Synthesis of Biobased Polyurethane from Oleic and Ricinoleic Acids as the Renewable Resources via the AB-Type Self-Condensation Approach

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Polyurethane (PU) from methyl oleate (derived from sunflower oil) and ricinoleic acid (derived from castor oil) was synthesized using the AB-type self-polycondensation approach for the first time. In the present work, three novel AB-type monomers, namely, a mixture of 10-hydroxy-9-methoxyoctadecanoyl azide/9-hydroxy-10-methoxyoctadecanoyl azide (HMODAz), 12-hydroxy-9-*cis*-octadecenoyl azide (HODEAz) and methyl-*N*-11-hydroxy-9-*cis*-heptadecen carbamate (MHHDC) were synthesized from methyl oleate and ricinoleic acid using simple reaction steps. Out of these, HMODAz and HODEAz monomers were polymerized by the acyl-azido and hydroxyl AB-type self-condensation approach, while MHHDC monomer was polymerized through AB-type self-condensation via transurethane reaction. The acyl-azido and hydroxyl self-condensations were carried out at various temperatures (50, 60, 80. and 110 °C) in bulk with and without catalyst. A FTIR study of the polymerization, using HMODAz at 80 °C without catalyst, indicates in situ formation of an intermediate isocyanate group in the first 15−30 min, and further onward, the molar mass increases as observed by SEC analysis. In the case of the MHHDC monomer, a transurethane reaction was used to obtain a similar PU (which was obtained by AB-type acyl-azido and hydroxyl self-condensation of HODEAz) in the presence of titanium tetrabutoxide as a catalyst at 130 °C. HMODAz, HODEAz, MHHDC, and corresponding polyurethanes were characterized by FTIR, ^{1}H NMR, ^{13}C NMR, and MALDI-TOF mass spectroscopy. Differential scanning calorimetric analysis of polyurethanes derived from HMODAz, HODEAz, and MHHDC showed two different glass transition temperatures for soft segments (at lower temperature) and hard segments (at higher temperature), indicating phase-separated morphology.

Introduction

Polyurethanes are among the most important polymeric materials, which exhibit versatile properties suitable for use in many fields, such as footwear, machinery industry, coatings and paints, rigid insulations, elastic fibers, soft flexible foam, and medical devices.[1] Additionally, the chemistry of PUs allows for the synthesis of different types of polymeric materials such as foams (flexible and rigid), thermoplastics (TPU), interpenetrating polymer networks (IPNs), and segmented PUs, depending on the polyols and isocyanates used as well as the method of polymerization.

Recently, intensive interest has been paid to the synthesis of PU starting from natural resources like vegetable oils and natural fats because of their important availability, sustainability, biodegradability, and added values. It is well-known that the products based on renewable resources are usually more eco-compatible in comparison with petrochemical-based products.[2–4] There have been many studies on the synthesis and characterization of a wide variety of polymers based on vegetable oils in the recent years.[5–12]

Vegetable oils are triglycerides and often have at least one unsaturated fatty acid in their chemical structure.[13,14] Many types of vegetable oils (from rapeseed, tung, linseed, canola, sunflower, and soybean) have been tested and reported for polyol synthesis as polyurethane precursors. The use of enzymes or chemicals to modify the structure of fatty acid and to introduce functional groups to obtain functional monomers has been known for a long time and, in some cases, particular vegetable oils can be utilized directly as monomers. For example, Ogunniyi[15] and Ehrilich[16] et al. reported that naturally hydroxylated castor oil can be used to replace the petroleum-based polyol to make polyurethane foams. Castor-oil-based polyurethanes have also been used for artificial bones.[17] Xiao et al. used polyurethane based on castor oil as a component of semi-interpenetrating polymer network (semi-IPNs) with nitroguar gum.[18] Castor-oil-based polyurethane composite proved also to be a material useful as a “corrosion sensor”.[19] Conveniently, Cramail and co-workers describe the synthesis of monodisperse PU nanoparticles by a miniemulsion technique in water as dispersant medium using castor oil as a monomer.[20] Polyester diol based on ricinoleic acid was also prepared to be used for conventional TPU applications. Nevertheless, it is expected that, like conventional TPU systems, appropriate stabilizers would promote even further thermal stability during melt processing.[21a] On the other hand, it is important to mention that Matsumura et al. utilized ricinoleic acid derived from castor oil as AB-type monomer for lipase-catalyzed polyester synthesis.[21b,c] Lu et al. used waterborne polyurethane made from rapeseed-oil-based polyol to modify glycerol-plasticized starch and develop

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biodegradable films.[22] Chang et al. added commercial soy flours into water-blown rigid polyurethane foams to improve the physical properties and lower the cost of these foams.[23,24] Petrovic and co-workers have been doing extensive research in the field and investigated the structure and properties of vegetable-oil-based polyols, their applications in polyurethane foams, and the foam's biodegradation behavior and thermal stability.[25–27]

With the views on academic research considering this field, our goal is to design new monomers and polymers using vegetable oils as precursors. To our knowledge, while vegetable oils have been studied as polyol precursors for PU synthesis, there is no report on the AB-type self-condensation approach to PU from vegetable oils. Recently, Hojabri et al. synthesized 1,7-heptane diisocyanate utilizing oleic acid as a renewable source from sunflower oil, and from that PU was prepared with petroleum- and canola-oil-based polyols, respectively. The properties of PU obtained from fatty-acid derived diisocyanate was comparable with PU obtained from petroleum-derived 1,6-hexane diisocyanate.[28] Isocyanates are highly reactive and toxic chemicals, hence, nonisocyanate routes for PU synthesis are required. Among the nonisocyanate routes to polyurethanes one can cite the two most used: self-condensation approach in which the AB-type monomer contains hydroxyl and acyl azide groups[29–31] and the other one is the ring-opening of cyclic carbonate by amines.[32] Kumar et al. showed that the acyl azide route produces PU of moderately high molar mass, but highly branched structures are also observed. Self-polycondensation of an AB-type monomer makes the advantage of built-in stoichiometric control for attaining high molar mass. Finally, it is worth mentioning that the transurethane process is also important in view of the nonisocyanate and nonsolvent route to PU. For instance, Jayakannan and Deepa have reported PU synthesis via a transurethane reaction of bisurethane and diol in the presence of titanium tetrabutoxide as a catalyst.[33]

In this article, we wish to report the first example of vegetable-oil-derived AB-type self-condensable monomers for the synthesis of biosourced PU. The AB-type monomers described below are composed of acyl-azide, hydroxyl, and methyl urethane functionalities, namely, 10-hydroxy-9-methoxyoctadecanoyl azide/9-hydroxy-10-methoxyoctadecanoyl azide (HMODAz), 12-hydroxy-9-*cis*-octadecenoyl azide (HODEAz), and methyl-*N*-11-hydroxy-9-*cis*-heptadecen carbamate (MHHDC). Self-condensation of HMODAz and HODEAz was carried out at different temperatures, and the detailed reaction progress was monitored by FTIR, ^{1}H NMR, and SEC. MHHDC was polymerized by a transurethane polycondensation reaction in the presence of titanium tetrabutoxide as a catalyst at 130 °C.

Materials and Methods

Materials. Methyl oleate (84.5%) and ricinoleic acid (88.5%) were kindly provided by ITERG Pessac, France, and used as received (detailed analysis carried out using AFNOR methods, NF EN ISO 5509 and NF EN ISO 5508, is presented in Supporting Information, Table 1). *meta*-Chloroperbenzoic acid (mCPBA), dibutyl tin dilaurate (DBTDL), titanium tetrabutoxide [$Ti(n\text{-}BuO)_4$], sodium bicarbonate, 1 M methanolic potassium hydroxide solution, 1 N hydrochloric acid, triethyl amine, and sodium azide were purchased from Aldrich and used as received. Ethyl chloroformate (Fluka), methanol, ethanol, tetrahydrofuran dichloromethane (J. T. Baker), and anhydrous sodium sulfate were purchased and used as received.

