Novel Long Chain Unsaturated Diisocyanate from Fatty Acid: Synthesis, Characterization, and Application in Bio-Based Polyurethane

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ABSTRACT: A novel long chain linear unsaturated terminal diisocyanate, 1,16-diisocyanatohexadec-8-ene (HDEDI) was synthesized from oleic acid via Curtius rearrangement. Its chemical structure was identified by FTIR, ^{1}H NMR, ^{13}C NMR, and HRMS. This diisocyanate was used as a starting material for the preparation of entirely bio-based polyurethanes (PUs) by reacting it with canola diol and canola polyol, respectively. The physical properties and crystalline structure of the PUs prepared from this diisocyanate were compared to their counterparts prepared from similar fatty acid-derived diisocyanate, 1,7-heptamethylene diisocyanate (HPMDI). The HDEDI based PUs demonstrated various different properties compared to those of HPMDI based PUs. For example, HDEDI based PUs exhibited a triclinic crystal form; whereas HPMDI based PUs exhibited a hexagonal crystal lattice. In addition, canola polyol-HDEDI PU demonstrated a higher tensile strength at break than that of canola polyol-HPMDI, attributed to the higher degree of hydrogen bonding associated with the former sample. Nevertheless, lower Young's modulus and higher elongation in canola polyol-HDEDI PU were obtained because of the flexibility of the long chain introduced by the HDEDI diisocyanate. © 2010 Wiley Periodicals, Inc. J Polym Sci Part A: Polym Chem 48: 3302–3310, 2010

KEYWORDS: biomaterials; diisocyanates from renewable sources; metathesis; nonlinear polymers; polyurethanes; polyurethanes from renewable sources

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INTRODUCTION Polyurethanes (PUs) form a versatile class of polymers, which are used in a broad range of applications, for example, as elastomers, sealants, fibers, foams, coatings, adhesives, and biomedical materials.[1] The synthesis of polyurethanes is carried out by a variety of methods, although the most widely used method starts from di- or polyfunctional hydroxycompounds (polyol) with di- or polyfunctional isocyanates, which are usually industrially produced from petroleum.[1] The progressive dwindling of fossil resources, coupled with the drastic increase in oil prices in the long-term, have driven research to develop alternatives based on renewable resources for the production of polymer materials. In recent years, the utilization of renewable materials such as plant oils and natural fatty acids for replacing petroleum derived raw materials for the production of polymeric materials has attracted great attention, due to social, environmental and economic considerations. In terms of bio-based PUs, almost all current available scientific publications[2–11] have been focused on preparing such types of polymers using polyol derived from vegetable oil in combination with petrochemical-based diisocyanates. It has been demonstrated[12] that these bio-based PUs have comparable properties in many aspects with PUs derived from petrochemical polyol. Over the past few years, our research effort has been part of the growing worldwide interest in developing methodologies for the synthesis of vegetable oil based PUs.[3–5,7–10]

Isocyanates, the other primary building blocks of polyurethanes, are normally petroleum-derived. These can be prepared via several routes.[13] The only route that is practiced on a significant industrial scale is phosgenation of primary amines or their salts. The high toxicity of phosgene, the rather high temperature necessary to decompose the intermediate carbamoyl chloride, and the poor selectivity toward different nucleophiles are some disadvantages that limit the synthetic use of phosgene. Some other methods which are used on laboratory scale include the Curtius rearrangement of acylazides, the dissociation of blocked isocyanates, the conversion of alkyl halides with alkali cyanates, and the dehydration of carbamic acid derivatives (adducts of amines and carbon dioxide).[14]

In the past few decades, researchers have sought different ways and technologies to viably produce isocyanates from renewable resources. However, literature available regarding the synthesis of diisocyanate from vegetable oils is very limited. The one instance of diisocyanate production from fatty

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acids is reported in a US Patent.[15] It describes the synthesis of diisocyanates from diamine precursors prepared from the hydrogenation of dinitrile compounds which were obtained from hydroxyl-substituted fatty nitrile and unsaturated nitrile starting materials. In addition, a fatty acid-based diisocyanate known as dimer acid diisocyanate containing 36 carbon atoms in the chain has been commercialized by Henkel Corportion Company and General Mills. This diisocyanate has been utilized for the preparation of PU coatings.[16–18] Recently, soybean oil derived isocyanate has been synthesized, which involved substitution of the allylic bromides of plant oil triacylglycerols (TAGs) with AgNCO.[19]

More recently, a new linear saturated terminal diisocyanate, 1,7-heptamethylene diisocyanate (HPMDI) has been synthesized from azelaic acid via Curtius rearrangement using oleic acid as starting materials by our research group.[20] It has been established that this fatty acid-derived diisocyanate was capable of reacting with lipid-based polyol to produce entirely bio-based PUs with comparable properties within acceptable tolerances. However, in the Curtius rearrangement azelaic diazide intermediate can be explosive because the ratio of carbon and oxygen atoms numbers ($N_C + N_O$) to nitrogen atoms numbers (N_N) is less than 2. This can be a barrier to larger scale batch type processes because extreme care is required. For organic azides to be safely manipulated, $(N_C + N_O)/N_N$ should be at least 3.[21] To minimize this issue, we report on our efforts in this work as the first example of the preparation of aliphatic diisocyanate with longer chains from fatty acid, which could be a valuable agent for organic reactions, for example, the formation of resinous materials by reaction with glycols and diamines to from polyurethanes and polyureas. Moreover, this report also provides a new monomer for the production of polymers which are capable of vulcanization or cross-linking due to the unsaturation in the monomer unit. The introduction of C=C double bonds into aliphatic polymer chains would offer a starting point for a very diverse manifold of reactivity.[22] For example, Hartwig and Hillmyer have reported the borylation of polybutene[23] and polypropylene[24] and the oxyfunctionalization of polypropylene.[25] Furthermore, a partially unsaturated polymer could be cross-linked with standard techniques to give materials with enhanced mechanical properties.[26]

To the best of our knowledge, this is the first time that a linear long chain unsaturated terminal aliphatic diisocyanate was synthesized using a cheap and short procedure from fatty acid. We also demonstrate the feasibility of this new type of fatty acid-derived diisocyanate in the preparation of entirely bio-based PUs by reacting it with canola diol and canola polyol, respectively. It is expected that these PUs exhibit various different properties to their counterparts produced from the same polyol but HPMDI.

