Macromolecules

Renewable Thermoplastics Based on Lignin-Derived Polyphenols

Shou Zhao[†] and Mahdi M. Abu-Omar^{*,†,‡}

[†]Department of Chemistry & Biochemistry and [‡]Department of Chemical Engineering, University of California, Santa Barbara, Santa Barbara, California 93106, United States

S Supporting Information

ABSTRACT: A series of renewable triphenylmethane-type polyphenols (TPs) were synthesized from lignin-derived guaiacols (methylguaiacol and propylguaiacol) and aldehydes (4-hydroxybenzaldehyde, vanillin, and syringaldehyde). By converting guaiacols to catechols through *ortho*-demethylation, the newly formed phenolic *para* site remarkably improved the reactivity as reflected by conversion of TPs. Optimized reagent molar ratios were aldehyde/catechol (1:4) and aldehyde/ H_2SO_4 (1:3). A typical TP (VAN-M-CAT) was converted to glycidyl ether (GE-VAN-M-CAT) to examine its feasibility as precursor to epoxy thermosets. The resulting network exhibited excellent glassy modulus (12.3 GPa), glass transition temperature (167 °C), and thermal stability, which were



attributed to the rigid triphenylmethane framework, high functionality (n = 5), and high cross-link density. A fully biobased epoxy comonomer (VAN-LIN-EPO), which was prepared by esterification of VAN-M-CAT with linoleic acid followed by epoxidation, could tune the material properties. This study widens the synthesis route of fully biobased polyphenols, which can yield polymers with excellent properties.

INTRODUCTION

Polyphenols are important precursors to polymers like epoxy thermosets. As development of renewable materials has become increasingly important, partially or fully biobased polyphenols have been prepared with the purpose to replace or supplement petroleum-based bisphenol A (BPA).^{1–3} Polyphenols are generally produced by condensation of phenol with ketone or aldehyde in the presence of an acid.⁴ Using this approach, several biobased polyphenols have recently been reported: (1) diphenolic acid based on cellulose-derived levulinic acid,⁵ (2) bisphenol obtained from cellulose-based 2,3-pentanedione,⁶ (3) bisphenol based on lignin-derived creosol,⁷ and (4) triphenol prepared from lignin-based vanillin and guaiacol.⁸

For phenol–aldehyde condensation, the phenolic *para* position is the preferred coupling site due to its higher reactivity over the *ortho* site.^{9,10} However, lignin-derived phenols are often characterized as *para* site occupied by alkyl groups, while partial *ortho* sites are substituted by methoxy groups,^{11,12} which makes them especially difficult to couple to aldehydes. Because of this obstruction, either *para*-available phenols like guaiacol⁸ or *ortho*-specified coupling catalysts like zinc acetate⁷ have been used as alternative methodologies, even though these approaches are frequently associated with limitations such as insufficient phenol candidates and limited orientation and stretch of functional hydroxyls obtained via *ortho* coupling.¹³

To increase the applications of lignin-based phenols, creating a *para* site on *para*-substituted phenol could be a more universal and straightforward methodology. This improvement can be realized through *ortho*-demethylation of *ortho* methoxy, a characteristic group of lignin-derived phenols.^{14,15} As illustrated in Scheme 1, *ortho*-demethylation of typical ligninbased guaiacols leads to new *para* and *ortho* sites. These newly formed sites, especially the *para* site, could enhance reactivity. Meanwhile, demethylation also increases the number of functional OH groups. TPs with higher OH content have the potential to further improve the cross-linking density and mechanical properties of subsequently formed polymers.^{13,16,17}

Recent development in catalytic lignin depolymerization techniques is capable of converting bulk lignin into various smaller aromatic molecules including aldehydes, e.g., 4-hydroxybenzaldehyde (HBA), vanillin (VAN), and syringaldehyde (SYA)^{18,19} and guaiacols such as 4-methylguaiacol (M-GUA) and 4-propylguaiacol (P-GUA).^{20,21} Condensation between aromatic aldehyde and phenol yields triphenylmethane-type phenol (TP). TP-based materials are supposed to be highly rigid due to the triphenylmethane framework and highly functional (n = 5). To tune the rigidity, vegetable oils with flexible carbon chains may represent a renewable modifier.^{22,23} Especially, unsaturated fatty acids (e.g., linoleic acid, LA) are often used as plasticizer or copolymer adjusting the rigidity of thermoplastics.^{24,25} The integration of lignin-based TPs and unsaturated fatty acids would yield renewable polymers with tunable mechanical properties.

Received: January 10, 2017 Revised: March 6, 2017 Scheme 1. Synthesis Route of Fully Renewable Triphenylmethane-Type Polyphenols from Lignin-Derived Aldehydes and Para-Substituted Guaiacols^a



^{*a*}Condensation reactions between aldehydes and guaiacols give conversions below 5%. *Ortho*-demethylation of guaiacols to corresponding catechols significantly improve the reactivity. The conversions of methylcatechol (M-CAT) based TPs are more than 90%, while propylcatechol (P-CAT)-based TPs are more than 45%. Reaction conditions: molar ratio of aldehyde:phenol = 1:4, aldehyde: H_2SO_4 = 1:3, room temperature for 2 days. Absolute ethanol is used as solvent. Conversions and isolated yields of different lignin-based TPs are listed in Table 2.

In this study, we first describe the effective synthesis of fully renewable polyphenols from the above-mentioned aldehydes and para-substituted guaiacols. By creating a para site on parasubstituted guaiacols through ortho-demethylation, reactivity of the afforded catechols significantly improves. The proposed TPs have unique molecular architecture: three aromatic rings and five functional OH groups. To explore their potential as precursors to epoxy resin, a typical TP (VAN-M-CAT, prepared from condensation of vanillin and methylcatechol) is then reacted with epichlorohydrin to produce glycidyl ether prepolymer (GE-VAN-M-CAT). VAN-M-CAT was selected because it was easily separated from the reaction mixture, giving the highest yield (88%) among all TPs. Meanwhile, VAN-M-CAT is reacted with chlorinated linoleic acid via esterification followed by epoxidation to make an epoxy comonomer (VAN-LIN-EPO), which acts as a plasticizer that tunes the rigidity of the resulting thermosets. The mixture of GE-VAN-M-CAT and VAN-LIN-EPO with different mass ratios is cured with a hardener (diethylenetriamine, DETA) to make epoxy networks. Thermal and mechanical performances of biobased thermosets are characterized to evaluate their potential for replacing BPAbased counterparts.

