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# Synthesis of chiral ADMET polymers containing repeating D-*chiro*-inositol units derived from a biocatalytically prepared diene diol

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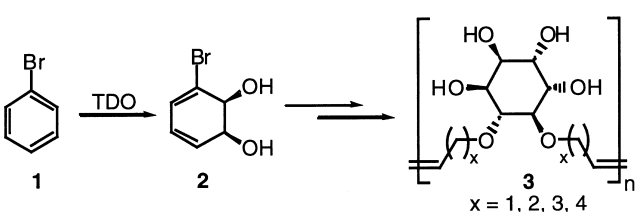
**Abstract**—Several chiral hydroxylated polymers have been prepared, via ADMET techniques, from the diene diol derived from bromobenzene, obtained by means of whole-cell fermentation with *Escherichia coli* (JM109 pDTG601).


Chiral polymers[1–3] are used in a number of interesting applications: in catalysis for asymmetric induction in organic synthesis,[1,2,4] in chiral separations,[5] and in ferroelectric and nonlinear optical applications.[6] Achiral monomers can be induced to form polymers with a helical conformation by means of 'helix-sense-selective' polymerization with either a chiral initiator or catalyst.[3] These include poly(chloral), poly(isocyanates), poly(isocyanides), and poly(triarylmethylmethacrylates). Other polymers, obtained, for example, by cyclopolymerization of diolefins,[7] diisocyanides,[8] vinyl ethers,[9–12] bis(styrenes),[1,2,11,12] dimethyacylates,[13–16] and diepoxides,[17] derive their optical activity from chirality in the main chain or in side chains. Synthetic peptide-like polymers are also included in this group.[18,19] The introduction of metal catalysts by Ziegler and Natta in the late 1940s provided an approach to making chiral polymers on an industrial scale.[20,21] Development of methods for the preparation chiral polymers remains a challenging field, as radical, anionic, and cationic methods are generally neither stereo- nor enantioselective.[22–24]

We have become interested in polyhydroxylated polymers, or high oligomers, such as **3**, derived from the monomers of established configuration via acyclic diene metathesis (ADMET) of vicinally bis-alkylated olefinic side chains.[25,26] The corresponding monomers are easily obtained from diene diol **2**, the product of the whole-cell fermentation of bromobenzene with a *E. coli* JM109 pDTG601A,[27] recombinant organism expressing toluene dioxygenase (TDO), Scheme 1. The central inositol unit can readily be synthesized in any of the nine possible configurations, as we have demonstrated previously.[28–31] It is also possible to approach the monomer synthesis from protected synthons—in such cases the number of isomeric possibilities in intermediates of this type would approach the theoretical limit of 64. As described in recent papers on combinatorial possibilities of oligoinositols,[32,33] the number of possible isomers increases exponentially with higher oligomers once secondary and tertiary structures develop through hydrogen-bonded forms and β-turns initiated by the 1,2 *trans* connectivity in **3**.[29–31,34] We were interested primarily in generating relatively low molecular weight polymers and investigating physical and chemical properties of these compounds in anticipation of further cross-linking and testing of these compounds as materials for chiral separations.

To test our approach to this problem, bis-allyl ether **8**, Scheme 2, was prepared and subjected to polymerization with Grubbs' first-generation catalyst. The bis-ether was generated by first protecting the *cis*-diol of the diene diol **2** as the acetonide followed by epoxidation of the more electron-rich double bond to afford epoxide **4**. The $BF_3{\cdot}Et_2O$-catalyzed epoxide opening of epoxide **4** with allyl alcohol led to a low yield of ether **5** at the expense of




