

Development of environment-friendly materials based on renewable resources

B. W. GUAN*, H. X. CHEN, R. XIONG

School of Material Science and Engineering, Chang'an University, Xi'an 710064, China

Biobased aromatic triols were synthesized using two different methods. Alkyne alcohol derivatives were obtained from the corresponding fatty acids by bromination, dehydrobromination, and reduction of carboxylic acid using well-established procedures. Alkyne fatty derivatives were obtained from the corresponding fatty acids by bromination, dehydrobromination, and esterification using well-established procedures. The crystalline structure and thermal stability of these polyurethanes were compared to their counterparts made from a similar O-BAT, E-BAT, and U-BAT, respectively. The corresponding polyurethane networks with hard-segment were prepared by the reaction of the polyol, BD, and MDI. The final results show the feasibility of utilizing the new biobased aromatic triols to react with diisocyanate for the production of biobased polyurethanes. In particular, the present study provides a promising direction for the use of exploit renewable resources to achieve environment-friendly materials.

(Received July 9, 2015; accepted August 3, 2016)

Keywords: Renewable, Environment-friendly, Green materials

1. Introduction

In order to protect the environment and to reduce our dependence on fossil fuels, a great deal of research effort has been and is still being devoted to the development of innovative technologies using renewable resources [1-7]. Vegetable oils are abundant and cheap renewable resources which represent a major potential alternative source of chemicals suitable for developing safe environmentally products [8-10]. The use of vegetable oils and natural fatty acids as starting raw materials offers numerous advantages: for example, inexpensive, abundant, low toxicity, and inherent biodegradability, thus they are considered to be one of the most important classes of renewable resources for the production of biobased polymeric materials [11-17]. 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. The industrial production of PUs is normally accomplished through the polyaddition reaction between organic isocyanates and compounds containing active hydroxyl groups, such as polyols. Comparing with polyurethanes derived from petrochemical polyols, the vegetable-oil-based polyols used to produce polyurethanes has been the subject of many studies [9-12]. Moreover, due to the hydrophobic nature of triglycerides, vegetable oils produce PUs that have excellent chemical and physical properties such as enhanced hydrolytic, high tensile strength and elongation, high tear strength, and thermal stability [13-18].

Vegetable oils are one of the most important sources of renewable raw materials for the chemical industry and provide versatile opportunities for transformation to meet specific applications. In 1980s, Baumann et al. mainly focused on the carboxyl group of fatty acids, these include hydrolysis of fats to make soaps, and synthesis of fatty amines from fatty acids [10]. Recently, increasing interest in industrial and academic research has been focused towards reactions on the hydrocarbon chains of fatty acids, especially on the double bonds of unsaturated fatty acids. Guo et al. had applied the epoxidation of the double bonds of fatty acids, followed by nucleophilic ring opening of the epoxide to make polyols for producing polyurethanes [11,12].

To further expand applications of the biobased polymeric materials, the previous studies have been focusing on converting vegetable oils into useful PUs. Based on these studies, now it has become a main research field to functionalize vegetable oils by the introduction of aromatic comonomers into the polymer structure, which could be suitable in the search for new viable polymeric materials [12]. Transition metal-catalyzed trimerization of alkyne fatty acid compounds provides an alternative method for the preparation of highly functionalized aromatic polyols [10,11].

In the present study, we have synthesized three kinds of biobased aromatic triols prepared by oleic acid, 10-undecenoic acid, and erucic acid, which could be obtained from sunflower oil, castor oil, and rapeseed oil, respectively. PUs were synthesized by these aromatic

triols and 4,4'-methylenebis(phenyl isocyanate), 1,4-butanediol as a chain extender. The chemical structures, molecular characteristics, physical properties, and thermal properties were studied and compared using nuclear magnetic resonance (NMR) spectroscopy, fourier transform infrared (FTIR) spectroscopy, X-ray diffraction (XRD), differential scanning calorimetry (DSC), and thermogravimetry-differential thermal analysis (TG-DTA).

2. Experimental

2.1. Materials

The following chemicals were obtained from the sources indicated: Oleic acid (AR, from Sinopharm), 10-undecenoic acid (from Sinopharm), erucic acid (from Aldrich), copper (II) chloride, CuCl_2 (99%, from Sinopharm), palladium (II) chloride, PdCl_2 (AR, from Sinopharm), palladium on carbon, Pa/C (10 wt%, from Aldrich), potassium hydroxide, KOH (AR, from Kermel), n-propanol (AR, from Kermel), dimethyl sulfoxide, DMSO (AR, from Kermel), bromine (AR, from Xilong), chlorotrimethylsilane, TMSCl (CP, from Sinopharm), lithium aluminum hydride, LiAlH_4 (97%, from Aldrich), 1,4-butanediol, BD (AR, from Bodi) and 4,4'-methylenebis(phenyl isocyanate), MDI (98%, from Aldrich) were used as received.

2.2. Synthesis of aromatic triol 4 from oleic acid

Dibromide carboxylic acid 1. To a solution of oleic acid (10.6 g, 33.6 mmol) in diethyl ether (150 mL) was cooled to 0 °C in an ice-water bath, bromine (2.7 mL, 52.3 mmol) was added dropwise over 30 min. Then the ice-water bath was removed and the solution was stirred for another 2 h at room temperature. Saturated sodium sulfite ($\text{Na}_2\text{S}_2\text{O}_3$) solution (20 mL) was added to reduce the excess bromine. The resulting organic phase was separated, washed with brine (20 mL) and dried over anhydrous magnesium sulfate (MgSO_4). The solvent was evaporated by reduced pressure to give a pale yellow powder **1** (yield 73%).