EXPERIMENTAL SECTION

General. 4-Hydroxybenzaldehyde, vanillin, syringaldehyde, 4methylguaiacol, 4-propylguaiacol, 4-methylcatechol, 48% aqueous hydrobromic acid, epichlorohydrin, tetrabutylammonium bromide, diethylenetriamine (DETA), peracetic acid (32 wt % in dilute acetic acid), linoleic acid, and oxalyl chloride were purchased from Aldrich Chemical Co. Ethanol (200 proof) was purchased from Decon Laboratories, Inc. Sulfuric acid (98%) was obtained from Fisher Scientific. All chemicals were used as received without further purification. **Ortho-Demethylation of 4-Methylguaiacol and 4-Propylguaiacol.** Lignin-based phenols were *ortho*-demethylated as previously reported.¹⁴ Briefly, 4-propylguaiacol (P-GUA, 16.6 g, 0.1 mol) was added to 83 g of 48% aqueous hydrobromic acid. The reaction mixture was magnetically stirred at 120 °C for 20 h, cooled to ambient temperature, saturated with NaCl, and extracted three times with diethyl ether. The organic layer was dried over MgSO₄ and concentrated using rotary evaporation to yield P-GUA-derived catechol (P-CAT) as a yellow oil (94% yield). M-GUA demethylated product (M-CAT) was prepared using the same method with 92% yield. Proton NMR spectra of M-GUA, M-CAT, P-GUA, and P-CAT are shown in Figures S1 and S2.

Synthesis of Lignin-Based Triphenylmethane-Type Phenols (TP). M-CAT-Based TPs. Vanillin (VAN, 1.05 g, 7 mmol) and M-CAT (3.47 g, 28 mmol) were dissolved in 3 mL of absolute ethanol. To this solution, 2.0 g of concentrated sulfuric acid, dissolved in 1.5 mL of absolute ethanol, was slowly added while stirred. An ice bath was used to control the temperature below 10 °C. After the addition of sulfuric acid, the temperature was increased to room temperature. The system was gently stirred for 2 days under room temperature. Then, 100 mL of H₂O and 15 mL of diethyl ether were successively added to precipitate flakes. The precipitate was then collected through filtration, washed with water three times, and dried at 65 °C under vacuum for 2 days to obtain the TP product (VAN-M-CAT) as a white powder (2.35 g, 88% isolated yield). ¹H NMR (acetone- d_6 , 400 MHz) δ : 7.64 (s, 2H, Ar–OH), 7.39 (s, 2H, Ar–OH), 6.74 (d, J = 8.1, 1H, Ar–H), 6.69 (s, 1H, Ar-H), 6.65 (s, 2H, Ar-H), 6.42 (d, J = 7.8, 1H, Ar-H), 6.23 (s, 2H, Ar-H), 5.39 (s, 1H, Ar₃-CH), 3.69 (s, 3H, -OCH₃), 2.00 (s, 6H, $-CH_3$). ¹³C NMR (acetone- d_{6} , 400 MHz) δ : 148.09, 145.54, 143.71, 143.08, 136.21, 135.08, 128.24, 122.76, 118.18, 117.24, 115.31, 113.98, 56.13 (-OCH₃), 49.70 (Ar₃-CH), 18.80 (-CH₃). $[C_{22}H_{22}O_6 - H^+]$: 381.4.

SYA-M-CAT was obtained from M-CAT and syringaldehyde (SYA) using the above-mentioned method (2.05 g, 71% isolated yield). ¹H NMR (acetone- d_{6} , 400 MHz) δ : 7.65 (s, 2H, Ar–OH), 7.40 (s, 2H, Ar–OH), 7.08 (s, 1H, Ar–OH), 6.63 (s, 2H, Ar–H), 6.33 (s, 2H, Ar–H), 6.23 (s, 2H, Ar–H), 5.37 (s, 1H, Ar₃–CH), 3.67 (s, 6H, –

Scheme 2. Glycidylation of VAN-M-CAT with Epichlorohydrin^a



^{*a*}Three major products with mono-epoxy-substituted (GE-VAN-M-CAT-1), tri-epoxy-substituted (GEVAN-M-CAT-3), and penta-epoxy-substituted (GEVAN-M-CAT-5) were isolated using a preparative HPLC, and their molar ratio was measured to be 14:55:31 using analytical HPLC spectra.

OCH₃), 2.00 (s, 6H, -CH₃). ¹³C NMR (acetone- d_6 , 400 MHz) δ : 148.45, 143.75, 143.09, 135.30, 135.06, 134.93, 128.25, 118.15, 117.16, 108.10, 56.54 (-OCH₃), 50.03 (Ar₃-CH), 18.76 (-CH₃). [C₂₃H₂₄O₇ - H⁺]: 411.4.

For HBA-M-CAT that is derived from 4-hydroxybenzaldehyde (HBA) and M-CAT, only the isolation method is different from the above. In detail, after the reaction was complete, 100 mL of H₂O was poured into the mixture prior to the addition of 20 mL of diethyl ether to extract the product. The ethereal extract was dried with MgSO₄, and the solvent was allowed to evaporate slowly to yield colorless crystals, which were subsequently washed with cold ether and dried at 65 °C under vacuum for 2 days to yield a white powder (2.07 g, 84% isolated yield). ¹H NMR (acetone-*d*₆, 400 MHz) δ : 7.58 (s, 5H, Ar–OH), 6.84 (d, *J* = 8.4, 2H, Ar–H), 6.75 (d, *J* = 8.4, 2H, Ar–H), 6.64 (s, 2H, Ar–H), 6.20 (s, 2H, Ar–H), 5.38 (s, 1H, Ar₃–CH), 1.99 (s, 6H, –CH₃). ¹³C NMR (acetone-*d*₆, 400 MHz) δ : 156.32, 143.68, 143.10, 135.34, 135.53, 135.15, 131.27, 128.17, 120.93, 118.18, 117.27, 116.85, 115.89, 115.72, 49.24 (Ar₃–CH), 18.74 (–CH₃). [C₂₁H₂₀O₅ – H⁺]: 351.4.

P-CAT-Based TPs. P-CAT-based TPs (HBA-P-CAT, VAN-P-CAT, and SYA-P-CAT) were prepared using the same reaction conditions as VAN-M-CAT. The desired TPs were separated from unreacted phenols and aldehydes using silica gel chromatography (hexane/ethyl acetate, 3:1 to 1:1) to give:

HBA-P-CAT, orange solid, 1.20 g, 42% isolated yield. ¹H NMR (acetone- d_{6} , 400 MHz) δ : 7.53 (s, 4H, Ar–OH), 6.81 (d, J = 8.2, 2H, Ar–H), 6.73 (d, J = 8.1, 2H, Ar–H), 6.66 (s, 2H, Ar–H), 6.22 (s, 2H, Ar–H), 5.57 (s, 1H, Ar₃–CH), 2.35 (t, J = 7.2, 4H, –CH₂–), 1.47 (dt, J = 15.0, 7.4, 4H, –CH₂–), 0.85 (t, J = 7.2, 6H, –CH₃). ¹³C NMR (acetone- d_{6} , 400 MHz) δ : 156.27, 143.82, 143.04, 136.82, 134.81, 132.66, 131.07, 117.79, 117.34, 115.68, 47.99 (Ar₃–CH), 34.85 (–CH₂–), 24.84 (–CH₂–), 14.45 (–CH₃). [C₂₃H₂₈O₅ – H⁺]: 407.4.