EXPERIMENTAL

Materials

Oleic acid (90% purity), 1,3-Bis-(2,4,6-trimethylphenyl)-2-(imidazolidinylidene) (dichlorophenylmethylene)(tricyclohexylphosphine)ruthenium (grubbs catalyst 2th generation), ethyl vinyl ether, triethylamine, sodium azide, dibutyltin dilaurate (DBTDL), Tin(II) 2-ethylhexanoate ($Sn(OCT)_2$), anhydrous DMF, and anhydrous THF were purchased from Sigma-Aldrich. Ethylchloroformate was obtained from BDH, Methanol, chloroform, ethyl acetate, and hexane were purchased from Fisher. Canola polyol was synthesized using an ozonolysis and hydrogenation technology developed by our group—the detailed procedure was reported elsewhere.[9,10] The chemical reaction procedure is illustrated in Scheme 1, as an example. The hydroxyl number of the canola polyol was 237 mg KOH/g, as determined according to the ASTM D1957–86. The polyol contained 60.18% ± 1.16 wt %, 26.00% ± 0.48 wt%, and 4.72% ± 0.03 wt% of triol, diol and mono-ol, respectively.[10] The remainder consists of ~9 wt% saturated TAGs. The canola diol was separated from canola polyol by flash chromatography using the procedure developed by Yue and coworkers[9] HPMDI was synthesized from oleic acid according to the reported procedure.[20]

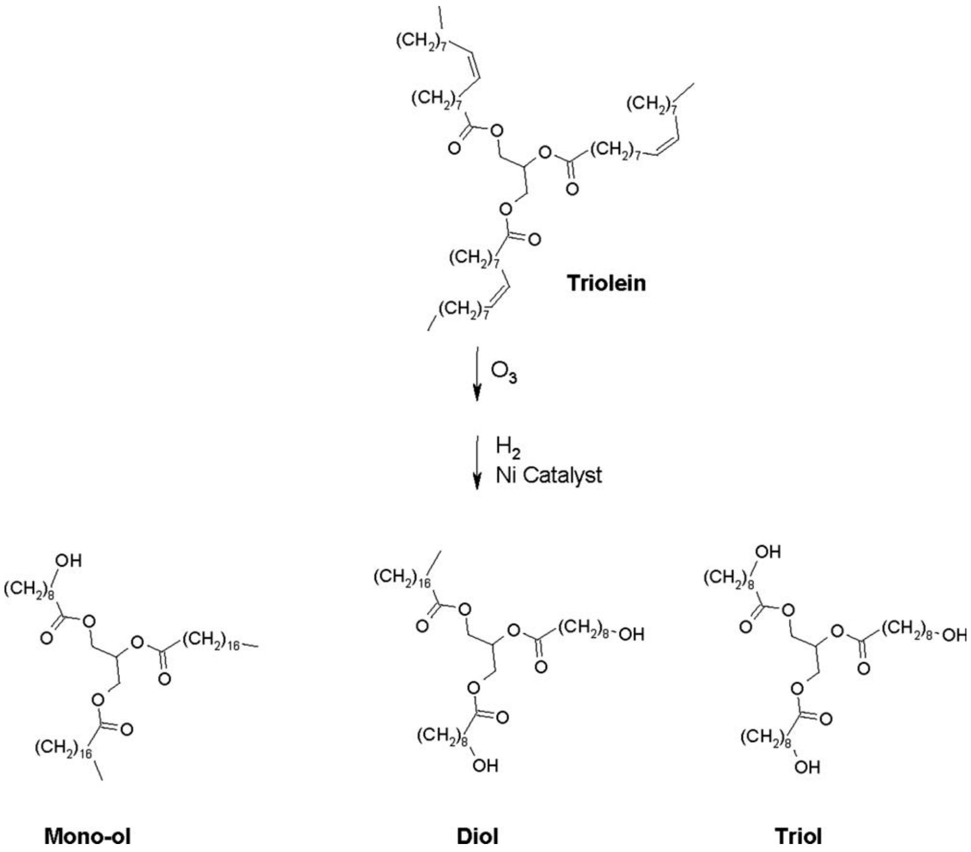
Fatty Acid-Derived Unsaturated Diisocyanate Synthesis

1,18-Octadec-9-enedioic Acid 2

Oleic acid [28.2 g (90%), 0.1 mol] was transferred into a 250-mL three-necked round-bottomed flask and stirred at 45 °C under nitrogen gas for 0.5 h. Grubbs catalyst 2th generation (89 mg, 0.01 mmol) was then added. The reaction mixture was kept at 45 °C and stirred with a stirrer bar. After ~5 minutes, the diacid began to precipitate from the reaction mixture. After 24 h, the crude product was quenched with ethyl vinyl ether (6.5 mL), and excess ether was removed under reduced pressure. The residue was purified by column chromatography using a hexane: ethyl acetate eluting solvent (4:1, 3:1, 2:1, 1:1, 1:0) to give 10.0 g of pure 1,18-octadec-9-enedioic acid **2** (Scheme 2) as a white solid (64%).[27] The other option for purification is recrystallization of the product in hexane/ethyl actetate several times.

1,16-Diisocyanatohexadec-8-ene (HDEDI) 3

A suspension of product **2** (5 g, 16 mmol) and triethylamine (5.4 mL, 38.4 mmol) in anhydrous THF (100 mL) was cooled to 0 °C and ethylchloroformate (3.36 mL, 35.2 mmol) was added dropwise. The resulting mixture was stirred for 3 hours at 0 °C under N_2 atmosphere. Then it was added dropwise to a solution of sodium azide (4.17 g, 64 mmol) in water (70 mL) that was cooled to 0 °C and kept for 1 hour, followed by another hour at 5 °C. The reaction mixture was added to a separatory funnel containing 100 mL of cold water, and the organic layer was separated and dried over $MgSO_4$. After filtering, the solvent was completely removed under reduced pressure at room temperature (because of the long carbon chain of this diazide, it is safe under dry conditions). Anhydrous THF (50 mL) was then added to the flask and the resulting solution was heated to reflux for 3 hours under N_2 atmosphere, then solvent was removed under reduced pressure. 10 mL of hexane was added to the residue and the solution was passed through a very short silicagel column under N_2 pressure and washed out by extra hexane. After removing the solvent under reduced pressure, 2.8 g of diisocyanate **3** was obtained as a pale yellow oil.