IR (thin film): 3440 (OH), 1703 (C=O) cm^{-1} .

^1H NMR (CDCl_3/TMS , δ ppm): 11.34 (s, 1H, COOH), 4.23–4.14 (m, 2H, CHBr), 2.38–2.33 (t, 2H, CH_2COOH), 2.06–1.99 (m, 2H, CHCHBr), 1.88–1.80 (m, 2H, CHBr), 1.64–1.56 (m, 6H), 1.35–1.25 (m, 16H), 0.88 (t, 3H, CH_3).

Stearic acid 2. Dibromide compound **1** (5.5 g, 15 mmol) was dissolved in DMSO (18 mL, 250 mmol). KOH (20 g, 360 mmol) and 1-propanol (150 mL) were added. The mixture was heated at 110 °C under reflux for 4 h. Then the solution was poured into 2N hydrochloric acid (HCl) (150 mL) at room temperature. The resulting organic layer was separated, washed with brine (20 mL) and dried over MgSO_4 . The solvent was evaporated by

reduced pressure to give a pale yellow powder **2** (yield 76%).

IR (thin film): 3446 (OH), 2356 (C≡C), 1712 (C=O) cm^{-1} .

^1H NMR (CDCl_3/TMS , δ ppm): 11.34 (s, 1H, COOH), 2.33 (t, 2H, CH_2COOH), 2.12 (m, 4H, CH_2CC), 1.26–1.62 (m, 22H), 0.88 (t, 3H, CH_3)

Stearoyl alcohol 3. Stearic acid **2** (2.4 g, 8.6 mmol) was dissolved in 50 mL diethyl ether and added dropwise to a dispersion of LiAlH_4 (0.4 g, 10.2 mmol) in 100 mL of anhydrous diethyl ether. The mixture was stirred for 2 h at room temperature, and then the excess LiAlH_4 was decomposed by adding 20 mL of water dropwise. A 2N HCl (30 mL) aqueous solution was added until the pH was neutral. The resulting organic layer was separated, washed with brine (20 mL) and dried over MgSO_4 . The solvent was evaporated by reduced pressure to give pale yellow oil **3** (yield 82%).

IR (thin film): 3392 (OH), 2360 (C≡C) cm^{-1} .

^1H NMR (CDCl_3/TMS , δ ppm): 3.65 (t, 2H, CH_2OH), 2.14 (t, 4H, CH_2CC), 1.58–1.48 (m, 6H), 1.41–1.23 (m, 18H), 0.90 (t, 3H, CH_3).

Aromatic triols 4a and 4b. Stearoyl alcohol **3** (1.05 g, 4.0 mmol) was dissolved in tetrahydrofuran (THF) (50 mL). 0.25 g of Pd/C (10 wt %) and TMSCl (0.75 mL, 6.0 mmol) were added. The reaction mixture was heated at 65 °C refluxed for 8 h. The resulting mixture was cooled to room temperature and filtered to remove the Pd/C. The resulting organic layer was separated, washed with brine (20 mL) and dried over MgSO_4 . The solvent was evaporated by reduced pressure to give dark yellow oil **4a** and **4b** (yield 58%).

IR (thin film): 3438 (OH), 1652 (C=C of benzene) cm^{-1} .

^1H NMR (CDCl_3/TMS , δ ppm): 3.56 (t, 6H, CH_2OH), 2.43 (m, 12H, CH_2Ph), 1.49–1.20 (m, 72H), 0.83 (t, 9H).

^{13}C NMR (CDCl_3/TMS , δ ppm): 136.77 (PhCH_2), 62.94 (CH_2OH), 31.94, 31.86, 29.68, 29.64, 29.57, 29.33, 29.26, 25.72, 22.68, 22.66, 14.12 (CH_3).

2.3. Synthesis of aromatic triol 4' from 10-undecenoic acid

Dibromide carboxylic acid 1'. 10-Undecylenic acid (9.2 g, 50 mmol) in diethyl ether (150 mL) was cooled to 0 °C in an ice-water bath. Bromine (4.2 mL, 81 mmol) was added dropwise over 30 min. Then the ice-water bath was removed and the solution was stirred for another 2 h at room temperature. Saturated $\text{Na}_2\text{S}_2\text{O}_3$ solution (20 mL) was added to reduce the excess bromine. The resulting organic phase was separated, washed with brine (20 mL) and dried over MgSO_4 . The solvent was evaporated by reduced pressure to give a gray solid **1'** (yield 78%).

IR (thin film): 3433 (OH), 1705 (C=O) cm^{-1} .

^1H NMR (CDCl_3/TMS , δ ppm): 11.58 (s, 1H, COOH), 3.85–3.80 (q, 1H, CHCHBr), 3.64–3.57 (t,

2H, CH₂Br), 2.35–2.30 (t, 2H, CH₂COOH), 2.17–2.05 (m, 3H), 1.84–1.50 (m, 3H), 1.30–1.23 (m, 8H).

10-Undecynic acid 2^ˆ. Dibromide compound **1^ˆ** (5.2 g, 15 mmol) was dissolved in DMSO (18 mL, 250 mmol). KOH (20 g, 360 mmol) and 1-propanol (150 mL) were added. The mixture was heated at 110 °C under reflux for 4 h. Then the solution was poured into 2N HCl (150 mL) at room temperature. The resulting organic layer was separated, washed with brine (20 mL) and dried over MgSO₄. The solvent was evaporated by reduced pressure to give a white solid **2^ˆ** (yield 63%).