VAN-P-CAT, orange solid, 1.07 g, 35% isolated yield. ¹H NMR (acetone- d_{6} , 400 MHz) δ : 7.66 (s, 2H, Ar–OH), 7.39 (s, 1H, Ar–OH), 7.37 (s, 2H, Ar–OH), 6.72 (d, J = 8.0, 1H, Ar–H), 6.66 (s, 2H, Ar–H), 6.63 (s, 1H, Ar–H), 6.41 (d, J = 7.2, 1H, Ar–H), 6.24 (s, 2H, Ar–H), 5.58 (s, 1H, Ar₃–CH), 3.68 (s, 3H, –OCH₃), 2.36 (t, J = 7.2, 4H, –CH₂–), 1.48 (dt, J = 15.0, 7.4, 4H, –CH₂–), 0.85 (t, J = 7.2, 6H, – CH₃). ¹³C NMR (acetone- d_{6} , 400 MHz) δ : 148.06, 145.54, 143.85, 143.02, 137.48, 134.75, 132.71, 122.78, 117.52, 117.27, 115.33, 113.85, 107.64, 56.16 (–OCH₃), 48.44 (Ar₃–CH), 34.85 (–CH₂–), 24.78 (–CH₂–), 14.47 (–CH₃). [C₂₆H₃₀O₆ – H⁺]: 437.4.

SYA-P-CAT, orange solid, 1.08 g, 33% isolated yield. ¹H NMR (acetone- d_{6} , 400 MHz) δ : 7.68 (s, 2H, Ar-OH), 7.36 (s, 2H, Ar-OH), 7.05 (s, 1H, Ar-OH), 6.66 (d, J = 1.8, 2H, Ar-H), 6.28 (dd, J = 15.7, 1.8, 4H, Ar-H), 5.57 (s, 1H, Ar₃-CH), 3.66 (s, 6H, -OCH₃), 2.36 (t, $J = 7.2, 4H, -CH_2-$), 1.45 (dt, $J = 15.0, 7.4, 4H, -CH_2-$), 0.85 (t, $J = 7.2, 6H, -CH_3$). ¹³C NMR (acetone- d_6 , 400 MHz) δ : 148.45, 143.89, 143.01, 136.58, 135.11, 134.64, 132.76, 117.68, 117.48, 108.11, 56.58 (-OCH₃), 48.81 (Ar₃-CH), 34.85 (-CH₂-), 24.75 (-CH₂-), 14.48 (-CH₃). [C₂₇H₃₂O₇ - H⁺]: 467.6.

Preparation of Glycidylated Ether of VAN-M-CAT (GE-VAN-M-CAT). GE-VAN-M-CAT was prepared by reaction of VAN-M-CAT (2 g, 5.2 mmol) and epichlorohydrin (30 g, 320 mmol). Tetrabutylammonium bromide (0.84 g, 2.6 mmol) was used as a phase transfer catalyst. The mixture was heated at 95 °C for 1 h and followed by a dropwise addition of 10 g of 20% w/w NaOH solution. The reaction was kept for another 3 h, and the mixture was washed with water, extracted with ethyl acetate, and concentrated with a rotary evaporator to yield GE-VAN-M-CAT as a viscous oil (2.8 g). The catechol-like structure of VAN-M-CAT is likely to produce benzodioxane derivatives during glycidylation (Scheme 2). Using a preparative scale HPLC, three major glycidylated products, i.e., monoepoxy-substituted (GE-VAN-M-CAT-1), tri-epoxy-substituted (GE-VAN-M-CAT-3) and penta-epoxy-substituted GE-VAN-M-CAT-5) were isolated. Structures of the major glycidylated products were measured by NMR and mass spectra. An analytical HPLC was used to detect peaks of each epoxidized product and determine their molar ratio in the mixture to be GE-VAN-M-CAT-1:GE-VAN-M-CAT-3:GE-VAN-M-CAT-5 = 14:55:31. Epoxy equivalent value of GE-VAN-M-CAT mixture was determined to be 495 mmol epoxy/100 g by HCl/acetone chemical titration method. This is in accordance with the calculated value (531 mmol epoxy/100 g) using the above ratio.

GE-VAN-M-CAT-1, yellow oil, 14 mol % in epoxidized product mixture. ¹H NMR (CDCl₃, 400 MHz) δ : 6.27–6.80 (7H, Ar–H), 5.37 (1H, f), 4.13–4.28 (5H, c', g', h), 3.94–4.10 (3H, c, g), 3.82–3.87 (4H, i, i'), 3.76 (3H, d), 3.37 (1H, b), 2.89 (1H, a), 2.73 (1H, a'), 2.03 (6H, e). ¹³C NMR (CDCl₃, 400 MHz) δ : 113.58–140.51 (Ar–C), 73.31 (h), 70.07 (c), 65.07 (g), 61.74 (i), 55.89 (d), 50.14 (f), 48.99 (b), 44.99 (a), 18.66 (e). [C₃₁H₃₄O₉ + Na⁺]: 573.

GE-VAN-M-CAT-3, brown oil, 55 mol % in epoxidized product mixture. ¹H NMR (CDCl₃, 400 MHz) δ : 6.23–6.80 (7H, Ar–H), 5.37 (1H, f), 4.18–4.25 (5H, c', g', h), 3.92–4.07 (4H, c, g), 3.78–3.82 (2H, i, i'), 3.74 (3H, d), 3.22–3.37 (3H, b), 2.61–2.88 (6H, a, a'), 1.99–2.03 (6H, e). ¹³C NMR (CDCl₃, 400 MHz) δ : 113.40–149.39 (Ar–C), 73.29 (h), 70.08 (c), 65.18 (g), 61.74 (i), 55.84 (d), 50.12 (f), 49.09 (b), 44.66 (a), 18.93 (e). [C₃₄H₃₈O₁₀ + Na⁺]: 629.

GE-VAN-M-CAT-5, brown oil, 31 mol % in epoxidized product mixture. ¹H NMR (CDCl₃, 400 MHz) δ : 6.32–6.80 (7H, Ar–H), 5.40 (1H, f), 4.09–4.25 (5H, c'), 3.88–4.99 (5H, c), 3.74 (3H, d), 3.22–3.36 (5H, b), 2.60–2.87 (10H, a, a'), 2.03 (6H, e). ¹³C NMR (CDCl₃, 400 MHz) δ : 113.29–146.78 (Ar–C), 70.28 (c), 55.77 (d), 50.23 (b), 49.20 (f), 45.26 (a), 18.89 (e). [C₃₇H₄₂O₁₁ + Na⁺]: 686.

