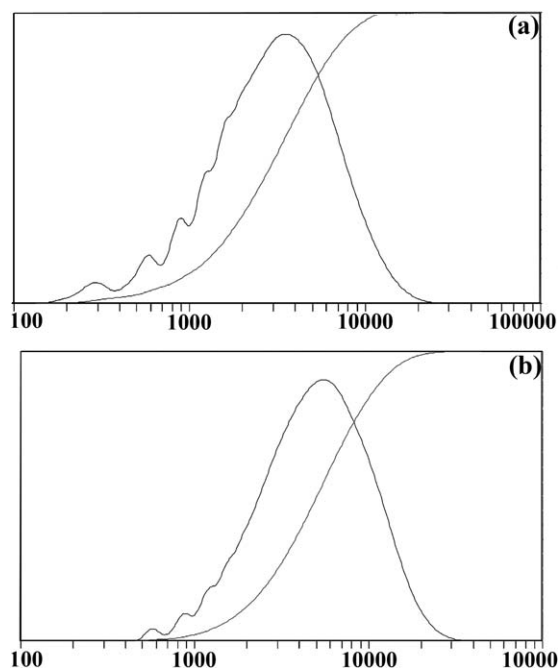


Figure 6. Effect of reaction time on SEC distribution of synthesized HTPBS after adding catalyst: (a) 1 min and (b) 5 min.

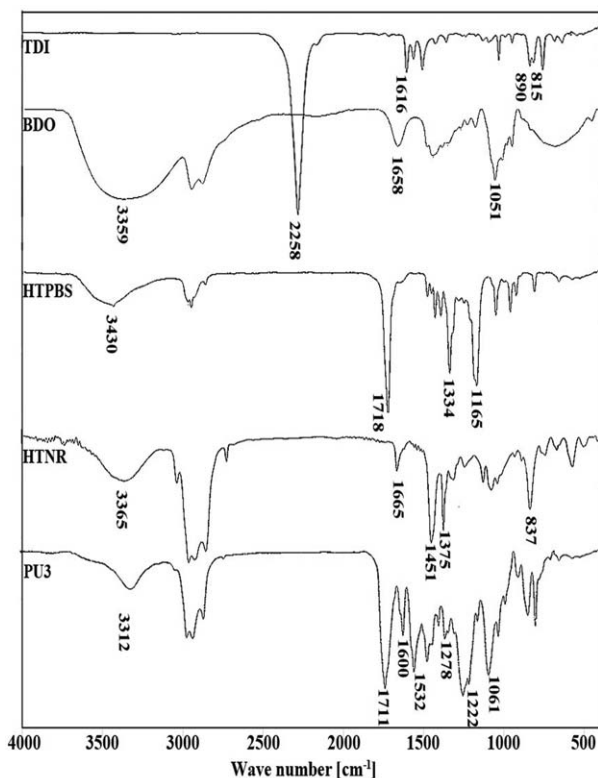


Figure 7. FTIR spectra of PU3 and its precursors.

of succinic acid with the excess of BDO leading to hydroxyl telechelic oligomers. Furthermore, we can also observe the peaks of ester groups at 1.67 (H_b), 2.65 (H_d), and 4.10 (H_c) ppm. The ratio of the integration of the methylene protons adjacent to the hydroxyl end groups ($I_{3,65}$) to the methylene protons of the ester linkage at 4.10 ppm ($I_{4,10}$) was used to calculate the degree of polymerization (\bar{X}_n) according to eq. (1).

$$\bar{X}_n = I_{4,10}/I_{3,65} \quad (1)$$

The number average-molecular weight (\bar{M}_n) of HTPBS was then calculated by eq. (2).

$$\bar{M}_n = 172 * \bar{X}_n + 90 \quad (2)$$

where:

172: is the molecular weight of PBS repeating unit.

90: is the molecular weight of chain-ends.

The average molecular weights and distributions of PBS during the two steps of the polymerization process after are depicted in Table I. It is apparent that the \bar{M}_n values obtained from the

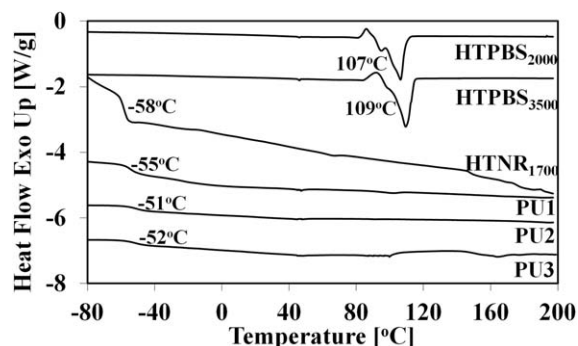


Figure 8. DSC Second heating scan of PU1 to PU3 and their precursors.