IR (thin film): 3440 (OH), 2360 (C≡C), 1710 (C=O) cm⁻¹.

¹H NMR (CDCl₃/TMS, δ/ppm): 11.54 (s, 1H, COOH), 2.31 (t, 2H, CH₂COOH), 2.17–2.11 (m, 2H), 1.92 (t, 1H), 1.55–1.44 (m, 4H), 1.33–1.23 (m, 8H).

10-Undecyn-1-ol 3^ˆ. 10-Undecynic acid **2^ˆ** (1.6 g, 8.8 mmol) was dissolved in 50 mL diethyl ether and added dropwise to a dispersion of LiAlH₄ (0.4 g, 10.2 mmol) in 100 mL of anhydrous diethyl ether. The mixture was stirred for 2 h at room temperature, and then the excess LiAlH₄ was decomposed by adding 20 mL of water dropwise. A 2N HCl (30 mL) aqueous solution was added until the pH was neutral. The resulting organic layer was separated, washed with brine (20 mL) and dried over MgSO₄. The solvent was evaporated by reduced pressure to give a pale yellow solid **3^ˆ** (yield 72%).

IR (thin film): 3335 (OH), 2358 (C≡C) cm⁻¹.

¹H NMR (CDCl₃/TMS, δ/ppm): 3.59 (t, 2H, CH₂OH), 2.20–2.14 (m, 4H), 1.76 (t, 1H, CH₂C), 1.56–1.50 (m, 4H), 1.35–1.26 (m, 8H).

Aromatic triols 4^ˆa and 4^ˆb. 10-Undecyn-1-ol **3^ˆ** (0.68 g, 4.0 mmol) was dissolved in n-butyl alcohol (9 mL) and benzene (150 mL). PdCl₂ (0.15 g, 0.85 mmol) and CuCl₂ (2.05 g, 12 mmol) were added. The reaction mixture was heated at 40 °C refluxed for 8 h. The resulting mixture was cooled to room temperature and filtered to remove the PdCl₂ and CuCl₂. The resulting organic layer was separated, washed with brine (20 mL) and dried over MgSO₄. The solvent was evaporated by reduced pressure to give dark yellow oil **4^ˆa** and **4^ˆb** (yield 68%).

IR (thin film): 3456 (OH), 1639 (C=C of benzene) cm⁻¹.

¹H NMR (CDCl₃/TMS, δ/ppm): 6.40 (s, 3H, Ph), 3.64 (t, 6H, CH₂Ph), 2.29 (t, 6H), 1.61–1.24 (m, 42H).

¹³C NMR (CDCl₃/TMS, δ/ppm): 138.22 (Ph-CH₂), 120.35 (Ph-H), 64.11 (CH₂OH), 39.86, 34.35, 30.68, 29.70, 29.08, 28.54, 27.46, 24.96.

2.4 Synthesis of aromatic triol 4^ˆ from erucic acid

Dibromide carboxylic acid 1^ˆ. Erucic acid (15.88 g, 33.6 mmol) in diethyl ether (150 mL) was cooled to 0 °C in an ice-water bath. Bromine (2.7 mL, 52.3 mmol) was

added dropwise over 30 min. Then the ice-water bath was removed and the solution was stirred for another 2 h at room temperature. Saturated Na₂S₂O₃ solution (20 mL) was added to reduce the excess bromine. The resulting organic phase was separated, washed with brine (20 mL) and dried over MgSO₄. The solvent was evaporated by reduced pressure to give a gray solid **1^ˆ** (yield 78%).

IR (thin film): 3425 (OH), 1706 (C=O) cm⁻¹.

¹H NMR (CDCl₃/TMS, δ/ppm): 11.89 (s, 1H, COOH), 4.27–4.18 (m, 2H, CH₂Br), 2.35 (t, 2H, CH₂COOH), 2.10–1.95 (m, 2H, CH₂CHBr), 1.65–1.54 (m, 2H), 1.47–1.26 (m, 30H), 0.89 (t, 3H, CH₃).

Behenolic acid 2^ˆ. Dibromide compound **1^ˆ** (7.5 g, 15 mmol) was dissolved in DMSO (18 mL, 250 mmol). KOH (20 g, 360 mmol) and 1-propanol (150 mL) were added. The mixture was heated at 110 °C under reflux for 4 h. Then the solution was poured into 2N hydrochloric acid (HCl) (150 mL) at room temperature. The resulting organic layer was separated, washed with brine (20 mL) and dried over MgSO₄. The solvent was evaporated by reduced pressure to give a pale yellow powder **2^ˆ** (yield 72%).

IR (thin film): 3454 (OH), 2361 (C≡C), 1705 (C=O) cm⁻¹.

¹H NMR (CDCl₃/TMS, δ/ppm): 11.62 (s, 1H, COOH), 2.37 (t, 2H, CH₂COOH), 2.15 (m, 4H, CH₂CC), 1.69–1.23 (m, 30H), 0.90 (t, 3H, CH₃).

Behenolic ester 3^ˆ. To a solution of behenolic acid **2^ˆ** (4.5 g, 12.9 mmol) in methanol (100 mL) was added about 5 mL concentrated sulphuric acid. The reaction mixture was heated at 95 °C refluxed for 3 h. The resulting organic layer was separated, washed with brine (20 mL) and dried over MgSO₄. The solvent was evaporated by reduced pressure to give pale yellow oil **3^ˆ** (yield 62%).