SCHEME 1 The chemical reaction procedure of polyol from triolein.

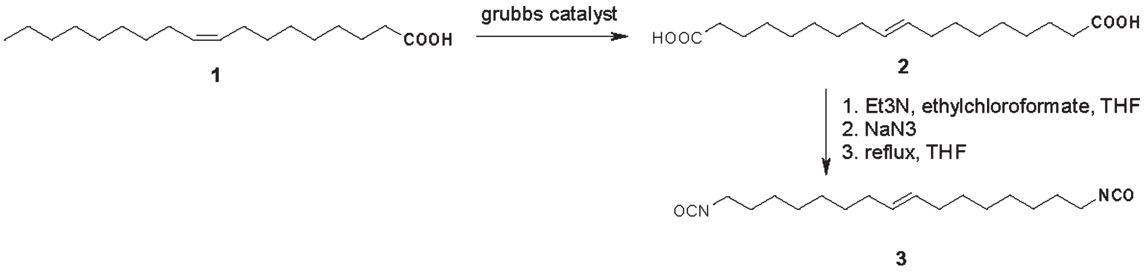
(57% yield and 98% purity). Purity of compound was determined by GC-FID (Fig. 1).

^{1}H NMR: δ 1.28–1.37 (m, 16H, 8CH$_2$), 1.59–1.62 (m, 4H, 2CH_2CH$_2$NCO), 1.95–1.98 (m, 4H, 2CH_2—CH=CH), 3.28 (t, $^3J_{HH}$ = 6.5 Hz, 4H, 2 OCN—CH$_2$), 5.37–5.39 (m, 2H, CH=CH); ^{13}C NMR: δ 26.5 (CH$_2$), 28.8 (CH$_2$), 28.9 (CH$_2$), 29.5 (CH$_2$), 31.3 (CH$_2$), 32.5 (CH$_2$), 43.0 (N—CH$_2$), 121.9 (NCO), 130.3 (CH=CH), IR (cm^{-1}): 967, 1354, 1464 (CH$_2$ Scissoring), 2272 (N=C=O), 2855, 2927 (C—H). HRMS(EI) calcd for $C_{18}H_{30}O_2N_2$ 306.2307, found m/z 306.2305.

Polyurethane Preparation

Polyurethanes Prepared from Canola Oil-Based Diol

1 mmol of HPMDI or HDEDI was dissolved in 1 mL of anhydrous DMF in a stirred three-neck flask. Canola diol (~0.65 g, 1 mmol) and one drop of Sn(OCT)$_2$ were dissolved in 4 mL of anhydrous DMF and added to an addition funnel fitted to the three-neck flask. The canola diol and catalyst solution was slowly (over 0.5 h) dropped into the diisocyanate solution at room temperature. The reaction mixture was increased to 85 °C and kept at this temperature for 18 hours with stirring. After cooling, the reaction mixture was precipitated into a large excess of warm distilled water. The polymer was filtered and washed with methanol. The resulting polymer was then dissolved in 10 mL of chloroform and precipitated in 300 mL of methanol. The white solid was filtered and washed by methanol and dried in vacuum oven (50 °C) for 3 days. The yield for polymerization of canola diol and HPMDI was 76% and for canola diol and HDEDI was 74%. The samples were coded as canola diol-HPMDI, canola diol-HDEDI for PUs produced from canola diol with HPMDI and HDEDI, respectively.



SCHEME 2 Synthesis of unsaturated diisocyanates from oleic acid.

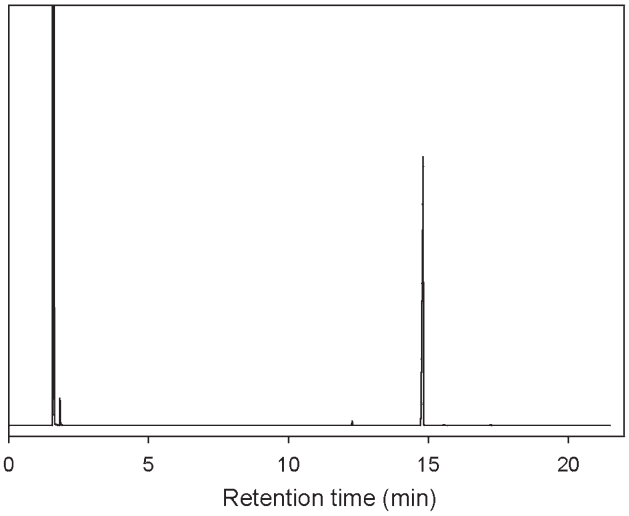


FIGURE 1 GC-FID chromatogram of fatty acid-derived unsaturated diisocyanate.

Polyurethane Prepared from Canola Oil-Based Polyol

PU sheets were prepared by reacting canola polyol with diisocyanates at molar ratios of the OH group to the NCO group, that is OH/NCO of 1.0/1.1. The desired OH/NCO molar ratio satisfies the equation:

$$M_{\mathrm{ratio}} = \frac{W_{\mathrm{polyol}}/EW_{\mathrm{polyol}}}{\left(W_{\mathrm{PU}} - W_{\mathrm{polyol}}\right)/EW_{\mathrm{isocyanate}}} \tag{1}$$

where W_{polyol} is the weight of the polyol, EW_{polyol} is the equivalent weights of polyol, W_{PU} is the total weight of PU to produce and $EW_{\mathrm{isocyanate}}$ is the equivalent weight of the isocyanate.

The equivalent weights of both HPMDI and HDEDI were calculated based on their molar mass. The equivalent weight of canola polyol was determined using the equation:

$$\begin{aligned} EW_{\mathrm{polyol}} &= \frac{\text{molecular weight of KOH} \times 1000}{\text{OH Number}} \\ &= \frac{56110}{\text{OH Number}} \text{ g per mole of hydroxyl group.} \end{aligned}$$

Canola polyol-HPMDI, canola polyol-HDEDI represent PUs produced from canola oil-based polyol with HPMDI and HDEDI, respectively.