Analysis. ^{1}H and ^{13}C NMR spectra were recorded using a Bruker AC-400 NMR at room temperature by dissolving the samples in $CDCl_3$. Size exclusion chromatography (SEC) analyses were performed at room temperature in THF with a setup consisting of a WATERS 880-PU pump and a series of three microstyragel columns with pore sizes of 103, 105, and 106 Å. The elution of the filtered samples was monitored using simultaneous UV and refractive index detections. The elution times were converted to molar mass using a calibration curve based on low dispersity (M_w/M_n) polystyrene (PS) standards. Infrared spectra were obtained on a Bruker-Tensor 27 spectrometer using the attenuated total reflection (ATR) mode. Matrix-assisted laser desorption ionization time-of-flight mass spectrometry (MALDI-TOF MS) spectra were performed by the CESAMO (Bordeaux, France) on a Voyager mass spectrometer (Applied Biosystems). The instrument is equipped with a pulsed nitrogen laser (337 nm) and a time-delayed extracted ion source. Spectra were recorded in the positive-ion mode using the reflectron and with an accelerating voltage of 20 kV. Polymer samples were dissolved in THF at 10 mg mL^{-1}. The dithranol matrix solution was prepared by dissolving 10 mg in 1 mL of dichloromethane. A methanol solution of cationization agent (NaI, 10 mg mL^{-1}) was also prepared. The solutions were combined in a 10:1:1 volume ratio of matrix to polymer to cationization agent. Several microliters of the obtained solution were deposited onto the sample holder and vacuum-dried. 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 the glass transition temperatures were calculated from a second heating run. All runs were performed at a rate of 10 °C min^{-1}.

1. Synthesis of AB-Type Monomers for Self-Condensation. *(i) Synthesis of 10-Hydroxy-9-methoxyoctadecanoyl Azide (HMODAz) AB-Type Monomer (***5***). (a) Synthesis of Methyl cis-9,10-Epoxyoctadecanoate (***2***).* Methyl oleate (**1**; 5.0 g, 0.017 mol) and *meta*-chloroperbenzoic acid (4.3 g, 0.025 mol) were dissolved into dichloromethane (100 mL) and the reaction mixture was stirred at room temperature for 5 h. The reaction mixture was filtered, and the solution was washed with aqueous saturated sodium bicarbonate (3 × 50 mL) and then with water (3 × 50 mL). The organic layer was separated and dried with anhydrous sodium sulfate. The solvent was removed by rotary evaporator to obtain intermediate **2**. Yield: 4.8 g (91%). IR: 1740 ($COOCH_3$), 841 cm^{-1} (epoxy). ^{1}H NMR (400 MHz, $CDCl_3$): 0.87 (3H, t, CH_3, $J = 6.4$ Hz), 1.20−1.70 (methylene protons), 2.29 (2H, t, CH_2-$COOCH_3$, $J = 7.6$ Hz), 2.99 (2H, epoxy ring proton), 3.66 (3H, s, $COOCH_3$).

*(b) Synthesis of Methyl 10-Hydroxy-9-methoxyoctadecanoate/Methyl 9-Hydroxy-10-methoxyoctadecanoate (***3/3′***).* Methyl *cis*-9,10-epoxyoctadecanoate (**2**; 4.8 g, 0.015 mol), amberlyst 15 (0.05 g), and excess methanol (100 mL) were refluxed for 12 h. The reaction mixture was filtered and methanol was removed using a rotary evaporator. The reaction mixture was dissolved into dichloromethane (100 mL) and washed with water (3 × 50 mL). The dichloromethane solution was separated and evaporated to obtain intermediate **3/3′** as a mixture of regioisomers. Yield: 4.7 g (89%). IR: 3480 (OH), 1740 cm^{-1} ($COOCH_3$). ^{1}H NMR (400 MHz, $CDCl_3$): 0.88 (3H, t, CH_3, $J = 6.4$ Hz), 1.20−1.70 (methylene protons), 2.29 (2H, t, CH_2-COOH, $J = 7.6$ Hz), 2.99 (1H, dd, CH-OCH_3, $J = 5.2$, 10.8 Hz), 3.41 (3H, s, OCH_3), 3.49 (1H, m, CH-OH), 3.66 (3H, s, $COOCH_3$).

*(c) Synthesis of 10-Hydroxy-9-methoxyoctadecanoic Acid/9-Hydroxy-10-methoxyoctadecanoic Acid (***4/4′***).* A mixture of regioisomer intermediates (**3/3′**; 4.0 g, 0.012 mol) was dissolved into 1 N methanolic potassium hydroxide solution (100 mL) and refluxed for 12 h. The methanol was removed from the reaction mixture and the crude product was dissolved into 100 mL of water. The water solution was neutralized with hydrochloric acid and the product was extracted with 3 × 50 mL dichloromethane. The dichloromethane solution was washed with 3 × 50 mL of water and dried on anhydrous sodium sulfate. The dichloromethane solution was filtered and solvent was removed to obtain a mixture of intermediates **4/4′**. Yield: 3.50 g (91%). IR: 3435 (OH), 1709 cm^{-1} (COOH). ^{1}H NMR (400 MHz, $CDCl_3$): 0.86 (3H, t, CH_3, $J = 6.8$ Hz), 1.20 to 1.70 (methylene protons), 2.34 (2H, t, CH_2-COOH, $J = 7.6$ Hz), 2.98 (1H, dd, CH-OCH_3, $J = 5.2$, 11.2 Hz), 3.39 (3H, s,

OC*H*$_3$), 3.47 (1H, m, C*H*-OH). ^{13}C NMR (400 MHz, CDCl$_3$, ppm): 179.3 (COOH), 84.4 (CH-OMe), 72.2 (CH-OH), 58.3 (OCH$_3$), 22−35 (alkyl chain protons), 13.9 (CH$_3$).

*(d) Synthesis of 10-Hydroxy-9-methoxyoctadecanoyl Azide/9-Hydroxy-10-methoxyoctadecanoyl Azide (HMODAz) AB-Type Monomer (**5/5′**).* Into a 100 mL round-bottom flask equipped with a magnetic stirring bar and an addition funnel were charged a mixture of hydroxyl acid intermediates **4/4′** (2.0 g, 0.006 mol), triethyl amine (1.8 g, 0.018 mol), and THF/water mixture (7:3 v/v, 30 mL). The reaction mixture was cooled to 0 °C and ethylchloroformate (1.96 g, 0.018 mol) was added dropwise over a period of 10 min. The reaction mixture was stirred for 2 h and then sodium azide (1.2 g, 0.018 mol) in water (7 mL) was added dropwise for 10 min and stirred at 0 °C for 4 h. THF was removed using a rotary evaporator and crude product was dissolved into dichloromethane (100 mL). The dichloromethane solution was washed with water (2 × 50 mL), dried over anhydrous sodium sulfate, and filtered and the solvent was removed to obtain HMODAz as an oil with a slightly yellow in color. Yield: 2.0 g (92%). IR: 3465 (OH), 2138 (N$_3$), 1720 cm$_{-1}$ (CO). ^{1}H NMR (400 MHz, CDCl$_3$): 0.87 (3H, t, C*H*$_3$, J = 6.4 Hz), 1.20−1.70 (methylene protons), 2.32 (2H, t, C*H*$_2$-CON$_3$, J = 7.6 Hz), 2.98 (1H, dd, C*H*-OCH$_3$, J = 6, 11.6 Hz), 3.39 (3H, s, OC*H*$_3$), 3.47 (1H, m, C*H*-OH). ^{13}C NMR (400 MHz, CDCl$_3$, ppm): 180.1 (CON$_3$), 84.1 (CH-OMe), 72.2 (CH-OH), 57.7 (OCH$_3$), 21−37 (alkyl chain protons), 13.5 (CH$_3$).

*(ii) Synthesis of 12-Hydroxy-9-cis-octadecenoyl Azide (HODEAz) AB-Type Monomer (**8**).* The procedure for the synthesis of HODEAz is similar to HMODAz synthesis except ricinoleic acid was used. Yield: 90%. IR: 3400 (OH), 3008 (=C−H), 2133 (N$_3$), 1720 cm^{-1} (CO). ^{1}H NMR (400 MHz, CDCl$_3$): 0.87 (3H, t, C*H*$_3$), 1.20−1.70 (methylene protons), 2.31 (2H, t, C*H*$_2$-CON$_3$), 3.58 (1H, m, C*H*-OH), 5.3−5.6 (C*H*=C*H*). ^{13}C NMR (400 MHz, CDCl$_3$, ppm): 180.5 (CON$_3$), 132.9 and 125.3 (CH=CH), 71.3 (CH−OH), 42.8 ($\underline{C}H_2CON_3$), 36.7 and 35.2 ($\underline{C}H_2$-CH(OH)-$\underline{C}H_2$), 21−37 (alkyl chain protons), 13.5 (CH$_3$).