IR (thin film): 2360 (C≡C), 1745 (C=O), 1170 (C-O) cm⁻¹.

¹H NMR (CDCl₃/TMS, δ/ppm): 3.66 (s, 3H, CH₃O), 2.30 (t, 2H, CH₂COOCH₃), 2.13 (m, 4H, CH₂CC), 1.68–1.20 (m, 30H), 0.88 (t, 3H, CH₃).

Aromatic triester 4^ˆa and 4^ˆb. Behenolic ester **3^ˆ** (2.8 g, 8.0 mmol) was dissolved in n-butyl alcohol (9 mL) and benzene (150 mL). PdCl₂ (0.15 g, 0.85 mmol) and CuCl₂ (2.05 g, 12 mmol) were added. The reaction mixture was heated at 40 °C refluxed for 12 h. The resulting mixture was cooled to room temperature and filtered to remove the PdCl₂ and CuCl₂. The resulting organic layer was separated, washed with brine (20 mL) and dried over MgSO₄. The solvent was evaporated by reduced pressure to give yellow oil **4^ˆa** and **4^ˆb** (yield 68%).

IR (thin film): 1745 (C=O), 1641 (C=C of benzene), 1174 (C-O) cm⁻¹.

¹H NMR (CDCl₃/TMS, δ/ppm): 3.68 (s, 9H, CH₃O), 2.54–2.43 (m, 12H, CH₂Ph), 2.32 (t, 6H, CH₂COOCH₃), 1.70–1.26 (m, 90H), 0.90 (t, 9H, CH₃).

¹³C NMR (CDCl₃/TMS, δ/ppm): 174.41 (C=O),

136.71 (Ph-CH₂), 51.48 (CH₃-O), 34.13, 33.76, 31.96, 31.46, 30.69, 30.17, 29.71, 29.52, 29.42, 29.36, 29.31, 29.10, 24.97, 22.72, 14.16 (CH₃).

Aromatic triols 5^a and 5^b. Aromatic triester 5^a (2.1g, 2.0 mmol) was dissolved in 50 mL diethyl ether and added dropwise to a dispersion of LiAlH₄ (0.4 g, 10.2 mmol) in 100 mL of anhydrous diethyl ether. The mixture was stirred for 2 h at room temperature, and then the excess LiAlH₄ was decomposed by adding 20 mL of water dropwise. A 2N HCl (30 mL) aqueous solution was added until the pH was neutral. The resulting organic layer was separated, washed with brine (20 mL) and dried over MgSO₄. The solvent was evaporated by reduced pressure to give pale yellow oil 5^a and 5^b (yield 88%).

IR (thin film): 3430 (OH), 1465 (C=C of benzene) cm⁻¹.

¹H NMR (CDCl₃/TMS, δ/ppm): 3.63 (t, 6H, CH₂OH), 2.56–2.40 (m, 12H), 1.64–1.26 (m, 96H), 0.89 (t, 9H, CH₃).

¹³C NMR (CDCl₃/TMS, δ/ppm): 136.71 (PhCH₂), 63.06 (CH₂OH), 34.12, 32.81, 32.61, 31.96, 31.49, 30.68, 29.70, 29.51, 29.42, 29.26, 25.75, 24.97, 22.70, 22.70, 19.15, 14.13(CH₃).

2.5 Synthesis of Polyurethanes

Polyurethane powders were prepared by reacting aromatic triol with diisocyanate at molar ratios of the OH group to the NCO group. The desired OH/NCO molar ratio satisfies the equation:

$$M_{\text{ratio}} = \frac{W_{\text{polyol}} / EW_{\text{polyol}}}{(W_{\text{PU}} - W_{\text{polyol}}) / EW_{\text{diisocyanate}}} \quad (1)$$

where W_{polyol} is the weight of the polyol, EW_{polyol} is the equivalent weights of polyol, W_{PU} is the total weight of polyurethane, and $EW_{\text{diisocyanate}}$ is the equivalent weight of the diisocyanate.

The equivalent weight for the diisocyanate was calculated based on the molar mass and was $EW_{\text{diisocyanate}} = 250$ g/mol. The equivalent weights of aromatic triol were determined using the equation:

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

The weight of the polyol and diisocyanate were calculated using the above-calculated equivalent weight.

Polyurethane elastomers are block copolymers and their domain structure can be controlled through the selection of the materials and their relative proportions. The polyurethanes were prepared using a single-stage process. In our investigation the hard-segment

composition was controlled by the molar ratios of poly-ol/diisocyanate/diol and aromatic triol used in the synthesis [18]. The molar ratios of the OH group to the diisocyanate (NCO) group chosen for the formulations were 0.9. The $OH_{\text{diol}}/OH_{\text{aromatic triol}}$ molar ratio used was of 1.0/2.0 in each of the synthesized polyurethane samples. After 10 min of mixing the appropriate amount of aromatic triols and chain extender (BD) at 75°C, diisocyanate at the OH/NCO ratio of 0.9 was added. The mixture was cured for 2 h at 75°C and the postcured at 110°C for 16 h.

2.6. Measurements and analysis

The X-ray diffraction (XRD) patterns obtained on an X-ray diffractometer (type Bruker AXS D8) using Cu-Kα radiation at a scan rate (2θ) of 0.02° s⁻¹ were used to determine the identity of any phase present and their crystallite size. The accelerating voltage and the applied current were 15 kV and 20 mA, respectively.

