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(54) Title: NOVEL BIO-BASED DIOLS FROM SUSTAINABLE RAW MATERIALS, USES THEREOF TO MAKE DIGLYCIDYL ETHERS, AND THEIR COATINGS

(57) Abstract: The invention relates to diols derived from 5-hydroxymethyl furfural, diformyl furan, or derivatives thereof. The invention further relates to diglycidyl ethers derived from the diols of the invention, curable coating compositions containing the diglycidyl ethers, and objects coated with the curable coating compositions. The invention also relates to composites, composites, adhesives, and films containing the diglycidyl ethers of the invention. The invention also relates to methods of making the diols, diglycidyl ethers, and curable coating compositions.

Novel Bio-based Diols From Sustainable Raw Materials, Uses Thereof to Make Diglycidyl Ethers, and Their Coatings

Dean C. Webster, Mukund P. Sibi, Catherine Sutton, Deep J. Kalita, and Eric M. Serum

Cross-Reference to Related Application

[0001] This application claims priority to U.S. Application No. 62/871,387, filed July 8, 2019, which is incorporated herein by reference.

Statement of U.S. Government Support

[0002] This invention was made with government support under grant IIA-1355466 awarded by the National Science Foundation. The U.S. government has certain rights in the invention.

Background

[0003] The development of green chemical methods for the synthesis of novel monomers for polymer applications has received intense scrutiny in the past two decades. Furthermore, the use of bio-based feedstocks for monomer synthesis has become important due to the projected depletion of fossil fuels in the near future [Kucherov et al., *ACS Sustainable Chemistry & Engineering* **2018**, 6(7):8064-8092; Isikgor et al., *Polymer Chemistry* **2015**, 6(25):4497-4559; Delidovich et al., *Chemical Reviews* **2016**, 116(3):1540-1599; Mülhaupt et al., *Macromolecular Chemistry and Physics* **2013**, 214(2):159-174; Galbis et al., *Chemical Reviews* **2016**, 116(3):1600-1636]. Diols serve as important monomers for the synthesis of a variety of polymers such as polyesters and polyurethanes. Currently, most of the diols used in polymer applications are derived from petroleum.

[0004] Of the three important sources of biomass, cellulosic biomass provides access to compounds with a furan skeleton. Two compounds derived from cellulose, 5-hydroxymethyl furfural (HMF) [Yu et al., *Bioresource Technology* **2017**, 238:716-732; van Putten et al., *Chemical Reviews* **2013**, 113(3):1499-1597] and 2,5-furandicarboxylic acid (FDCA) [Jong et al., Furandicarboxylic Acid (FDCA), A Versatile Building Block for a Very Interesting Class of Polyesters. In *Biobased Monomers, Polymers, and Materials*, American Chemical Society: 2012;

Vol. 1105, pp 1-13; Sousa et al., *Polymer Chemistry* **2015**, 6(33):5961-5983], have been identified as the top feedstock compounds for monomer synthesis. HMF has two functional groups at different oxidation states that can be selectively manipulated to provide access to other furan-based monomers. Diformylfuran (DFF) is readily available by selective oxidation of HMF.

[0005] The diols are useful monomers in the synthesis of a variety of polymers [Mou et al., *ACS Sustainable Chem. Eng.* **2016**, 4(12):7118-7129]. For example, they are used extensively in the synthesis of polyesters [Li et al., *J. Polym. Sci., Part A: Polym. Chem.* **2018**, 56:968-976]. Also, the glycidyl ethers derived from diols can be cured with diamines to furnish epoxies. The different diols currently used extensively in polymer synthesis are (1) aliphatic diols, (2) bisphenols, and (3) mixed diols. In contrast, the use of diol monomers derived from cellulosic biomass with a furan skeleton has received only limited attention.

Summary of the Invention

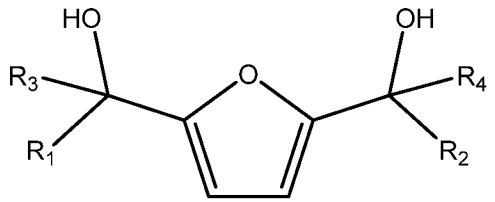
[0006] The invention relates to novel diols derived from 5-hydroxymethyl furfural (HMF), diformyl furan (DFF), or derivatives thereof. The invention also relates to the synthesis of the diols.

[0007] The invention further relates to diglycidyl ethers derived from the diols of the invention. The invention also relates to the synthesis of the diglycidyl ethers. The invention also relates to composites and adhesives containing the diglycidyl ethers.

[0008] The invention further relates to curable coating compositions containing the diglycidyl ethers with amine curing agents, and object coating with the curable coating compositions.

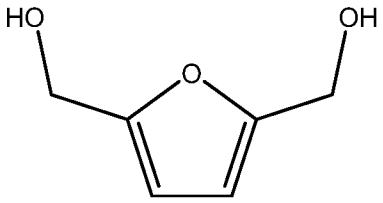
Detailed Description of the Invention

[0009] The invention relates to a diol having the following structure:



wherein R_1, R_2, R_3, and R_4 are independently selected from the group consisting of H, C_1-C_6 alkyl, C_1-C_6 alkenyl, aryl, and C_1-C_6 alkyl-aryl,

with the proviso that the diol cannot have the following structure:



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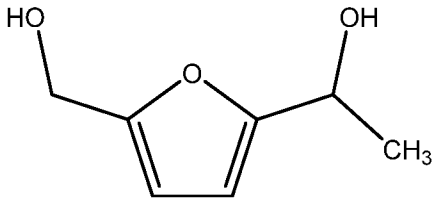

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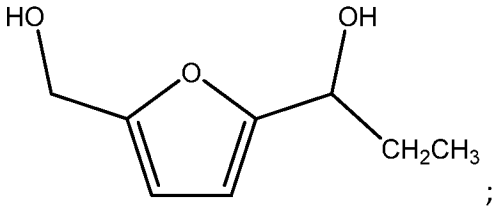

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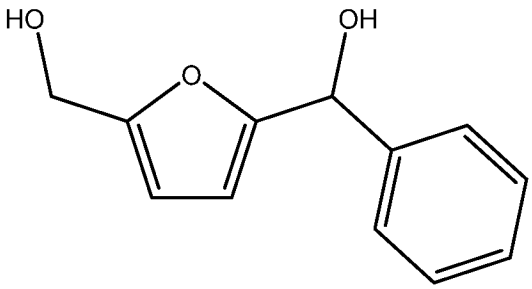

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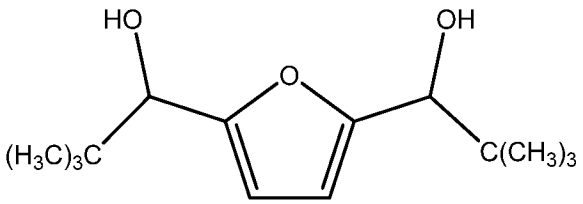

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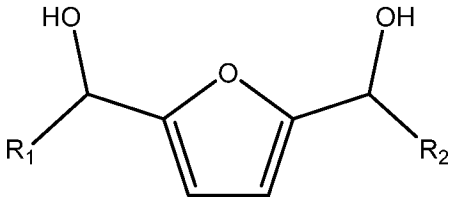
[00010] As used herein, the term "alkyl" refers to a linear, branched, saturated hydrocarbon group, such as methyl, ethyl, n-propyl, iso-propyl, n-butyl, iso-butyl, tert-butyl, pentyl, hexyl, and the like.

[00011] As used herein, the term "alkenyl" refers to a linear, branched hydrocarbon group containing at least one double bond, such as ethenyl, n-propenyl, iso-propenyl, n-butenyl, iso-butenyl, pentenyl, hexenyl, and the like.

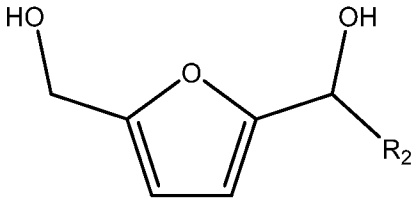
[00012] As used herein, the term "aryl" refers to an aromatic substituent containing a single aromatic ring or multiple aromatic rings that are fused together, directly linked, or indirectly linked (such that the different aromatic rings are bound to a common group such as a methylene or ethylene moiety). Preferred aryl groups contain 5 to 24 carbon atoms, and particularly preferred aryl groups contain 6 to 10 carbon atoms. Exemplary aryl groups contain one aromatic ring or two fused or linked aromatic rings, e.g., phenyl (Ph), naphthyl, biphenyl, diphenylether, diphenylamine, benzophenone, phenanthryl, and the like.

[00013] The diol preferably has the following structure:



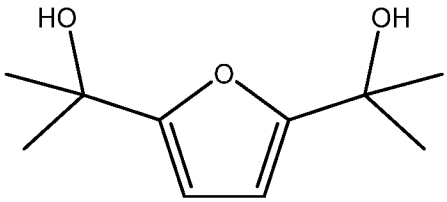
, wherein R_1 and R_2 are as defined above. Preferably, R_1 and R_2 are both methyl, ethyl, n-butyl, c-pentyl, allyl, or benzyl.

[00014] The diol also preferably has the following structure:



, wherein R_2 is as defined above. Preferably, R_2 is n-butyl, t-butyl, c-pentyl, allyl, or benzyl.

[00015] The diol also preferably has the following structure:



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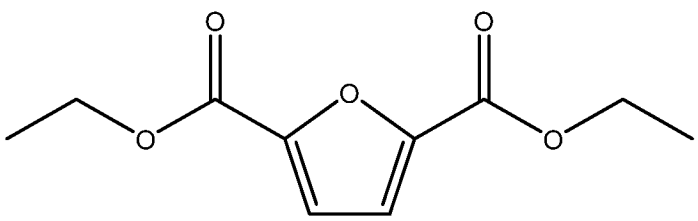
[00016] The invention also relates to a method of making the diols of the invention, comprising, consisting essentially of, or consisting of:

reacting 5-hydroxymethyl furfural (HMF), diformyl furan (DFF), or a derivative thereof with a Grignard reagent,

under conditions sufficient to form the diol.

[00017] Preferably, the Grignard reagent is RMgCl, wherein R is H, C_1-C_6 alkyl, C_1-C_6 alkenyl, aryl, or C_1-C_6 alkyl-aryl.

[00018] Preferably, the derivative used in the method of making the diols of the invention has the following structure:



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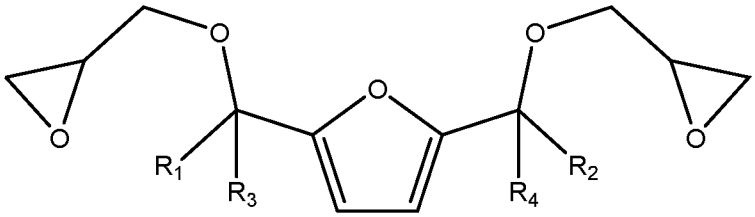
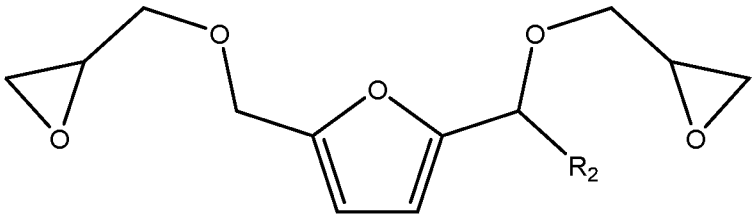
[00019] The invention also relates to a diglycidyl ether having the following structure:



wherein R_1, R_2, R_3, and R_4 are independently selected from the group consisting of H, C_1-C_6 alkyl, C_1-C_6 alkenyl, aryl, and C_1-C_6 alkyl-aryl,

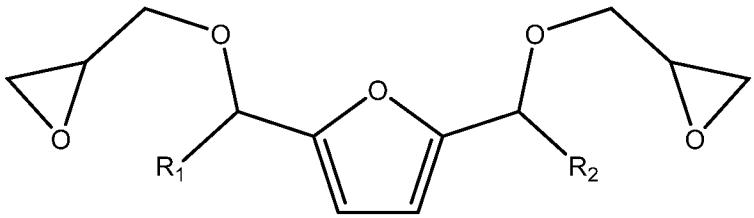
with the proviso that R_1, R_2, R_3, and R_4 cannot all be H.

[00020] Preferably, the diglycidyl ethers have the following structure:



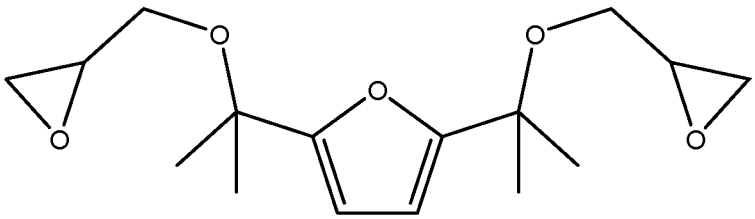
, wherein R_2 is as defined above. Preferably, R_2 is methyl or phenyl.

[00021] Preferably, the diglycidyl ethers also have the following structure:



, wherein R_1 and R_2 are as defined above. Preferably, R_1 and R_2 are both methyl, n-butyl, or allyl.