*(iii) Synthesis of Methyl-N-11-hydroxy-9-cis-heptadecene Carbamate (MHHDC), AB-Type Monomer for Transurethane Process (**10**).* Into a 100 mL round-bottom flask equipped with a magnetic stirring bar and refluxed condenser were charged 12-hydroxy-9-*cis*-octadecenoyl azide (**8**; 2.0 g, 0.006 mol) and dry methanol (50 mL). The reaction mixture was refluxed for 4 h, and after that, the excess of methanol was removed on a rotary evaporator. The crude urethane product was dissolved into dichloromethane (100 mL), washed with water (2 × 50 mL), dried over anhydrous sodium sulfate, and filtered, and the solvent was removed to obtain the carbamate product (**10**). Yield: 1.85 g (92%). IR: 3600−3400 (OH), 3334 (NH), 3008 (=C−H), 1703 cm^{-1} (CO). ^{1}H NMR (400 MHz, CDCl$_3$): 0.87 (3H, t, C*H*$_3$, J = 6.6 Hz), 1.20−1.70 (methylene protons), 3.14 (2H, dd, C*H*$_2$-NHCOO-, J = 6.4, 12.8 Hz), 3.59 (1H, m, C*H*-OH), 3.64 (3H, s, NHCOO-C*H*$_3$), 4.63 (1H, N*H*-COO), 5.3−5.6 (C*H*=C*H*). ^{13}C NMR (400 MHz, CDCl$_3$, ppm): 157 (NHCOO−), 133 (CH=CH), 71.4 (CH−OH), 51.8 (NHCOO$\underline{C}H_3$), 24−37 (alkyl chain carbons).

(2) AB-Type Self-Condensation of HMODAz (5/5′) and HODEAz (8). Into a 50 mL two necked round-bottom flask equipped with a magnetic stirring bar and a nitrogen inlet were charged HMODAz (2.0 g, 0.005 mol) and kept in an oil bath at different temperatures (50, 60, 80, and 110 °C) for various times. Yield: 1.80 g (90%). IR: 3338 (NH), 1695 (CO), 1526 (NH deformation), 1230 cm^{-1} (C−N). ^{1}H NMR (400 MHz, CDCl$_3$): 0.87 (C*H*$_3$), 1.20−1.70 (methylene protons), 3.18 (−C*H*$_2$-NHCOO), 3.39 (OC*H*$_3$), 4.88 (N*H*).

(3) Progress of AB-Type Self-Condensation Monitored by FTIR, ^{1}H NMR Spectroscopy, and SEC. Into a 50 mL two-necked round-bottom flask equipped with a magnetic stirring bar and a nitrogen inlet, were charged HMODAz (**5/5′**; 2.0 g, 0.005 mol) and kept in an oil bath at 80 °C for 24 h. Aliquots (15 mg) were taken out after 15, 45, 60, and so on, minute reaction time intervals and immediately analyzed by FTIR spectroscopy. After FTIR analysis, samples were reacted with an excess of ethanol into a nitrogen atmosphere at 40 °C for 12 h and dried under vacuum. The complete dried samples were analyzed by ^{1}H NMR and SEC.

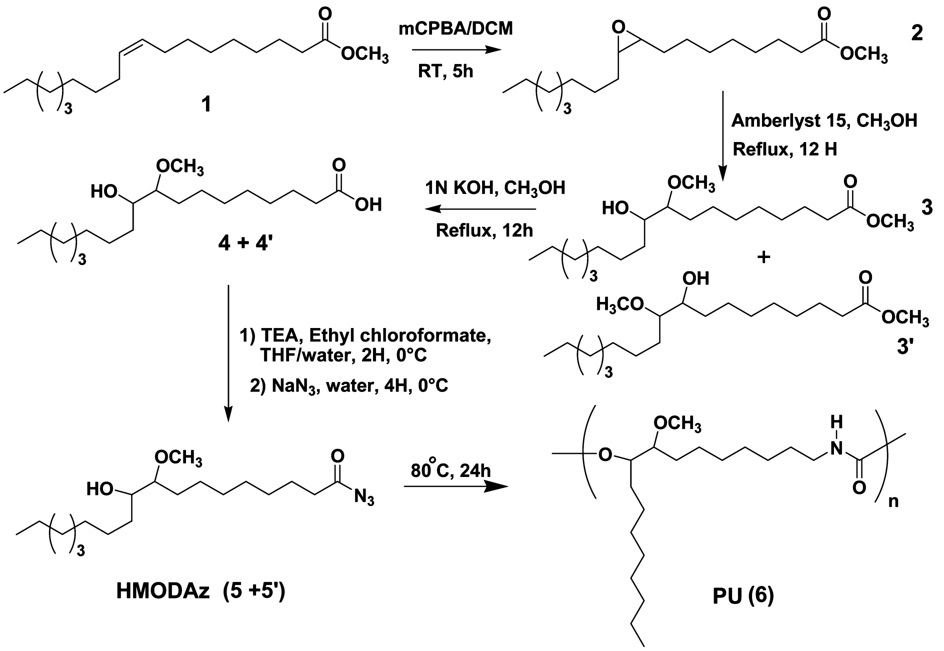
(4) Polycondensation of MHHDC via Melt-Transurethane (9). Into a 50 mL two-necked round-bottom flask equipped with a magnetic stirring bar, vacuum adapter, and a nitrogen inlet were charged methyl-*N*-11-hydroxy-9-*cis*-heptadecen carbamate (**10**; 1.0 g, 0.003 mol) and titanium tetrabutoxide (0.035 g, 1 × 10^{-4} mol). The reaction mixture was purged with nitrogen, followed by vacuum twice. The reaction flask was kept in an oil bath at 130 °C for 4 h under a nitrogen purge and then under vacuum at 130 °C for 2 h. Yield: 0.80 g (80%). IR: 3338 (NH), 1695 (CO), 1526 (NH deformation), 1230 cm^{-1} (C−N). ^{1}H NMR (400 MHz, CDCl$_3$): 0.86 (C*H*$_3$), 1.20−1.70 (methylene protons), 3.13 (−C*H*$_2$-NHCOO), 3.63 (OC*H*$_3$), 4.86 (N*H*), 5.3−5.6 (C*H*=C*H*).

Results and Discussion

(1). Synthesis and Characterization of HMODAz AB-Type Monomer (5/5′). For the synthesis of PU via AB-type self-condensation approach, the monomer should contain at least one hydroxyl and one isocyanate group. In the present work, HMODAz was designed as an AB-type self-condensable monomer with one secondary hydroxyl group and one acyl azide group as an isocyanate precursor.