The fourier transform infrared spectroscopy (FTIR) spectra were recorded on a Bruker Tensor 27 spectrometer in the range of 400-4000 cm⁻¹ using KBr disks. ¹H NMR and ¹³C NMR were recorded on Bruker Advance III 300MHz spectrometers with CDCl₃ as a solvent.

DSC measurements were carried out on a Diamond DSC instrument (TA instruments, DE, USA), equipped with a refrigerated cooling system. The samples were heated at a rate of 10 °C/min from 25 °C to 200 °C to erase thermal history and cooled down to -65 °C at cooling rate of 5 °C/min. The DSC experiments were carried out with a liquid nitrogen cooler under a dry nitrogen atmosphere.

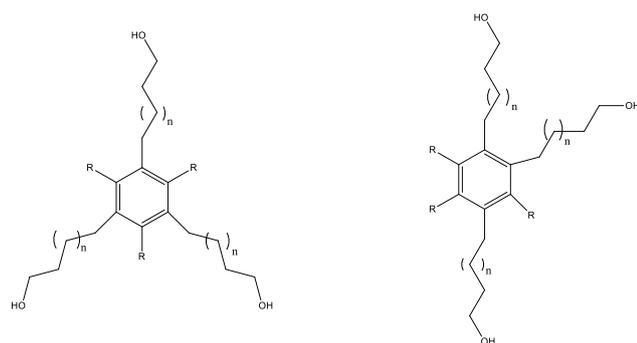
For thermal stability analysis, 10 mg of the dried polyurethanes powders was used in TG-DTA thermal analyzer (type PerkinElmer Diamond TG/DTA, America) at a heating rate of 10 °C/min from 20 to 800 °C in an inert gas atmosphere.

3. Results and discussion

3.1. Synthesis of biobased aromatic triols

The synthesis of triols monomers from oleic acid, erucic acid and 10-undecenoic through a cyclotrimerization reaction yielded a mixture of asymmetrical and symmetrical molecules (Chart 1). Biobased aromatic triols oleic acid-based aromatic triols (O-BAT), erucic acid-based aromatic triols (E-BAT) and 10-undecenoic-based aromatic triols (U-BAT) were synthesized by two different methods. Alkyne alcohol derivatives were obtained in moderate yields from the corresponding fatty acids by bromination, dehydrobromination, and reduction of carboxylic acid using well-established procedures (Scheme 1). Alkyne fatty derivatives were obtained in moderate yields from

the corresponding fatty acids by bromination, dehydrobromination, and esterification using well-established procedures (Scheme 1) [9,12]. Cyclotrimerization of the 10-undecyn-1-ol **3**^ˆ and behenic ester **3**^{ˆˆ} were carried out using PdCl₂ as transition metal catalyst. However, when cyclotrimerization of stearoyl alcohol **3** was carried out in the same conditions, some side products were slowly generated or no indication of trimer formation was obtained. The reaction was then carried out using Pd/C as transition metal catalyst, and the expected product was obtained in moderate yield [10,11].



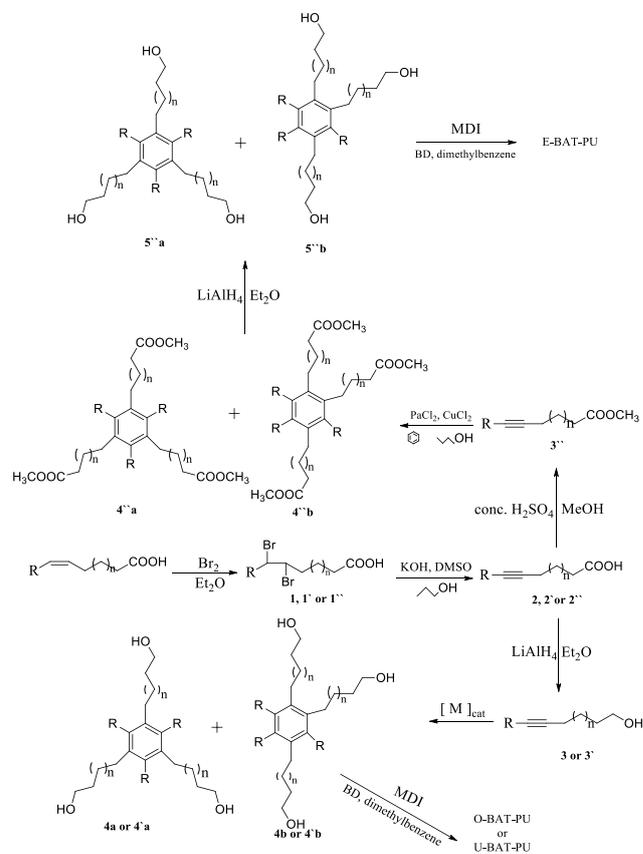
- (A) Oleic acid and derivatives: $n=5$, $R=(CH_2)_7CH_3$
 (B) Erucic acid and derivatives: $n=9$, $R=(CH_2)_7CH_3$
 (C) 10-undecenoic acid and derivatives: $n=6$, $R=H$

Chart 1. Chemical structures of aromatic triols monomers obtained by oleic acid, erucic acid and 10-undecenoic, respectively.