Esterification of VAN-M-CAT with Linoleic Acid and Epoxidation. Linoleic acid was first converted to linoleoyl chloride (LC) to increase its reactivity.²⁶ To a solution of linoleic acid (4.2 g, 15 mmol) dissolved in 35 mL of dry dichloromethane was added slowly 4.23 g (33.3 mmol) of oxalyl chloride at 0 °C. The temperature was then raised to room temperature and stirred for 4 h. The reaction mixture was concentrated with rotary evaporator to yield LC as a yellowish oil (4.13 g, 92% isolated yield).

Esterification between VAN-M-CAT and LC was then performed by a solvent-free and catalyst-free condition as established by a previous study.²⁷ In detail, VAN-M-CAT (1 g, 2.6 mmol) and LC (8.97 g, 30 mmol) were introduced in a 50 mL reactor with a nitrogen—gas bubbling system and an outlet connected to a wash bottle holding a NaOH solution. The mixture was then stirred and heated at 130 °C for 15 h under a continuous nitrogen stream. The obtained esterified product, VAN-M-CAT-LIN, was washed using cold ethanol to remove the excess acid chloride and further purified by a silica column using an eluent of hexane/ethyl acetate (10:1) to yield 2.79 g, 63% isolated yield.

VAN-M-CAT-LIN was then epoxidized using peracetic acid to make epoxy comonomer. 1.5 g (0.88 mmol, 8.8 mmol of double bond) of VAN-M-CAT-LIN was dissolved in 25 mL of dichloromethane in a 50 mL round-bottomed flask. To this flask was added dropwise peracetic acid (4.2 g, 17.6 mmol). The reaction mixture was stirred at room temperature overnight, washed 3 times with brine, and extracted with ethyl acetate. The ethyl acetate was removed using a rotary evaporator to yield epoxidized VAN-M-CAT-LIN (VAN-M-CAT-LIN-EPO) as a yellowish oil (1.4 g, 86% isolated yield).

Formation of Biobased Epoxy Networks. Three epoxy monomer mixtures with weight ratio GE-VAN-M-CAT to VAN-M-CAT-LIN-EPO of 100:0, 75:25, and 50:50 are respectively mixed with diethylenetriamine (DETA) with stoichiometric ratio of epoxy vs –NH for curing. The mixtures were stirred for 10 min, degassed under vacuum to remove entrapped air, and poured into molds for curing. Given GE-VAN-M-CAT was highly reactive with DETA, the mixtures were cured at room temperature for 8 h, followed by 60 °C for 4 h and 80 °C for 4 h. The obtained cured epoxy thermosets, denoted as VAN₁₀₀LIN₀, VAN₇₅LIN₂₅, and VAN₅₀LIN₅₀, were subjected to mechanical and thermal analyses.

Analysis Methods. The chemical structure of TPs was followed using NMR and Fourier transform infrared (FTIR) spectroscopy. The NMR spectra were performed on a Bruker Avance ARX-400 spectrometer while a Bruker Avance-III-800 was used for taking 2D HMQC spectra. Deuterated acetone or chloroform was used as solvent. FTIR analyses were conducted using a Thermo-Nicolet Nexus 470 FTIR spectrometer equipped with an ultrahigh-performance, versatile attenuated total reflectance (ATR) sampling accessory. The spectra were scanned over a wavenumber range of 400–4000 cm⁻¹ with a resolution of 4 cm⁻¹.

Conversions of phenol–aldehyde condensation reaction were measured by high-performance liquid chromatography (HPLC, Agilent 1260 Infinity Quaternary), with a Zorbax Eclipse XDB-C₁₈ Column (250 × 74.6 mm). ESI–MS analyses in negative mode were performed using a 7 T Thermo Scientific LQIT/FT–ICR mass spectrometer. A Waters Delta Prep 4000 HPLC was used to separate and collect each of the glycidylated products of VAN-M-CAT in 50 mg scale.

Crystal of VAN-M-CAT was obtained from slow evaporation of an ether solution at room temperature. Single crystals were mounted on Mitegen microloop mounts using a trace of mineral oil and cooled in situ to 100(2) K for data collection on a Nonius KappaCCD diffractometer equipped with a graphite crystal, incident beam monochromator using Mo K α radiation ($\lambda = 0.71073$ Å). Data were collected using the Nonius Collect software and processed using HKL3000 and corrected for absorption and scaled using Scalepack.

Dynamic mechanical properties were characterized using a DMA 2980 (TA Instruments). Rectangular specimens with dimensions of 30 mm length, 10 mm width, and 2.5 mm thickness were measured in a single-cantilever mode. The measurements were conducted from 25 to 200 °C at a heating rate of 3.00 °C/min and a frequency of 1 Hz. The temperature at the maximum in the tan δ curve was taken as T_{α} (related to glass transition).

Thermal stability studies were carried out on a TGA Q500 (TA Instruments) under a nitrogen flow of 40 mL/min. Samples (15–20 mg) were placed in a platinum pan and scanned from 30 to 600 $^{\circ}$ C at a ramp rate of 20 $^{\circ}$ C/min.

RESULTS AND DISCUSSION

Synthesis of Renewable TPs under Optimized Conditions. Molar ratios of aldehyde/phenol and aldehyde/ H_2SO_4 are capable of affecting the yield of TPs. To obtain optimal conditions, reaction between vanillin and methylcatechol was studied as an example due to the facile isolation and purification of the product VAN-M-CAT. Isolated yields of VAN-M-CAT under various synthesis conditions are listed in Table 1. Effect of vanillin/methylcatechol molar ratio was

Table 1. Effect of Stoichiometric Ratio of Reactants and Amount of Catalyst and Solvent on the Isolated Yield of VAN-M-CAT

entry	vanillin/ M-CAT ^a	$\begin{array}{c} \text{vanillin} / \\ \text{H}_2 \text{SO}_4^{\ a} \end{array}$	vanillin/ EtOH	isolated yield (%)
1	1:2	1:3	1:3	72
2	1:3	1:3	1:3	83
3	1:4	1:3	1:3	88
4	1:4	1:1	1:3	75
5	1:4	1:5	1:3	89
6	1:4	1:3	1:6	83

^{*a*}Molar ratio. ^{*b*}Weight ratio. Condensation was conducted at room temperature for 2 days.

studied first. For entry 1, condensation of 1 equiv of vanillin with 2 equiv of methylcatechol gave a yield of 72%. Increasing methylcatechol/vanillin ratio to 3:1 (entry 2) readily improved isolated yield to 83%. As the ratio raised to 4:1, the yield increased further to 88% (entry 3). The effect of catalyst amount was then investigated (entries 3-5). The amount of H₂SO₄ was insufficient when equal moles of H₂SO₄ and vanillin were used (entry 4, 75% isolated yield). After increasing the H₂SO₄/vanillin ratio to 3:1 (entry 3), the yield increased to 88%. It is noteworthy that the yields of entry 5 (89%) and entry 3 are similar, even though the H₂SO₄/vanillin ratio is increased to 5:1. Thus, H₂SO₄/vanillin ratio of 3:1 is effective at catalyzing the coupling reaction and considered optimal.