HMODAz as an AB-type monomer was synthesized in four step reactions (Scheme 1), and the structure of all the intermediates were confirmed by FTIR and ^{1}H and ^{13}C NMR spectroscopy. FTIR analysis of methyl oleate (**1**) shows a band at 1654 cm^{-1} due to the presence of vinylic double bond (C=C) and a band at 1740 cm^{-1} due to the presence of an ester bond, while a C=C−H stretching vibration band is observed at 3005 cm^{-1} (Figure 1). Further, the structure elucidation of methyl oleate was carried out by ^{1}H NMR spectroscopy in which vinylic protons appeared at 5.32 ppm and methyl ester protons at 3.65 ppm. In the first step, methyl oleate (**1**) was epoxidized using *meta*-chloroperbenzoic acid reagent to yield intermediate (**2**). FTIR spectrum of intermediate **2** shows the absence of a band at 3005 cm^{-1} due to C=C−H group. The appearance of a new peak in ^{1}H NMR spectrum due to epoxy ring protons (Hc) at 2.9 ppm and absence of vinylic protons at 5.32 ppm confirms the epoxidation of the vinylic bond. The second step consists of the epoxide ring-opening of **2** using methanol in the presence of acid catalyst amberlyst 15 to obtain a mixture of two regioisomers (**3/3′**) containing a secondary hydroxyl group. Further onward, for the simplicity of the reaction schemes, we write one isomer structure in the scheme as well as in the figures 1 and 2. The ring-opening of epoxide was confirmed on the basis of an appearance of a band at 3480 cm^{-1} due to hydroxyl group and a band at 1100 cm^{-1} due to ether bond in the IR spectrum (Figure 1). The ^{1}H NMR spectrum of a mixture of regioisomers (**3/3′**; Figure 2) shows significant three new peaks at 2.99, 3.41, and 3.49 ppm that correspond, respectively, to CH to which the methoxy group is attached, methoxy protons, and CH to which hydroxyl group is attached along with other peaks. In the third step, methyl ester hydrolysis of intermediate **3/3′** using methanolic potassium hydroxide was carried out to obtain corresponding hydroxy acid **4/4′**. The FTIR spectrum of hydroxy acid **4/4′** shows a broad band due to acid hydroxyl at 3435 cm^{-1} and disappearance of the ester band at 1740 cm^{-1}. Moreover, the disappearance of a peak at 3.66 ppm corresponding to methyl ester protons (COOC*H*$_3$) in ^{1}H NMR spectrum of intermediate **4/4′** confirms the formation of carboxylic acid. A peak for carboxylic acid **4/4′** appeared at 179.3 ppm in ^{13}C NMR spectrum. In the last step, hydroxy acid **4/4′** was converted into hydroxyl acyl azide monomer **5/5′** using a reported

Scheme 1. Synthesis of HMODAz (**5**/**5′**) Derived from Methyl Oleate and Corresponding Polyurethane (**6**)



method.[35,36] Hydroxy acid was reacted with ethyl chloroformate in the presence of triethyl amine to form in situ mixed anhydride and subsequently reacted with sodium azide to afford acyl azide HMODAz. The structure of hydroxyl azide **5**/**5′** was confirmed by FTIR and ^{1}H and ^{13}C NMR spectroscopy. The IR spectrum shows a strong absorption band at 2138 cm^{-1} due to the asymmetric stretching vibration of the azide group (N_3) and also a shift of the carbonyl group band from 1709 to 1720 cm^{-1} due to formation of the more electron withdrawing azide group than the carboxylic acid precursor. The presence of a hydroxyl group could not interfere with the reaction of ethyl chloroformate, as noticed by FTIR spectroscopy (because if there was the reaction, a carbonate band in the FTIR should appear). A peak of the methylene group attached to an azide group (CH_2-CON_3) appears at 2.32 ppm in the ^{1}H NMR spectrum of **5**/**5′**, and the ^{13}C NMR spectrum shows a peak at 180.09 ppm for the carbonyl attached to an azide group, confirming the transformation from carboxylic acid to an acyl-azide group.

(2) Synthesis and Characterization of 12-Hydroxy-9-*cis*-octadecenoyl Azide (HODEAz) AB-Type Monomer (8). Ricinoleic acid is a potential important hydroxyl containing C18 fatty acid with a cis-configuration double bond in the ninth position.[34] In comparison with methyl oleate as a starting material for PU synthesis by the self-condensation approach, ricinoleic acid is advantageous due to the hydroxyl group naturally being present in the fatty ester backbone, thus, reducing the number of chemical reactions to obtain an acyl-azide hydroxy AB-type monomer.

For the synthesis of 12-hydroxy-9-*cis*-octadecenoyl azide AB-type monomer (**8**), a reported method was used.[35,36] Ricinoleic acid was reacted with ethyl chloroformate in presence of triethyl

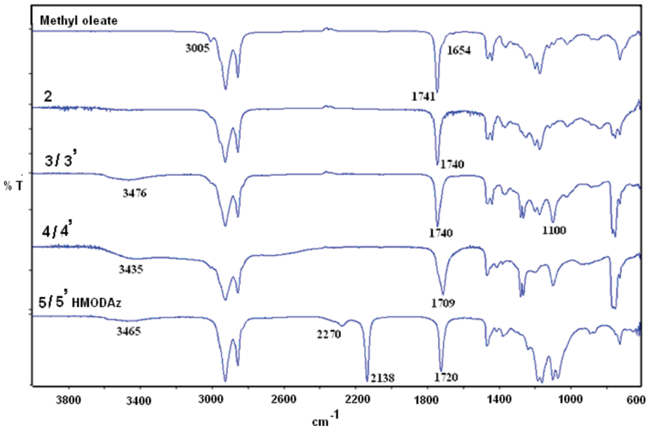


Figure 1. FTIR spectra of intermediates based on methyl oleate: (a) methyl oleate, (b) **2**, (c) **3**/**3′**, (d) **4**/**4′**, and (e) HMODAz (**5**/**5′**).

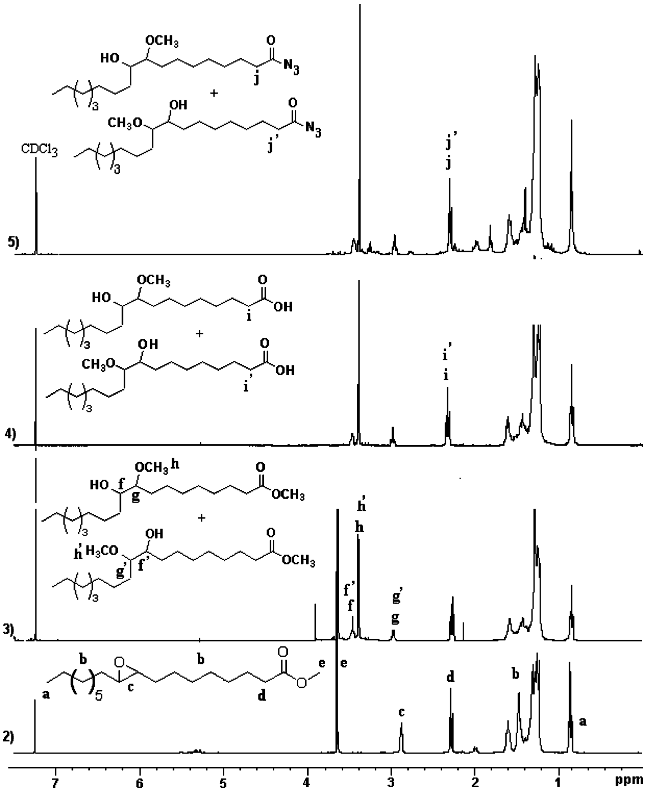
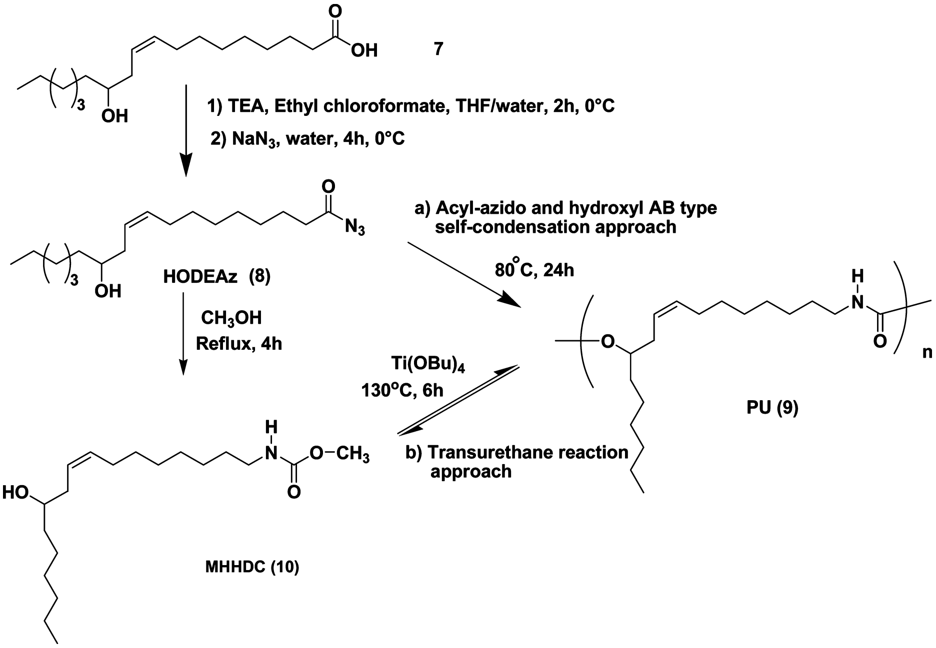


Figure 2. ^{1}H NMR spectra of intermediates based on methyl oleate, **2**, **3**/**3′**, **4**/**4′**, and HMODAz (**5**/**5′**): solvent, $CDCl_3$; *T* = 25 °C.

