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Polycondensation of Butenediol: Synthesis of Telechelic 2-Butene-1,4-diol Oligomers

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S *Supporting Information*

ABSTRACT: The catalytic condensation of *cis*-2-butene-1,4-diol with CpRu(MQA)(C$_3$H$_5$) (Cp = cyclopentadienyl, MQA = 4-methoxyquinoline-2-carboxylate) generates poly-(2-butenediol), an unsaturated telechelic polyether diol with molecular weights between 400 and 4600 g/mol. This Ru(IV) allyl catalyst enchains 2-butene-1,4-diol primarily as the linear *trans*-2-butenyl ether (92%) along with vinyl branches (8%). These telechelic oligomers are useful chain extenders and macromonomers, as demonstrated by their use in the synthesis of poly(lactide)-*b*-poly(butenediol)-*b*-poly(lactide) triblock copolymers. Model studies support a proposed mechanism involving the formation of Ru(IV) allyl intermediates from allylic alcohols and chain growth by selective nucleophilic displacement at the terminus of the Ru(IV) allyl to generate *trans*-2-butenyl ether linkages.
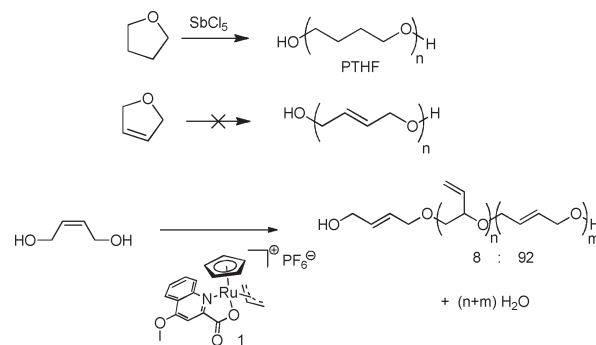
Figure 1. Ring-opening polymerization of furans and step-growth polymerization of butene-1,4-diol.

Telechelic polymers are valuable building blocks for the construction of an array of polymeric materials that are useful as adhesives and biomedical and elastomeric materials.[1−7] Polytetrahydrofuran (PTHF) (Figure 1) is a commodity telechelic polymer of which ~200 000 tons are produced annually.[8] In contrast, the corresponding unsaturated analogue poly(1,2-dihydrofuran) is unknown. This is a potentially attractive material, as unsaturated telechelic polymers such as hydroxytelechelic butadiene (HTPB)[9] are widely used commercially as components for elastomers and as binders for solid rocket fuels.[10−12] However, poly(1,2-dihydrofuran) cannot be readily produced from 1,2-dihydrofuran because of side reactions that occur under the conditions typically used in the Lewis acid-mediated ring-opening polymerization (ROP) of THF (Figure 1).[13,14] Herein we report a strategy for obtaining unsaturated telechelic oligoethers by a different route involving the Ru-catalyzed step-growth polymerization of 2-butene-1,4-diol.

Our approach was inspired by Kitamura's pioneering studies[15−17] on the formation of allyl ethers and our own investigations of the catalytic behavior of Ru allyl complex **1**,[18] a modified version of a Ru(IV) (de)allylation catalyst first reported by Kitamura.[15−17] Complex **1** catalyzes the hydrolysis or alcoholysis of allyl carbonates in either aqueous or alcohol solution.[19] Kinetic and mechanistic studies indicated that the Ru(IV) allyl complex can be generated from allyl alcohols and that the corresponding Ru(IV) allyl species are readily attacked by alcohols to generate allyl ethers. While these catalysts are known to catalyze the hydrolysis of allyl ethers,[20] our kinetic studies implied that allyl ether hydrolysis is slower than allyl ether formation. This reactivity

suggested a novel strategy for generating polyethers by the CpRu(IV) allyl-catalyzed condensation of 2-butene-1,4-diol (Figure 1).