A suitable amount of polyol and diisocyanate were weighed in a plastic container, stirred for 2 min before trace amounts of DBTDL was added. The mixture was further mixed for 5 min, poured in another container and placed in a vacuum oven at 40 °C for 5 to 8 min to degas the CO_2 released during the side reaction of diisocyanate with moisture or carboxylic acid and the air trapped during mixing. Air was then introduced to the oven to avoid the deformation of the sample under vacuum and the sample was postcured for about 24 hours at 70 °C, 10 hours at 110 °C.

Characterization

Gas Chromatograph-Flame Ionization Detector (GC-FID) System

Gas chromatograms were obtained on an Agilent 6890N capillary GC (Santa Clara, CA) equipped with a flame ionization detector and Agilent 7683B auto sampler. The 30 m × 0.32 mm × 0.1 μm DB-5HT column was used for the determination of diisocyanate compound purity. The temperature of the column was initially set at 85 °C then increased to 250 °C at a rate of 10 °C/min and held for 5 min.

NMR, Mass and FTIR

^{1}H NMR and ^{13}C NMR were recorded at larmor frequencies of 500 and 125 MHz, respectively, using a Varian UNITY 500 NMR spectrometer (Varian, CA). Deuterated chloroform ($CDCl_3$) was used as solvent. Mass spectra were acquired on a Kratos Analytical MS-50 (Kratos Analytical, Manchester, UK) EI high-resolution spectrometer. FTIR spectrum of diisocyanate was measured with a Mattson Galaxy series 3000 FTIR spectrophotometer. The analysis of polymer specimens was performed using a Bruker Vertex 70 FTIR main bench with an attached Hyperion FTIR microscope using OPUS software. The spectra were obtained using a micro-ATR objective with an analysis area ~100 μm in diameter. The spectra were acquired using 128 scans at a resolution of four wavenumbers.

Molecular Weight Measurements by Gel Permeation Chromatography (GPC)

The number and weight-average molecular weights (M_n and M_w, respectively) were determined by GPC (Santa Clara, CA). The tests were carried out using GPC with an Agilent G1311A quaternary pump, G1362A refractive index detector, and a PL gel column (5 μm mixed-D). Chloroform and DMSO (1:1) was used as the eluent at a flow rate of 0.8 mL/min. Sample concentrations of 0.4% (w/v) and injection volumes of 10 μL were used. Polystyrene (PS) standards were used to generate a calibration curve.

Wide Angle X-Ray Diffraction (WAXD)

A Bruker AXS X-ray diffractometer (Madison) equipped with a filtered Cu-Kα radiation source ($\lambda = 0.1542$ nm) and a 2D detector was used to record the WAXD patterns. The procedure was automated and controlled by the Bruker AXS's "GADDs V 4.1.08" software. The frames were processed using GADDS software and the resulting spectra were analyzed using Bruker AXS's "Topas V 2.1" software.

Thermal Properties

MDSC measurements were carried out on a DSC Q100 (TA Instruments, DE), equipped with a refrigerated cooling system. The samples were heated at a rate of 10 °C/min from 25 °C to 100 °C to erase thermal history, then cooled down to –50 °C at a cooling rate of 5 °C/min. MDSC measurements were performed with a modulation amplitude of 1 °C/min and a modulation period of 60 s at a heating rate of 3 °C/min to 100 °C. The second heating stage was selected for the analyzing of heating data. All the DSC measurements were performed following the ASTM E1356–03 standard procedure under a dry nitrogen gas atmosphere.

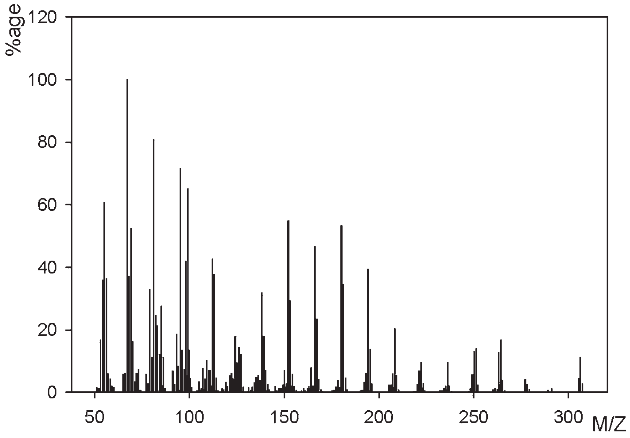


FIGURE 2 HRMS spectrum of fatty acid-derived unsaturated diisocyanate.

Mechanical Properties

Mechanical properties were tested using an Instron (MA) tensile testing machine (model 4202) equipped with a 50 Kgf load cell and activated grips which prevented slippage of the sample before break. Specimens were cut out from the PUs sheets using an ASTM D638 Type V cutter. The measurements were performed at room temperature with cross-head speed of 50 mm/min, as suggested by the aforementioned ASTM standard. The data presented were average of five different measurements. The reported errors are the subsequent standard deviations.

RESULTS AND DISCUSSION

Characterization of Diisocyanate

The self-metathesis of readily available monounsaturated fatty acids has the potential of being an important pathway for the synthesis of symmetrical long-chain unsaturated dicarboxylic acids. By using Grubbs catalyst and the self-metathesis procedure, unsaturated dicarboxylicacid **2** (Scheme 2) was synthesized.[27] It has been reported that the double bond on the alkyl chain of diacid **2** is in a trans geometry, determined from IR spectrum.[27] Unsaturated diacylazide was prepared from the diacid **2** via the Curtius reaction route.[20] The white solid diacyl azide was dissolved in anhydrous THF and decomposed by heating at reflux to give the corresponding pale yellow diisocyanate **3** that was further purified by passing through a very short chromatograghy column of silicagel. The ^{1}H NMR spectra of the diisocyanate **3** showed a triplet at δ3.28, related to the CH_2 group attached to N=C=O and a multiplet at δ5.38, related to the C—H groups of double bond. Also ^{13}C NMR showed a signal at δ121.9 and 130.3, which corresponds to the isocyanate group and double bonded carbons. High resolution mass spectrum (Fig. 2) of the diisocyanate **3** was in accordance with the structure proposed. The chemical structure of the diisocyanate obtained was further confirmed by FTIR. As shown in Figure 3 (curve a), a strong characteristic band at 2274 cm^{-1} which corresponds to the N=C=O stretching vibration was observed.