Scheme 2. Synthesis of HODEAz (**8**) and MHHDC (**10**) Derived from Ricinoleic Acid and Corresponding Polyurethane (**9**) by (a) Acyl Azido and Hydroxyl AB-Type Self Condensation Approach and (b) Transurethane Reaction Approach



amine to form in situ a mixed anhydride, and then it was subsequently reacted with sodium azide to afford acyl azide **8** (Scheme 2). The structure of HODEAz (**8**) was confirmed by FTIR and ^{1}H and ^{13}C NMR spectroscopy. The FTIR spectrum shows a strong absorption band at 2133 cm^{-1} due to asymmetric stretching vibration of azide group (N_3) and also a shift of the carbonyl group band from 1707 to 1720 cm^{-1} due to the formation of a more electron withdrawing azide group (Figure 3). In addition, a band due to the C=C−H stretching vibration appeared at 3008 cm^{-1}. In the ^{1}H NMR spectrum of HODEAz (**8**), a triplet peak of the methylene group attached to an azide group (CH_2-CON_3) appears at 2.31 ppm and vinylic protons (CH=CH) appear at 5.2−5.60 ppm (Figure 4). ^{13}C NMR spectrum shows a peak at 180.53 ppm for the carbonyl carbon attached to an azide group, confirming the carboxylic acid to acyl azide transformation.

(3) Synthesis and Characterization of Methyl-*N*-11-hydroxy-9-*cis*-heptadecen Carbamate, AB-Type Monomer for Transurethane Process (10). An AB-type self-condensable monomer specially dedicated to transurethane reaction namely, methyl-*N*-11-hydroxy-9-*cis*-heptadecen carbamate (**10**) was designed from ricinoleic acid as a biobased source. It was synthesized by refluxing excess methanol with 12-hydroxy-9-*cis*-octadecenoyl azide (**8**) and obtained in quantitative yield (Scheme 2). The formation of **10** was easily confirmed by FTIR spectroscopy (Figure 5). In the spectrum, a band of azide at 2238 cm^{-1} vanished and a carbonyl band was shift to 1702 cm^{-1}. A band appeared at 3334 cm^{-1}, confirming the presence of the N−H bond of urethane. In the ^{1}H NMR spectrum of **10**, a signal

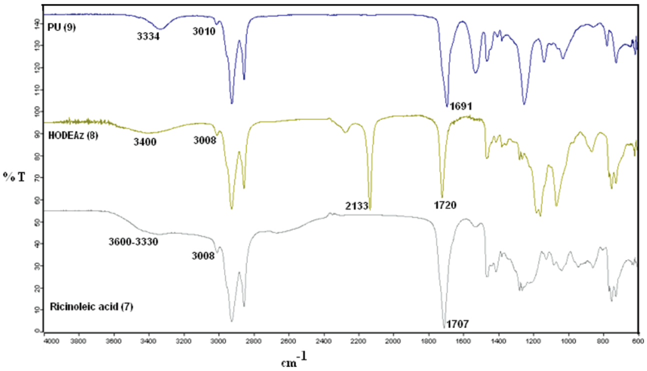


Figure 3. FTIR spectra of ricinoleic acid (**7**), HODEAz (**8**), and PU (**9**).

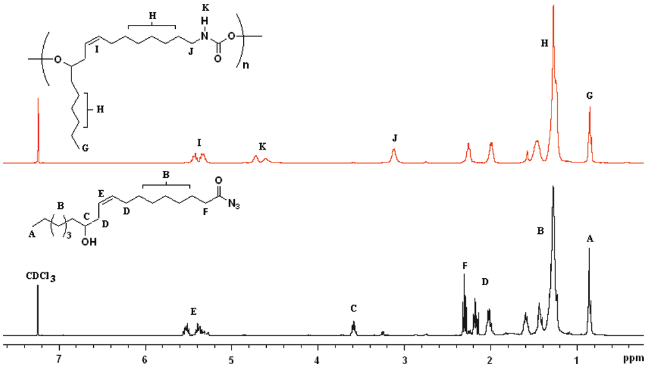


Figure 4. ^{1}H NMR spectra of HODEAz (**8**) and PU (**9**; solvent, $CDCl_3$, T = 25 °C).

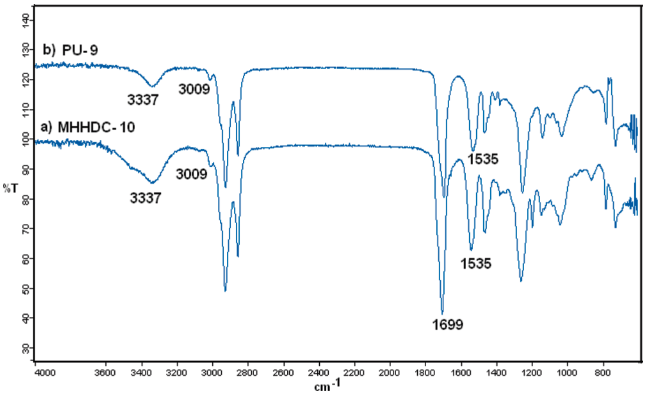


Figure 5. FTIR spectra of (a) methyl-*N*-11-hydroxy-9-*cis*-heptadecen carbamate (**10**) and polyurethane (**9**), obtained by a transurethane reaction.

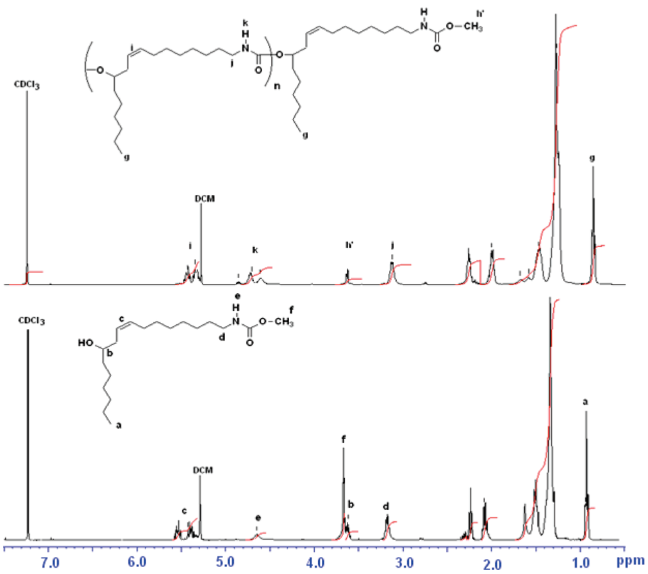


Figure 6. ^{1}H NMR spectra of methyl-*N*-11-hydroxy-9-*cis*-heptadecen carbamate (**10**) and ricinoleic acid derived biobased polyurethane (**9**), obtained by transurethane reaction.

Table 1. Experimental Conditions and Results for Polymerization of HMODAz (**5**/**5′**) and HODEAz (**8**)

				SEC^a		
run	AB-type monomer	T (°C)	time (h)	M_n	M_w	M_w/M_n
1	HMODAz	50	20	3210	4880	1.5
2^b	HMODAz	50	5	2720	4280	1.6
3 (i)	HMODAz	60	8	1040	1620	1.6
3 (ii)	HMODAz	60	23	2475	3780	1.5
4^c (i)	HMODAz	80	1	740	1740	2.3
4 (ii)	HMODAz	80	2	1640	3240	2.0
4 (iii)	HMODAz	80	3	2510	4820	1.9
4 (iv)	HMODAz	80	5	2610	3880	1.5
4 (v)	HMODAz	80	7	3510	6030	1.7
4 (vi)	HMODAz	80	9	3660	6340	1.7
4 (vii)	HMODAz	80	23	6390	10450	1.6
5^b	HMODAz	80	6	8890	18740	2.1
6	HMODAz	110	4	3500	6310	1.8
7	HODEAz	60	24	5300	7770	1.5
8	HODEAz	80	10	6210	9330	1.5
9	HODEAz	80	24	6880	10030	1.5

[a] Based on PS calibration, [b] Reaction in presence of DBTDL (0.1 wt % on HMODAz) as catalyst. [c] Runs 4(i) to 4(vii) carried out for FTIR, ^{1}H NMR and SEC studies.

for methyl group protons (Hf) attached to urethane bond appeared at 3.65 ppm, while a signal for methylene protons (Hd) attached to the NH bond appeared at 3.14 ppm (Figure 6). A signal appeared at 4.63 ppm corresponding to the protons (He) of the NH group, while the other protons are matching well with the expected structure. The carbamate formation was also confirmed by the ^{13}C NMR spectrum, the carbonyl carbon appearing at 157 ppm.