The amount of solvent ethanol was also found to impact product yields (compare entries 3 and 6). In entry 3, to fully dissolve 1 equiv of vanillin and 4 equiv of methylcatechol, the weight ratio of ethanol/vanillin had to be at least 3. For production of VAN-M-CAT, using the least amount of solvent is advantageous since it minimizes the product dissolved in solvent and facilitates isolation of product. This was confirmed when weight ratio of ethanol/vanillin increased to 6 in entry 6. Even though increasing solvent could facilitate mixing of reactants, the yield in entry 6 (83%) was still slightly lower than that in entry 3. Therefore, overall evaluation of the abovementioned conditions revealed entry 3 as the optimal synthesis condition (molar ratio of vanillin/M-CAT = 1:4, vanillin/H₂SO₄ = 1:3), which produced high isolated yield while consuming relatively less H₂SO₄ and ethanol.

The optimized condition was subsequently used for condensation of other lignin-based aldehydes and phenols. Initially, direct condensation of aldehydes (HBA, VAN, or SYA) with *para*-substituted guaiacols (M-GUA or P-GUA) was studied using HPLC to measure the conversion. However, it turned out that conversions of all reactions were negligible (<5%). In an effort to increase the conversion, reaction time was increased up to 7 days, but with no enhancement in conversion. As *ortho* site of M-GUA and P-GUA is the only available position for condensation, low reactivity due to steric

effect of the *ortho* sites significantly decreased the reactivity of guaiacols. To increase the reactivity, M-GUA and P-GUA were demethylated to the corresponding catechols (M-CAT and P-CAT).

Compared to the negligible conversions of *para*-substituted guaiacols, Table 2 shows significant increase in conversion and

Table 2. Conversions and Isolated Yields of TPs Derived from Lignin-Based Aldehydes and Catechols^a

entry	aldehyde	catechol	polyphenol	conv (%)	isolated yield (%)
1	HBA	M-CAT	HBA-M-CAT	97	84
2	HBA	P-CAT	HBA-P-CAT	50	42
3	VAN	M-CAT	VAN-M-CAT	95	88
4	VAN	P-CAT	VAN-P-CAT	48	35
5	SYA	M-CAT	SYA-M-CAT	90	71
6	SYA	P-CAT	SYA-P-CAT	45	33

"Reaction conditions: molar ratio of aldehyde:phenol = 1:4, aldehyde: $H_2SO_4 = 1:3$, room temperature for 2 days. Absolute ethanol is used as solvent.

yield when the corresponding catechols are used. For example, TPs based on M-CAT have conversions in the range of 90–97%, with isolated yields of 71–88%. By comparison, P-CAT-based TPs have lower conversion (45–50%) and isolated yields (33–42%), which might be attributed to the greater steric effect of the propyl group. Structure of aldehydes also has impact on conversion. Generally, conversion follows the order: HBA >

VAN > SYA. As the number of electron-donating (methoxy) groups increases from HBA to SYA, the electrophilicity decreases, which reduces their reactivity in electrophilic substitution reactions.

Structure of TPs. Proton and carbon NMR spectra of VAN-M-CAT are shown in Figure 1. The proton peak at 5.39 ppm corresponds to the triphenyl methyl group, which indicates successful coupling of vanillin with methylcatechol. Aromatic protons are found at 6.74, 6.69, 6.65, 6.42, and 6.23 ppm. The methoxy group is observed at 3.69 ppm while the methyl peak at 2.00 ppm. As for the carbon NMR, the methoxy, triphenylmethyl, and methyl groups are observed at 56.13, 49.70, and 18.80 ppm, respectively. The characteristic triphenyl methyl peak is also observed for other lignin-based TPs (as depicted in Figures S3–S7), which confirms the formation of triphenylmethane framework. The structure of M-CAT and P-CAT based TPs are also confirmed by IR and mass spectra in Figures S8–S14.

X-ray structure of VAN-M-CAT is also measured to confirm the structure and determine the coupling site. It is observed in Figure 2 that vanillin couples exclusively at the *para* sites of both methylcatechol molecules. This can be explained by higher reactivity of the *para* site. Meanwhile, the *para* site has less steric hindrance compared to *ortho* sites when subjected to condensation. The high reactivity of phenolic *para* position highlights the role of demethylation, which could be an effective way of modifying lignin-derived phenols, especially for those with *para* substituted and *ortho* occupied by methoxy group. Besides, the stretched orientation of functional hydroxyls of



Figure 1. Proton (A) and carbon (B) NMR spectra of VAN-M-CAT. Solvent: acetone- d_6 .

Figure 2. X-ray structure of VAN-M-CAT. Crystal was obtained from the slow evaporation of an ether solution at room temperature.

TPs is also advantageous for making polymers with desirable properties.

Epoxy Monomers from VAN-M-CAT and Fatty Acid. Glycidylation of VAN-M-CAT with epichlorohydrin yields three products with different substitution of oxirane groups (Scheme 2). Proton, carbon, HMQC NMR spectra, and mass spectra of each product are illustrated in Figures S15-S21. Formation of epoxy groups is also confirmed using IR spectra. As seen in Figure 3, panel A, after VAN-M-CAT is glycidylated to GE-VAN-M-CAT, its broad hydroxyl band at 3401 cm⁻¹ decreases significantly, and it is accompanied by the presence of an epoxy ring band at 912 cm^{-1} and a C–O–C ether linkage at 1027 cm⁻¹. The catechol groups of VAN-M-CAT make it inevitable to cause side reactions like intramolecular cyclization between two adjacent oxiranes. Benzodioxane derivative can occur in either one or both catechols to form mono-epoxysubstituted (GE-VAN-M-CAT-1) or tri-epoxy-substituted (GE-VAN-M-CAT-3) products. From the viewpoint of functionality, the appearance of benzodioxane derivative is unfavorable since it is unreactive with amine hardener/cross-linker and is likely to create dangling chain ends that impair cross-linking in the resulting polymers.²⁸ However, if the penta-epoxy-substituted (GE-VAN-M-CAT-5) is the only glycidylation product, the formed network could be highly brittle due to the high rigidity and functionality (related to cross-link density) of VAN-M-CAT.²⁹ Therefore, from the viewpoint of processing and application, the presence of certain amount of benzodioxane byproducts is favorable since it helps adjust the rigidity of cured networks. As the major product, tri-epoxy-substituted product (55%) could effectively reduce the rigidity while still keep crosslinked within the network. Meanwhile, hydroxyl groups of Article

benzodioxane can also catalyze the reaction between monomer and cross-linker. $^{30\!,31}$

Introduction of flexible components is another way of adjusting rigidity. By esterifying VAN-M-CAT and linoleic acid, followed by epoxidation, a fully biobased epoxy monomer with rigid core and flexible branches was synthesized (VAN-LIN-EPO) as shown in Figure 4. Figure 5, panel A, exhibits the



Figure 4. Structure of fully biobased epoxy prepolymer VAN-LIN-EPO, which is synthesized via esterification between VAN-M-CAT and linoleic acid, and followed by epoxidation.