Transition-metal-catalyzed cyclotrimerization of alkynes can be considered as one of the most powerful and general methodologies used to assemble arene rings, and a large number of transition metal catalyst have been developed for alkyne cyclotrimerization in organic media [12,24,25]. A simple method utilizes heterogeneous Pa/C catalyst in nitrogen atmosphere with refluxing THF as the solvent and commercial grade chlorotrimethylsilane [10,26]. Cyclotrimerization of Stearoyl alcohol **3** was carried out following this procedure, and the symmetric and asymmetric isomers, such as aromatic triols **4a** and **4b**, have almost identical IR or ¹³C NMR spectra in CDCl₃. The formation of the aromatic derivative was confirmed by the appearance of the signal at 136.77 ppm in the ¹³C NMR spectrum corresponding to the aromatic core. The two compounds could not be separated by flash chromatography due to their similar polarities. Therefore, the presence of two compounds could not be ruled out.

The preparation of benzene derivatives via palladium-chloride-catalyzed cyclotrimerization of alkynes in the presence of CuCl₂ has been described as a smooth and regioselective method [12]. When cyclotrimerization of 10-undecyn-1-ol **3**^ˆ was carried out using PdCl₂ and CuCl₂ as transition metal catalyst, a 1,3,5-trisubstituted benzene derivative was obtained

regioselectively in a moderate yield. The appearance of signals at 6.39 ppm in the ¹H NMR spectrum and 120.35 and 137.63 ppm in the ¹³C NMR spectrum confirms the formation of the symmetric product.



- Oleic acid and derivatives: $n=5$, $R=(CH_2)_7CH_3$
 Erucic acid and derivatives: $n=9$, $R=(CH_2)_7CH_3$
 10-undecenoic acid and derivatives: $n=6$, $R=H$

Scheme 1. Synthesis of aromatic triols from oleic acid, erucic acid and 10-undecenoic acid, respectively.

The attempt to cyclotrimerize behenic ester **3**^{ˆˆ} via Pa/C catalyst in nitrogen atmosphere with refluxing THF as the solvent and chlorotrimethylsilane, some side products were slowly generated. The preparation of benzene derivatives via palladium-chloride-catalyzed cyclotrimerization of alkynes in the presence of CuCl₂ has been described as a smooth and regioselective method [12,27,28]. When we applied the reaction to behenic ester **3**^{ˆˆ}, the symmetric and asymmetric isomers, such as aromatic triols **4**^{ˆˆ}**a** and **4**^{ˆˆ}**b**, have almost identical IR or ¹³C NMR spectra in CDCl₃. The formation of the aromatic derivative was confirmed by the appearance of the signal at 136.71 ppm in the ¹³C NMR spectrum corresponding to the aromatic core. The two compounds could not be separated by flash chromatography due to their similar polarities. Therefore, the presence of two compounds could not be ruled out. The reaction can also proceed with behenyl alcohol.

However, when cyclotrimerization of the behenolyl alcohol was carried out in the same conditions, a lot of side products were slowly generated and the yields of aromatic triester **4`a** and **4`b** were lower. So, aromatic ester derivatives were used as starting material for the reduction of the carboxylate groups to synthesize two triols with primary hydroxyl groups.

3.2. Synthesis and characterization of polyurethanes

Vegetable-oil-based polyols have been widely used to produce segmented and nonsegmented polyurethanes [19-22]. Segmented polyurethanes are elastomeric block copolymers that generally exhibit a phase-segregated morphology made up of soft rubbery segments and hard glassy or semicrystalline segments [23,24]. The soft segment usually consists of polyether or polyester diols whereas the hard segment consists of the diisocyanate component and a low molecular weight consists of the

diisocyanate component and a low molecular weight chain extender. The advantage of segmented polyurethanes is that their segmental and domain structure can be controlled over a considerable range through the selection of the materials, their relative proportions, and the processing conditions [12].

In the study, biobased polyurethanes were prepared using the one-shot technique from O-BAT, E-BAT or U-BAT, BD as a chain extender, and MDI as a coupling agent. The biobased aromatic triols/MDI part is considered the soft phase even though its glass transition is above room temperature (Table 1). These hard segments are polar, crystallizable and likely to form a separate phase if the hard-segment content is high enough. The chemical composition and hard-segment content of the synthesized polyurethanes are also shown in Table 1. The OH/NCO molar ratio was kept at 1.5. Reactants were mixed at 75 °C and cured at this temperature for 2 h and postcured at 110 °C for 18 h to give the polyurethanes.

Table 1. Formulations and hardness of the polyurethanes obtained.

Sample code	Ratio (OH:NCO)	Ratio (Polyol/BD/MDI)	% Hard segment ^a
O-BAT-PU	0.9	1:3:3	56.9
E-BAT-PU	0.9	1:3:3	52.1
U-BAT-PU	0.9	1:3:3	67.6

^aThe hard-segment percentage is calculated as the wt % of BD and MDI per total material weight.

To investigate the molecular structure of polyurethanes WAXD and FTIR were employed. The amorphous character of both the asymmetric and symmetric polyurethanes was verified by WAXD (Fig. 1). All samples show similar WAXD curves with a broad peak at about $2\theta \approx 22^\circ$. This broad peak is atypical characteristic of amorphous polymers [12,13,15,16,17], which confirms that there are no crystals in O-BAT-PU, E-BAT-PU and U-BAT-PU.

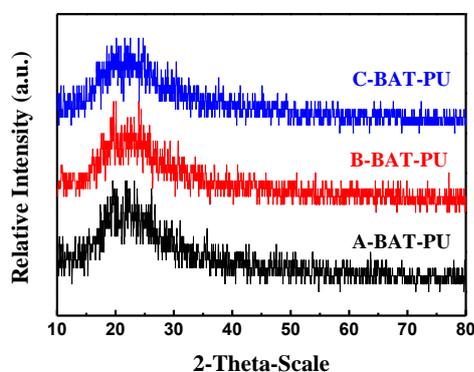


Fig. 1. Wide-angle X-ray diffraction patterns of O-BAT, E-BAT, and U-BAT polyurethane.