**Scheme 1.** Chemoenzymatic approach to polyhydroxylated chiral polymers (D-*chiro*-inositol configuration shown).

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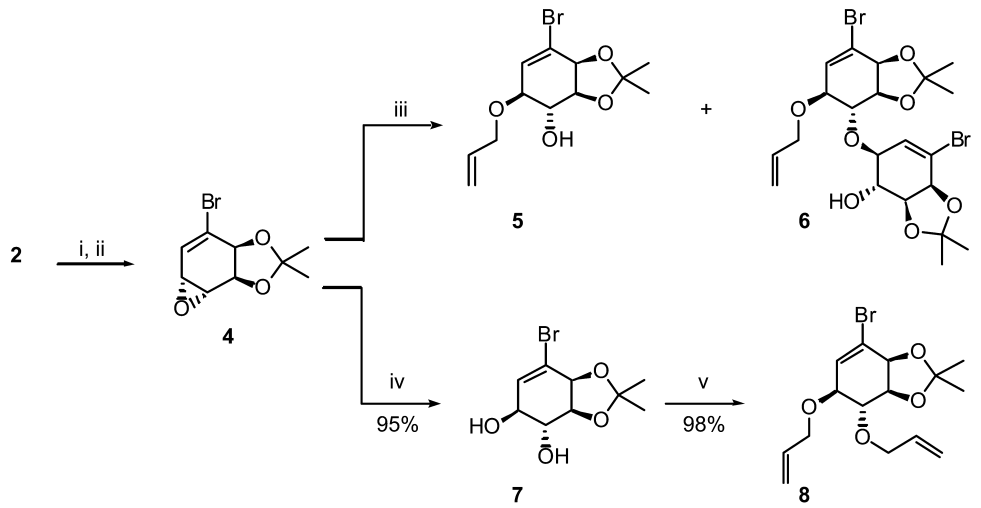
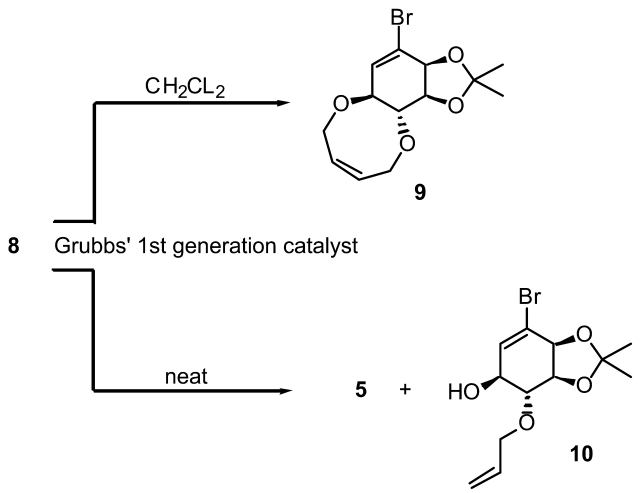



**Scheme 2.** Synthesis of monomer bis-allyl ether **8**. Key: (i) DMP, *p*TsOH; (ii) *m*CPBA, $CH_2Cl_2$; (iii) $BF_3{\cdot}Et_2O$, allyl alcohol; (iv) Amberlyst resin; (v) DMF; NaH, allyl bromide.

generating the conduritol dimer **6**. The problem was circumvented by treating epoxide **4** first with Amberlyst resin to afford *trans* diol **7**, which was alkylated with allylbromide to afford allyl ether **8** in 98% yield (Scheme 2).

Allyl ether **8** was subjected to ADMET conditions with Grubbs' first-generation catalyst under several conditions. In dilute methylene chloride, no polymerization occurred, and only the cyclic dioxocane **9** formed (Scheme 3). When the reaction was conducted neat, again no polymer formed,



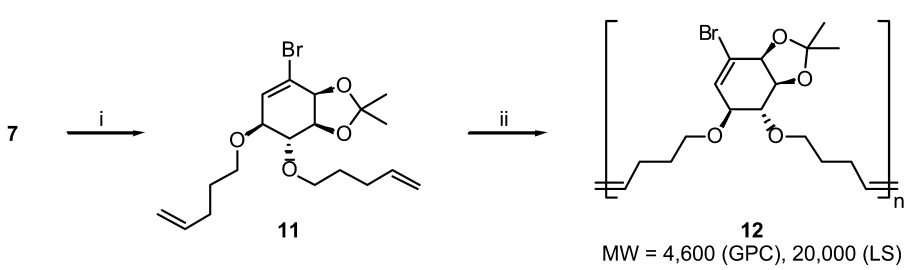

**Scheme 3.** Polymerization of **8** with Grubbs' first-generation catalyst.

and a mixture of de-allylated products **5** and **10**, along with starting material, was isolated.