(4) Self-Polycondensation of HMODAz, Characterization, and Reaction Progress Monitored by FTIR, ^{1}H NMR spectroscopy, and SEC. Self-polycondensation of acyl azide and hydroxyl groups was adapted as an approach for the synthesis of polyurethane. The advantages of this approach are (i) the reaction proceeds smoothly by simple heating of the monomer in a one-pot reaction, and (ii) there is no need for optimization of the molar ratios between OH and CO-N_3. Self-condensation of novel HMODAz AB-type monomer was carried out at different temperatures, such as 50, 60, 80, and 110 °C. Table 1 shows the detailed reaction conditions and results of polymerization. It was found that all the temperatures used for polymerizations were useful. There was a crucial effect of temperature on the decomposition of acyl azide as well as polymerization rate observed by FTIR analysis. An increase in the reaction temperature leads to an increase in the acyl azide decomposition, as already observed by Theato and co-workers,[37] yielding a faster rate of polymerization. Hence, compared to run 1, which was carried out at 50 °C, run 4 (vii; Table 1) carried out at 80 °C shows a higher molar mass for similar time reactions.

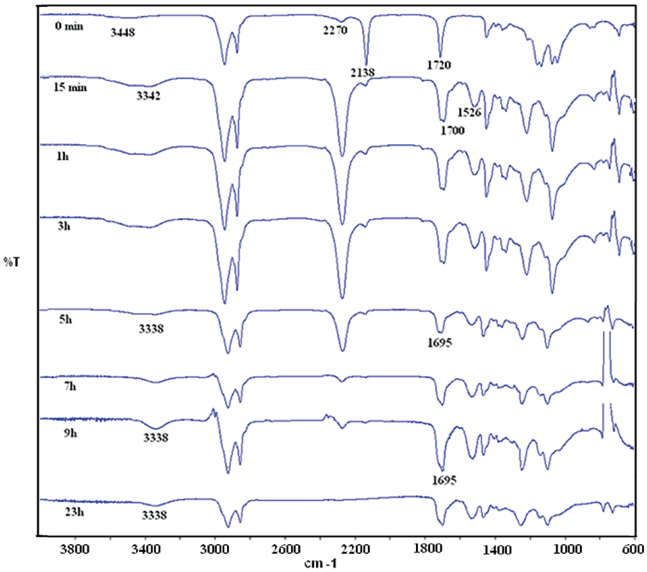


Figure 7. FTIR spectra of HMODAz (**5**/**5′**) polymerization samples taken at different intervals.

For further analysis of the reaction progress, polymerization was carried out at 80 °C and monitored by FTIR, ^{1}H NMR spectroscopy, and SEC. The monomer (**5**/**5′**) initially forms in situ isocyanate by the decomposition of acyl azide group via Curtius rearrangement[38a] and then isocyanate functions react with the hydroxyl group to form urethane. It is known that the reactivity of isocyanates are high toward the hydroxyl group, and hence, to stop the further increase in molar mass, aliquots taken at different intervals were reacted with an excess of ethanol after IR spectroscopic analysis and used for further SEC and ^{1}H NMR analyses. Figures 7 and 8 show, respectively, FTIR and ^{1}H NMR spectra of polymerization progress, while Figure 9 shows SEC traces along the polymerization progress upon heating at 80 °C. The band at 2138 cm^{-1} (Figure 7) due to presence of acyl azide groups (CON_3) converts into a new band attributed to isocyanate functions located at 2270 cm^{-1}. The absorption band at 3341 cm^{-1} is observed due to the formation of N−H urethane bonds. Aliquots taken after 15 min of reaction show almost complete transformation of acyl azido group into isocyanate function on the basis of FTIR spectrum (Figure 7). The aliquots after FTIR analysis were reacted with ethanol and analyzed by ^{1}H NMR spectroscopy, which shows a peak at 4.06 ppm (Hg) due to methylene group protons attached to urethane group (Figure 8).

FTIR spectra of aliquots taken along the polymerization reaction allowed us to observe evolution of characteristic bands, such as, isocyanate band at 2270 cm^{-1}, which decreases in intensity, N−H band from polyurethane at 3338 cm^{-1}, which increases in intensity, the band at 1526 cm^{-1} due to N−H bending vibration, and the band of the carbonyl group of acyl azide at 1720 cm^{-1} shifts to lower frequency (1695 cm^{-1}) due to formation of the urethane bond.

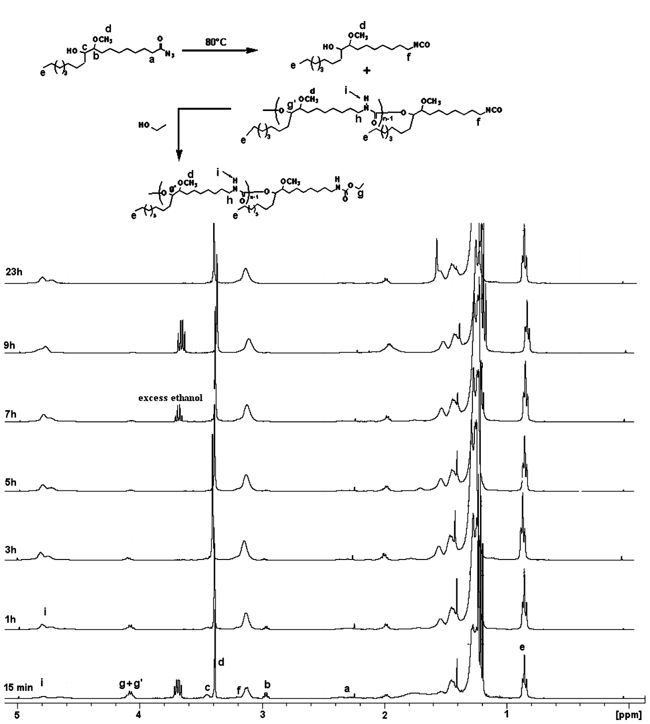


Figure 8. ^{1}H NMR spectra of HMODAz (**5**/**5′**) polymerization samples at different intervals (quenched with ethanol).

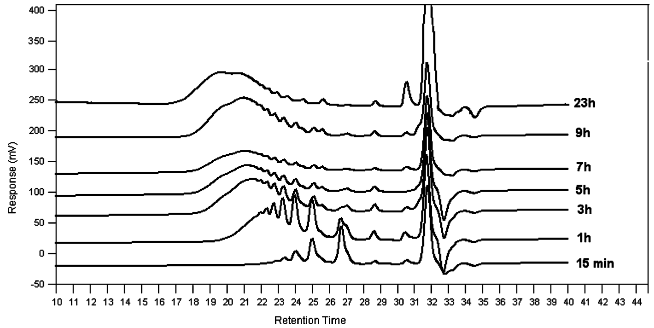


Figure 9. SEC traces of HMODAz (**5**/**5′**) polymerization samples as a function of time.

Similar kind of observations was seen in ^{1}H NMR spectra of aliquots. The intensity of a peak at 4.06 ppm due to methylene protons attached to the carbamate group (NH-COO-CH_2CH$_3$) as an end-group decreases with time (15 min, 1 h, 3 h, etc.) due to an increase in molar mass of polyurethane (Figure 8). There were also increases in the peak intensities at 4.80 ppm due to N*H* protons of urethane groups and the peak at 3.16 ppm due to methylene protons attached to the urethane group of polyurethane (-CH_2-NH-COO-).