[00022] Preferably, the diglycidyl ether also has following structure:



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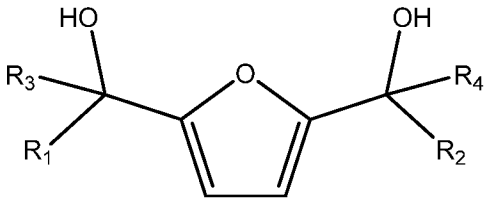
[00023] The invention also relates to a method for making the diglycidyl ethers of the invention comprising, consisting essentially of, or consisting of:

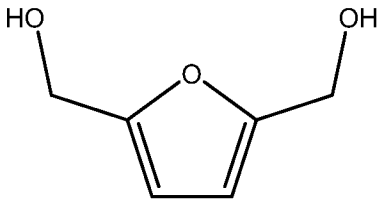
reacting a diol with epichlorohydrin under conditions sufficient to form the diglycidyl ether,

wherein the diol has the following structure:



wherein R_1, R_2, R_3, and R_4 are independently selected from the group consisting of H, C_1-C_6 alkyl, C_1-C_6 alkenyl, aryl, and C_1-C_6 alkyl-aryl.

[00024] Preferably, the diols used in the methods for making the diglycidyl ethers of the invention cannot have the following structure:



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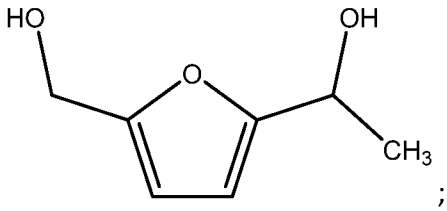

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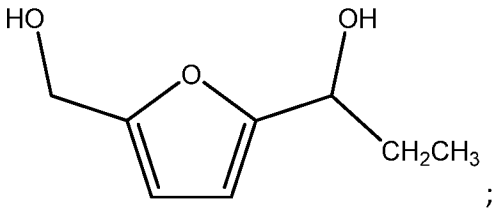

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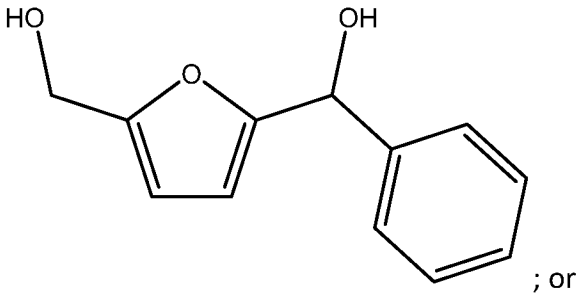

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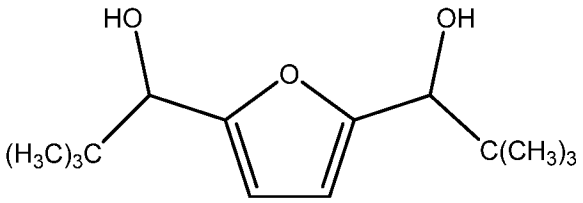

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[00025] The invention also relates to a coating, composite, adhesive, or film comprising, consisting essentially of, or consisting of at least one diglycidyl ether of the invention.

[00026] The invention further relates to a curable coating composition comprising, consisting essentially of, or consisting of:

a) at least one diglycidyl ether of the invention; and

b) an amine.

[00027] Preferably, the amine is an aliphatic, an aromatic, a cycloaliphatic, or a polyether amine. For example, the aliphatic amine may be Priamine 1075, 1,8-diaminooctane, diethylenetriamine, or tetraethylenepentamine; the aromatic amine may be m-xylylenediamine; the cycloaliphatic amine may be 1,3-bis(aminomethyl)cyclohexane, isophorone diamine, or bis(p-aminocyclohexyl) methane; and the polyether amine may be JEFFAMINE EDR-148 (XTJ-504), JEFFAMINE D-400, JEFFAMINE D-230, or JEFFAMINE T-403.

[00028] The curable coating compositions of the invention may be coated onto a substrate and cured using techniques known in the art. The substrate can be any common substrate such as paper, polyester films such as polyethylene and polypropylene, metals such as aluminum and steel, glass, urethane elastomers, primed (painted) substrates, and the like.

[00029] Pigments and other additives known in the art to control coating rheology and surface properties can also be incorporated in a curable coating composition of the invention. For example, a curable coating composition of the invention may further contain coating additives. Such coating additives include, but are not limited to, one or more leveling, rheology, and flow control agents such as silicones, fluorocarbons, or cellulosics; extenders; reactive coalescing aids such as those described in U.S. Pat. No. 5,349,026, incorporated herein by reference; plasticizers; flatting agents; pigment wetting and dispersing agents and surfactants; ultraviolet (UV) absorbers; UV light stabilizers; tinting pigments; colorants; defoaming and antifoaming agents; anti-settling, anti-sag and bodying agents; anti-skinning agents; anti-flooding and anti-floating agents; biocides, fungicides and mildewcides; corrosion inhibitors; thickening agents; or coalescing agents. Specific examples of such additives can be found in Raw Materials Index, published by the National Paint & Coatings Association, 1500 Rhode Island Avenue, N.W., Washington, D.C. 20005. Further examples of such additives may be found in U.S. Pat. No. 5,371,148, incorporated herein by reference.

[00030] Solvents may also be added to the curable coating formulation in order to reduce the viscosity. Hydrocarbon, ester, ketone, ether, ether-ester, alcohol, or ether-alcohol type solvents may be used individually or in mixtures. Examples of solvents can include, but are not limited to, benzene, toluene, xylene, aromatic 100, aromatic 150, acetone, methylethyl ketone, methyl amyl

ketone, butyl acetate, t-butyl acetate, tetrahydrofuran, diethyl ether, ethylethoxy propionate, isopropanol, butanol, butoxyethanol, etc.

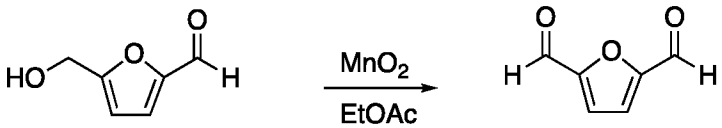
[00031] The invention further relates to a cured coating composition, wherein the curable coating composition of the invention is cured at ambient conditions or by heating.

[00032] The invention also relates to an object coated with the curable coating composition of the invention.

[00033] Examples:

[00034] ***Materials***

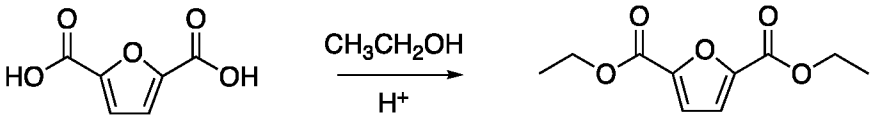
[00035] Commercially available HMF was purified by column chromatography or by dissolving it in diethyl ether and drying with anhydrous sodium sulfate and decolorizing with Norrit A. The compound was stored in a freezer prior to use. Diformylfuran (**2**) was synthesized by oxidation of pure HMF with manganese dioxide and ethyl acetate as a solvent (**Scheme 1**). The product was recrystallized from iso-propanol before use.



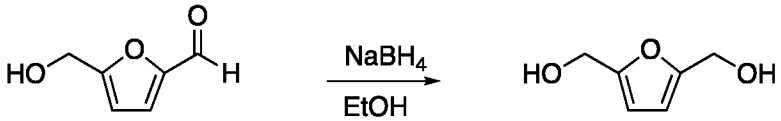
1 HMF **2 DFF**

Scheme 1. Synthesis of diformylfuran

[00036] Fischer esterification of 2,5-furandicarboxylic acid (FDCA) **3** with ethanol provided the diethyl ester **4** in high yield. The diol, 2,5-bihydroxymethylfuran (**5**) was synthesized by sodium borohydride reduction of HMF **1** in ethanol (**Scheme 2**) [Li et al., *ACS Sustainable Chem. Eng.* **2017**, 5(12):11752-11760; Vijjamarri et al., *ACS Sustainable Chem. Eng.* **2018**, 6(2):2491-2497].



3 FDCA **4 FDCA-Et Ester**



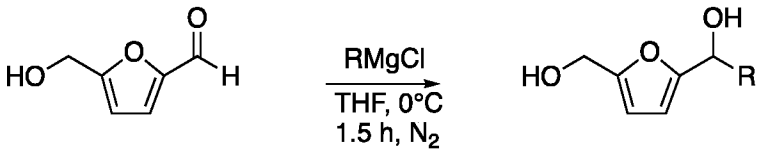
1 HMF **5 Diol**

Scheme 2. Synthesis of starting materials

[00037] *Synthesis of symmetric and unsymmetrical diols*

[00038] The formyl group in HMF was converted to a secondary alcohol by the addition of a Grignard reagent. Several variables such as solvent, temperature, stoichiometry and counterion of the Grignard reagent were investigated for obtaining the product diols in high purity and yield. **Table 1** lists isolated yields for the unsymmetrical diol **6**. The table also lists the physical state of the diol. As can be discerned from the table, the diols are obtained in excellent yield from the Grignard addition. Also, most of the compounds have not been reported previously (References are given for known compounds in **Table 1**). The product diols were extensively characterized by spectroscopic techniques. The synthesis of diols from HMF is shown **Scheme 3** ("R" defined in **Table 1**).

[00039] Typical experimental procedure: A reaction vessel containing solution of purchased Grignard reagent (6.6 mmol, diluted from 1.0 -3.4 M to a 0.5 M solution in inhibitor-free drysolv THF) was flushed with N_2 and kept under positive N_2 pressure. A solution of HMF (3 mmol) dissolved to form a 0.2 M solution in inhibitor-free drysolv THF) was added dropwise via syringe into the dry 50 mL round bottom flask reaction vessel. The reaction was monitored by TLC, until the reaction was complete (1-2 h). To quench the reaction, 6 mL of 0.1 M trisodium citrate (aq) was added via syringe. The reaction mixture was filtered through filter paper, then the THF was removed *in vacuo*. The resulting oil was then diluted with ethyl acetate (40 mL) and washed with brine (10 mL x 3) in a 60 mL separatory funnel. The organic layer was dried over sodium sulfate, then filtered and solvent removed *in vacuo* to obtain the product.



1 HMF **6**

Scheme 3. Synthesis of unsymmetrical diols from HMF

Table 1. Synthesis of unsymmetrical Diols from HMF: Yield and Physical State

Entry	R	Yield (%)	State	Reference
1	Methyl (**6a**)	77	liquid	Finiels, A. et al., Studies in Surface Science and Catalysis, 135(Zeolites and Mesoporous Materials at the Dawn of the 21st Century), 3612-3619; 2001
2	Ethyl (**6b**)	91	liquid	Nishimura, Shun; Ebitani, Koki, Jpn. Kokai Tokkyo Koho (2018), JP 2018193353 A 20181206. -
3	n-Butyl (**6c**)	94	liquid	-
4	t-Butyl (**6d**)	95	liquid	
5	c-Pentyl (**6e**)	78	liquid	-
6	Allyl (**6f**)	88	liquid	
7	Phenyl (**6g**)	87	solid	Rajmohan, Rajamani et al., RSC Advances, 5(121), 100401-100407; 2015
8	Benzyl (**6h**)	80	liquid	-

HMF Based Diols

Compound 6a: ^{1}H (400 MHz, $CDCl_3$) δ 6.20 (d, *J* = 3.2 Hz, 1H), 6.15 (d, *J* = 3.1 Hz, 1H), 4.83 (q, *J* = 6.6 Hz, 1H), 4.54 (s, 2H), 3.01 (s, 2H), 1.51 (d, 6.6 Hz, 3H); ^{13}C (101 MHz, $CDCl_3$) δ 157.5, 153.3, 108.2, 105.8, 63.3, 57.1, 21.0. FTIR (neat) cm^{-1} 3316, 2979, 2932, 1635, 1557, 1369, 1320,1239, 1187, 1072. HRMS calculated for $C_7H_{10}O_3Na$: 165.0528; Found: 165.0537.

Compound 6b: ^{1}H (400 MHz, $CDCl_3$) δ 6.17 (d, *J* = 3.2 Hz, 1H), 6.13 (d, *J* = 2.8 Hz, 1H), 4.50 (s, 3H), 3.46 (s, 1H), 3.29 (s, 1H), 1.94 – 1.75 (m, 2H), 0.93 (t, *J* = 7.4 Hz, 3H); ^{13}C (101 MHz, $CDCl_3$) δ 156.5, 153.3, 108.7, 106.5, 69.0, 57.0, 28.3, 10.0. FTIR (neat) cm^{-1} 3304, 2965, 2933, 2876, 1556, 1378,

1318, 1242, 1183, 960. HRMS calculated for $C_8H_{12}O_3Na$: 179.0684; Found: 179.0730.