The FTIR spectra for O-BAT-PU, E-BAT-PU, and U-BAT-PU are shown in Fig. 2. From Fig. 2 it is noticed

that the spectra are similar for the PUs prepared from the same diisocyanate but different aromatic triols sources. The unreacted diisocyanate (NCO group) is clearly shown by a peak centered at 2362 cm^{-1} . A strong stretching band located at around 3317 cm^{-1} characteristic of the N-H group and a stretching vibration band centered around 1708 cm^{-1} characteristic of the C=O group are present in the FTIR spectra [7,8,15]. There are also two stretching regions attributed to the C=O group. The band centered at around 1768 cm^{-1} corresponds to the free carbonyl group while the band centered at around 1768 cm^{-1} . These results indicated that the three kinds of PU materials undergo physical bonding [16,18].

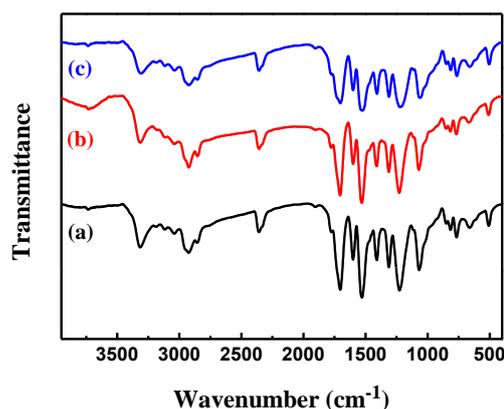


Fig. 2. FTIR spectra of (a) O-BAT-PU, (b) E-BAT-PU, and (c) U-BAT-PU.

3.3. Thermal stability of polyurethanes

Thermal analysis of the polyurethanes obtained was performed to provide insights into the morphological structure of the material. Fig. 3 shows the DSC thermogram for the polyurethanes. There were two endothermic peaks at about 45-50 °C and 175-190 °C. The glass transition temperature of the samples measured by DSC was 45-50 °C. The transition appeared in the region from 45 to 50 °C and were attributed to the soft-segment glass transition temperature (T_g). The T_g value is a measure of relative purity of the soft-segment regions; when there are hard segments dispersed in the soft domains, the T_g is raised [12]. The addition of bifunctional components such as MDI/BD reduces cross-linking density but increases phenyl ring content. In principle, reduced cross-linking density should decrease the T_g , but increased aromatic content should have the opposite [12]. The peak in the region from 175 to 190 °C was ascribed to the melting point of hard-segment domains, which supports the development of a phase-separated morphology and indicates that hard-segment content is high enough to achieve phase separation [12].

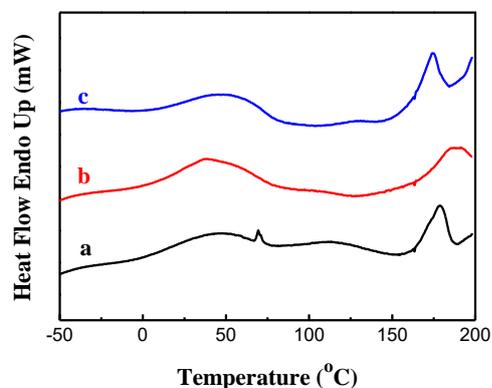


Fig. 3. DSC thermograms (10 °C/min) of (a) O-BAT-PU, (b) E-BAT-PU, and (c) U-BAT-PU.

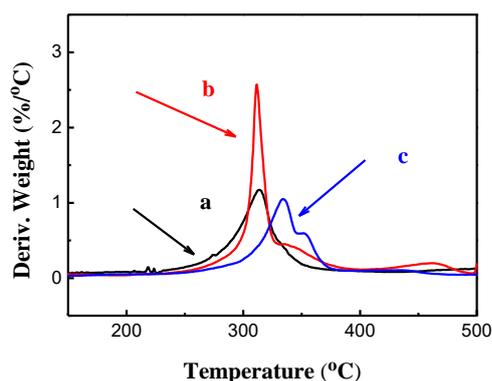


Fig. 4. DTG curves of (a) O-BAT-PU, (b) E-BAT-PU, and (c) U-BAT-PU.

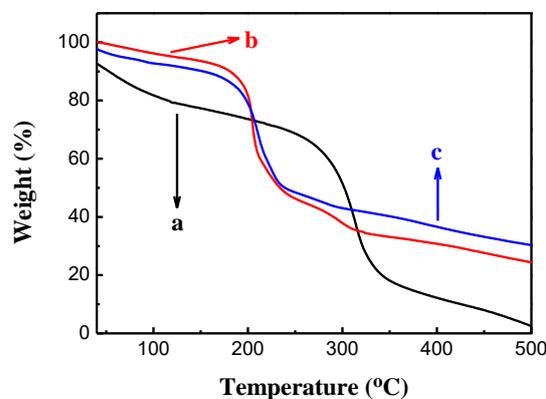


Fig. 5. TGA curves of (a) O-BAT-PU, (b) E-BAT-PU, and (c) U-BAT-PU.