SEC results reveal that an aliquot after 15 min shows formation of traces of *di*-, *tri*-, and tetramer along with the isocyanate monomer (Figure 9). As the time of polymerization increases the intensities of SEC peaks corresponding to oligomers reduce and SEC peaks shift to higher molar mass showing polycondensation mechanism. The self-condensation (Run 5) in presence of DBTDL as a catalyst was faster than self-condensation without catalyst (Run 4 (v), 7 h) on the basis of molar mass obtained by SEC.

(5) Self-Polycondensation of HODEAz (8) and Characterization of PU (9). As previously described, self-polycondensation of HODEAz was carried out at 60 and 80 °C in bulk reaction without catalyst (Scheme 2). Polyurethanes obtained were characterized by SEC and results are given in Table 1. The molar mass of the polyurethane synthesized at 60 °C was found to be less compared with self-condensation carried out at 80 °C, which indicates that 80 °C is a better temperature for the formation of an in situ isocyanate intermediate as well as polycondensation.

Table 2. Experimental Conditions and Results for Transurethane Polycondensation of MHHDC (**10**)

				SEC[a]		
run	catalyst	*T* (°C)	time (h)	M_n	M_w	M_w/M_n
1	Ti(*n*-BuO)$_4$	130	5	3840	5480	1.4
2	Ti(*n*-BuO)$_4$	130	6	6950	9850	1.4
3[b]	no catalyst	130	6			
4[c]	Ti(*n*-BuO)$_4$	130	5	4510	9020	2.0
5[d]	Ti(*n*-BuO)$_4$	130	6	5370	9290	1.7
6	Ti(*n*-BuO)$_4$	150	6	5000	10120	2.0

[a] Based on PS calibration. [b] No polymer. [c] Oligomers obtained from acyl-azido and hydroxyl self-condensation approach (M_n, 3430; M_w, 5870; M_w/M_n, 1.7). [d] Oligomers obtained from acyl-azido and hydroxyl self-condensation approach (M_n, 5100; M_w, 7820; M_w/M_n, 1.5).

PU (**9**) formation was confirmed by FTIR, ^{1}H NMR, and ^{13}C NMR spectroscopy. The conversion of acyl azide group into intermediate isocyanate via "Curtius rearrangement" and followed by condensation with the secondary hydroxyl group was confirmed on the basis of bands observed at 3334 and 1691 cm^{-1} due to the urethane N−H stretching vibration and the C=O stretching vibrations of the PU (Figure 3). The vinylic double bond in the PU remains intact, showed by the =C−H bond stretching vibration band at 3010 cm^{-1}. Urethane formation was also confirmed by ^{1}H NMR spectroscopy, with the peak corresponding to methylene protons attached to acyl azide group in the monomer HODEAz (**8**) is shifted to downfield due to urethane formation as well a new peak appearing in the range of 4.6 to 4.8 ppm due to NH protons of the urethane group (Figure 4). ^{13}C NMR spectrum shows an urethane carbonyl function at 156.57 ppm confirming self-condensation.

(6) Self-Polycondensation of MHHDC via Melt-Transurethane Reaction. Transurethane is a condensation between bisurethane (A−A) and diol (B−B) in the presence of catalyst and, similarly, it can be AB-type self-condensation in the presence of catalyst.[33] Transurethane polycondensation was carried out on MHHDC at 130 °C in the presence of titanium tetrabutoxide as catalyst in two stages (Scheme 2). In the first stage, the reaction was performed at 130 °C by stirring under nitrogen flow for 2 h to obtain oligomers and in the second stage reaction was carried out at 130 °C under vacuum for 3 h for further condensation. It was also possible to carry out transurethane reaction at 150 °C to achieve slightly better results. The obtained polymer was characterized by IR, ^{1}H NMR, and SEC. Table 2 shows reaction conditions and results of transurethane polycondensation. It was observed that the transurethane reaction was only possible in presence of titanium tetrabutoxide, as shown by the experiment performed in the absence of catalyst (Table 2, run 3).

In another two reactions, an attempt was made to synthesize PU by transurethane reaction using the PU oligomers obtained from acyl-azido and hydroxyl AB-type self-condensation approaches. For this purpose, isocyanate-terminated PU oligomers were synthesized and reacted with excess of methanol to obtained PU oligomers resembling the structure with MHHDC. These oligomers were characterized by IR, ^{1}H NMR, and SEC. Further, the transurethane polycondensation was carried out in presence of titanium tetrabutoxide under vacuum at 130 °C to obtain high molar mass PU. As it can be seen in Table 2 (run 4), M_w increases from 5870 to 9020 g/mol after a transuretha-

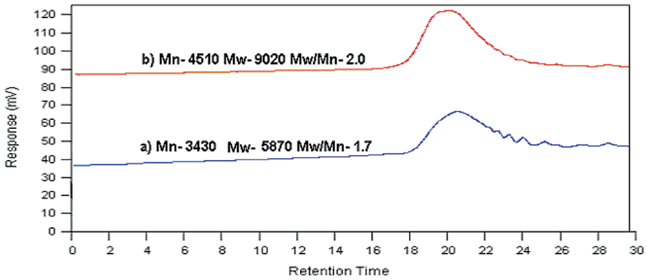
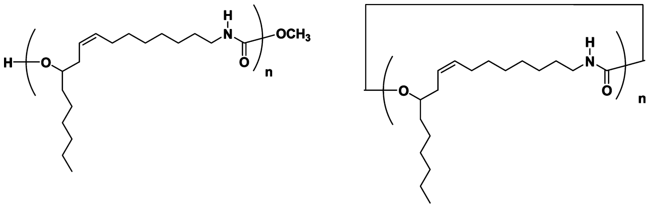


Figure 10. SEC traces of (a) PU oligomers obtained from acyl-azido and hydroxyl AB-type self-condensation approach, and (b) PU obtained by transurethane reaction on oligomers.



a) b)

Figure 11. PU with linear structure (a) and macrocyclic structure (b).

nization reaction and low molar mass oligomers vanished as observed in SEC traces (Figure 10).

Figure 5b shows FTIR of polyurethane synthesized by transurethane polycondensation. IR spectrum of PU is similar to monomer (**10**) except the hydroxyl band that is shifted to 3337 cm^{-1}. ^{1}H NMR spectrum of PU (**9**) confirms the structure of polyurethane by transurethane reaction (Figure 6). Transurethane reaction was also confirmed on the basis of a decrease of intensity of OC**H**$_3$ protons (Hh′) of chain end-group due to molar mass increase compare with signal intensity of -C**H**$_2$NHCOO- protons at 3.13 ppm. At this reaction temperature, the presence of double bond in the polymer suggests that no side reactions have occurred.

(7) MALDI-TOF Mass Spectroscopy Analysis. Low molar masses of these PU obtained by both methods made us analyze whether macrocycles were formed. Indeed, it is known that AB-type monomers can form macrocycles during polymerization.[38b–e] A typical MALDI-TOF MS spectrum is shown in the Figures 12 and 13 for PU obtained by transurethane process (run 1, Table 2). It should be noted that these spectra are very complicated, probably due to the monomer source as well as the polydispersity of PU,[33] whatever the matrix used, for

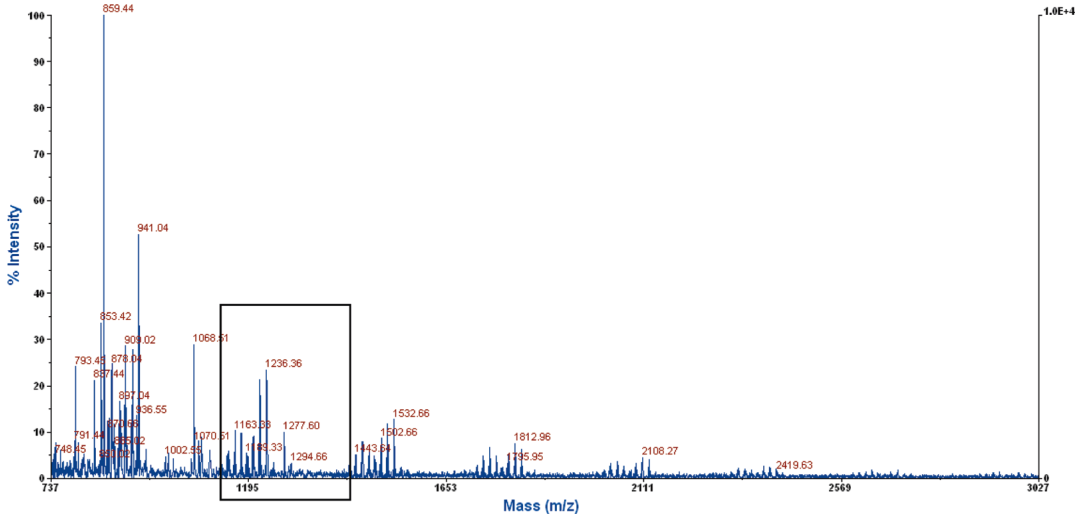


Figure 12. MALDI-TOF mass spectrum of PU (run 1, Table 2).