Compound 6c: ^1H (400 MHz, $CDCl_3$) δ 6.20 (d, *J* = 3.1 Hz, 1H), 6.15 (d, J = 3 Hz, 1H), 4.61 (t, *J* = 6.9 Hz, 1H), 4.53 (s, 2H), 2.93 (s, 1H), 2.82 (s, 1H), 1.83 (dtd, *J* = 8.0, 6.3, 1.2 Hz, 2H), 1.42 – 1.30(m, 4H), 0.91 (t, *J* = 7.0 Hz, 3H); ^{13}C (101 MHz, $CDCl_3$) δ156.9, 153.3, 108.2, 106.4, 67.6, 57.2, 35.0, 27.7, 22.4, 14.0. FTIR (neat) cm^{-1} 3315, 2955, 2931, 2861, 1724, 1559, 1457, 1377, 1243, 1182. HRMS calculated for $C_{10}H_{16}O_3Na$: 207.0997; Found: 207.0982.

Compound 6d: ^1H (400 MHz, $CDCl_3$) δ 6.24 (d, *J* = 3.1 Hz, 1H), 6.17 (d, *J* = 3.1 Hz, 1H), 4.57 (s, 2H), 4.35 (s, 1H), 2.25 (s, 2H), 0.98 (s, 9H); ^{13}C (101 MHz, $CDCl_3$) δ 155.7, 152.8, 108.2, 107.8, 76.4, 57.4, 35.7, 25.8. FTIR (neat) cm^{-1} 3396, 2955, 2870, 1723, 1552, 1479, 1464, 1394, 1364, 1197. HRMS calculated for $C_{10}H_{16}O_3Na$: 207.0997; Found: 207.0997

Compound 6e: ^1H (400 MHz, $CDCl_3$) δ 6.19 (d, *J* = 3.1 Hz, 1H), 6.15 (d, *J* = 3.1 Hz, 1H), 4.53 (s, 2H), 4.37 (d, *J* = 8.6 Hz, 1H), 2.85 (s, 1H), 2.74 (s, 1H), 2.37 (q, *J* = 8.1 Hz, 1H), 1.90 – 1.84 (m, 1H), 1.66-1.47 (m, 6H), 1.25 – 1.18 (m, 1H); ^{13}C (101 MHz, $CDCl_3$) δ 156.7,153.2, 108.2, 106.9, 71.8, 57.3, 44.4, 29.2, 25.5. FTIR (neat) cm^{-1} 3327, 2949, 2867, 1704, 1559, 1449, 1362, 1311, 1885, 931. HRMS calculated for $C_{11}H_{16}O_3$ Na: 219.0997; Found: 219.0999.

Compound 6f: ^1H (400 MHz, $CDCl_3$) δ 6.19 (d, *J* = 3.2 Hz, 1H), 6.16 (d, *J* = 3.2 Hz, 1H), 5.80 (td, *J* = 17.2, 7.0 Hz, 1H), 5.18 – 5.11 (m, 2H), 4.67 (t, *J* = 6.5 Hz, 1H), 4.51 (s, 2H), 3.26 (s, 1H), 3.20 (s, 1H), 2.59 (t, *J* = 7.2 Hz, 2H); ^{13}C (101 MHz, $CDCl_3$) δ156.0, 153.4, 133.8, 118.3, 108.3, 106.8, 66.9, 57.2, 39.8. FTIR (neat) cm^{-1} 3320, 2923, 1641, 1557, 1416, 1316, 1182, 916, 860, 793. HRMS calculated for $C_9H_{12}O_3Na$: 191.0684; Found: 191.0721.

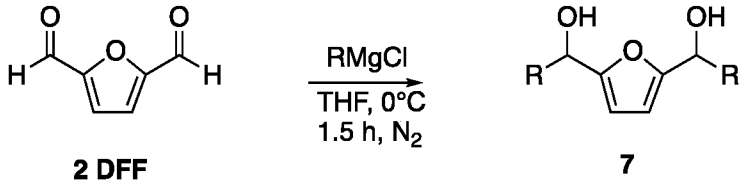
Compound 6g: ^1H NMR (400 MHz, DMSO-d6) δ 7.41 (dd, *J* = 8.3, 1.3 Hz, 2H), 7.37 – 7.32 (m, 2H), 7.30 – 7.24 (m, 1H), 6.18 (d, *J* = 3.1 Hz, 1H), 6.04 (d, *J* = 3.1 Hz, 1H), 5.96 (d, *J* = 5.0 Hz, 1H), 5.65 (d, *J* = 5.0 Hz, 1H), 5.15 (t, *J* = 5.7 Hz, 1H), 4.33 (d, *J* = 5.7 Hz, 2H); ^{13}C NMR (101 MHz, DMSO-d6) δ 157.1, 155.1, 143.1, 128.4, 127.6, 127.0, 107.8, 107.3, 68.9, 56.1. FTIR (neat) cm^{-1} 3242, 2881,

1601, 1555, 1491, 1452, 1291, 1263, 1193, 1008. HRMS calculated for $C_{12}H_{12}O_3Na$: 227.0684; Found: 227.0686.

Compound 6h: ^1H NMR (400 MHz, $CDCl_3$) δ 7.31 – 7.17 (m, 5H), 6.17 (d, *J* = 3.1 Hz, 1H), 6.12 (d, *J* = 3.1 Hz, 1H), 4.84 (dd, *J* = 7.9, 5.9 Hz, 1H), 4.51 (s, 2H), 3.31 (s, 1H), 3.13 (qd, *J* = 13.7, 6.9 Hz, 2H), 2.76 (s, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.7, 153.4, 137.5, 129.4, 128.4, 126.6, 108.4, 107.1, 68.6, 57.2, 42.0. FTIR (neat) cm^{-1} 3379, 3027, 2922, 1702, 1602, 1495, 1453, 1416, 1360, 1221. HRMS calculated for $C_{13}H_{14}O_3Na$: 241.0841; Found: 241.0839.

[00040] Reaction of DFF **2** with excess Grignard reagent gave access to diols **7** (**Scheme 4**) ("R" defined in **Table 2**). **Table 2** lists the isolated yield of the symmetric diols. As can be seen from the table, the diols are produced in high yields and all of them are liquids. Another noteworthy feature of the diols is that most of them are new compounds. The diols are produced as a mixture of meso and DL products. The products were extensively characterized by spectroscopic techniques. No attempt was made to ascribe chemical shifts to meso and DL products.

[00041] Typical experimental procedure: A reaction vessel containing solution of purchased Grignard reagent (6.6 mmol, diluted from 1.0 -3.4 M to a 0.5 M solution in inhibitor-free drysolv THF) was flushed with N_2 and kept under positive N_2 pressure. A solution of DFF (3 mmol) dissolved to form a 0.2 M solution in inhibitor-free drysolv THF) was added dropwise via syringe into the dry 50 mL round bottom flask reaction vessel. The reaction was monitored by TLC, until the reaction was complete (1-2 h). To quench the reaction, 6 mL of 0.1 M trisodium citrate (aq) was added via syringe. The reaction mixture was filtered through filter paper, then the THF was removed *in vacuo*. The resulting oil was then diluted with ethyl acetate (40 mL) and washed with brine (10 mL x 3) in a 60 mL separatory funnel. The organic layer was dried over sodium sulfate, then filtered and solvent removed *in vacuo* to obtain the product.



2 DFF **7**

Scheme 4. Synthesis of symmetrical diols from DFF

Table 2. Synthesis of symmetrical diols from DFF: Yield and Physical State

Entry	R	Yield (%)	State	Reference
1	Methyl (**7a**)	98	liquid	-
2	Ethyl (**7b**)	95	liquid	-
3	n-Butyl (**7c**)	90	liquid	-
4	t-Butyl (**7d**)	94	liquid	Fuentes, Jose A. et al., Chemistry Central Journal (2012), 6, 151.
5	c-Pentyl (**7e**)	95	liquid	-
6	Allyl (**7f**)	80	liquid	-
7	Benzyl (**7g**)	83	liquid	-

DFF-based Diols

Compound 7a: ^{1}H (400 MHz, $CDCl_3$) δ 6.15 (d, *J* = 1.3 Hz, 2H), 4.84 (q, *J* = 6.6 Hz, 2H), 2.79 (s, 2H), 1.52 (d, *J* = 6.6 Hz, 6H); ^{13}C (101 MHz, $CDCl_3$) δ 156.9, 105.6, 63.5, 21.0. FTIR (neat) cm^{-1} 3391, 2980, 2934, 1764, 1702, 1446, 1370, 1302, 1238, 1192. HRMS calculated for $C_8H_{12}O_3Na$: 179.0684; Found: 179.0713.

Compound 7b: ^{1}H (400 MHz, $CDCl_3$) δ 6.13 (s, 2H), 4.51 (t, *J* = 6.8 Hz, 2H), 2.94 (s, 2H), 1.86 – 1.79 (h, 7.2 Hz, 4H), 0.93 (t, *J* = 7.4 Hz, 6H); ^{13}C (101 MHz, $CDCl_3$) δ 195.9, 106.3, 69.0, 28.4, 9.9. FTIR (neat) cm^{-1} 3316, 2964, 2934, 2876, 1557, 1456, 1377, 1315, 1187, 1094. HRMS calculated for $C_{10}H_{16}O_3Na$: 207.0997; Found: 207.1007.

Compound 7c: ^{1}H (400 MHz, $CDCl_3$) δ 6.19 (d, *J* = 3.1 Hz, 1H), 6.14 (d, *J* = 3.1 Hz, 1H), 4.60 (t, *J* = 6.9 Hz, 2H), 2.96 (s, 2H), 1.83 (q, *J* = 7.4 Hz, 4H), 1.44 – 1.29 (m, 8H), 0.91 (t, *J* = 7.0 Hz, 6H); ^{13}C (101 MHz, $CDCl_3$) δ 156.0, 106.1, 67.4, 36.9, 27.7, 22.4, 13.9. FTIR (neat) cm^{-1} 3337, 2955, 2930, 2860, 1725, 1557, 1457, 1376, 1242, 1104. HRMS calculated for $C_{14}H_{24}O_3Na$: 263.1623; Found: 263.1639.

Compound 7d: ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.19 (s, 1H), 6.17 (s, 1H), 4.36 (s, 1H), 4.34 (s, 1H), 2.49 (s, 2H), 0.97 (m, 18H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 154.6, 107.5, 76.4, 35.7, 25.8. FTIR (neat) cm^{-1} 3429, 3101, 2956, 2871, 1561, 1513, 1413, 1365, 1241, 1189. HRMS calculated for $C_{14}H_{24}O_3Na$: 263.1623; Found: 263.1628.

Compound 7e: ^{1}H (400 MHz, $CDCl_3$) δ 6.20 (d, *J* = 3.1 Hz, 1H), 6.15 (d, *J* = 3.1 Hz, 1H), 4.53 (s, 1H), 4.37 (d, *J* = 8.7 Hz, 1H), 2.86 (s, 1H), 2.72 (s, 1H), 2.37 (q, *J* = 8.2 Hz, 2H), 1.91 – 1.85 (m, 2H), 1.65 – 1.47 (m, 12H), 1.25 – 1.19 (m, 2H); ^{13}C (101 MHz, $CDCl_3$) δ 156.6, 153.2, 108.2, 106.9, 71.8, 57.3, 44.4, 29.3, 29.2, 25.6, 25.5. FTIR (neat) cm^{-1} 3332, 2951, 2867, 1710, 1650, 1450, 1187, 1011, 794, 622. HRMS calculated for $C_{16}H_{24}O_3Na$: 287.1623; Found: 287.1623.

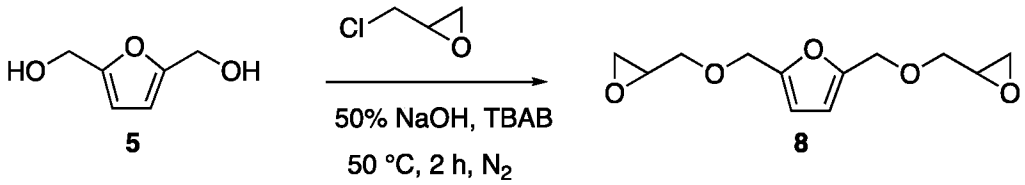
Compound 7f: ^{1}H (400 MHz, $CDCl_3$) δ 6.20 (s, 2H), 5.88 – 5.76 (m, 2H), 5.21 (q, 1.8 Hz, 2H), 5.17 (m, 1H), 5.14 (m, 1Hf), 4.73 (t, *J* = 5.9 Hz, 3H), 2.62 (m, 3H), 2.39 (s, 2H); ^{13}C (101 MHz, $CDCl_3$) δ 155.4, 133.8, 118.3, 106.6, 66.9, 39.9. FTIR (neat) cm^{-1} 3309, 3076, 2914, 1640, 1431, 1310, 1186, 859, 794, 643. HRMS calculated for $C_{12}H_{16}O_3Na$: 231.0997; Found: 231.1004.

Compound 7g: ^{1}H NMR (400 MHz, $CDCl_3$) δ7.39 – 7.20 (m, 10H), 6.15 (d, *J* = 3.1 Hz, 2H), 4.91 (ddd, *J* = 8.0, 5.6, 3.8 Hz, 2H), 3.20 – 3.10 (s, 4H), 1.91 (s, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.2, 137.3, 129.4, 128.5, 126.7, 107.1, 68.7, 42.1. FTIR (neat) cm^{-1} 3346, 2955, 2905, 2869, 1682, 1557, 1479, 1462, 1389, 1365. HRMS calculated for $C_{20}H_{20}O_3Na$: 331.1310; Found: 331.1311.