NMR spectra of linoleic acid. The peak at δ 5.4 corresponds to C=C double bonds, while peaks at δ 0.9–2.8 are related to the saturated part of the carbon chain. After linoleic acid is esterified with VAN-M-CAT to yield VAN-M-CAT-LIN (VAN-LIN), characteristic peaks of both linoleic acid and VAN-M-CAT (δ 6.5–6.9, aromatic H; δ 5.5, Ar₃–CH; δ 3.7, $-OCH_3$ and δ 2.0, $-CH_3$) are evident (Figure 5, panel B). To produce epoxy comonomer, VAN-LIN is epoxidized using peracetic acid to yield VAN-LIN-EPO. As seen in Figure 5, panel C, the double bond peak of VAN-LIN-EPO disappears while a new epoxy peak at δ 2.9 appears. As for the FTIR spectra of VAN-LIN in Figure 3, panel B, it reveals a C=C stretching vibration band at 3008 cm⁻¹ and an ester bond at 1764 cm⁻¹. When VAN-LIN is epoxidized with peracetic acid, the C=C band is gone while a new epoxy band at 912 cm^{-1} appears.



Figure 3. FTIR spectra of (A) VAN-M-CAT and its epoxidized product GE-VAN-M-CAT and (B) VAN-LIN and its epoxidized product VAN-LIN-EPO.



Figure 5. Proton NMR structure of (A) linoleic acid, (B) VAN-LIN, product of esterification between VAN-M-CAT and linoleoyl chloride and (C) epoxidized VAN-LIN (VAN-LIN-EPO). Solvent: CDCl₃.

Dynamic Mechanical Analysis (DMA). Cross-link density (ν_e) is a key parameter that determines performance of epoxy thermosets.³² ν_e can be reflected from α -relaxation temperature $(T_{\alpha}$, related to glass transition temperature) since increased covalent cross-links restricts the mobility of polymer segments, which leads to higher T_{α} . Inset of Figure 6 illustrates T_{α} of VAN₁₀₀LIN₀ (167 °C), VAN₇₅LIN₂₅ (111 °C), and VAN₅₀LIN₅₀ (82 °C), which gradually decreases as portion of VAN-LIN-EPO increases from 0 to 50 wt %. Even though GE-VAN-M-CAT mixture and VA-LIN-EPO are calculated to have



Figure 6. DMA curve of epoxy networks with different weight ratio of GE-VAN-M-CAT and VA-LIN-EPO as a function of temperature. VAN₇₅LIN₂₅, for example, represents epoxy network with 75 wt % GE-VAN-M-CAT and 25 wt % VAN-LIN-EPO in prepolymer mixture. Temperature at the maximum in tan δ curve is taken as T_{α} (related to glass transition).

similar epoxy equivalent value (531 and 539 mmol epoxy/100 g, respectively), the flexible nature of VAN-LIN-EPO remarkably decreases cross-linking density of the resulting polymer. On one hand, the saturated component of the carbon side chain introduces void volume and yields a network that deforms more readily.³³ On the other hand, closed looping could be formed by the hardener and epoxies of VAN-LIN-EPO in adjacent carbon chains, which limits the direction of the resulting network. The plasticizer role of VAN-LIN-EPO can also be reflected through height of tan δ , which is the ratio of loss to storage modulus. As seen in Figure 6, height of tan δ decreases from VAN₅₀LIN₅₀ to VAN₁₀₀LIN₀, suggesting lower segmental mobility and fewer relaxing species in VAN₁₀₀LIN₀.

Storage modulus (E') values are also presented in Figure 6. Without addition of VAN-LIN-EPO, VAN₁₀₀LIN₀ exhibits a high glassy E' of 12.3 GPa, which could be attributed to the high rigidity and functionality of GE-VAN-M-CAT mixture. Addition of flexible VAN-LIN-EPO comonomer effectively decreases the modulus, as E' of VAN₇₅LIN₂₅ and VAN₅₀LIN₅₀ decreases to 6.2 and 3.2 GPa, respectively. This confirms the plasticizer nature of VAN-LIN-EPO. It is noteworthy that T_{α} and E' of BPA diglycidyl ether (DGEBA)/DETA network were reported to be 137 °C and 3.6 GPa,³⁶ which are lower than those of GE-VAN-M-CAT/DETA. This finding highlights renewable TP-based epoxy networks possess marked mechanical performance to replace or supplement petroleum-based thermosets.

Thermogravimetric Analysis (TGA). Figure 7 exhibits a one-step degradation profile for all epoxy networks. Thermal



Figure 7. Thermogravimetric analysis thermograms of epoxy networks with different weight ratio of GE-VAN-M-CAT and VAN-LIN-EPO. VAN₇₅LIN₂₅, for example, represents epoxy network with 75 wt % GE-VAN-M-CAT and 25 wt % VAN-LIN-EPO in the prepolymer mixture.

stability of cured thermosets increases with cross-linking density. This can be reflected from the shift of onset degradation temperature (expressed as T_{d5} , temperature at 5% weight loss) from 220 °C of VAN₅₀LIN₅₀ to 245 and 269 °C of VAN₇₅LIN₂₅ and VAN₁₀₀LIN₀. As cross-linking density increases, polymer chains become more constrained, which causes lower molecular mobility during thermal expansion. Meanwhile, the tortuous pathway in highly cross-linked network postpones mass exchange. Statistic heat-resistant

index temperature (T_s) , which is calculated using T_{d5} and T_{d30} (temperature at 30% weight loss) (eq 1), reflects the thermal stability of cured networks.³⁷ Table 3 illustrates T_s increases