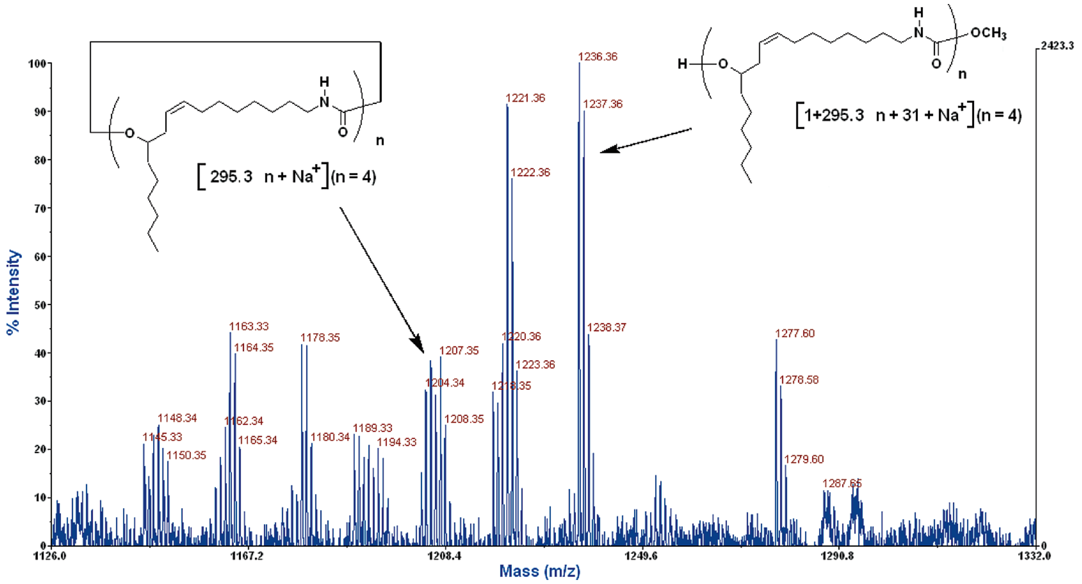


Figure 13. MALDI-TOF mass spectrum of PU (run 1, Table 2) in the mass range 1126–1332.

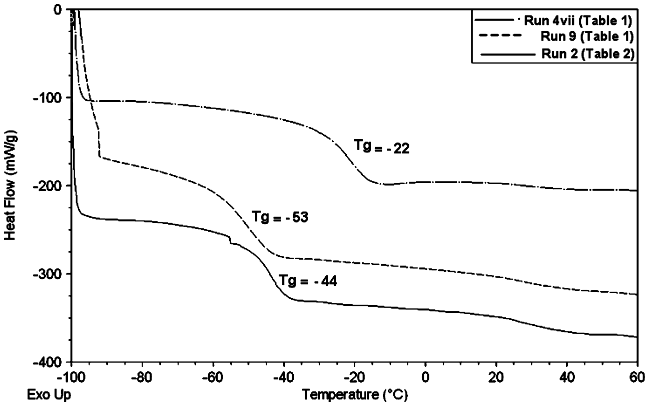


Figure 14. DSC traces of PU obtained by polymerization of HMODAz (**5**/**5′**) derived from methyl oleate (run 4 (vii), Table 1), PU obtained by polymerization of HODEAz (**8**) derived from ricinoleic acid (run 9, Table 1), and PU obtained by polymerization of MHHDC (**10**) derived from ricinoleic acid (run 2, Table 2).

example, dithranol, *trans*-3-indoleacrylic acid, or *trans*-2-[3-(4-*tert*-butylphenyl)-2-methyl-2-propenylidene]-malononitrile.

Figures 12 and 13 show several series of signals but one of the major series of signals have an interval of 295.3 which corresponds to molar mass of major repeating unit of the polymer. Peaks at m/z $(1 + 295.3n + 31 + \mathrm{Na}^+) = 941.04$ ($n = 3$), 1236.38 ($n = 4$), 1532.66 ($n = 5$), and so on correspond to the PU with a linear structure (Figure 11a). Another series of peaks found at interval of 295.3 at m/z $(295.3\, n + \mathrm{Na}^+) = 909.02$ ($n = 3$), 1204.34 ($n = 4$), 1500.64 ($n = 5$) matches with PU macrocycles having a structure presented in Figure 11b. MALDI-TOF MS analysis of PU obtained by acyl azido-hydroxyl self-condensation of HMODAz (**5**/**5′**) and HODEAz (**8**) were also carried out, and the results also revealed PU having a linear structure and partly formed macrocycles (see Supporting Information for MALDI-TOF MS spectra, Figures 5−11).

(8) Differential Scanning Calorimetry Analysis. Figure 14 shows DSC thermograms for the PU derived from HMODAz (**5**/**5′**), HODEAz (**8**), and MHHDC(**10**) by self-condensation approach at a heating rate of 10 °C/min. Two different glass transition temperatures were observed for all PU derived from methyl oleate and ricinoleic acid based monomers. The observed glass transition temperature at lower temperature results due to soft segments and at higher temperature due to hard ones. HMODAz derived PU showed T_gs at −22 and 27 °C. In case of PU synthesized from HODEAz, T_gs observed at −53 and 26 °C, while MHHDC-derived PU exhibited T_gs at −44 and 26 °C.

Conclusions

Three new AB-type self-condensable monomers, namely, 10-hydroxy-9-methoxyoctadecanoyl azide/9-hydroxy-10-methoxyoctadecanoyl azide (HMODAz) (**5**/**5′**), HODEAz (**8**), and MHHDC (**10**) were synthesized from methyl oleate (sunflower oil) and ricinoleic acid (castor oil), respectively, using simple reaction steps. Self-condensation of HMODAz was studied at 50, 60, 80, and 110 °C, while self-condensation of HODEAz (**8**) was carried out at 80 °C. The acyl azide group of AB-type monomer decomposes to form in situ isocyanate as an intermediate within 15−30 min at 80 °C. Further, the isocyanate containing AB-type intermediate condenses each other to form polyurethane. Transurethane reaction was carried out on MHHDC to obtain similar PU to the one formed by AB-type self-condensation of HODEAz (**8**). The comparatively low molar masses of all the PU formed by both the processes were observed and explained by the formation of macrocycles. Two glass transition temperatures due to soft and hard segments, respectively, were observed for all PU synthesized from methyl oleate and ricinoleic acid. DSC analysis revealed that both PU obtained from ricinoleic acid by different methods had nearly the same T_g.

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Supporting Information Available. Methyl oleate and ricinoleic acid composition analysis using AFNOR methods, NF EN ISO 5509 and NF EN ISO 5508. ^{13}C NMR spectra of 10-hydroxy-9-methoxyoctadecanoic acid/9-hydroxy-10-methoxyoctadecanoic acid (**4**/**4′**), 10-hydroxy-9-methoxyoctadecanoyl azide/9-hydroxy-10-methoxyoctadecanoyl azide (HMODAz) (**5**/**5′**), 12-hydroxy-9-*cis*-octadecenoyl azide (HODEAz) (**8**), and methyl-*N*-11-hydroxy-9-*cis*-heptadecen carbamate (MHHDC) (**10**). MALDI-TOF mass spectrum of PU (run 8 and run 4 (v), Table 1) and PU (run 6, Table 2). This material is available free of charge via the Internet at http://pubs.acs.org.

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