[00042] *Synthesis of glycidyl ethers*

[00043] The formation of glycidyl ethers began by synthesizing a known compound as shown in **Scheme 5**. Treatment of bishydroxymethylfuran **5** with epichlorohydrin, 50% NaOH, tetra n-butylammonium bromide (TBABr, catalyst) at 50 °C gave the diglycidyl ether **8** in 85% isolated yield. The physical and spectral characteristics of **8** were in complete agreement with those reported in the literature [Shen et al., *Ind. Eng. Chem. Res.* **2017**, 56(38):10929-10938; Ding et al., *ACS Sustainable Chem. Eng.* **2017**, 5(9):7792-7799; Hu et al., Macromolecules **2014**, 47(10):3332-3342].

[00044] Typical experimental procedure:



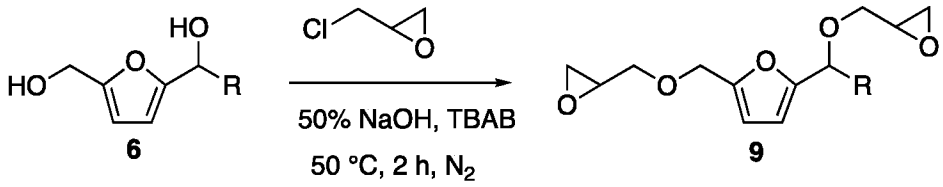
Scheme 5. Synthesis of diglycidyl ether from 2,5-bishydroxymethylfuran

Compound 8: ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.31 (s, 2H), 4.58 – 4.43 (m, 4H), 3.78 (dd, *J* = 11.5, 3.1 Hz, 2H), 3.46 (dd, *J* = 11.5, 5.9 Hz, 2H), 3.17 (ddt, *J* = 5.8, 4.1, 2.9 Hz, 2H), 2.81 (dd, *J* = 5.0, 4.2 Hz, 2H), 2.63 (dd, *J* = 5.0, 2.7 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 151.8, 110.3, 70.7, 65.1, 50.7, 44.3; FTIR (neat) cm^{-1} 2930, 2871, 1734, 1636, 1457, 1373, 1243, 1090, 929, 855.

[00045] After establishing reaction conditions for glycidation, the synthesis of diglycidyl ethers of unsymmetrical diols **6** was undertaken (**Scheme 6**) ("R" defined in **Table 3**). The goal was to prepare a diverse set of diglycidyl ethers and evaluate them in epoxy formation using different diamines. The reaction with diol **6** was optimized to obtain the diglycidyl ether **9** in high yield (**Table 3**). The products were characterized by spectroscopy. The NMR spectra of the products were complex because of the presence of multiple chiral centers. Two different sources for epichlorohydrin were evaluated. A 100% biobased epichlorohydrin gave diglycidyl ethers with a better impurity profile.

[00046] Typical experimental procedure: A 50 mL round bottom flask reaction vessel under N_2, containing 50 w/v % NaOH, aq. (4.0 g in 4 mL DI H_2O), tetrabutylammonium bromide (32.2 mg, 0.1 mmol) and epichlorohydrin (20 mL) was placed in a 50 °C water bath. Before stirring and placing reaction vessel into hot oil bath, a solution of diol (1 mmol) in epichlorohydrin (10 mL) was added to the reaction vessel dropwise. The vessel was lowered into the hot oil bath (50 °C) and stirring started. The reaction was monitored via TLC, and upon completion (2-14 h), the hot reaction mixture was poured over ice. The resulting liquid was transferred to a 125 mL separatory funnel and diluted with ethyl acetate (40 mL). Then the aqueous layer was removed and the organic layer was washed with brine (20 mL x 3). The organic layer was dried over magnesium

sulfate, filtered through filter paper, and then the organic solvent was removed *in vacuo* to obtain the diglycidyl ether.



Scheme 6. Synthesis of diglycidyl ethers from diols **6**

Table 3. Diglycidyl ethers derived from unsymmetrical diols **6**

ENTRY	R	YIELD (%)
1	Methyl (**9a**)	92
2	Phenyl (**9b**)	80

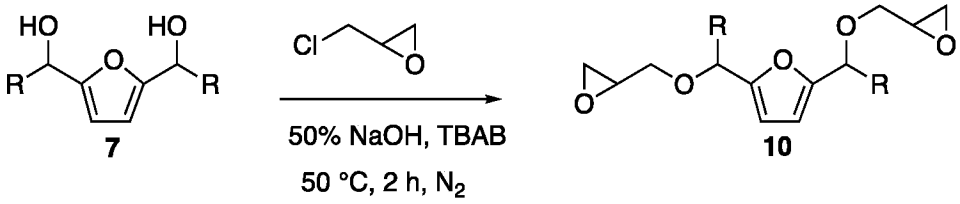
HMF-based diglycidyl ethers

Compound 9a: ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.28 (d, *J* = 3.0 Hz, 1H), 6.23 (d, *J* = 3.2 Hz, 1H), 4.56 – 4.43 (m, 3H), 3.76 (dd, *J* = 12.3, 3.1 Hz, 1H), 3.65 (ddd, *J* = 20.7, 11.4, 3.3 Hz, 1H), 3.48 – 3.29 (m, 2H), 3.15 (dq, *J* = 6.0, 3.0 Hz, 1H), 3.10 (dq, *J* = 7.6, 3.9, 3.3 Hz, 1H), 2.80 – 2.75 (m, 2H), 2.63 – 2.52 (m, 2H), 1.52 (dd, *J* = 8.6, 6.6 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.7, 155.5, 151.1, 151.0, 110.1, 110.0, 107.9, 107.7, 71.1, 71.0, 70.6, 69.5, 68.6, 65.1, 50.9, 50.7, 44.6, 44.4, 44.2, 19.7, 19.5; ^{13}C-DEPT-135 (101 MHz, $CDCl_3$) δ 110.0 (CH_2), 107.9 (CH_2), 107.7 (CH_2), 71.1 (CH_2), 71.0 (CH/CH_3), 69.5 (CH/CH_3), 68.6 (CH/CH_3), 65.1 (CH/CH_3), 50.7 (CH_2), 44.6(CH/CH_3), 44.4(CH/CH_3), 44.2 (CH/CH_3), 19.7 (CH_2), 19.7 (CH_2); ^{1}H- ^{13}C HSQC (400 MHz/101MHz, $CDCl_{13}$) δ (6.28, 110.1), (6.23, 107.8), (4.54, 71.1), (4.50, 65.1), (3.77, 70.6), (3.68, 69.5), (3.44, 70.6), (3.33, 69.5), (3.15, 50.7), (2.78, 44.3), (2.62, 44.3), (2.54, 44.4), (1.52, 19.7). FTIR (neat) cm^{-1} 2986, 2867, 1711, 1443, 1372, 1322, 1252, 1090, 1013, 911. HRMS calculated for $C_{13}H_{18}O_5Na$: 277.1052; Found: 277.1062.

Compound 9b: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 – 7.29 (m, 5H), 6.26 (d, *J* = 3.1 Hz, 1H), 6.11 – 6.06 (m, 1H), 5.48 (d, *J* = 2.8 Hz, 1H), 4.54 – 4.44 (m, 2H), 3.75 (ddd, *J* = 18.9, 11.4, 3.2 Hz, 2H), 3.58 – 3.38 (m, 2H), 3.22 – 3.11 (m, 2H), 2.80 – 2.75 (m, 2H), 2.62 – 2.56 (m, 2H); ^{13}C NMR (101

MHz, $CDCl_3$) δ 154.6, 154.5, 151.6, 138.7, 138.6, 128.4, 128.1, 128.1, 127.3, 127.1, 110.2, 109.5, 109.3, 77.5, 70.5, 69.8, 69.5, 65.1, 50.8, 50.6, 44.4; ^{13}C-DEPT-135 (101 MHz, $CDCl_3$) δ 128.4(CH/CH_3), 127.3(CH/CH_3), 127.1(CH/CH_3), 110.2(CH/CH_3), 109.5(CH/CH_3), 109.3(CH/CH_3), 77.5(CH/CH_3), 70.5(CH_2), 69.8(CH_2), 69.56(CH_2), 65.1(CH_2), 50.7(CH/CH_3), 50.6(CH/CH_3), 44.4(CH_2); ^{1}H- ^{13}C HSQC (400 MHz/101MHz, $CDCl_3$) δ (7.44, 127.2), (7.37, 128.2), (6.27, 110.2), (6.09, 109.5), (5.48, 77.5), (4.49, 65.1), (3.76, 69.6), (3.74, 70.5), (3.62, 69.8), (3.55, 70.5), (3.48, 69.6), (3.42, 70.5), (3.20, 50.7), (3.13, 50.6), (2.77, 44.4), (2.59, 44.3). FTIR (neat) cm^{-1} 2998, 2921, 1555, 1494, 1452, 1334, 1252,1060, 1021, 845. HRMS calculated for $C_{18}H_{20}O_5Na$: 339.1208; Found: 339.1208.

[00047] The diglycidyl ethers of symmetrical diols **7** were also synthesized (**Scheme 7**) ("R" defined in **Table 4**). The reactions were slightly less efficient as compared to reactions with unsymmetrical diols (**Table 4**). The products were fully characterized by spectroscopy.



Scheme 7. Synthesis of diglycidyl ethers from diols **7**

Table 4. Diglycidyl ethers derived from symmetrical diols **7**

ENTRY	R	YIELD (%)
1	Methyl (**10a**)	65
2	Allyl (**10b**)	74
3	n-Butyl (**10c**)	82

DFF-based diglycidyl ethers

Compound 10a: ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.22 (s, 2H), 4.54 (p, *J* = 6.5 Hz, 2H), 3.64 (ddd, *J* = 16.4, 11.4, 3.3 Hz, 2H), 3.54 – 3.30 (m, 2H), 3.15 – 3.06 (m, 1H), 2.84 – 2.74 (m, 2H), 2.63 (dd, *J* = 4.8, 2.8 Hz, 2H), 2.59 – 2.51 (m, 1H), 1.59 – 1.46 (t, *J* = 6.6 Hz, 6H); ^{13}C-DEPT-135 (101 MHz, $CDCl_3$)

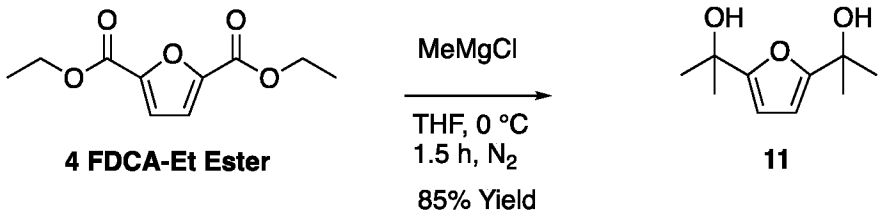
δ 155.0, 107.6, 71.1, 69.5, 68.6, 50.9, 44.4, 19.4; FTIR (neat) cm^{-1} 3061, 2985, 2928, 2864, 1446, 1372, 1253, 1089, 913, 851. HRMS calculated for $C_{14}H_{20}O_5Na$: 291.1208; found:

Compound 10b: ^1H NMR (400 MHz, $CDCl_3$) δ 6.25 (q, *J* = 1.6 Hz, 2H), 5.76 (dqd, *J* = 17.2, 6.9, 3.5 Hz, 2H), 5.18 – 4.96 (m, 4H), 4.48 – 4.34 (m, 2H), 3.72 – 3.55 (m, 2H), 3.47 (dt, *J* = 11.5, 4.4 Hz, 1H), 3.32 (ddd, *J* = 11.4, 6.1, 2.4 Hz, 1H), 3.11 (tt, *J* = 8.5, 4.8 Hz, 1H), 2.78 (q, *J* = 4.7 Hz, 2H), 2.75 – 2.49 (m, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 153.7, 133.8, 117.4, 108.8, 108.6, 75.1, 75.0, 69.6, 68.8, 50.8, 50.6, 44.6, 44.3, 38.5; ^{13}C-DEPT-135 (101 MHz, $CDCl_3$) δ 133.9(CH_2), 117.4(CH/CH_3), 108.9(CH_2), 108.6(CH_2), 75.2(CH_2), 74.9(CH_2), 69.6(CH/CH_3), 68.7(CH/CH_3), 50.9(CH_2), 50.6(CH_2), 44.6(CH/CH_3), 44.3(CH/CH_3), 38.5(CH/CH_3); ^1H- ^{13}C HSQC (400 MHz/101MHz, $CDCl_{13}$) δ (6.25, 108.8), (5.76, 133.7), (5.12, 117.3), (5.06, 117.3), (4.40, 75.0), (3.71, 69.5), (3.59, 68.8), (3.48, 68.7), (3.33, 69.5), (3.10, 50.8), (2.79, 44.5), (2.68, 38.5), (2.64, 44.5), (2.53, 44.3). FTIR (neat) cm^{-1} 3074, 2998, 2918, 1641, 1431, 1316, 1252, 1160, 1190, 992. HRMS calculated for $C_{18}H_{24}O_5Na$: 343.1521; found: 343.1519.