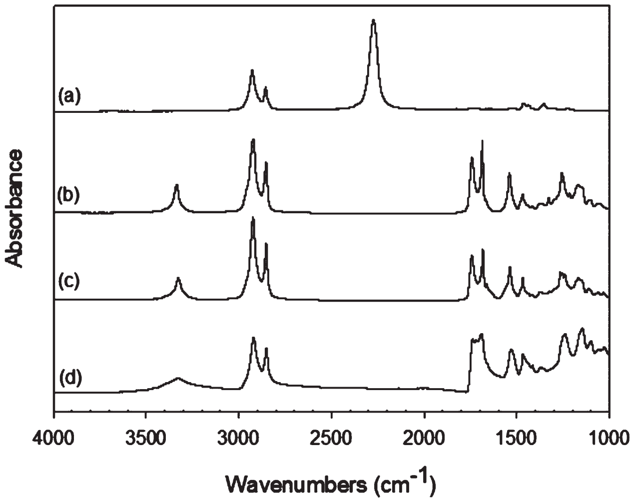


FIGURE 3 FTIR spectra of (a) fatty acid-derived unsaturated diisocyanate, (b) canola diol-HPMDI, (c) canola diol-HDEDI, and (d) canola polyol-HDEDI polyurethane.

Canola Diol-Based Polyurethane

In addition to the presence of C=C double bond, the number of methylene groups of the synthesized HDEDI diisocyanate monomer is 14, which will offer different characteristics when it is compared with HPMDI (whose methylene groups number is 7) synthesized previously in our group. Moreover, all of the current available vegetable oils-based polyol, including canola polyol, is a mixture of triol, diol and monool due to the nature of vegetable oils feedstock.[10] To synthesize model renewable resources based PUs whose purity and structure could be ensured, canola diol was separated from the mixture of canola polyol by flash chromatography using the procedure developed by Yue and coworkers[9] and its structure was illustrated in Scheme 1. The obtained canola diol was utilized to react with HDEDI and HPMDI to prepare polyurethanes, respectively. The number average molecular weights are 4.0 × 10^4 (PDI = 1.5) for canola diol-HDEDI PU

TABLE 1 Average Molecular Weight Determined by GPC and Thermal Properties of Polyurethane Made from Different Raw Materials Determined by MDSC

	M_w	M_n	PDI	T_g (°C)	T_m (°C)
Canola diol-HDEDI	6.0 × 10^4	4.0 × 10^4	1.5		80
Canola diol-HPMDI	5.0 × 10^4	3.6 × 10^4	1.4		73
Canola polyol-HDEDI				−23	48
Canola polyol-HPMDI				−16	62

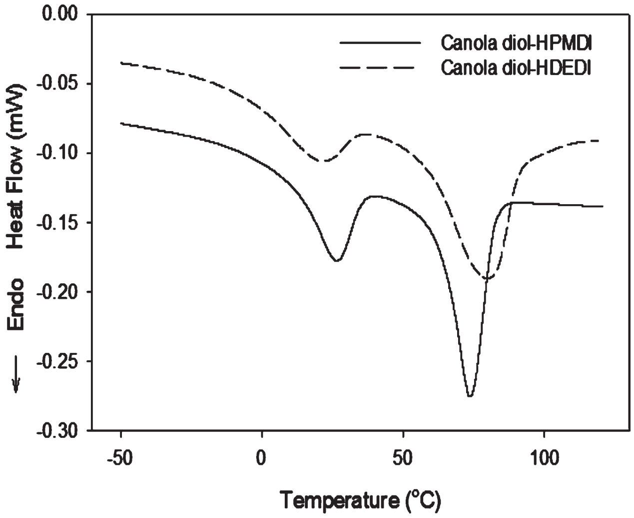


FIGURE 4 MDSC curves of canola diol-HPMDI, and canola diol-HDEDI polyurethane.

and 3.6 × 10^4 (PDI = 1.4) for canola diol-HPMDI PU determined by GPC (Table 1). It is worthmentioning that the number-average molecular weight values determined by GPC are relative to those of PS, however, the chemical structure difference between TPU and PS might cause errors, therefore, further work needs to be done to obtain reliable average molecular weights by utilizing other techniques such as vapor phase osmometry, light scattering and so forth.

The FTIR spectra for canola diol-HPMDI and canola diol-HDEDI PUs are shown in Figure 3 (curves b and c, respectively). It is clear that in both specimens, the N=C=O stretching vibration band was missing, meanwhile, a strong stretching band located around 3330 cm^{-1} characteristic of the N—H group, and stretching vibration bands characteristic of free nonhydrogen bonded C=O groups (ca. 1740 cm^{-1}) and hydrogen bonded urethane C=O groups in ordered (crystalline) domains (ca. 1685 cm^{-1}) were present in the FTIR spectra. These results indicates that this novel fatty acid-derived unsaturated diisocyanate was successfully reacted with canola diol produced PUs. Nevertheless, it is worth pointing out that the wave number of N—H stretching band of canola diol-HDEDI PU is 3327 cm^{-1} and that of canola diol-HPMDI PU is 3336 cm^{-1}. Because higher bond strength is generally characterized by lower wave numbers,[28] this result suggests that the hydrogen bond strength for the former specimen is higher than the latter one, even though the higher number of methylene groups in HDEDI decreases the concentration of urethane groups and hydrogen bond strength. This difference is mainly attributed to the fact that a fully saturated and optimum hydrogen bonding scheme with all trans conformation in the entire polymer backbone could be active in the former specimen.