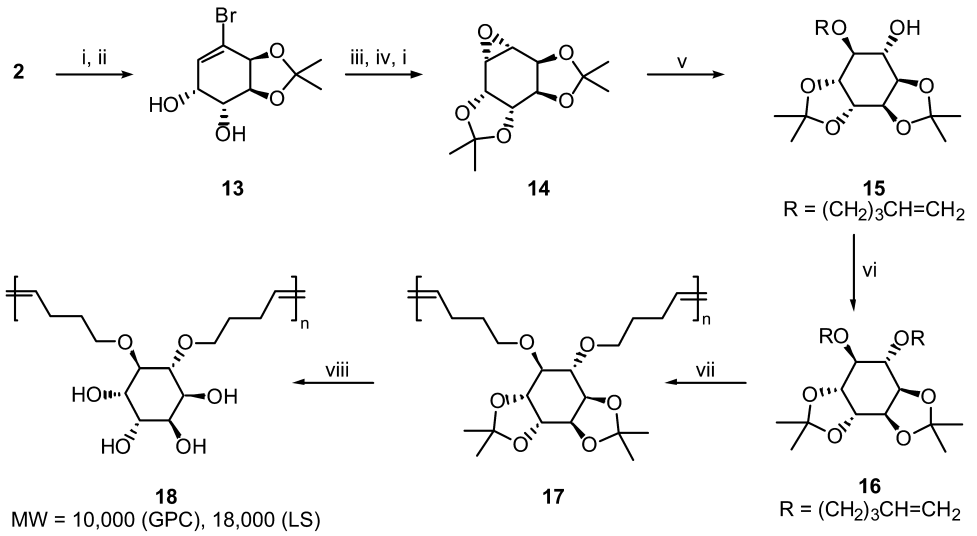
Diol **7** was alkylated with 5-bromopentene to furnish bis-alkylated ether **11**, which polymerized with Grubbs' first-generation catalyst. The result was polymer **12** having an estimated molecular weight of 4600. When monomer **11** was polymerized with Grubbs' second-generation catalyst, a polymer with an average molecular weight of 20,000 was obtained, determined by light-scattering (LS) analysis (Scheme 4).

The synthesis of the fully hydroxylated polymer was carried out as outlined in Scheme 5.

In the approach to polyhydroxylated polymer **18**, the *cis* diol in **2** was protected, and the more electron rich double bond was converted to *cis* diol **13**. Reduction under radical conditions with tri-*n*-butyltinhydride and subsequent epoxidation with *m*CPBA followed by protection of the *cis* diol provided epoxide **14**. $BF_3{\cdot}Et_2O$-catalyzed epoxide opening with 4-penten-1-ol gave alcohol **15**, which was alkylated with 5-bromopentene to furnish the desired monomer **16**. Exposure of this material to Grubbs' first generation of catalyst (neat) gave polymer **17** whose deprotection under acidic condition gave the fully hydroxylated polymer **18**, with a molecular weight estimated at ~10,000 via GPC analysis, as a viscous oil. Light scattering analysis of polymer **18** estimated the average molecular weight of the polymer at 18,000.




**Scheme 4.** Preparation and polymerization of pentenyl ether **11**. Key: (i) 5-bromopentene, DMF, NaH; (ii) Grubbs' catalyst (1st generation), neat, or Grubbs' catalyst (2nd generation), neat.




**Scheme 5.** Approach to fully hydroxylated chiral polymers. Key: (i) DMP, *p*TsOH; (ii) acetone, $H_2O$, NMO, $OsO_4$; (iii) $Bu_3SnH$, AIBN, PhH; (iv) *m*CPBA, $CH_2Cl_2$; (v) $BF_3{\cdot}Et_2O$, $CH_2Cl_2$, 4-penten-1-ol; (vi) DMF, NaH, 5-bromopentene; (vii) Grubbs' first-generation catalyst; (viii) THF–TFA–$H_2O$, 4:1:1.