Compound 10c: ^1H NMR (400 MHz, $CDCl_3$) δ 6.21 (t, *J* = 1.8 Hz, 2H), 4.31 (dt, *J* = 13.8, 7.0 Hz, 2H), 3.65 – 3.50 (m, 2H), 3.48 – 3.35 (m, 2H), 3.29 (ddt, *J* = 11.4, 6.1, 1.8 Hz, 2H), 3.08 (tq, *J* = 7.9, 3.8 Hz, 2H), 2.75 (q, *J* = 4.9 Hz, 2H), 2.60 (dd, *J* = 5.1, 2.7 Hz, 2H), 2.50 (dt, *J* = 5.1, 2.7 Hz, 4H), 1.97 – 1.72 (m, 4H), 1.44 – 1.10 (m, 6H), 0.87 (t, *J* = 7.1 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 154.2, 108.3, 75.4, 69.5, 68.7, 50.9, 50.6, 44.6, 44.3, 33.7, 27.7, 22.4, 13.9; ^{13}C-DEPT-135 (101 MHz, $CDCl_3$) δ 108.5 (CH/CH_3), 75.7 (CH/CH_3), 69.5 (CH_2), 68.7(CH_2), 50.9(CH/CH_3), 50.6(CH/CH_3), 44.6 (CH_2), 44.3 (CH_2), 33.7(CH_2), 27.7(CH_2), 22.44(CH_2), 13.9(CH/CH_3); ^1H- ^{13}C HSQC (400 MHz/101MHz, $CDCl_{13}$) δ (6.21, 108.0), (4.32, 75.5), (3.62, 69.5), (3.54, 68.7), (3.45, 68.7), (3.29, 69.5), (3.07, 50.8), (2.75, 44.5), (2.60, 44.6), (2.50, 44.3), (1.89, 33.7), (1.82, 33.7), (1.34, 27.7), (1.33, 22.4), (1.21, 27.6), (0.88, 14.0). FTIR (neat) cm^{-1} 2955, 2930, 2861, 1466, 1379, 1320, 1253, 1090, 1013, 795. HRMS calculated for $C_{20}H_{32}O_5Na$: 375.2147; found: 375.2146.

[00048] A tertiary diol **11** was synthesized from by the addition of excess methylmagnesium chloride to FDCA diethyl ester **4** in 85% yield (**Scheme 7**). The solid diol was not stable and

underwent dehydration readily. However, the compound could be stored in a freezer without decomposition.



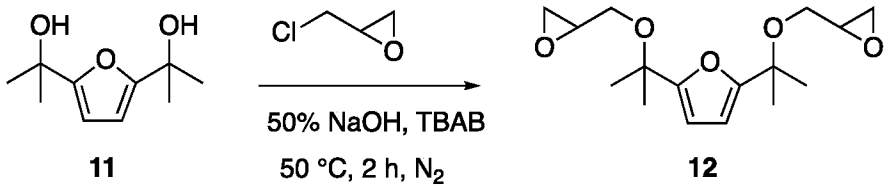
Scheme 7. Synthesis of a tertiary diol

Procedure: A reaction vessel containing solution of purchased Grignard reagent (13.5 mmol eq, diluted from 1.0 -3.4 M to a 0.5 M solution in inhibitor-free drysolv THF) was flushed with N_2 and kept under positive N_2 pressure. A solution of substrate (3 mmol, dissolved to form a 0.1 M solution in inhibitor-free drysolv THF) was added dropwise via syringe into the dry 50 mL round bottom flask reaction vessel. The reaction was monitored by TLC, until the reaction was complete (1-2 h). To quench the reaction, 6 mL of 0.1 M trisodium citrate (aq) was added via syringe. The reaction mixture was filtered through filter paper, then the THF was removed *in vacuo*. The resulting oil was then diluted with ethyl acetate (40 mL) and washed with brine (10 mL x 3) in a 60 mL separatory funnel. The organic layer was dried over sodium sulfate, then filtered, and solvent removed *in vacuo* to obtain the diol product in 85% yield.

Compound 11: ^{1}H (400 MHz, $CDCl_3$) δ 6.09 (s, 2 H), 2.49 (s, 2 H), 1.58 (s, 12 H); ^{13}C (101 MHz, $CDCl_3$) δ 159.0, 104.0, 68.7, 28.5. FTIR (neat) cm^{-1} 3362, 2979, 2900, 1375, 1267, 1164, 1115, 1022, 959, 840. HRMS calculated for $C_{10}H_{16}O_3Na$: 207.0997; Found: 207.0994.

[00049] The glycidation of **11** to provide diglycidyl ether **12** was successful and gave the product in 75% yield (**Scheme 8**). It is interesting to note highly hindered ether such as **12** could be accessed. However, the glycidation was slow as compared to reactions with less hindered alcohols.

[00050]



Scheme 8. Synthesis of a diglycidyl ether from a tertiary diol

Compound 12: ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.17 (d, *J* = 3.2 Hz, 1H), 6.12 (d, *J* = 3.2 Hz, 1H), 3.37 (dd, *J* = 11.0, 3.7 Hz, 2H), 3.22 (dd, *J* = 11.0, 5.5 Hz, 2H), 3.06 – 2.99 (m, 2H), 2.75 (t, 5 Hz, 2H), 2.53 (dd, *J* = 5.1, 2.7 Hz, 2H), 1.59 (s, 6H), 1.56 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.87, 155.8, 107.5, 103.7, 73.3, 68.7, 64.4, 51.0, 44.9, 28.5, 25.7. FTIR (neat) cm^{-1} 2968, 2905, 1375, 1350, 1252, 1168, 1112, 1018, 963, 837. HRMS calculated for $C_{16}H_{24}O_5Na$: 319.1521; found: 319.1513.

[00051] *Reaction of diglycidyl ethers with diamines*

[00052] To evaluate the curing ability of the diglycidyl ether bis-epoxymonomers with four different types of amine curatives, high throughput and conventional methods were used to extract maximum property information of the crosslinked networks with minimal material in a short period of time. The properties of the networks formed from the novel diglycidyl ether bis-epoxymonomers as a function of curative type, cure temperature, and time of curing are disclosed. For comparison, commercial BPA based epoxy resin EPON 828 (Momentive) was used as reference. To evaluate the relative crosslink density of the crosslink networks high throughput dye extraction and nano-indentation technique were used. Conventional methods such as König pendulum hardness and differential scanning calorimetry (DSC) were used to further evaluate the crosslinked networks.

[00053] 1.1. Materials

[00054] The materials used are described in **Table 5**.

Table 5. Starting materials

Chemical	Designation	Vendor
Bisphenol A diglycidyl ether	EPON 828	Momentive
Perylene, 98+%	Perylene	Alfa Aesar
Toluene	Toluene	BDH Chemicals
Methyl ethyl ketone, 99%	MEK	Alfa Aesar
Perylene, 98+%,	Perylene	Alfa Aesar
Aluminum panels 4”×8”	Aluminum panels	Q-LAB
polypropylene microtiter plates		Evergreen Scientific.

[00055] 1.2. Preparation of formulations

[00056] Formulations from the diglycidyl ether bis-epoxymonomers and EPON 828 were prepared with four types of amine curatives (total twelve amine curatives listed in **Table 6**) to

investigate the reactivity of the diglycidyl ether bis-epoxymonomers towards different amine curatives and simultaneously the impact of the nature of amine curative on the properties of the cured coatings. To evaluate the relative performance of curatives towards crosslinking, the dye extraction method previously reported by Bach et al. [Bach et al., *Farbe Lack* **2002**, 108:30; 2. Bach et al., in *High-Throughput Analysis: A Tool for Combinatorial Materials Science*, eds. R. A. Potyrailo and E. J. Amis, Springer US, Boston, MA, 2003, pp. 525-549.] was used. Prior to making formulations, a 3 mM solution of perylene dye in toluene was prepared. A representative procedure for making dye incorporated formulation of EPON 828 with isophorone diamine as curative is as follows: 1.14 g of EPON 828 resin was transferred into a 20 mL glass vial, where, 2.56 mL of methyl ethyl ketone (MEK) solvent and 202 µL of perylene dye solution were subsequently added and mixed using Teflon coated magnetic stir bar at 900 rpm on multi-position magnetic stirring plates for 25 min. Next, 0.26 g of isophorone diamine (Epoxy to amine ratio was 1:1) was added to the mixture and mixed for another 20 min prior to deposition on primed aluminum discs. For all the formulations and the amount of dye per formulation unit volume was kept constant.

Table 6. List of amine curatives used to study properties of crosslinked networks.

Type	**Name of curative**	**Designation**	**Amine hydrogen equivalent weight (AHEW)**	**Vendors**
Aliphatic	Priamine 1075	Priamine	267	Croda
	1,8-Diaminooctane	1,8-DA Octane	36.07	Sigma Aldrich
	Diethylenetriamine	DETAA	20.63	Sigma Aldrich
	Tetraethylenepentamine	TEPAA	24.37	Sigma Aldrich

Type	Name of curative	Designation	Amine hydrogen equivalent weight (AHEW)	Vendors
Aromatic	m-Xylylenediamine	Xylene DA	34.05	Sigma Aldrich
Cycloaliphatic	1,3-Bis(Aminomethyl)cyclohexane	1,3 BAC	35.55	Mitsubishi gas chemicals
	Isophorone diamine	IPDA	42.68	
	bis(p-aminocyclohexyl) methane	PACM	52.5	Sigma Aldrich
Polyether	JEFFAMINE EDR-148 (XTJ-504)	XTJ-504	37.05	Huntsman Corporation
	JEFFAMINE D-400	Jeff. D-400	115	Huntsman Corporation
	JEFFAMINE D-230	Jeff. D-230	60	Huntsman Corporation
	JEFFAMINE T-403	Jeff. t-403	81	Huntsman Corporation

[00057] 2. Methods and Instruments

[00058] 2.1. Dye Extraction

[00059] Preparation for the dye extraction method was carried out by punching out 10 mm epoxy primed aluminum discs and affixing them to a 4" × 8" aluminum panel in a 6 × 11 array format. 75 µL of each formulation was deposited on six discs using an Eppendorf repeat pipettor. Coatings were then allowed to dry overnight under ambient conditions. Array panels were then

cured at room temperature for 7 days, 60 °C and 100 °C using preheated oven for 1 h., 3 h., or 6 h. to evaluate the optimum curing condition. After curing, three discs from each set (same formulation and curing regime) were transferred into 24 well (6x4) polypropylene microtiter plates, each row of wells containing two sets of discs. The discs were affixed to the bottom of each well with double-sided tape and were allowed to adhere for 18+ hours prior to dye extraction.

[00060] Dye extraction was performed by adding 500 µL of toluene to each well of the microtiter plate using an Eppendorf repeat pipettor. Toluene was quickly added to each row of the microtiter plate with 15 s intervals between the rows. Formulations were allowed to soak for 10 min on an orbital shaker, then 150 uL of each extraction sample was collected and transferred to a 96 well microtiter plate using a 6-channel, adjustable spacing, multichannel pipette. Each row of two sets with three replicates was collected at the same time, aspirating twice to ensure a homogenous mixture. The timing of collection for each individual formulation was held to 15 second intervals to ensure that the soaking time was precise. Fluorescence measurements (415ex/471em) of all extraction samples using a TECAN Saffire2 plate reader were taken immediately following collection.

[00061] 2.2. Nano-Indentation

[00062] Depth sensing indentation, also called instrumented indentation or nanoindentation, was performed using a Hysitron TriboIndenter with automation (9 samples per run) using a diamond Berkovich tip. Since accurate determination of the elastic modulus from the indentation load-displacement responses requires flat sample surfaces, indentation was performed mostly near the center of the coated discs. Before every indent, the indenter was held in contact with the surface, to allow for piezoactuator stabilization (35 s) and drift correction (40 s), at a contact load of only 0.5 mN to prevent any deformation prior to the indentation experiment. The drift rate (typically 0.1 nm s21) was automatically determined over the last 20 s of the 40 s period. After lifting the tip up to 30 nm and re-approaching the surface (surface detection at a load of 0.5 mN), the tip was loaded to maximum load of 300 µN in 5 s, held at maximum load for 5 s and unloaded in 5 s. Nine measurements with a spacing of 60 µm apart

were performed per sample and the first one was left out from the analysis to further reduce the influence of drift.

[00063] 2.3. Differential Scanning Calorimetry

[00064] Thermal properties of the cured coatings were characterized using Q1000 Modulated Differential Scanning Calorimeter from TA Instruments with a cooling limit up to -90 °C. About 6-8 mg of the cured film was scraped out from the disc and the following heat/cool/heat regime was used: the sample was first equilibrated at 23 °C and then cooled to -10 °C at 10 °C/minute, held at -10 °C for 2 min and heated to 100 °C at 10 °C/minute.

[00065] 2.4. König Pendulum Hardness

[00066] König pendulum hardness was measured according to ASTM D 4366-16 by sticking two cured coated discs on a steel panel on top of which steel balls of the pendulum were placed; the result was reported in seconds.