TGA is the most favored technique for the evaluation of the thermal stability of polymers. Polyurethanes have relatively low thermal stability, mainly because the presence of urethane bonds. From the DTG curves it can be seen that in nitrogen only one process occurs during thermal degradation. Petrovic et al. observed a similar behavior in the case of vegetable-oil-based polyurethanes [12]. They showed that poly-(oxypropylene)-based polyurethanes degrade in a single step, whereas vegetable-oil-based polyurethane shows one-step decomposition [4,7,15]. Figure 4 shows the DTG curve and Fig. 5 shows the TGA curves of different polyurethanes, which reveals a degradation stage at temperatures between 300 and 400 °C. The results are similar to the three biobased polyurethanes systems. That can be associated with the decomposition of urethane bonds, which takes place through the dissociation to diisocyanate and alcohol, the formation of primary amines and olefins, or the formation of secondary amines [16,18].

4. Conclusions

Biobased aromatic triols, O-BAT, E-BAT and U-BAT have been synthesized using two different methods. It is demonstrated that alkyne alcohol derivatives can be obtained in the moderate yields from the corresponding fatty acids by bromation, dehydrobromination, and reduction of carboxylic acid, and alkyne fatty derivatives can also be obtained in moderate yields from the corresponding fatty acids by bromation, dehydrobromination, and esterification. Such a synthesis methodology has indicated a practical feasibility of utilizing the new biobased aromatic triols

for the production of biobased polyurethanes. The crystalline structure and thermal stability of these polyurethanes have been compared to their counterparts made from a similar O-BAT, E-BAT, and U-BAT, respectively. The corresponding polyurethane networks with hard-segment have been further prepared by the reaction of the polyol, BD, and MDI. The synthesized materials have been characterized using the spectroscopic techniques, WAXD, DSC and TG-DTA. The results have showed that it is possible to exploit renewable resources to achieve environment-friendly green materials.

Acknowledgments

The authors wish to thank the financial support from the National Natural Science Foundation of China (No.51308062), and the National Key Technology R&D Program (No.2011BAE27B04).

References

- [1] L. Hu, A. Zhang, Y. Yu, Z. Zheng, S. Du, X. Cheng, *Polym J* **23**, 689 (2014).
- [2] A. S. Singha, H. Kapoor, *Iran Polym J*, **23**, 655 (2014).
- [3] S. J. Li, L. Bouzidi, S. S. Narine, *Ind Eng Chem Res* **52**, 2209 (2013).
- [4] L. Raghunanan, S. S. Narine, *J Phys Chem B* **117**, 14754 (2013).
- [5] L. Raghunanan, J. Yue, S. S. Narine, *J Am Oil Chem Soc* **91**, 349 (2014).
- [6] M. Desroches, M. Escouvois, R. Auvergne, S. Caillol, B. Boutevin, *Polym Rev* **52**, 38 (2012).
- [7] P. C. Blasco, J. M. M. Martinez, I. V. Antoniac, *Int J Adhes Adhes* **42**, 11 (2013).
- [8] D. V. Palaskar, A. Boyer, E. Cloutet, J. F. L. Meins, B. Gadenne, C. Alfes, C. Farcet, H. Cramail, *J Polym Sci Pol Chem* **50**, 1766 (2012).
- [9] G. Lligadas, J. C. Ronda, M. Galia, V. Cadiz, *Biomacromolecules* **11**, 2825 (2008).
- [10] H. Baumann, M. Bühler, H. Fochem, *Angewandte Chemie International Edition in English* **27**, 41 (1988).
- [11] J. Yue, S. S. Narine, *Chem Phys Lipids* **152**, 1(2008)
- [12] G. Lligadas, J. C. Ronda, M. Galia, V. Cadiz, *Biomacromolecules* **8**, 1858 (2007).
- [13] M. J. Dumont, S. S. Narine, *J Appl Polym Sci* **118**, 3211 (2010).
- [14] G. Ligadas, J. C. Ronda, M. Galia, V. Cadiz, *Polymers* **2**, 440 (2010).
- [15] L. Hojabri, X. H. Kong, S. S. Narine, *Biomacromolecules* **10**, 884 (2009).
- [16] M. J. Dumont, X. Kong, S.S. Narine, *J Appl Polym Sci* **117**, 3196 (2010).
- [17] L. Hojabri, X. H. Kong, S. S. Narine, *J Polym Sci Pol Chem* **48**, 3302 (2010).
- [18] S. Oprea, *J Am Oil Chem Soc* **87**, 313 (2010).
- [19] J. H. Li, Y. Liang, Y. X. Xie, *J Org Chem* **69**, 8125 (2004).
- [20] J. H. Li, S. Tang, Y. X. Xie, *J Org Chem* **70**, 477 (2005).
- [21] J. H. Li, H. F. Jiang, M. C. Chen, *J Org Chem* **66**, 3627 (2001).
- [22] H. Dietl, H. Reinheimer, J. Moffat, P. M. Maitlis, *J Am Chem Soc* **92**, 2276 (1970).
- [23] J. S. Cheng, H. F. Jiang, *Eur J Org Chem* **3**, 643 (2004).
- [24] M. A. R. Meier, J. O. Metzger, U. S. Schubert, *Chem Soc Rev* **36**, 1788 (2007).
- [25] L. M. D. Espinosa, M. A. R. Meier, *Eur Polym J* **47**, 837 (2011)
- [26] A. Gandini, *Green Chem* **13**, 1061 (2011).
- [27] Y. Xia, R. C. Larock, *Green Chem* **12**, 1893 (2010).
- [28] A. K. Jhingan, W. F. Maier, *J Org Chem* **52**, 1161 (1987).

*Corresponding author: hyqgxu@126.com