## 1. Conclusions

New homochiral polymeric materials have been prepared from metabolites of type **2**. Further exploitation of the properties of these hydroxylated polymers in the area of chiral separation and catalyst development are ongoing and will be reported in due course.

## 2. Experimental

### 2.1. General

All commercial chemicals and solvents are reagent grade and were used without further purification unless otherwise specified. Standard techniques for the exclusion of moisture were used in all reactions. Reactions were monitored by thin-layer chromatography on 0.25 mm silica gel plates (60F-254, Silicycle) and visualized with UV light, iodine vapors, or 5% phosphomolybdic acid in 95% ethanol. Final compounds were typically purified by flash chromatography on silica gel (230–400 mesh). All $^1$H- and $^{13}$C NMR spectra were recorded at 300 and 75 MHz, respectively, using a Varian 300 spectrometer. Chemical shifts are reported relative to TMS, $CDCl_3$, or DMSO-$d_6$. Coupling constants are measured in Hz. Infrared spectra, recorded on a Perkin–Elmer FT-IR, are reported as wavenumbers ($cm^{-1}$). High-resolution mass spectra were performed at the University of Florida, elemental analyses at Atlantic Microlab, Inc. Optical rotations were recorded on a Perkin–Elmer 241 digital polarimeter ($10^{-1}$ deg $cm^2$ $g^{-1}$). Melting points were obtained on a Thomas–Hoover capillary melting point apparatus and are uncorrected. Gel permeation chromatography (GPC) was performed on two 300 mm Polymer Laboratories 5 μm mixed-C columns with a Rainin SD-300 pump, a Hewlett–Packard 1047-A RI detector, a TC-45 Eppendorf column heater set to 35 °C and a Waters U6K injector.

**2.1.1. 5-(5-Allyloxy-7-bromo-2,2-dimethyl-3a,4,5,7a-tetrahydro-benzo[1,3]dioxol-4-yloxy)-7-bromo-2,2-dimethyl-3a,4,5,7a-tetrahydro-benzo[1,3]dioxol-4-ol (6).** Bromoepoxide **4** (0.5 g) was added to a flame-dried 50 mL round-bottomed flask containing a stirred solution of allyl alcohol (0.56 g, 9.66 mmol) in freshly distilled methylene chloride (5 mL) under argon atmosphere. The reaction mixture was cooled to −78 °C for 20 min. $BF_3{\cdot}Et_2O$ (10 mol%) was added, and the reaction mixture was stirred overnight. The reaction was quenched with water (10 mL), and the mixture was extracted with methylene chloride (3×10 mL). The organic layers were combined and washed with 5% $NaHCO_3$ (10 mL), dried ($MgSO_4$) and concentrated under reduced pressure to afford a reddish residue. The products were purified by flash chromatography (hexanes–EtOAc, 4:1) to yield dimer **6** as a white solid (356 mg, 63%) with trace amount of alcohol **5** (8 mg, 3%).

**2.1.2. 5-Allyloxy-7-bromo-2,2-dimethyl-3a,4,5,7a-tetrahydro-benzo[1,3]dioxol-4-ol (5).** $R_f$=0.48 (hexanes–EtOAc, 3:1); $^1$H NMR (300 MHz, $CDCl_3$) $\delta$ 6.22 (m, 2H), 5.28 (ddd, $J$=17.2, 1.75, 1.46 Hz, 1H), 5.16 (ddd, $J$=10.5, 1.75, 1.46 Hz, 1H), 4.94 (bs, 1H), 4.70 (ddd, $J$=6.42, 1.75, 1.46 Hz, 1H), 4.25 (ddt, $J$=13.1, 5.26, 1.46 Hz, 1H), 4.16 (dd, $J$=9.64, 6.42 Hz, 1H), 3.98 (ddt, $J$=12.8, 5.84, 1.46 Hz, 1H), 3.60 (t, $J$=9.64 Hz, 1H), 1.55 (s, 3H), 1.43 (s, 3H).