Table 3. Thermogravimetric Data of T_{d5} , T_{d30} (Temperature at 5% and 30% Weight Loss), T_s (Statistic Heat-Resistant Index Temperature), and Char₆₀₀ (Char Residue at 600 °C) of Epoxy Networks with Different Ratio of GE-VAN-M-CAT and VAN-LIN-EPO

epoxy networks	T_{d5} (°C)	$T_{\rm d30}~(^{\circ}{\rm C})$	$T_{\rm s}$ (°C)	Char ₆₀₀ (%)
VAN ₅₀ LIN ₅₀	220	317	136	14.0
VAN ₇₅ LIN ₂₅	245	313	140	14.9
VAN ₁₀₀ LIN ₀	269	318	146	17.3

slightly from VAN₅₀LIN₅₀ (136 °C) to VAN₇₅LIN₂₅ (140 °C) and VAN₁₀₀LIN₀ (146 °C), verifying the role of cross-linking density on thermal stability. Besides, Char₆₀₀ (char formed at 600 °C) of networks is also observed to increase from VAN₅₀LIN₅₀ to VAN₁₀₀LIN₀.

$$T_{\rm s} = 0.49[T_{\rm d5} + 0.6(T_{\rm d30} - T_{\rm d5})] \tag{1}$$

CONCLUSIONS

Synthetic routes to renewable triphenylmethane-type polyphenols were demonstrated, widening the applications of typical lignin-based para-substituted guaiacols. Ortho-demethylation of para-substituted guaiacols to give the corresponding catechols was key in providing new and highly reactive para sites, which effectively improves the reactivity for aldehyde coupling. Under optimized conditions, M-CAT and P-CAT based TPs are obtained in high to moderate yields in the range 71-88% and 33-42%, respectively. Steric effect and electrondonating group influence the conversions and yields of TPs. The proposed TPs have rigid triphenylmethane framework and high functionality (n = 5). These advantageous structural properties make renewable TPs excellent precursors to epoxy thermosets. As an example, VAN-M-CAT based network exhibits excellent glassy modulus (12.3 GPa) and glass transition temperature (167 °C), which is attributed to the high cross-linking density of the obtained network. To adjust the brittleness of above-mentioned network, a fully biobased plasticizer and copolymer based on linoleic acid (VAN-LIN-EPO) was employed and found to effectively tune the storage modulus. With the advantages of moderate to high yields excellent mechanical and thermal parameters, and tunable properties, the proposed renewable TP-based epoxy thermosets exhibit sufficient potential to replace or supplement petroleumbased materials.

ASSOCIATED CONTENT

S Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.macro-mol.7b00064.

¹H and ¹³C NMR, 2D HMQC, FTIR, HPLC, and mass spectra of all new compounds (PDF) X-ray structure of VAN-M-CAT (CIF)

AUTHOR INFORMATION

Corresponding Author

*E-mail abuomar@chem.ucsb.edu (M.M.A.-O.).

ORCID [©]

Mahdi M. Abu-Omar: 0000-0002-4412-1985

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

Financial support for this research was provided by the University of California, Santa Barbara, and the Mellichamp Academic Initiative in Sustainability. S.Z. thanks Yuan Jiang for mass spectrometry measurements. Shou Zhao is the recipient of a Mellichamp graduate fellowship.

ABBREVIATIONS

TP, triphenylmethane-type phenol; HBA, 4-hydroxybenzaldehyde; VAN, vanillin; SYA, syringaldehyde; M-GUA, 4methylguaiacol; P-GUA, 4-propylguaiacol; M-CAT, 4-methylcatechol; P-CAT, 4-propylcatechol; DETA, diethylenetriamine; LA, linoleic acid; HBA-M-CAT, TP prepared from HBA and M-CAT; VAN-M-CAT, TP prepared from VAN and M-CAT; SYA-M-CAT, TP prepared from SYA and M-CAT; HBA-P-CAT, TP prepared from HBA and P-CAT; VAN-P-CAT, TP prepared from VAN and P-CAT; SYA-P-CAT, TP prepared from SYA and P-CAT; GE-VAN-M-CAT, glycidylated ether of VAN-M-CAT; VAN-LIN, esterification product of VAN-M-CAT and LA; VAN-LIN-EPO, epoxidized VAN-LIN; VAN₁₀₀LIN₀, cured resin with weight ratio of GE-VAN-M-CAT to VAN-LIN-EPO (100:0); $VAN_{75}LIN_{25}$, cured resin with weight ratio of GE-VAN-M-CAT to VAN-LIN-EPO (75:25); VAN₅₀LIN₅₀, cured resin with weight ratio of GE-VAN-M-CAT to VAN-LIN-EPO (50:50).

REFERENCES

 Laurichesse, S.; Avérous, L. Chemical modification of lignins: Towards biobased polymers. *Prog. Polym. Sci.* 2014, 39, 1266–1290.
 Auvergne, R.; Caillol, S.; David, G.; Boutevin, B.; Pascault, J. P. Biobased thermosetting epoxy: present and future. *Chem. Rev.* 2014, 114, 1082–1115.

(3) Isikgor, F. H.; Becer, C. R. Lignocellulosic biomass: a sustainable platform for the production of bio-based chemicals and polymers. *Polym. Chem.* **2015**, *6*, 4497–4559.

(4) Wang, L.; Meng, Y. Z.; Wang, S. J.; Shang, X. Y.; Li, L.; Hay, A. S. Synthesis and sulfonation of poly(aryl ethers) containing triphenyl methane and tetraphenyl methane moieties from isocynate-masked bisphenols. *Macromolecules* **2004**, *37*, 3151–3158.

(5) Maiorana, A.; Spinella, S.; Gross, R. A. Bio-based alternative to the diglycidyl ether of bisphenol A with controlled materials properties. *Biomacromolecules* **2015**, *16*, 1021–1031.

(6) Schutyser, W.; Koelewijn, S. F.; Dusselier, M.; Van de Vyver, S.; Thomas, J.; Yu, F.; Carbone, M. J.; Smet, M.; Van Puyvelde, P.; Dehaen, W. Regioselective synthesis of renewable bisphenols from 2,3pentanedione and their application as plasticizers. *Green Chem.* **2014**, *16*, 1999–2007.

(7) Meylemans, H. A.; Groshens, T. J.; Harvey, B. G. Synthesis of renewable bisphenols from creosol. *ChemSusChem* 2012, *5*, 206–210.
(8) Zhang, L.; Zhu, Y.; Li, D.; Wang, M.; Chen, H.; Wu, J. Preparation and characterization of fully renewable polybenzoxazines from monomers containing multi-oxazine rings. *RSC Adv.* 2015, *5*, 96879–96887.

(9) Zhou, Z.; Parr, R. G. Activation hardness: new index for describing the orientation of electrophilic aromatic substitution. *J. Am. Chem. Soc.* **1990**, *112*, 5720–5724.

(10) Hernandez, E. D.; Bassett, A. W.; Sadler, J. M.; La Scala, J. J.; Stanzione, J. F., III Synthesis and characterization of bio–based epoxy resins derived from vanillyl alcohol. *ACS Sustainable Chem. Eng.* **2016**, *4*, 4328–4339. (11) Xu, J.; Jiang, J.; Hse, C.; Shupe, T. F. Renewable chemical feedstocks from integrated liquefaction processing of lignocellulosic materials using microwave energy. *Green Chem.* **2012**, *14*, 2821–2830. (12) Liu, W. J.; Jiang, H.; Yu, H. Q. Thermochemical conversion of lignin to functional materials: a review and future directions. *Green Chem.* **2015**, *17*, 4888–4907.