[00067] 2.5. Drying Time Measurement

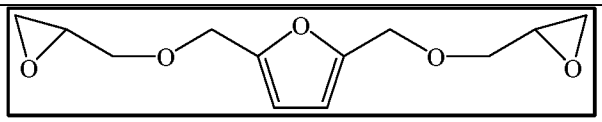
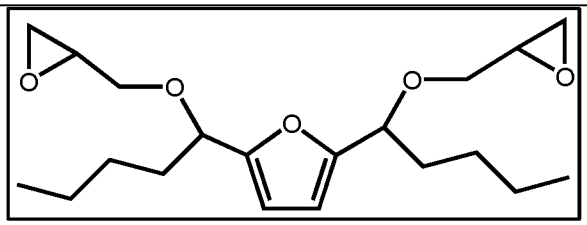
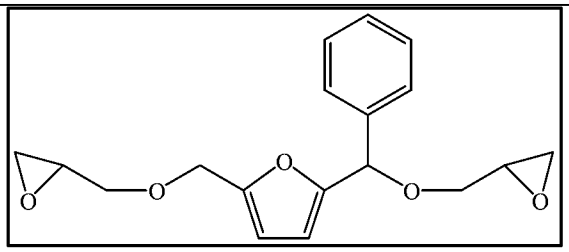
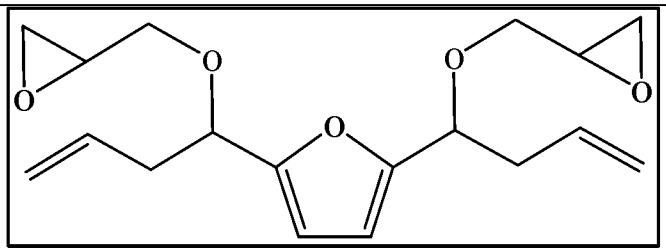
[00068] Drying time was measured according to ASTM D 1640. Due to small size of the coated discs dry-to-touch time was recorded when the coating no longer adheres to the finger and does not rub up appreciably when the finger was lightly rubbed across the surface.

[00069] 2.5. Measurement of Epoxy Equivalent Weight

[00070] Epoxy equivalent weight (EEW, g/eq.) of the diglycidyl ether bis-epoxymonomers and EPON 828 resin were evaluated by titrating epoxy samples with 0.0925 N solution of HBr in glacial acetic acid; 1 wt.% solution of crystal violet in acetic acid was used as an indicator. EEW value was calculated using the following equation (1) and the values are reported in **Table 7**, where W is the sample mass in grams, N is the normality of HBr solution, and V is the volume of HBr solution used for titration in mL.

$$EEW = \frac{100 \times W}{N \times V}$$

Table 7. Epoxy equivalent weight (EEW, g/eq.) of the diglycidyl ether bis-epoxymonomers and EPON 828 resin.

Resin		**EEW (g/eq)**
GLY 13/16		165.85
GLY 23/24		148.92
GLY 17		157.18
GLY 25		158.23
EPON 828		190

[00071] 3. Results

[00072] 3.1. Drying Time

[00073] Drying time was measured as a preliminary study to estimate the reactivity of the novel diglycidyl ether bis-epoxymonomers towards various amine curatives. See **Table 8**. Drying time of EPON 828 was measured with the curatives as a reference.

Table 8. Drying time of diglycidyl ether bis-epoxymonomers and EPON 828 with amine curatives.

	Dry-to-touch time (hr.)				
Amine Curatives	**EPON 828**	**GLY 23/24**	**GLY 17**	**GLY 13/16**	**GLY 25**
TEG-DA (XTJ-504)	16	PS	18	14	NI

	Dry-to-touch time (hr.)				
Amine Curatives	**EPON 828**	**GLY 23/24**	**GLY 17**	**GLY 13/16**	**GLY 25**
Jeffamine t403	13	42	23	24	33
Jeffamine D-230	25	77	24	17	56
Jeffamine D-400	NI	91	28	NI	62
PACM	8	18	22	15	19
1,3-BAC	8	17	20	22	16
IPDA	11	16	22	12	16
Xylene diamine	5	22	28	13.5	20
Diethylenetriamine	6	PS	20	16	17
Tetraethylenepentamine	5	PS	23	18	21
Priamine 1075	PS	PS	PS	PS	PS
1,8 DA Octane	6	17	20	14	15

S - Phase separation
NI – Not included in the study

[00074] 3.2. Dye Extraction Results

[00075] The dye extraction method described previously was used to estimate the relative crosslink density of the coatings. Higher values of dye extraction are related to lower crosslinked coatings and vice versa. The tables below show the dye extraction results for coatings made from the diglycidyl ethers and amine curing agents cured under room temperature (RT) conditions as well as at elevated temperatures for the times shown.

Table 9. Dye extraction results of coatings formulated from GLY 23/24 with amine curatives.

Curing Temperature (°C)	**RT**	**60**			**100**		
Curing Time	**7 Days**	**1h.**	**3h.**	**6h.**	**1h.**	**3h.**	**6h.**
TEG-DA (XTJ-504)	20578	20991	20042	20125	16544	15915	14557
Jeffamine t403	16333	14895	14522	16578	14166	13552	15073
Jeffamine D-230	20123	18786	19086	21048	16687	16101	17574
Jeffamine D-400	21019	20998	21705	24856	21326	20358	21549
PACM	11116	10935	10700	13334	10545	9585	10708
1,3-BAC	13703	14280	14332	16715	14072	13036	14344
IPDA	18306	13541	12157	13322	12930	11862	13441

Curing Temperature (°C)	RT	60			100		
Curing Time	**7 Days**	**1h.**	**3h.**	**6h.**	**1h.**	**3h.**	**6h.**
Xylene diamine	15516	12031	11821	12910	13804	13590	14816
Diethylenetriamine	15139	14594	16254	20919	17731	19418	21345
Tetraethylenepentamine	17050	16644	17776	25250	22196	19136	13935
Priamine 1075	24208	20580	20400	22766	19842	18530	19752
1,8 DA Octane	12018	6414	5302	5205	7972	8954	7946

Table 10. Dye extraction results of coatings formulated from GLY 13/16 with amine curatives.

Curing Temperature (°C)	RT	60			100		
Curing Time	**7 Days**	**1h.**	**3h.**	**6h.**	**1h.**	**3h.**	**6h.**
TEG-DA (XTJ-504)	204	214	152	129	168	124	142
Jeff. t403	3463	3611	3519	2492	2858	2473	1665
Jeff. D-230	8819	9187	9554	9955	8043	7003	7356
Jeff.D-400	NI						
PACM	304	1525	760	126	213	61	107
1,3-BAC	1376	324	250	426	679	234	124
IPDA	127	136	84	54	127	103	77
Xylene diamine	174	72	92	100	170	120	91
DETA	341	105	111	105	76	81	78
TEPA	703	126	748	148	548	166	525
Priamine 1075	44637	45440	46136	48543	37621	33993	30476
1,8 DA Octane	272	608	529	326	693	196	152

NI – Not included in the study

Table 11. Dye extraction results of coatings formulated from GLY 17 with amine curatives.

Curing Temperature (°C)	RT	60			100		
Curing Time	**7 Days**	**1h.**	**3h.**	**6h.**	**1h.**	**3h.**	**6h.**
TEG-DA (XTJ-504)	738	2114	2604	3033	4141	3087	2258

Curing Temperature (°C)	RT	60			100		
Curing Time	**7 Days**	**1h.**	**3h.**	**6h.**	**1h.**	**3h.**	**6h.**
Jeffamine t403	3720	3663	3703	2608	3016	2542	2072
Jeffamine D-230	27621	28338	28333	27862	23012	18084	13276
Jeffamine D-400	38468	40511	40735	40689	36651	32086	30629
PACM	3500	2994	2906	641	1145	286	130
1,3-BAC	2321	2042	790	163	6012	5233	4326
IPDA	2863	6772	7299	702	1885	203	116
Xylene diamine	7401	1100	1100	956	15431	23468	13669
Diethylenetriamine	931	1121	1409	678	1363	309	342
Tetraethylenepentamine	29781	25886	25229	27807	3889	1879	1293
Priamine 1075	44422	44165	44577	45501	40452	38352	35642
1,8 DA Octane	20532	12378	10432	8193	6087	6035	6005

Table 12. Dye extraction results of coatings formulated from GLY 25 with amine curatives.

Curing Temperature (°C)	RT	60			100		
Curing Time	**7 Days**	**1h.**	**3h.**	**6h.**	**1h.**	**3h.**	**6h.**
TEG-DA (XTJ-504)	NI						
Jeffamine t403	17277	16437	17283	15196	15751	15142	13292
Jeffamine D-230	12654	13080	14141	13358	9596	10105	10171
Jeffamine D-400	34037	35898	35054	36861	31008	28581	28691
PACM	3493	9923	7238	6320	11110	9384	7539
1,3-BAC	13117	13626	13394	11472	8623	2590	1397
IPDA	15948	15468	15904	15007	13542	11417	11280
Xylene diamine	2167	2264	2782	1396	7190	4469	2173
Diethylenetriamine	9138	5968	6416	5996	1483	1882	607
Tetraethylenepentamine	14755	10584	4889	4971	867	879	820
Priamine 1075	37500	32975	48161	45077	37220	35820	31653
1,8 DA Octane	1124	1811	2098	2595	1704	726	679

NI – Not included in the study

Table 13. Dye extraction results of coatings formulated from EPON 828 with amine curatives.

Curing Temperature (°C)	**RT**	**60**			**100**		
Curing Time	**7 Days**	**1h.**	**3h.**	**6h.**	**1h.**	**3h.**	**6h.**
TEG-DA (XTJ-504)	8648	1153	1124	1358	1124	887	501
Jeffamine t403	568	13751	3867	353	336	64	68
Jeffamine D-230	1327	17265	4245	247	212	115	96
PACM	1107	247	227	211	37	36	35
1,3-BAC	628	1172	917	1331	189	123	108
IPDA	132	426	130	84	44	56	36
Xylene diamine	8704	91	90	84	72	55	42
Diethylenetriamine	11478	7004	5431	3014	1198	885	487
Tetraethylenepentamine	18994	1604	391	643	425	335	338
Priamine 1075	5075	31762	31543	29461	26349	22649	23601
1,8 DA Octane	13289	995	488	157	589	63	63

[00076] 3.3. Pendulum Hardness Results

[00077] Konig pendulum hardness measurements were carried out on the coatings made by reacting the diglycidyl ethers with the amine curing agents at room temperature (RT) and elevated temperatures for the times indicated. Higher pendulum hardness value indicates a harder coating.

Table 14. Pendulum hardness of coatings formulated from GLY 23/24 with amine curatives.

Curing Temperature (°C)	**RT**	**60**			**100**		
Curing Time	**7 Days**	**1h.**	**3h.**	**6h.**	**1h.**	**3h.**	**6h.**
TEG-DA (XTJ-504)	PS, T						
Jeffamine t403	27	19	21	25	25	22	24
Jeffamine D-230	16	19	22	20	18	19	21
Jeffamine D-400	31	28	33	43	26	39	53
PACM	29	10	36	33	43	54	61
1,3-BAC	8	5	11	14	7	11	15

Curing Temperature (°C)	RT	60			100		
Curing Time	**7 Days**	**1h.**	**3h.**	**6h.**	**1h.**	**3h.**	**6h.**
IPDA	10	25	91	97	61	66	83
Xylene diamine	12	8	7	9	4	4	5, W
Diethylenetriamine	PS, W						
Tetraethylenepentamine							
Priamine 1075	PS, T						
1,8 DA Octane	17	24	32	19	21	15	19

PS- Phase separated
T- Tacky
W- Wrinkled

Table 15. Pendulum hardness results of coatings formulated from GLY 13/16 with amine curatives.

Curing Temperature (°C)	RT	60			100		
Curing Time	**7 Days**	**1h.**	**3h.**	**6h.**	**1h.**	**3h.**	**6h.**
TEG-DA (XTJ-504)	8	7	7	7	11	17	19
Jeffamine t403	75	59	134	143	44	154	153
Jeffamine D-230	10	7	7	9	7	7	11
Jeffamine D-400	NI						
PACM	32	163	173	191	173	151	177
1,3-BAC	7	13	20	23	61	95	108
IPDA	185	186	187	195	154	193	200
Xylene diamine	13	12	17	18	17	63	68
Diethylenetriamine	14	12	13	17	26	79	105
Tetraethylenepentamine	28	9	25	36	141	179	183
Priamine 1075	PS						
1,8 DA Octane	15	16	18	13	17	22	28

NI- Not included in the study
PS- Phase separated

Table 16. Pendulum hardness results of coatings formulated from GLY 17 with amine curatives.

Curing Temperature (°C)	**RT**	**60**			**100**		
Curing Time	**7 Days**	**1h.**	**3h.**	**6h.**	**1h.**	**3h.**	**6h.**
TEG-DA (XTJ-504)	6	6	7	14	7	13	W
Jeffamine t403	86	66	150	171	85	152	178
Jeffamine D-230	NI						
Jeffamine D-400							
PACM	44	113	109	116	152	174	176
1,3-BAC	39	38	36	42	71	140	173
IPDA	80	130	140	146	152	192	202
Xylene diamine	9	14	20	30	10	27	88
Diethylenetriamine	4	7	9	9	36	88	134
Tetraethylenepentamine	NI						
Priamine 1075	PS, T						
1,8 DA Octane	4	11	14	15	13	17	20

NI- Not included in the study
PS- Phase separated
T- Tacky

Table 17. Pendulum hardness results of coatings formulated from GLY 25 with amine curatives.