*Compound* **6**: $R_f$=0.65 (hexanes–EtOAc, 3:2); mp=176–177 °C; $[\alpha]_D^{31}$=+47.35 (c, 0.665, $CHCl_3$); IR (KBr) 3498, 2981, 1645, 1457, 1381, 1214, 1046, 998, 870, 513 $cm^{-1}$; $^1$H NMR (300 MHz, $CDCl_3$) $\delta$ 6.33 (d, $J$=1.71 Hz, 1H), 6.28 (d, $J$=1.71 Hz, 1H), 6.18–5.85 (m, 1H), 5.39–5.24 (m, 2H), 4.72 (d, $J$=6.84 Hz, 1H), 4.47 (d, $J$=6.84 Hz, 1H), 4.46 (s, 1H), 4.28–4.12 (m, 3H), 4.45–4.00 (m, 1H), 3.90 (d, $J$=8.30 Hz, 1H), 3.86–3.80 (m, 1H), 3.67 (m, 1H), 3.53 (t, $J$=8.7 Hz, 1H), 1.58 (s, 3H), 1.57 (s, 3H), 1.42 (s, 3H), 1.41 (s, 3H); $^{13}$C NMR (75 MHz, $CDCl_3$) $\delta$ 135.1, 133.5, 132.8, 118.8, 118.1, 117.9, 111.5, 111.1, 84.4, 84,1, 78.7, 77.6, 77.20, 77.1, 74.1, 74.0, 71.2, 28.2, 27.7, 25.9, 25.7. HRMS (FAB) calcd for

$C_{21}H_{29}O_7Br_2$: 551.0280. Found: 551.0045. Anal. calcd for $C_{21}H_{28}O_7Br_2$: C, 45.67; H, 5.11. Found: C, 45.92; H, 5.28.

**2.1.3. 4,5-*bis*-Allyloxy-7-bromo-2,2-dimethyl-3a,4,5,7a-tetrahydro-benzo[1,3]dioxole (8).** Into a 50 mL oven-dried round-bottomed flask, NaH (2.41 g, 45 mmol) was suspended in anhydrous DMF (20 mL) under argon atmosphere. Bromodiol **7** (2.41 g, 9.1 mmol) was added, and the reaction mixture was stirred for 1 h at room temperature. Allylbromide (5.46 g, 45 mmol) dissolved in 10 mL DMF was added dropwise to the reaction mixture. The reaction proceeded for 8 h after the addition of allylbromide. The reaction was quenched with water, and the mixture was extracted with diethyl ether (3×25 mL). The product was purified by flash chromatography (hexanes–EtOAc, 9:1). The fractions containing bis-allylether **8** were combined and concentrated to yield a yellowish oil, which was further purified by distillation at high temperature at under reduced pressure (150 °C, 0.2 mm Hg) using a Kugelrohr apparatus to afford bis-allylether **8** as a colorless oil (3.14 g, 98%). $R_f$=0.44 (hexanes–EtOAc, 6:1); $[\alpha]_D^{27}$=36.85 (*c* 1.1, $CDCl_3$); IR (film) 3078, 2987, 1646, 1456, 1381, 1246, 1218, 1073, 869, 794 $cm^{-1}$; $^1H$ NMR (300 MHz, $CDCl_3$) $\delta$ 6.21 (d, *J*=2.19 Hz, 1H), 6.02–5.84 (m, 2H), 5.33 (dt, *J*=1.47, 1.71 Hz, 1H), 5.28 (dt, *J*=1.47, 1.71 Hz, 1H), 5.24–5.14 (m, 2H), 4.65 (dd, *J*=1.22, 6.35 Hz, 1H), 4.40–4.25 (m, 2H), 4.24–4.19 (dd, *J*=6.35, 8.55 Hz, 1H), 4.16 (t, *J*=1.46 Hz, 1H), 4.14 (t, *J*=1.46 Hz, 1H), 3.90–3.84 (ddd, *J*=1.22, 0.98, 7.82 Hz, 1H), 3.52 (t, *J*=8.05 Hz, 1H), 1.55 (s, 3H), 1.41 (s, 3H); $^{13}C$ NMR (75 MHz, $CDCl_3$) $\delta$ 135.2, 134.5, 133.6, 119.0, 117.4, 117.4, 110.8, 79.2, 78.0, 77.9, 77.65, 73.5, 71.7, 28.2, 26.3; HRMS (EI) *m/z* calcd for $C_{14}H_{18}O_4Br$ $[M-CH_3]^+$: 329.0388. Found: 329.0271. Anal. calcd for $C_{15}H_{21}O_4Br$: C, 52.19; H, 6.13. Found C, 52.35; H, 6.23.