The reversing heat flow versus temperature curves obtained for canola diol-HPMDI and canola diol-HDEDI PUs samples are shown in Figure 4. In both cases, two endothermic peaks were observed. One is in the range of 20–25 °C, the other one is in the range of 70–80 °C. It has been reported[29–31] that the peak in the low temperature range can be ascribed to the disruption of urethane-polyol bonds, while peaks in the higher temperature range (usually assigned to the melting point of the polymers) was ascribed to the disruption of urethane-urethane bonds. Additionally, it should be noted that the melting point (T_m) of canola diol-HDEDI PU is 80 °C, while that of canola diol-HPMDI is 73 °C (Table 1). Both T_m values are much lower than that of the PUs (ca. 140 °C) produced from 1,6-hexamethylene diisocyanate (HDI) and long-chain, aliphatic α,ω-diol.[32] This was caused by the softening effect of the longer HDEDI chains on the crystal structures as well as the defects in the crystals of canola diol-based PUs due to the presence of dangling chains in canola diol as illustrated in Scheme 1. These long saturated fatty acid branches in canola-diol molecules interrupt the crystal packing, therefore resulting in a less effectively packed and less stable structure. Additionally, from a thermodynamic point of view, the decreasing of T_m in this study is due to the increasing of the entropic effect in the highly branched canola diol-based PUs. It is also worth mentioning that no glass transition was observed in these two PU samples. This might be due to the fact that heat capacity changes over the glass transition region of these types of materials are too small to be detected or the T_g's were overlapped by the endothermic peaks at low temperatures.

The WAXD patterns of canola diol-HPMDI and canola diol-HDEDI PUs are shown in Figure 5. Canola diol-HDEDI PU exhibited three peaks with d-spacings of 1.45 nm, 0.43 nm and 0.39 nm, which correspond to the (004), (100), and (010) planes of typical aliphatic polyurethanes in the usual triclinic crystal phase.[33] This triclinic crystal form consists of hydrogen-bonded sheets stacking via van der Waals forces, and the interchain hydrogen bonds are confined to the plane. The length of 1.45 nm of the chain axis repeat distance is

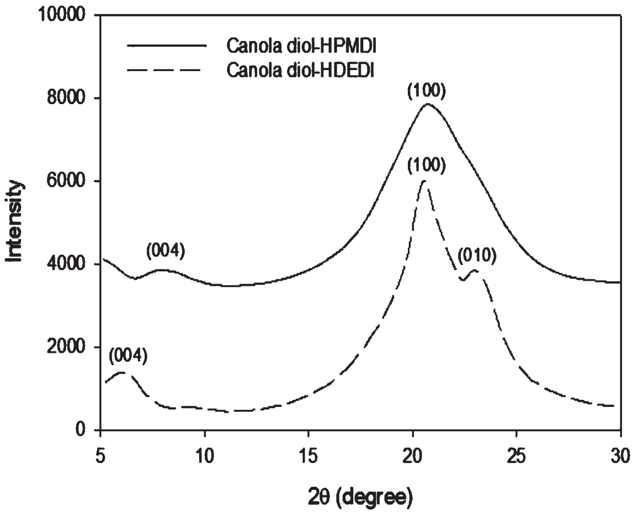


FIGURE 5 Wide angle X-ray diffraction patterns of canola diol-HPMDI, and canola diol-HDEDI polyurethane.

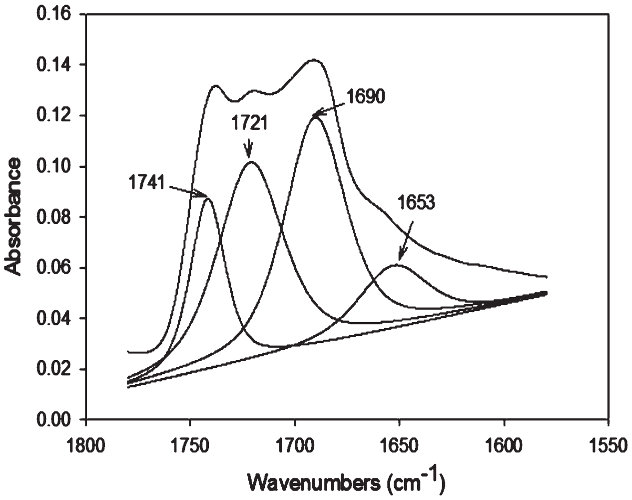


FIGURE 6 A representative spectrum in the carbonyl region for the canola polyol-HDEDI polyurethane, along with the individually fitted peaks from the deconvolution procedure.

slightly higher than the theoretical value, 1.39 nm, calculated for planar zigzag chains with the accepted bond angles and bond lengths. This is due to crystal structural distortion aroused from the presence of the double bond in HDEDI and the long branches in the canola diol. Canola diol-HPMDI PU exhibited two peaks in the WAXD patterns with d-spacings of 1.08 nm and 0.43 nm, which correspond to the (004) and (100) planes of the hexagonal lattice.[34–36] In this case, the chain axis is orthogonal to the lamellar surface with the hydrogen bonds built up within a crystal plane with a length of 0.43 nm.

The above results demonstrate that the synthesized fatty acid derived unsaturated diisocyanate is capable of producing entirely bio-based polyurethanes by reacting with canola oil derived diol. However, the separation of diol from polyol mixture consumes a large amount of solvent and time which would limit its application at an industrial scale. Therefore, it is necessary to study bio-based polyurethanes prepared from this fatty acid derived unsaturated diisocyanate and crude canola polyol.

Canola Polyol-Based Polyurethane

The FTIR spectrum for canola polyol-HDEDI (curve d, Fig. 3) clearly demonstrates that the N=C=O stretching vibration band is missing, meanwhile, a strong stretching band located at 3330 cm^{-1} characteristic of the N—H group and stretching vibration bands around 1700 cm^{-1} characteristic of the C=O group were present. Figure 6 is an enlarged FTIR spectrum in the carbonyl region along with the individual fitted bands from a deconvolution procedure performed on the spectrum. The four bands in the spectrum are identified as follows: free non hydrogen bonded C=O groups (1741 cm^{-1}), hydrogen bonded urethane C=O groups in disordered (amorphous) domains (1721 cm^{-1}), hydrogen bonded urethane C=O groups in ordered (crystalline) domains (1690 cm^{-1}), and the C=C double bond group in the diisocyanate chains (1653 cm^{-1}).