Curing Temperature (°C)	**RT**	**60**			**100**		
Curing Time	**7 Days**	**1h.**	**3h.**	**6h.**	**1h.**	**3h.**	**6h.**
TEG-DA (XTJ-504)	NI						
Jeffamine t403	9	11	11	11	9	12	13
Jeffamine D-230	NI						
Jeffamine D-400							
PACM	30	107	50	27	83	127	169
1,3-BAC	9	25	27	31	42	125	123
IPDA	30	18	17	13	11	9	10
Xylene diamine	7	6	7	38	40	38	45
Diethylenetriamine	NI						

Curing Temperature (°C)	RT	60			100		
Curing Time	**7 Days**	**1h.**	**3h.**	**6h.**	**1h.**	**3h.**	**6h.**
Tetraethylenepentamine							
Priamine 1075	PS						
1,8 DA Octane	158	159	152	157	127	174	169

NI- Not included in the study
PS- Phase separated

Table 18. Pendulum hardness of coatings formulated from EPON 828 with amine curatives.

Curing Temperature (°C)	RT	60			100		
Curing Time	**7 Days**	**1h.**	**3h.**	**6h.**	**1h.**	**3h.**	**6h.**
TEG-DA (XTJ-504)	13	33	22	46	85	93	95
Jeffamine t403	140	135	180	87	147	176	167
Jeffamine D-230	171	195	178	212	139	180	107
PACM	151	107	160	159	155	157	153
1,3-BAC	130	140	138	136	131	135	138
IPDA	133	89	150	175	160	171	166
Xylene diamine	56	49	104	92	118	137	134
Diethylenetriamine	9	35	44	48	78	107	117
Tetraethylenepentamine	32	32	82	71	122	159	121
Priamine 1075	HW						
1,8 DA Octane							

HW- Highly Wrinkled

[00078] 3.2. Results from DSC

Table 19. Glass transition temperature (T_g) of coatings formulated from GLY 23/24 with amine curatives.

Curing Temperature (°C)	RT	60	100
Curing Time	**7 Days**	**3h.**	**3h.**
TEG-DA (XTJ-504)	-1	3	5
Jeffamine t403	5	6	7
Jeffamine D-230	-1	-1	12

Curing Temperature (°C)	**RT**	**60**	**100**
Curing Time	**7 Days**	**3h.**	**3h.**
Jeffamine D-400	-3	0	40
PACM	30	29	32
1,3-BAC	56	21	19
IPDA	25	38	34
Xylene diamine	9	13	20
Diethylenetriamine	PS		
Tetraethylenepentamine			
Priamine 1075			
1,8 DA Octane	13	12	15

PS-Phase separated

Table 20. Glass transition temperature (T_g) of coatings formulated from GLY 13/16 with amine curatives.

Curing Temperature (°C)	**RT**	**60**	**100**
Curing Time	**7 Days**	**3h.**	**3h.**
TEG-DA (XTJ-504)	14	15	17
Jeffamine t403	38	40	60
Jeffamine D-230	11	12	14
Jeffamine D-400	NI		
PACM	39	50	63
1,3-BAC	15	22	45
IPDA	41	54	57
Xylene diamine	6	13	42
Diethylenetriamine	16	19	39
Tetraethylenepentamine	32	36	39
Priamine 1075	PS		
1,8 DA Octane	7	15	19

PS-Phase separated
NI- Not included in the study

Table 21. Glass transition temperature (T_g) of coatings formulated from GLY 17 with amine curatives.

Curing Temperature (°C)	**RT**	**60**			**100**		
Curing Time	**7 Days**	**1h.**	**3h.**	**6h.**	**1h.**	**3h.**	**6h.**
TEG-DA (XTJ-504)	-6	1	3	6	20	23	27
Jeffamine t403	39	36	39	40	40	41	45
Jeffamine D-230	NI						
Jeffamine D-400							
PACM	33	31	39	41	39	39	41
1,3-BAC	34	32	39	33	36	42	47
IPDA	-8	41	42	42	42	52	59
Xylene diamine	7	25	30	27	21	26	30
Diethylenetriamine	13	17	19	26	33	37	37
Tetraethylenepentamine	NI						
Priamine 1075							
1,8 DA Octane	29	8	16	26	26	27	30

NI- Not included in the study

Table 22. Glass transition temperature (T_g) of coatings formulated from GLY 25 with amine curatives.

Curing Temperature (°C)	**RT**	**60**			**100**		
Curing Time	**7 Days**	**1h.**	**3h.**	**6h.**	**1h.**	**3h.**	**6h.**
TEG-DA (XTJ-504)	NI						
Jeffamine t403	3	3	3	5	3	2	3
Jeffamine D-230	NI						
Jeffamine D-400							
PACM	14	9	23	28	27	29	33
1,3-BAC	16	15	28	29	25	30	35
IPDA	33	17	20	29	31	33	35

Curing Temperature (°C)	**RT**	**60**			**100**		
Curing Time	**7 Days**	**1h.**	**3h.**	**6h.**	**1h.**	**3h.**	**6h.**
Xylene diamine	17	11	16	35	27	30	31
Diethylenetriamine	NI						
Tetraethylenepentamine							
Priamine 1075							
1,8 DA Octane	-4	-4	4	11	6	11	21

NI- Not included in the study

Table 23. Glass transition temperature (T_g) of coatings formulated from EPON 828 with amine curatives.

Curing Temperature (°C)	**RT**	**60**	**100**
Curing Time	**7 Days**	**3h.**	**3h.**
TEG-DA (XTJ-504)	52	54	54
Jeffamine t403	53	58	63
Jeffamine D-230	47	56	57
Jeffamine D-400	50	49	51
PACM	47	49	51
1,3-BAC	44	46	48
IPDA	48	53	55
Xylene diamine	53	60	61
Diethylenetriamine	53	58	62
Tetraethylenepentamine	23	34	39
Priamine 1075	36	45	54
1,8 DA Octane	52	55	61

[00079] 3.2. Results from Nano-Indentation

Table 24. Hardness (GPa) of coatings formulated from GLY 23/24, GLY 13/16, GLY 17 and EPON

828 with amine curatives.

Resin	Curing Temperature (°C)	RT	60			100		
	Curing Time	**7 Days**	**1hr.**	**3hr.**	**6hr.**	**1hr.**	**3hr.**	**6hr.**
GLY 23/24	TEG-DA (XTJ-504)	PS						
	Jeffamine t403	1.94	1.85	2.07	1.57	1.78	1.80	1.39
	Jeffamine D-230	S						
	Jeffamine D-400							
	PACM	51.25	2.59	8.26	16.46	35.72	25.55	108.96
	1,3-BAC	1.37	1.25	6.72	7.25	1.34	2.54	2.55
	IPDA	67.34	5.38	140.12	152.38	46.27	21.76	94.22
	Xylene diamine	-	39.09	-	-	-	-	-
	Diethylenetriamine	PS						
	Tetraethylenepentamine							
	Priamine 1075							
	1,8 DA Octane	49.40	12.29	51.43	4.42	2.18	1.95	1.79
GLY 17	Jeffamine t403	222.06	3.71	46.69	260.36	167.28	146.40	268.56
GLY 13/16	Jeffamine t403	223.28	38.88	131.89	274.07	158.80	154.26	286.52
	PACM	225.24	299.19	221.63	362.53	244.32	253.11	332.73
	1,3-BAC	24.39	13.43	391.02	207.58	273.34	481.07	528.59
EPON 828	TEG-DA (XTJ-504)	-	130.70	102.86	-	-	-	-
	Jeffamine t403	323.52	204.75	255.74	258.47	263.74	500.88	461.72
	Jeffamine D-230	250.55	329.57	258.18	321.79	338.59	242.51	333.55
	PACM	440.05	263.58	286.69	303.08	372.51	361.02	650.28
	1,3-BAC	76.12	256.54	261.43	303.91	131.72	106.13	162.60
	IPDA	163.59	237.80	290.40	468.67	507.07	298.58	459.19
	Xylene diamine	176.39	91.36	98.11	149.09	214.12	228.24	141.20
	Diethylenetriamine	7.55	145.96	156.02	48.15	395.40	178.75	419.54
	Tetraethylenepentamine	129.76	104.91	331.80	103.05	428.99	324.58	472.33
	Priamine 1075	PS						
	1,8 DA Octane	HW						

PS-Phase separated
S- Soft, sticky surface
HW- Highly wrinkled

Table 25. Reduced elastic modulus (9MPa) of coatings formulated from GLY 23/24, GLY 13/16, GLY 17 and EPON 828 with amine curatives.

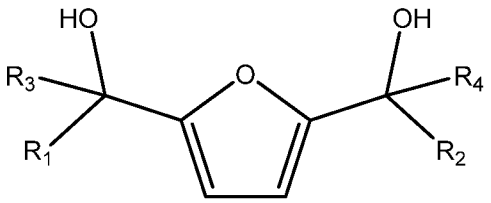
Resin	Curing Temperature (°C)	RT	60			100		
	Curing Time	**7 Days**	**1hr.**	**3hr.**	**6hr.**	**1hr.**	**3hr.**	**6hr.**
GLY 23/24	TEG-DA (XTJ-504)	PS						
	Jeffamine t403	11.2	5.6	9.5	9.3	7.8	8.1	8.3
	Jeffamine D-230	S						
	Jeffamine D-400							
	PACM	5.3	5.5	3.4	5.4	3.0	2.2	5.3
	1,3-BAC	50.4	45.1	65.8	125.1	38.1	45.4	118.0
	IPDA	2.7	303.0	3.3	2.3	4.0	5.1	3.2
	Xylene diamine	-	420.3	-	-	-	-	-
	Diethylenetriamine	PS						
	Tetraethylenepentamine							
	Priamine 1075							
	1,8 DA Octane	587.7	122.5	2.7	52.4	11.2	9.5	9.2
GLY 17	Jeffamine t403	4.6	1.2	4.4	4.3	4.7	4.3	5.4
GLY 13/16	Jeffamine t403	5.0	7.1	4.6	5.6	3.4	4.4	5.6
	PACM	5.3	5.5	3.4	5.4	3.0	2.2	5.3
	1,3-BAC	362.6	310.1	5.2	8.2	5.0	8.8	7.9
EPON 828	TEG-DA (XTJ-504)	-	189.1	252.8	-	-	-	-
	Jeffamine t403	7.1	4.4	5.1	4.7	4.9	7.3	8.3
	Jeffamine D-230	5.9	6.3	5.0	6.2	6.3	4.5	6.5
	PACM	9.8	4.5	4.8	4.4	4.9	5.1	10.0
	1,3-BAC	1.9	5.0	4.4	3.0	3.7	2.9	3.9
	IPDA	4.5	4.5	4.8	6.1	6.8	4.6	6.1
	Xylene diamine	3.9	3.3	3.1	12.6	4.4	5.4	4.1
	Diethylenetriamine	309.7	2.8	1.8	1.3	5.5	48.6	8.2
	Tetraethylenepentamine	3.3	2.4	5.1	2.0	6.4	4.4	8.4
	Priamine 1075	PS						
	1,8 DA Octane	HW						

PS-Phase separated
S- Soft, sticky surface
HW- Highly wrinkled

CLAIMS:

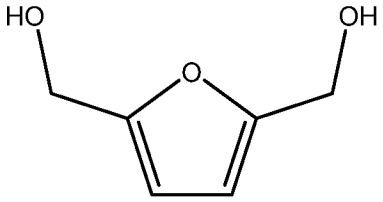
The claimed invention is:

1. A diol having the following structure:



wherein R_1, R_2, R_3, and R_4 are independently selected from the group consisting of H, C_1-C_6 alkyl, C_1-C_6 alkenyl, aryl, and C_1-C_6 alkyl-aryl,

with the proviso that the diol cannot have the following structure:



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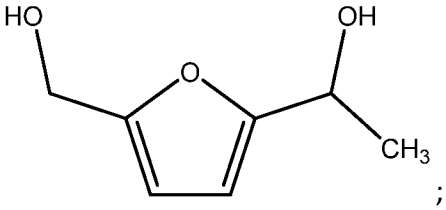

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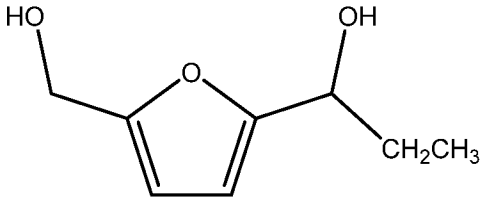

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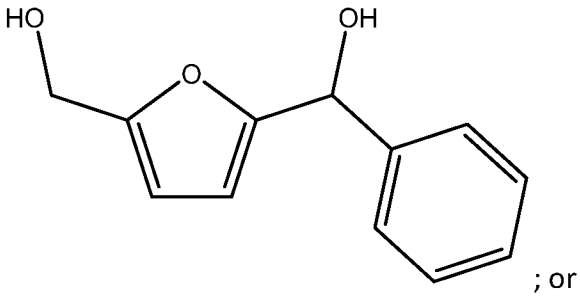
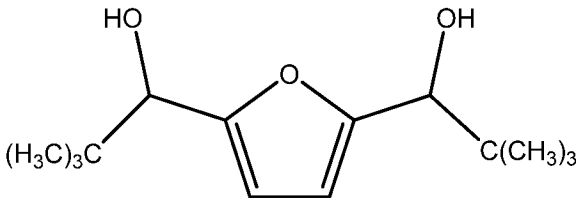


; or



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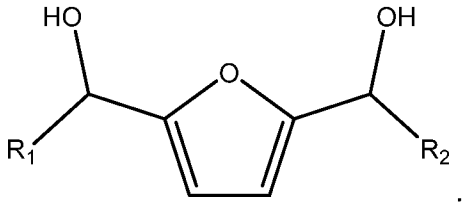
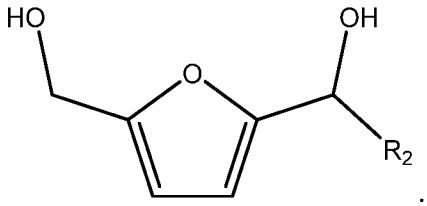
2. The diol of claim 1, having the following structure:



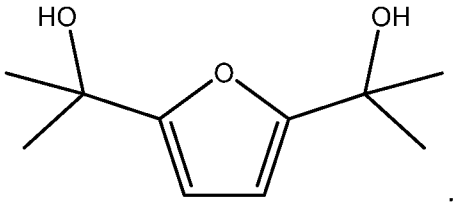
3. The diol of claim 2, wherein R_1 and R_2 are both methyl, ethyl, n-butyl, c-pentyl, allyl, or benzyl.