**2.1.4. ADMET polymerization of bis-allylether 8: 4-bromo-2,2-dimethyl-3a,5a,7,10,11a,11b-hexahydro-1,3,6,11-tetraoxa-cycloocta[*e*]indene (9).** Into an oven-dried 10 mL round-bottomed flask, bis-allylether **8** (76 mg, 0.2 mmol) was dissolved in freshly distilled methylene chloride (5 mL) at room temperature under argon atmosphere. Grubbs' first-generation catalyst (9.4 mg, 0.01 mmol) was then added, and the reaction mixture was stirred under argon for 24 h. The reaction was quenched with ethyl vinyl ether (0.2 mL), and the mixture concentrated under reduced pressure. The residue was purified via flash chromatography to yield the cyclic dioxocane **9** as a colorless oil (25 mg, 36%). $R_f$=0.45 (hexanes–EtOAc, 4:1); $^1H$ NMR (300 MHz, $CDCl_3$) $\delta$ 6.17 (d, *J*=2.1 Hz), 5.85–5.65 (m, 2H), 4.70–5.58 (m, 2H), 4.46–4.25 (m, 3H), 4.17 (dd, *J*=6.4, 9.0 Hz, 1H), 3.91 (td, *J*=8.47, 1.46 Hz, 1H), 3.47 (t, *J*=8.76 Hz, 1H), 1.56 (s, 3H), 1.42 (s, 3H); $^{13}C$ NMR (75 MHz, $CDCl_3$) $\delta$ 134.9, 130.1, 129.1, 118.2, 111.0, 81.5, 78.8, 77.4, 77.3, 69.5, 67.4, 28.4, 26.1; HRMS (EI) calcd for $C_{13}H_{17}BrO_4$: 316.0310. Found: 316.0309.

**2.1.5. 7-Bromo-2,2-dimethyl-4,5-bis-pent-4-enyloxy-3a,4,5,7a-tetrahydro-benzo[1,3]dioxole (11).** To a solution of bromodiol **7** (0.73 g, 2.75 mmol) in anhydrous DMF (10 mL) cooled in an ice bath, NaH (0.66 g, 22 mmol) was added under argon atmosphere. The reaction mixture was allowed to stir for 1 h. 5-Bromopentene (3.28 g, 22 mmol) dissolved in DMF (10 mL) was then added dropwise, and the reaction mixture was stirred for 6 h. The reaction was quenched with water (5 mL) and extracted with diethyl ether (3×25 mL). The ethereal extracts were combined, dried ($MgSO_4$), and concentrated. The residue was purified by flash chromatography (hexanes–EtOAc, 9:1). Fractions containing monomer **11** were combined and concentrated to yield a yellowish oil, which was distilled under reduced pressure (155 °C, 0.2 mm Hg) using a Kugelrohr apparatus to furnish monomer **11** as a colorless oil (0.35 g, 32%). $^1H$ NMR (300 MHz, $CDCl_3$) $\delta$ 6.2 (d, *J*=3.05 Hz), 5.92–5.74 (m, 2H), 5.05 (*J*=2.05, 1.54 Hz, 1H), 5.03–4.92 (m, 3H), 4.63 (dd, *J*=1.03, 6.41 Hz, 1H), 4.21–4.12 (dd, *J*=6.41, 8.46 Hz, 1H), 3.86–3.67 (m, 3H), 3.65–3.51 (m, *J*=2.56, 5.64, 6.41, 6.67 Hz, 2H), 3.39 (t, *J*=8.1 Hz), 2.20–2.08 (m, 4H), 1.77–1.63 (m, 4H), 1.54 (s, 3H), 1.41 (s, 3H); $^{13}C$ NMR (75 MHz, $CDCl_3$) $\delta$ 138.5, 138.2, 133.8, 118.8, 115.2, 114.8, 110.7, 80.0, 79.0, 78.0, 77.5, 72.3, 70.0, 30.4, 30.8, 29.5, 29.3, 28.3, 26.3; HRMS (EI) *m/z* calcd for $C_{19}H_{29}O_4Br$: 400.1249 Found: 400.1256.