The crystal structures of canola polyol-HDEDI and canola polyol-HPMDI PU are observed by WAXD as well (data not shown). Similar to the corresponding canola diol-based PUs, canola polyol-HDEDI PU exhibited three peaks with d-spacings of 1.41 nm, 0.44 nm, and 0.39 nm, and canola polyol-HPMDI exhibited two peaks with d-spacings of 1.10 nm and 0.42 nm. This result confirms that the diols in the canola polyol reacted with diisocyanate and formed crystals with similar structures to corresponding canola diol-based PUs. Nevertheless, the crystalline peaks in canola polyol-based PUs are broader which is due to the disturbance to the packing of the crystals due to the presence of mono-ols and saturated TAGs.

The reversing heat flow versus temperature curves obtained for both canola polyol-based PU samples are shown in Figure 7. T_ms are observed in both cases, which complement the FTIR and WAXD results. However, the low temperature endothermic peaks which occurred in canola diol-based PUs are missing, which might be due to the interruption of the complex structure of canola polyol-based PU. Meanwhile, in contrast to canola diol-based PUs, the T_m of canola polyol-HDEDI PU is lower than that of canola polyol-HPMDI PU. This probably results from the fact that canola polyol-HDEDI PU contains substantially longer segments which provide more spaces for inactive molecules (mono-ol and saturated TAG) to entrap between well packed molecules. Those entrapped molecules act as defects interrupting the crystal packing and causing a less well packed and less stable structure. In addition, the glass transition temperature (T_g) was determined from Figure 7 and the results were listed in Table 1. As expected, the T_g of canola polyol-HDEDI is about 7 °C lower than that of canola polyol-HPMDI, mainly because of the increasing flexibility caused by the long chain of HDEDI. Moreover, the presence of C=C double bonds in HDEDI molecules also contributes to the decreasing of T_g because there is little steric hindrance adjacent to this bond.

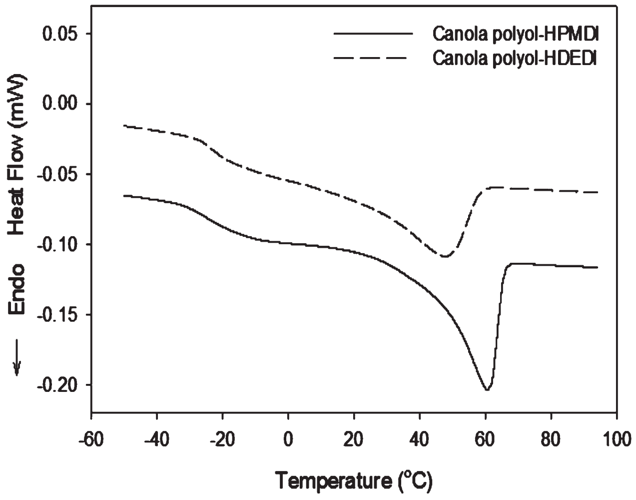


FIGURE 7 MDSC curves of canola polyol-HPMDI, and canola polyol-HDEDI polyurethane.

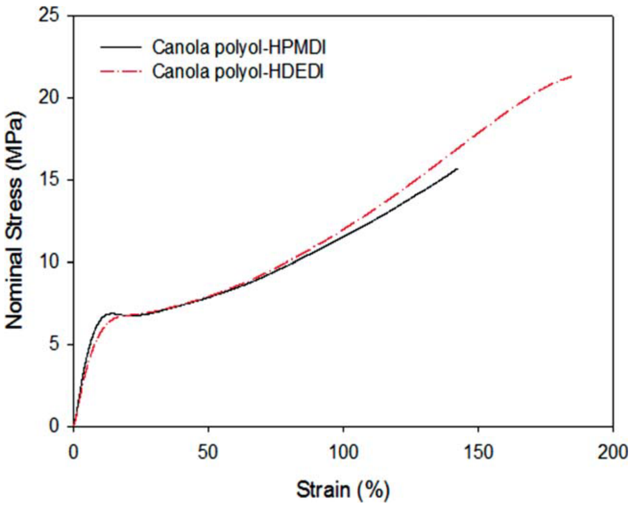


FIGURE 8 Nominal stress versus strain curves of canola polyol-HPMDI, and canola polyol-HDEDI polyurethane.

It is worth mentioning that the formation of vegetable oil-based PU networks (from three or more reactants) is more complicated because of the nature of the vegetable oil feedstock. In the case of the canola polyol-based PUs studied in this work, since the starting materials, that is canola polyol, is a mixture of triol, diol and mono-ol, the relative reactivity of functional groups are not equal, which results in structurally inhomogeneous systems containing various domains with different sizes. Each domain consists of alternate polyol (triol or diol)-isocyanate sequences. Part of the domain is chemically cross-linked through covalent bonds between diisocyanate with triol, diol and mono-ol, and part of it is crystalline domain resulting from physical cross-linking (hydrogen bonding) between segments. The packing of these crystals was interrupted by the mono-ol, saturated TAG and the dangling chains in the diol molecules. These chains would restrict the effective packing of the polymer chains into crystals by creating steric hindrances. Additionally, the chemical cross-links would reduce the mobility of molecular chains and cause a reduction of these chains to orient to form crystals.

The stress versus strain curves for canola polyol-HDEDI and canola polyol-HPMDI samples are shown in Figure 8. For canola polyol-HPMDI PU, the tensile strength at break is 15 ± 2 MPa, Young's modulus is 92 ± 3 MPa and maximum elongation is 133% ± 13%, whereas for canola polyol-HDEDI PU, the tensile strength at break is 21 ± 2 MPa, Young's modulus is 72 ± 4 MPa and maximum elongation is 175% ± 22%. The decreases in Young's modulus and increases in maximum elongation in canola polyol-HDEDI PU are due to the flexibility of the long chain introduced by the HDEDI diisocyanate. Additionally, the canola polyol-HDEDI sample demonstrated a higher tensile strength at break than that of canola polyol-HPMDI. This behavior is attributed to the higher intermolecular forces associated with the former sample, since fully saturated hydrogen bonding in the entire polymer backbone was generated. The mechanical properties of the PUs are greatly dependent on the intermolecular hydrogen bonding because the increased intermolecular hydrogen bonding improves the aggregating strength.[37] When HDEDI with longer molecular chains was used in the PU preparation, despite the decrease in the concentration of urethane groups, the overall hydrogen bond strength is still higher. Therefore, the canola polyol-HDEDI samples demonstrated a higher tensile strength at break.