4. The diol of claim 1, having the following structure:



5. The diol of claim 4, wherein R_2 is n-butyl, t-butyl, c-pentyl, allyl, or benzyl.

6. The diol of claim 1, having the following structure:



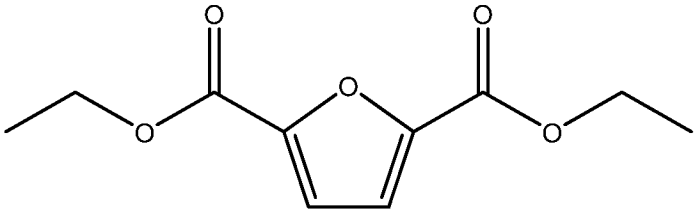
7. A method of making a diol of any of claims 1-6, comprising, consisting essentially of, or consisting of:

reacting 5-hydroxymethyl furfural (HMF), diformyl furan (DFF), or a derivative thereof with a Grignard reagent,

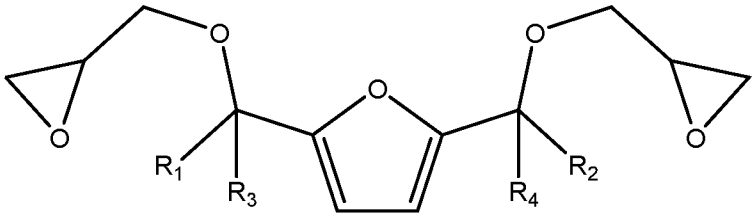
under conditions sufficient to form the diol.

8. The method of claim 7, wherein the Grignard reagent is RMgCl, wherein R is H, C_1-C_6 alkyl, C_1-C_6 alkenyl, aryl, or C_1-C_6 alkyl-aryl.

9. The method of claim 8 or claim 9, wherein the derivative has the following structure:



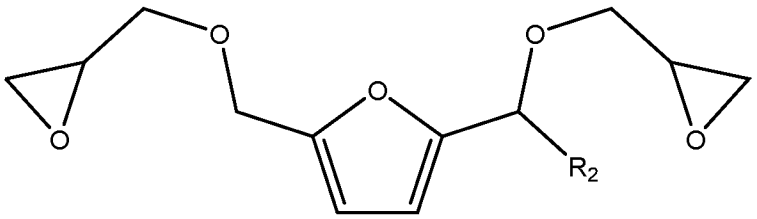
10. A diglycidyl ether having the following structure:



wherein R_1, R_2, R_3, and R_4 are independently selected from the group consisting of H, C_1-C_6 alkyl, C_1-C_6 alkenyl, aryl, and C_1-C_6 alkyl-aryl,

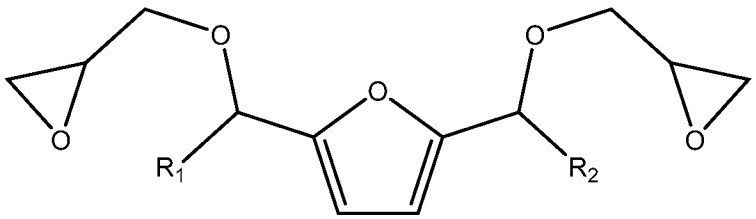
with the proviso that R_1, R_2, R_3, and R_4 cannot all be H.

11. The diglycidyl ether of claim 10 having the following structure:



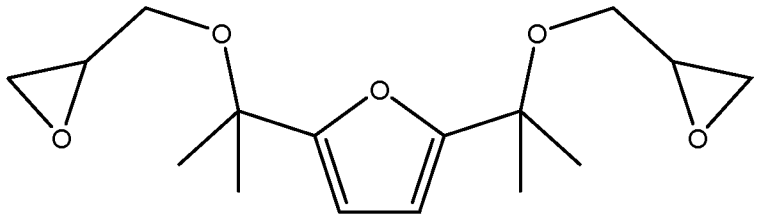
12. The diglycidyl ether of claim 11, wherein R_2 is methyl or phenyl.

13. The diglycidyl ether of claim 10 having the following structure:



14. The diglycidyl ether of claim 13, wherein R_1 and R_2 are both methyl, n-butyl, or allyl.

15. The diglycidyl ether of claim 10 having the following structure:



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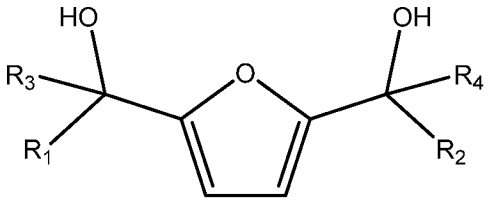
16. A method for making the diglycidyl ether of any of claims 10-15, comprising, consisting essentially of, or consisting of:

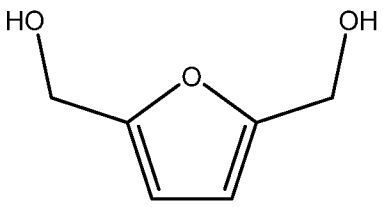
reacting a diol with epichlorohydrin under conditions sufficient to form the diglycidyl ether,

wherein the diol has the following structure:



wherein R_1, R_2, R_3, and R_4 are independently selected from the group consisting of H, C_1-C_6 alkyl, C_1-C_6 alkenyl, aryl, and C_1-C_6 alkyl-aryl.

17. The method of claim 16, wherein the diol cannot have the following structure:



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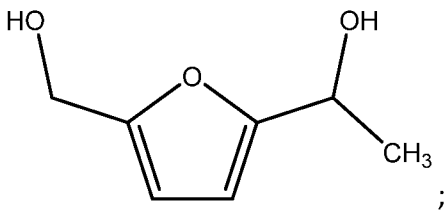

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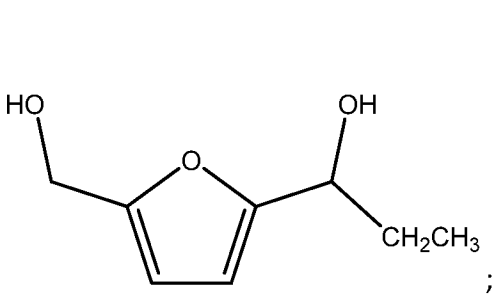

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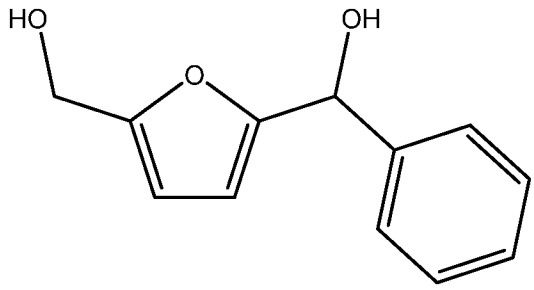
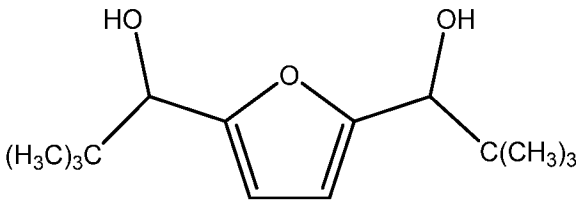


; or



.

18. A curable coating composition comprising, consisting essentially of, or consisting of:

a) at least one diglycidyl ether of any of claims 10-15; and

b) an amine.

19. The curable coating composition of claim 18, wherein the amine is an aliphatic, an aromatic, a cycloaliphatic, or a polyether amine.

20. The curable coating composition of claim 19, wherein the aliphatic amine is Priamine 1075, 1,8-diaminooctane, diethylenetriamine, or tetraethylenepentamine.

21. The curable coating composition of claim 19, wherein the aromatic amine is m-xylylenediamine.

22. The curable coating composition of claim 19, wherein the cycloaliphatic amine is 1,3-bis(aminomethyl)cyclohexane, isophorone diamine, or bis(p-aminocyclohexyl) methane.

23. The curable coating composition of claim 19, wherein the polyether amine is JEFFAMINE EDR-148 (XTJ-504), JEFFAMINE D-400, JEFFAMINE D-230, or JEFFAMINE T-403.

24. A cured coating composition, wherein the curable coating composition of any one of claims 18-23 is cured at ambient conditions or by heating.

25. An object coated with the curable coating composition of any one of claims 18-23.

26. A composite or adhesive comprising, consisting essentially of, or consisting of at least one diglycidyl ether of any of claims 10-15.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US2020/040918

A. CLASSIFICATION OF SUBJECT MATTER

IPC(8) - C07D 307/40; C07D 307/42; C07D 307/44; C08G 59/22; C08G 59/26 (2020.01)
CPC - C07D 307/40; C07D 307/42; C07D 307/44; C08G 59/22; C08G 59/26 (2020.08)

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
see Search History document

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched
see Search History document

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
see Search History document

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	PUBCHEM, Substance Record for SID 311663159, Available Date: 23 February 2016 [retrieved on 09 September 2020]. Retrieved from the Internet: <URL: https://pubchem.ncbi.nlm.nih.gov/substance/311663159>. entire document	1-3
X	PUBCHEM, Substance Record for SID 235901493, Available Date: 13 February 2015 [retrieved on 09 September 2020]. Retrieved from the Internet: <URL: https://pubchem.ncbi.nlm.nih.gov/substance/235901493>. entire document	1, 4
X	JP 2007-238570 A (KYOTO UNIVERSITY) 20 September 2007 (20.09.2007) see machine translation and original	1, 6
A	US 2013/0295399 A1 (SCHAEFER et al) 07 November 2013 (07.11.2013) entire document	1-8, 10-23, 26
A	US 2017/0121317 A1 (ROQUETTE FRERES) 04 May 2017 (04.05.2017) entire document	1-8, 10-23, 26
A	US 2016/0152764 A1 (RHODIA OPERATIONS) 02 June 2016 (02.06.2016) entire document	1-8, 10-23, 26
P, A	HU et al., Mechanically Triggered Small Molecule Release from a Masked Furfuryl Carbonate, Journal of the American Chemical Society, Vol. 141, No. 38, 13 September 2019 [retrieved on 11 September 2020]. Retrieved from the Internet: <URL: https://pubs.acs.org/doi/10.1021/jacs.9b08663>. Abstract and Supporting Information	1-8, 10-23, 26

☐ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

* Special categories of cited documents:
"A" document defining the general state of the art which is not considered to be of particular relevance
"D" document cited by the applicant in the international application
"E" earlier application or patent but published on or after the international filing date
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
"O" document referring to an oral disclosure, use, exhibition or other means
"P" document published prior to the international filing date but later than the priority date claimed
"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
11 September 2020	28 SEP 2020
Name and mailing address of the ISA/US Mail Stop PCT, Attn: ISA/US, Commissioner for Patents P.O. Box 1450, Alexandria, VA 22313-1450 Facsimile No. 571-273-8300	Authorized officer Blaine R. Copenheaver Telephone No. PCT Helpdesk: 571-272-4300

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US2020/040918

Box No. II Observations where certain claims were found unsearchable (Continuation of item 2 of first sheet)

This international search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:

2. ☐ Claims Nos.:
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:

3. ☒ Claims Nos.: 9, 24, 25
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box No. III Observations where unity of invention is lacking (Continuation of item 3 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.

2. ☐ As all searchable claims could be searched without effort justifying additional fees, this Authority did not invite payment of additional fees.

3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:

4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

☐ The additional search fees were accompanied by the applicant's protest and, where applicable, the payment of a protest fee.

☐ The additional search fees were accompanied by the applicant's protest but the applicable protest fee was not paid within the time limit specified in the invitation.

☐ No protest accompanied the payment of additional search fees.