**2.1.6. ADMET polymerization of monomer 11.** Freshly distilled monomer **11** (1.68 g, 4.19 mmol) was placed in a 10 mL round-bottomed flask equipped with a magnetic stir bar. The monomer was degassed by means of freeze-pump-thaw cycles under high vacuum ($<10^{-4}$ Torr). Grubbs' second-generation catalyst (35 mg, 1%) was then added under argon atmosphere. A few drops of dry $CDCl_3$ were added to initiate the polymerization process. After the addition of the catalyst, very slow to moderate bubbling of ethylene was observed. The bubbling reaction mixture was then exposed to intermittent vacuum until the viscosity increased, followed by exposure to high vacuum to remove ethylene, which is continuously generated during the course of the polymerization. The reaction was carried out at room temperature until increased viscosity prevented stirring, after which time the temperature was raised to 55 °C over a period of 5 days until a very high viscosity was obtained or bubbling ceased. The reaction mixture was then cooled to room temperature, and the reaction quenched by exposure to air. The viscous residue was dissolved in ethyl acetate and passed through a short column of silica to furnish a brown viscous oil (1.58 g), whose average molecular weight was estimated to be 20,000 by light-scattering analysis. $[\alpha]_D^{27}$=−12.1 (*c* 1.1, $CH_3OH$).

**2.1.7. 2,2,7,7-Tetramethyl-5-pent-4-enyloxy-hexahydro-benzo[1,2-d;3,4-d′]bis[1,3]dioxol-4-ol (15).** The diacetonide-protected epoxide **14** (1.0 g, 4.13 mmol) and 4-penten-1-ol (0.64 mL, 6.19 mmol) were dissolved in freshly distilled methylene chloride (15 mL), and the mixture cooled in an ice bath for 15 min. $BF_3{\cdot}Et_2O$ (10 mol%) was added, and the reaction was allowed to proceed overnight. The reaction was quenched with water, and the mixture was extracted with methylene chloride (3×25 mL). The organic layers were combined, dried ($Na_2SO_4$) and concentrated. The product was purified by flash chromatography (hexanes–EtOAc, 5:1) to yield alcohol **15** (0.794 g, 59%) as a colorless semi-solid material. $R_f$=0.25 (hexane–EtOAc, 5:1), $[\alpha]_D^{27}$=−29.4 (*c* 1.1, $CH_3OH$); IR (film) 3459, 2986, 1380, 1260, 1067, 1025 $cm^{-1}$; $^1H$ NMR (300 MHz, $CDCl_3$) $\delta$ 5.92–5.74 (m, 1H), 5.10–4.92 (m, 2H), 4.28–4.12 (m, 4H), 3.96–3.84 (m, 1H), 3.70–3.50 (m, 2H), 3.30–3.20 (m,

1H), 2.93 (s, exchanged with $D_2O$, 1H), 2.22–2.10 (m, 2H), 1.80–1.65 (m, 2H), 1.51 (s, 6H), 1.36 (s, 3H), 1.34 (s, 3H); $^{13}C$ NMR (75 MHz, $CDCl_3$) $\delta$ 138.42, 115.11, 110.3, 110.0, 80.0, 79.3, 78.5, 76.9, 76.8, 71.5, 70,9, 30.5, 29.2, 27.9, 27.8, 25.4, 25.2; HRMS (EI) *m/z* calcd for $C_{16}H_{25}O_6$ $[M-CH_3]^+$: 313.1651. Found: 313.1649.