A model study was first carried out by reacting the Ru(IV) allyl complex **1** with a stoichiometric amount of *cis*-2-butene-1,4-diol at room temperature in acetone-d_6 (eq 1). After 72 h at room temperature, 18% of the butenediol was converted to the allylic ether *cis*-4-(allyloxy)but-2-en-1-ol, indicating that butenediol is a competent nucleophile for displacing the allylic fragment from Ru(IV) complex **1**. In the presence of 5 mol % **1**, *cis*-2-pentenol was converted (53% conversion) in CD$_3$OH after 24 h to an 80:20 mixture of the linear *trans*-1-methoxy-2-pentene and branched 3-methoxy-1-pentene (7% yield for the branched product and 46% yield for the linear product; eq 2). These results indicate that allylic alcohols can function both as nucleophiles and electrophiles in allylic substitution reactions[21,22] mediated by Ru(IV) allyl complex **1**.
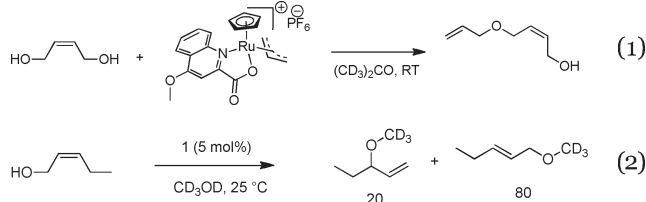
The catalytic oligomerization of *cis*-2-butene-1,4-diol (BD) was carried out by treating a 50/50 acetone/*cis*-2-butene-1,4-diol solution with Ru complex **1** (0.10 mol % relative to diol) at room temperature (Table 1, entry 1). Analysis of aliquots by

Table 1. Catalytic Oligomerization of *cis*-2-Butene-1,4-diol

entry	$[BD]_0$ (M)	$[Ru]$ (mM)	solvent	time (h)	temp	yield	M_n $(M_w/M_n)^a$
1	6.1	7.2	acetone	72	25 °C	1.71 g, 80%	415 (2.2)
2	1.24	12	acetone	22	55 °C	0.183 g, 65%	499 (1.4)
3	8.1	5	CH_2Cl_2/Et_2O	48	reflux	2.99 g, 70%	2300 (2.6)
4^b	8.1	5	CH_2Cl_2/Et_2O	72	reflux	1.90 g, 57%	5970 (2.2)

^{a} Determined by GPC vs polystyrene standards. The units of M_n are g/mol. ^{b} Reaction performed as in entry 3 followed by 24 h under high vacuum.
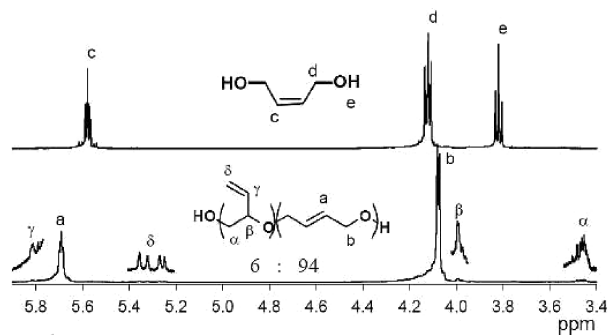

Figure 2. ^1H NMR spectra of (top) *cis*-2-butene-1,4-diol and (bottom) poly(2-butene-1,4-diol). Each inset above the bottom spectrum is a 10× enlargement of the section of the spectrum below that inset.

Figure 3. Chain extension of **2** with L-lactide to yield **3**. Asterisks indicate PLA end-group resonances.

gel-permeation chromatography (GPC) revealed an increase in molecular weight with time. Under these conditions, a molecular weight plateau ($M_n = 700$ g/mol) was reached at 48 h (as determined by GPC), which corresponds to 80% conversion from monomer (as determined by ^1H NMR). Evaporation of the reaction solvent yielded a mixture of products that was shown by electrospray ionization mass spectrometry (ESI-MS) to be composed of a mixture of cyclic [ESI-MS: $(C_4H_6O)_n$, $n = 3-10$; for $(C_4H_6O)_3 + H^+$, m/z 210.82 vs 211.12 g/mol] and linear polymer chains spaced by the mass of a butene ether repeat unit (Figure S2 in the Supporting Information). Dissolution of the crude material in CH_2Cl_2 followed by treatment with hexanes and drying yielded poly(2-butene-1,4-diol) [poly(BD), **2**] [GPC: $M_n = 770$ g/mol, $M_w/M_n = 2.97$. ESI: $HO(C_4H_6O)_nH$, $n = 5-27$; for $HO(C_4H_6O)_{16}H + Na^+$, m/z 1161.59 vs 1161.64 g/mol]. The concentrated supernatant contained primarily cyclic oligomers, as determined by ESI-MS (Figure S4). These cycles are the unsaturated versions of the $5n$-crown-n series of crown ethers.[23-25]