(13) Zhao, S.; Abu-Omar, M. M. Renewable epoxy networks derived from lignin-based monomers: effect of cross-linking density. ACS Sustainable Chem. Eng. 2016, 4, 6082-6089.

(14) Chung, H.; Washburn, N. R. Improved lignin polyurethane properties with Lewis acid treatment. *ACS Appl. Mater. Interfaces* **2012**, *4*, 2840–2846.

(15) Zhao, S.; Abu-Omar, M. M. Biobased epoxy nanocomposites derived from lignin-based monomers. *Biomacromolecules* **2015**, *16*, 2025–2031.

(16) Putz, K. W.; Palmeri, M. J.; Cohn, R. B.; Andrews, R.; Brinson, L. C. Effect of cross–link density on interphase creation in polymer nanocomposites. *Macromolecules* **2008**, *41*, 6752–6756.

(17) Pan, X.; Sengupta, P.; Webster, D. C. High biobased content epoxy-anhydride thermosets from epoxidized sucrose esters of fatty acids. *Biomacromolecules* **2011**, *12*, 2416–2428.

(18) Stärk, K.; Taccardi, N.; Bösmann, A.; Wasserscheid, P. Oxidative depolymerization of lignin in ionic liquids. *ChemSusChem* **2010**, *3*, 719–723.

(19) Mialon, L.; Pemba, A. G.; Miller, S. A. Biorenewable polyethylene terephthalate mimics derived from lignin and acetic acid. *Green Chem.* **2010**, *12*, 1704–1706.

(20) Xu, W.; Miller, S. J.; Agrawal, P. K.; Jones, C. W. Depolymerization and hydrodeoxygenation of switchgrass lignin with formic acid. *ChemSusChem* **2012**, *5*, 667–675.

(21) Parsell, T. H.; Owen, B. C.; Klein, I.; Jarrell, T. M.; Marcum, C. L.; Haupert, L. J.; Amundson, L. M.; Kenttämaa, H. I.; Ribeiro, F.; Miller, J. T.; Abu–Omar, M. M. Cleavage and hydrodeoxygenation (HDO) of C–O bonds relevant to lignin conversion using Pd/Zn synergistic catalysis. *Chem. Sci.* **2013**, *4*, 806–813.

(22) Xia, Y.; Larock, R. C. Vegetable oil-based polymeric materials: synthesis, properties, and applications. *Green Chem.* **2010**, *12*, 1893–1909.

(23) Miyagawa, H.; Misra, M.; Drzal, L. T.; Mohanty, A. K. Novel biobased nanocomposites from functionalized vegetable oil and organically-modified layered silicate clay. *Polymer* **2005**, *46*, 445–453.

(24) Meier, M. A. R.; Metzger, J. O.; Schubert, U. S. Plant oil renewable resources as green alternatives in polymer science. *Chem. Soc. Rev.* 2007, *36*, 1788–1802.

(25) Pleissner, D.; Lau, K. Y.; Zhang, C.; Lin, C. S. K. Plasticizer and surfactant formation from food-waste- and Algal biomass-derived lipids. *ChemSusChem* **2015**, *8*, 1686–1691.

(26) Wu, H.; Kelley, C. J.; Pino-Figueroa, A.; Vu, H. D.; Maher, T. J. Macamides and their synthetic analogs: evaluation of in vitro FAAH inhibition. *Bioorg. Med. Chem.* **2013**, *21*, 5188–5197.

(27) Laurichesse, S.; Huillet, C.; Avérous, L. Original polyols based on organosolv lignin and fatty acids: new bio–based building blocks for segmented polyurethane synthesis. *Green Chem.* **2014**, *16*, 3958– 3970.

(28) Nouailhas, H.; Aouf, C.; Le Guerneve, C.; Caillol, S.; Boutevin, B.; Fulcrand, H. Synthesis and properties of biobased epoxy resins. Part 1. Glycidylation of flavonoids by epichlorohydrin. *J. Polym. Sci., Part A: Polym. Chem.* **2011**, *49*, 2261–2270.

(29) Thompson, Z. J.; Hillmyer, M. A.; Liu, J.; Sue, H. J.; Dettloff, M.; Bates, F. S. Block copolymer toughened epoxy: role of cross-link density. *Macromolecules* **2009**, *42*, 2333–2335.

(30) Cole, K. C. A new approach to modeling the cure kinetics of epoxy/amine thermosetting resins. 1. Mathematical development. *Macromolecules* **1991**, *24*, 3093–3097.

(31) Mezzenga, R.; Boogh, L.; Månson, J. A. E.; Pettersson, B. Effects of the branching architecture on the reactivity of epoxy–amine groups. *Macromolecules* **2000**, *33*, 4373–4379.

(32) Wu, S.; Guo, Q.; Kraska, M.; Stühn, B.; Mai, Y. W. Toughening epoxy thermosets with block ionomers: the role of phase domain size. *Macromolecules* **2013**, *46*, 8190–8202.

(33) de Espinosa, L. M.; Ronda, J. C.; Galià, M.; Cádiz, V. A new route to acrylate oils: crosslinking and properties of acrylate triglycerides from high oleic sunflower oil. *J. Polym. Sci., Part A: Polym. Chem.* **2009**, *47*, 1159–1167.

(34) Pan, Y.; Xu, Y.; An, L.; Lu, H.; Yang, Y.; Chen, W.; Nutt, S. Hybrid network structure and mechanical properties of rodlike silicate/cyanate ester nanocomposites. *Macromolecules* **2008**, *41*, 9245–9258.

(35) Gu, H.; Tadakamalla, S.; Zhang, X.; Huang, Y.; Jiang, Y.; Colorado, H. A.; Luo, Z.; Wei, S.; Guo, Z. Epoxy resin nanosuspensions and reinforced nanocomposites from polyaniline stabilized multi-walled carbon nanotubes. *J. Mater. Chem. C* **2013**, *1*, 729– 743.

(36) Garcia, F. G.; Soares, B. G.; Pita, V. J. R. R.; Sánchez, R.; Rieumont, J. Mechanical properties of epoxy networks based on DGEBA and aliphatic amines. *J. Appl. Polym. Sci.* **2007**, *106*, 2047–2055.

(37) Chiu, Y. C.; Tsai, H. C.; Imae, T. Thermal degradation analysis of the isocyanate polyhedral oligomeric silsequioxanes (POSS)/ sulfone epoxy nanocomposite. *J. Appl. Polym. Sci.* **2012**, *124*, 1234–1240.