**2.1.8. 2,2,7,7-Tetramethyl-4,5-bis-pent-4-enyloxy-hexahydro-benzo[1,2-d;3,4-d′]bis[1,3]dioxole (16).** In a 10 mL round-bottomed flask NaH (169 mg, 4.2 mmol) was suspended in anhydrous DMF (5 mL). Alcohol **15** (138 mg, 0.42 mmol) dissolved in DMF (5 mL) was then added dropwise to the reaction flask and allowed to stir at room temperature for 45 min. 5-Bromopentene (0.62 mL, 4.2 mmol) was then added, and the reaction was allowed to proceed for 5 h. The reaction was quenched with $H_2O$ (5 mL) and extracted with $Et_2O$ (3×10 mL). The ethereal portions were combined, washed with saturated NaCl (10 mL), $H_2O$ (10 mL), dried ($MgSO_4$), and concentrated. The product was purified by flash chromatography (hexanes–EtOAc, 9:1) to yield a thick red oil (96 mg, 93%). $R_f$=0.68 (hexane–EtOAc, 5:1), $^1H$ NMR (300 MHz, $CDCl_3$) $\delta$ 5.90–5.72 (m, 2H), 5.08–5.02 (m, 1H), 5.02–4.90 (m, 3H), 4.50–4.32 (m, 1H), 4.24–4.10 (m, 4H), 3.80–3.66 (m, 4H), 3.36–3.26 (m, 2H), 2.20–2.06 (m, 4H), 1.76–1.63 (m, 4H), 1.49 (s, 6H), 1.40 (s, 6H); $^{13}C$ NMR (75 MHz, $CDCl_3$) $\delta$ 138.6, 114.8, 114.7, 112.3, 109.6, 80.3, 79.4, 77.3, 76.7, 75.6, 74.2, 71.7, 70.9, 30.4, 29.9, 29.5, 29.3, 28.0, 26.5, 25.6, 24.3.

**2.1.9. ADMET polymerization of diene 16 to generate polymer 17.** Monomer **16** (240 mg, 0.61 mmol) was placed in a 10 mL round-bottomed flask equipped with a stir bar and was degassed through several freeze-pump-thaw cycles under high vacuum ($<10^4$ Torr). Grubbs' first-generation catalyst (5 mg) was then added under argon atmosphere. After the addition of Grubb's catalyst, very slow to moderate bubbling of ethylene was observed. The bubbling reaction was then exposed to intermittent vacuum until the viscosity increased, followed by exposure to high vacuum to remove the ethylene, which was continuously generated during the course of the polymerization. The reaction was maintained at room temperature until the increase in viscosity prevented stirring. At this point, the reaction temperature was slowly raised to 45 °C over a period of 5 days until bubbling ceased. The reaction mixture was then cooled to room temperature, and quenched by exposure to air. The viscous residue was dissolved in ethyl acetate and passed through a short column of silica to furnish polymer **17** as a brown viscous oil. $^1H$ NMR (300 MHz, $CDCl_3$) $\delta$ 5.50–5.40 (b, 2H), 4.25–4.15 (b, 4H), 3.80–3.65 (m, 4H), 3.31 (s, 2H), 2.20–1.80 (b, 4H), 1.75–1.55 (m, 4H), 1.50 (s, 6H), 1.33 (s, 6H).

**2.1.10. Deprotection of polymer 17.** Polymer **17** was dissolved in 5 mL of a 4:1:1 mixture of THF, TFA and $H_2O$. The reaction was stirred at room temperature for 4 h. The reaction mixture was diluted with brine (3 mL) and extracted with ethyl acetate (4×10 mL). The organic fractions were combined, dried ($Na_2SO_4$), and concentrated. After the solvent was removed, the residue was introduced onto a silica-gel column and eluted with ethyl acetate to arrive at fully hydroxylated polymer **18**, whose molecular weight was estimated at 10,000 via GPC analysis. Light scattering analysis of polymer **18** estimated the average molecular weight of the polymer to be at around 18,000. $[\alpha]_D^{27}$=25.1 (c 2.1, $CH_3OH$).

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## References and notes

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