SEC experiment are very close to the values obtained from the NMR. During the first step, the dispersity was higher than 2 and the \bar{M}_n values were lower than 2000 g mol⁻¹. In addition, the SEC chromatogram displayed multiple peaks indicating different oligomers, suggesting that the polycondensation reaction was incomplete (Figure 5). However, in the second step, after adding the catalyst while increasing temperature and reducing the pressure, the molecular weight of HTPBS increased rapidly and the polydispersity was decreased below 2 (Table I and Figure 6). Thus, this process was successful to prepare HTPBS as starting material for polyurethane synthesis. The oligomers with \bar{M}_n of 2000 and 3500 g mol⁻¹, determined by SEC, were used in the next part.

Preparation of Polyurethanes

Several parameters were varied, i.e. hard segment (TDI+BDO) to soft segment (HTPBS+HTNR) ratio (PU1 to PU3), molar ratio between HTPBS and HTNR (PU3 to PU5) as well as the molecular weight of HTPBS (PU3 and PU6). The NCO/OH ratio was kept at 1.05, which provided satisfactory film in terms of apparent physical properties. The physical appearances and hard segment content are listed in Table II. The yellow tint was directly related to the HTNR content. Increasing the BDO content increased the hard segment content which resulted in films that are not as soft.

The FTIR analysis of PU sheets (Figure 7) absorption bands of N—H stretching, C=O stretching and N—H bending vibrations in the urethane links at 3312, 1711, and 1532 cm⁻¹, respectively. The band of isocyanate groups at 2258 cm⁻¹ has totally disappeared suggesting that the reaction went to completion and that the materials acquired their optimal properties.

However, the obtained polyurethanes were not soluble in classical solvents used for NMR and SEC analyses. Thus, the molecular weight of these new polyurethanes could not be determined.

Table III. DSC Data of the Prepared Hydroxyl Terminated Oligomers

Code	1st heating scan			2nd heating scan			1st cooling scan				
	T_g (°C)	T_m (°C)	ΔH_m (J g ⁻¹)	T_g (°C)	T_{cc} (°C)	ΔH_{cc} (J g ⁻¹)	T_m (°C)	ΔH_m (J g ⁻¹)	T_g (°C)	T_c (°C)	ΔH_f (J g ⁻¹)
HTNR ₁₇₀₀	-58	-	-	-58	-	-	-	-	-60	-	-
HTPBS ₂₀₀₀	-	107	123.8	-	83	10.1	94	58.9	-	70	89.9
HTPBS ₃₅₀₀	-	109	114.3	-	85	10.2	107	78.2	-	73	79.1

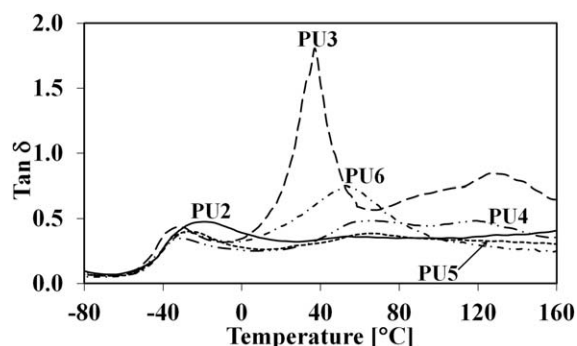


Figure 9. Tan δ curves versus temperature of PU2 to PU6.

Thermal Properties

The glass transition temperature (T_g), cold crystallization temperature (T_{cc}), and melting point temperature (T_m), as well as the enthalpy of cold crystallization (ΔH_{cc}) and melting (ΔH_m) obtained from the first heating, first cooling and second heating of diol precursors are listed in Table III. It was found that HTPBS with molecular weight of 2000 g mol⁻¹ displayed double melting peak at 94 and 107°C because of the different types of crystalline lamellae,³⁶ whereas T_m of HTPBS with molecular weight of 3500 g mol⁻¹ were 107 and 109°C. Glass transition temperature of HTPBS was not observed. In contrast, T_g of HTNR appeared at -58°C. The second heating scan of the DSC curves for HTPBS (with 2000 and 3500 g mol⁻¹), HTNR and PU cast film samples are shown in Figure 8. All the PUs exhibited only one glass transition temperature without any melting or crystallization peak in both of heating and cooling scan. The T_g value of all PUs were those of HTNR segment within the range of -51 to -55°C, which is in consistency with our previous works.²⁶ Their T_g were almost not significantly changed with the hard segment content, suggesting an absence of physical interaction between HTNR and hard segments. However, the T_m of HTPBS as well as T_g and T_m of hard segments were not observed in all the prepared PUs. This result can be explained by the weak proportion of hard segment and of HTPBS within these materials (<30%), which is consistent with our previous works.^{15,17,22}