To characterize the structure of poly(BD) **2**, the crude sample isolated by precipitation ($M_n = 415$ g/mol, $M_w/M_n = 2.2$) was purified and fractionated by dialysis in CH_2Cl_2/MeOH to afford a higher-molecular-weight fraction ($M_n = 5000$ g/mol, $M_w/M_n = 1.3$) that could be analyzed by NMR spectroscopy (Figure 2 and Figure S3). Analysis of the ^1H NMR (Figure 2) and ^{13}C NMR (Figures S5 and S6) spectra of **2** revealed that the butenediol is enchained predominantly as linear *trans*-2-butenyl ether (94%) and 2-vinyl ethyl ether (6%) repeating units (linear/branched ratio = 94/6).

Small-scale screening experiments revealed that for oligomerizations carried out in acetone solvent at 25 or 55 °C, the molecular weights (300-500 g/mol) and yields (60-80%) were modest. However, when a solution of *cis*-2-butene-1,4-diol (3.9 mL, 0.047 mol) and **1** (14.8 mg, 0.025 mmol) in a mixture of ethyl ether (1.9 mL) and CH_2Cl_2 (3.8 mL) was refluxed for 48 h beneath a condenser column packed with 4 Å molecular
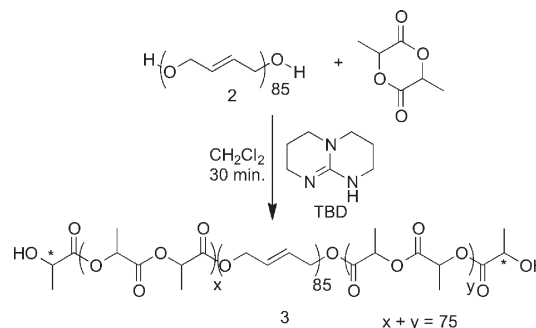
sieves,[26] the molecular weight of the polymer was 2300 g/mol as determined by GPC. Continuing the reaction for an additional 24 h under high vacuum further increased the molecular weight to 5970 g/mol (Table 1, entry 4), and linear enchainment of butene-diol predominated (linear/branched = 93/7). These results suggest that higher-molecular-weight telechelics can be generated by removing the water byproduct of the condensation reaction.

Analysis of the ^{13}C NMR spectra of low-molecular-weight samples provided clear evidence for allylic alcohol end groups (Figure S6). The presence of alcohol end groups on both ends of oligomers **2** was confirmed by a chain-extension experiment in which oligomer **2** was used as a macromolecular initiator for ROP of L-lactide (L-LA). ROP of L-LA (0.417 g; 2.89 mmol) initiated with a sample of **2** (202 mg, 0.035 mmol; $M_n = 6000$ g/mol, $M_w/M_n = 2.2$) in the presence of 1,5,7-triazabicyclo[4.4.0]dodec-1-ene (TBD) (0.004 mmol, 2.9 mM)[27,28] in CH_2Cl_2 afforded the poly(LA)-*b*-poly(butenediol)-*b*-poly(LA) triblock copolymer **3** ($M_n = 12700$ g/mol, $M_w/M_n = 1.97$).[4] The ^1H NMR spectrum of **3** exhibited a quartet at 4.4 ppm consistent with the assignment (assisted by $^1H-^1H$ COSY) as poly(LA) (PLA) methine end groups (* in Figure 3). Integration of this end-group signal versus the sum of the signals for the internal olefinic Hs of the enchained butenediol yielded 1.99 end groups/chain and $M_n = 6000$ g/mol for the butenediol block, in close agreement with that measured for **2**. Each of the PLA blocks had $M_n = 5500$ g/mol, giving an overall M_n of 17000 g/mol, in good agreement with that measured by GPC for **3** ($M_n = 12700$ g/mol). Integrations of the resonances of the PLA versus the resonances due to the butenediol gave a poly(BD):PLA ratio of 1.13:1.00, consistent with a poly(LA)-*b*-poly(butenediol)-*b*-poly(LA) triblock copolymer.[4]