CONCLUSIONS

A novel long chain linear unsaturated terminal diisocyanate has been successfully synthesized from oleic acids via Curtius rearrangement. The feasibility of utilizing this new diisocyanate for the production of bio-based polyurethanes has been demonstrated by reacting it with canola diol and canola polyol, respectively. The crystalline structure and physical properties of these polyurethanes were compared to their counterparts made from a similar fatty acid-derived diisocyanate, 1,7-heptamethylene diisocyanate. For model PUs produced from canola diol, the overall hydrogen bond strength of canola diol-HDEDI PU is higher than that of canola diol-HPMDI PU. In addition, both HDEDI based PUs exhibit the triclinic crystal subcell, whereas HPMDI based PUs exhibit a hexagonal crystal lattice subcell. Because of the flexibility of the long chain introduced by the HDEDI diisocyanate, lower Young's modulus and higher elongation in canola polyol-HDEDI PU were observed. On the other hand, canola polyol-HDEDI PU demonstrated a higher tensile strength at break than that of canola polyol-HPMDI, which is attributed to the higher intermolecular forces (hydrogen bonding) associated with the former sample.

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REFERENCES AND NOTES

1 Szycher, M. Szycher's Handbook of Polyurethanes; CRC Press: Boca Raton, FL, 1999.

2 Heidbreder, A.; Höfer, R.; Grützmacher, R.; Westfechtel, A.; Blewett, C. W. Fett/Lipid 1999, 101, 418–424.

3 Kong, X.; Narine, S. S. Biomacromolecules 2007, 8, 2203–2209.

4 Kong, X.; Yue, J.; Narine, S. S. Biomacromolecules 2007, 8, 3584–3589.

5 Kong, X. H.; Narine, S. S. Biomacromolecules 2008, 9, 1424–1433.

6 Lu, Y. S.; Larock, R. C. Biomacromolecules 2007, 8, 3108–3114.

7 Narine, S. S.; Kong, X.; Bouzidi, L.; Sporns, P. J Am Oil Chem Soc 2007, 84, 55–63.

8 Narine, S. S.; Kong, X.; Bouzidi, L.; Sporns, P. J Am Oil Chem Soc 2007, 84, 65–72.

9 Narine, S. S.; Yue, J.; Kong, X. J Am Oil Chem Soc 2007, 84, 173–179.

10 Yue, J.; Narine, S. S. J Am Oil Chem Soc 2007, 84, 803–807.

11 Zlatanic, A.; Lava, C.; Zhang, W.; Petrovic, Z. S. J Polym Sci Part B: Polym Phys 2004, 42, 809–819.

12 Javni, I.; Zhang, W.; Petrovic, Z. S. J Appl Polym Sci 2003, 88, 2912–2916.

13 Ulrich, H. Chemistry and Technology of Isocyanates; Wiley: Chichester, 1996.

14 Waldman, T. E.; McGhee, W. D. Chem Commun 1994, 8, 957–958.

15 Kamal, M. R.; Dhahran, S. A.; Kuder, R. C. U.S. Pat. 3,691,225, 1972.

16 Coady, C. J.; Krajewski, J. J.; Bishop, T. E. U.S. Pat. 4,608,409, 1986.

17 Bishop, T. E.; Coady, C. J.; Zimmerman, J. M. U.S. Pat. 4,609,718, 1986.

18 Cacella, A. F. U.S. Pat. 3,622,435, 1971.

19 Cayli, G.; Kusefoglu, S. J Appl Polym Sci 2008, 109, 2948–2955.

20 Hojabri, L.; Kong, X.; Narine, S. S. Biomacromolecules 2009, 10, 884–891.

21 Bräse, S.; Friedrich, A.; Gartner, M. Synthesis of Heterocycles via Cycloadditions I; Springer: Berlin/Heidelberg, 2008; Vol. 12, pp 45–115.

22 Ray, A.; Zhu, K. M.; Kissin, Y. V.; Cherian, A. E.; Coates, G. W.; Goldman, A. S. Chem Commun 2005, 3388–3390.

23 Kondo, Y.; Garcia-Cuadrado, D.; Hartwig, J. F.; Boaen, N. K.; Wagner, N. L.; Hillmyer, M. A. J Am Chem Soc 2002, 124, 1164–1165.

24 Bae, C.; Hartwig, J. F.; Harris, N. K. B.; Long, R. O.; Anderson, K. S.; Hillmyer, M. A. J Am Chem Soc 2005, 127, 767–776.

25 Boaen, N. K.; Hillmyer, M. A. Macromolecules 2003, 36, 7027–7034.

26 Ho, T.; Martin, J. M. Structure, Properties and Applications of Polyolefin Elastomers Produced by Constrained Geometry Catalysts; Wiley: New York, 2000.

27 Ngo, H. L.; Jones, K.; Foglia, T. A. J Am Oil Chem Soc 2006, 83, 629–634.

28 Petrovic, Z. S.; Ferguson, J. Prog Polym Sci 1991, 16, 695–836.

29 Seymour, R. W.; Cooper, S. L. Macromolecules 1973, 6, 48–53.

30 Seymour, R. W.; Cooper, S. L. J Polym Sci Part B: Polym Lett 1971, 9, 689–694.

31 Clough, S. B.; Schneider, N. S. J Macromol Sci Phys 1968, 2, 553–566.

32 McKiernan, R. L.; Gido, S. P.; Penelle, J. Polymer 2002, 43, 3007–3017.

33 McKiernan, R. L.; Sikorski, P.; Atkins, E. D. T.; Gido, S. P.; Penelle, J. Macromolecules 2002, 35, 8433–8439.

34 Kinoshita, Y. Makromol Chem 1959, 33, 1–20.

35 Kinoshita, Y. Makromol Chem 1959, 33, 21–31.

36 Cui, X. W.; Li, W. H.; Yan, D. Y. Polym Eng Sci 2005, 45, 1673–1679.

37 Zia, K. M.; Barikani, M.; Bhatti, I. A.; Zuber, M.; Bhatti, H. N. J Appl Polym Sci 2008, 109, 1840–1849.