The variation of tan δ as a function of temperature for PU2 to PU6 is depicted in Figure 9. Sample PU1 is not included in this figure due to the soft nature of this polymer which caused rela-

tively high experimental error in this test. The mechanical transition temperature T_∞ , which is assimilated to T_g , can be determined from the maximum of the tan δ curve. Table IV displayed the mechanical transition temperature values corresponding to HTNR, HTPBS, and hard segments within the PU materials. The T_g values of HTNR segments ranged from -33 to -19°C while T_g values of HTPBS and hard segments ranged from 37 to 66°C, and from 120 to 127°C, respectively. In addition, the T_g increased with an increase of molecular weight of HTPBS (comparison between PU3 and PU6) owing to the limitation of molecule motion in the polyurethane chain.

The thermal stability by TGA of diol precursors and PU samples are shown in Figure 10. The TGA curves of precursors [Figure 10(a)] indicated that BDO and HTNR₁₇₀₀ provided the lowest and highest thermal stability, respectively, while HTPBS₂₀₀₀ and HTPBS₃₅₀₀ had similar and intermediate thermal degradation. As shown in Figure 10(b), the thermal stability of PUs in terms of weight loss decreased with an increase of hard segment content which is consistent with the fact that the degradation of hard segments occurs at higher temperatures than the soft segments.^{15,17,22} The influence of HTNR:HTPBS ratio on thermal stability was also investigated as shown in Figure 10(c) (PU5, PU3, and PU4). A slight difference has been observed. Nevertheless, the thermal stability could be ranked in the following order: PU5 > PU3 > PU4, which is consistent with the decrease of HTNR content from PU5 to PU4. Finally, like their precursors HTPBS₂₀₀₀ and HTPBS₃₅₀₀, PU3 and PU6 exhibited similar TGA curves, suggesting that the molecular weight of HTPBS segments has not any influence in their thermal stability.

Mechanical Properties

The mechanical properties of the prepared polyurethanes were carried out by tensile, hardness Shore A and tear strength tests. The obtained results are summarized in Table IV. The stress-strain curves were illustrated in Figure 11. Except, PU1 which showed rubber-like behavior with no plastic yielding, all samples exhibited thermoplastic deformation behavior. The influence of hard segment to soft segment ratio can be viewed from samples PU1 to PU3 since these PUs had similar molar ratio of HTPBS:HTNR. It was found that Young's modulus, tensile strength, tear strength, and hardness increased significantly with the increase of hard segment content in the polyurethane

Table IV. The Mechanical and Thermo-mechanical Properties of PU1 to PU6

Code	Tensile properties			Tear strength (N mm ⁻¹)	Hardness (shore A)	T_g from DMTA (°C)		
	E (MPa)	σ_b (MPa)	ϵ_b (%)			HTNR	HTPBS	HS ^a
PU1	0.7 ± 0.0	2.9 ± 0.4	339 ± 29	9.3 ± 1.7	30 ± 2	-	-	-
PU2	4.9 ± 0.9	4.1 ± 0.2	466 ± 4	15.3 ± 4.8	28 ± 2	-19	-	-
PU3	13.5 ± 1.2	8.7 ± 0.4	389 ± 34	22.7 ± 0.4	38 ± 2	-31	37	127
PU4	17.9 ± 2.1	4.9 ± 0.1	365 ± 5	31.3 ± 2.7	51 ± 3	-33	66	120
PU5	10.5 ± 0.1	14.2 ± 2.0	335 ± 17	27.2 ± 4.7	34 ± 2	-24	-	-
PU6	29.8 ± 3.5	8.9 ± 0.4	344 ± 24	40.1 ± 4.0	61 ± 3	-28	52	-

^aHard segment.