The internal butenediol block can be readily degraded by catalytic olefin metathesis.[29,30] Treatment of **3** (102 mg, 0.0080 mmol) with 1-hexene and the Grubbs-II catalyst (1,3-bis(2,4,6-trimethylphenyl)-2-imidazolidinylidene)dichloro-(phenylmethylene)(tricyclohexylphosphine)ruthenium (2 mg,
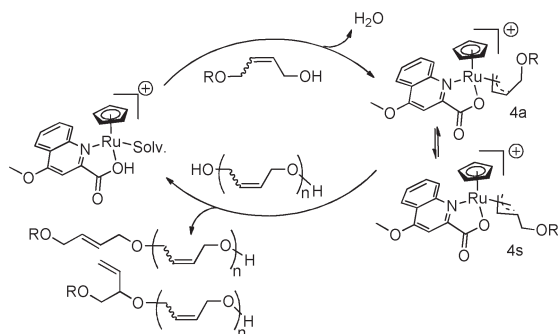
Figure 4. Polymerization mechanism (PF_6 anions have been omitted for clarity).

0.0024 mmol) in anhydrous 1:1 hexene/benzene (4 mL) for 12 h afforded PLA with M_n = 6700 g/mol, and ^{1}H NMR analysis indicated the absence of poly(butenediol). Taken together, these results suggest that the poly(butenediol)s generated from condensation of *cis*-2-butene-1,4-diol are oligomeric telechelic diols that can function as macroinitiators for the generation of triblock copolymers.[4]

Shown in Figure 4 is one proposed mechanism for the oligomerization. On the basis of previous studies[15,18,31] and model reactions (eqs 1 and 2), we propose that the Ru(IV) allyl precursor **1** reacts with *cis*-2-butene-1,4-diol with the elimination of *cis*-4-(allyloxy)but-2-en-1-ol to generate a solvated Ru(II) species. This Ru(II) complex can react with either the monomer or an allylic alcohol chain end to generate Ru(IV) allyl **4** with concomitant elimination of water. Nucleophilic displacement of the allyl ligand of **4** by either monomer or ROH chain ends results in chain extension.[18,31−33] Attempts to isolate or characterize intermediate **4** have proven unsuccessful, but we propose that the endo-syn Ru allyl species **4s** is formed from Ru(II) and *cis*-2-butene-1,4-diol. As we observed only *trans*-butenyl ethers in the polymer chain, we propose that syn-anti isomerization of the Ru(IV) allyl[21,22] is competitive with chain growth. This was corroborated by model studies in which an aqueous solution of *cis*-2-butene-1,4-diol was observed to isomerize to *trans*-2-butene-1,4-diol in the presence of 1.5 mol % **1**.

The high selectivity for linear enchainment in the oligomerization of *cis*-2-butene-1,4-diol (80−96% linear, depending on the conditions) or allylation of methanol with *cis*-2-pentenol (eq 2) implies that terminal attack of the alcohol on the allyl intermediate **4** is preferred. This atypical regioselectivity is important for chain growth, as branched allylic alcohol termini can function as nucleophiles but not as readily as electrophiles. Complexes of CpRu typically exhibit low regioselectivity in favor of the linear isomer;[34,35] the more sterically demanding pentamethylcyclopentadienylruthenium (Cp*Ru) complexes (including those ligated by quinaldic acid) exhibit high selectivities for branched isomers.[35−40]

In summary, we have reported the synthesis of unsaturated telechelic diols by Ru-catalyzed step-growth condensation of *cis*-2-butene-1,4-diol. While step-growth polymerization of allylic AB monomers or combinations of AA and BB monomers (where A = allylic electrophile and B = nucleophile) is known,[41,42] the ability of allylic alcohols to function as both nucleophiles and electrophiles in the presence of Ru catalyst **1** enables the facile formation of polyethers with the elimination of water as the only byproduct. The unsaturated telechelic polyether diols can be used as macromonomers for the synthesis of triblock copolymers and should also prove useful as cross-linkable chain extenders in polyurethanes and polyetheresters.

■ ASSOCIATED CONTENT

ⓢ **Supporting Information.** Experimental details; ^{1}H, ^{13}C, and [1]H−^{1}H COSY NMR spectra; and ESI-MS and differntial scanning calorimetry traces. This material is available free of charge via the Internet at http://pubs.acs.org.

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■ ACKNOWLEDGMENT

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