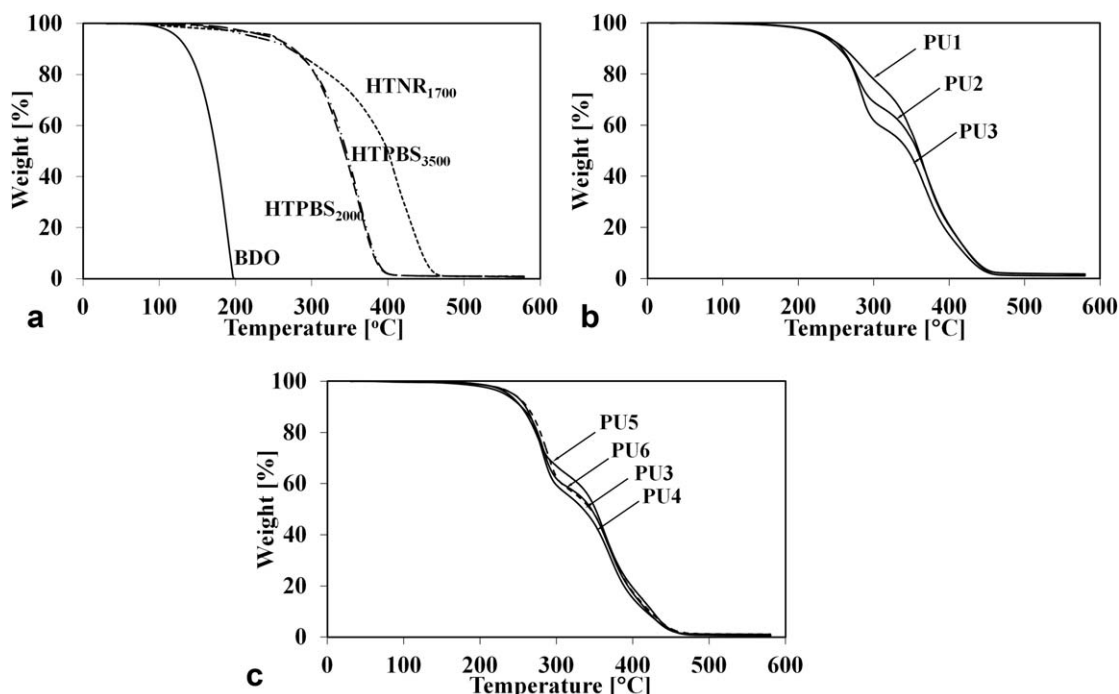


Figure 10. TGA thermograms of (a) diol precursors (b) PU1 to PU3 and (c) PU3 to PU6.

chain.¹ Indeed, hard segments enhanced inter and intramolecular attraction of polymer chains and acts as reinforcing filler.²

Comparing to PU5, the incorporation of an increasing HTPBS content in PU3 and PU4 led to an increase of Young's modulus and hardness, but led to reduction in tensile strength, whereas the elongation at break and tear strength were close to each other. Undeniably, when hard segment content has been considered, it was found that PU5, PU3 and PU4 are quite similar, i.e. 29.5, 29.1, and 28.8%, respectively (Table II). We can assume that poly(butylene succinate) had more interaction (hydrogen bonding) with hard phases than with HTNR, resulting in an increase of modulus and hardness in PU3 and PU4, comparing to PU5. The influence of molecular weight of HTPBS by keeping constant HTPBS:HTNR and NCO:OH ratios was determined from PU3 and PU6. The modulus, tear strength and hardness of PU increased with the increasing molecular weight of HTPBS, though PU6 had lower hard segment amount than PU3, i.e. 19.2 and 29.5%, respectively. This result suggested that the increase of mechanical properties with an increase of

HTPBS content and molecular weight was probably caused by the strong intermolecular attraction of ester and urethane groups. Indeed, a supramolecular assembly which may be in the form of glassy domain or crystallites can result from strong polar interaction in polyurethane blocks.¹

CONCLUSIONS

In summary, we have successfully synthesized HTPBS and HTNR as diols precursors for polyurethane synthesis. The chemical structure, average functionality and molecular weight of these oligomers were determined by FTIR, ¹H NMR and SEC. Several polyurethanes were prepared from HTNR, HTPBS using 1,4-butanediol (BDO) as a chain extender and TDI as an isocyanate agent, by a one-step solution polymerization. The urethane linkage formation was determined by FTIR technique. The physical parameters of the crystalline region of these PUs were not detected by the different techniques because of their weak amount. The effect of selected parameters on physical and thermal properties was investigated. Except PU1, all prepared PUs showed a plastic like deformation and good mechanical properties. The hard segment to soft segment ratio and molecular weight of HTPBS played an important role on materials' thermo-mechanical properties. The presence of HTNR segments increased the thermal stability of polyurethanes.

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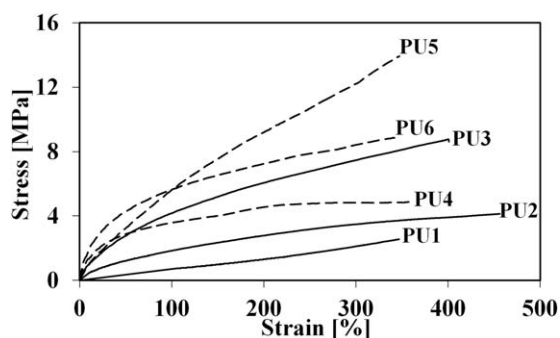


Figure 11. Stress-strain curves of PU1 to PU6.

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