Chapter 8

Synthesis and Characterization of Stereoregular Ethylene-Vinyl Alcohol Copolymers Made by Ring-Opening Metathesis Polymerization

8.1 Abstract

The synthesis of regioregular as well as stereoregular ethylene vinyl alcohol (EVOH) copolymers by ring-opening metathesis polymerization (ROMP) with ruthenium catalysts is reported. Symmetric cyclooctene-diol monomers were protected as acetates, carbonates, or acetonides to temporarily add ring strain as well as impart solubility to the monomer. Polymer molecular weights could be easily controlled by either varying the monomer-to-catalyst ratio or by the addition of a chain transfer agent. Hydrogenation and subsequent deprotection of the ROMP polymers afforded the EVOH materials in high yields and the structures were confirmed by ^{1}H NMR and ^{13}C NMR spectroscopies. Thermal properties of the corresponding EVOH copolymers are reported and suggest that differences in diol stereochemistry drastically affect the polymer morphology.

8.2 Introduction

Ethylene vinyl alcohol (EVOH) copolymers have found commercial utility in food packaging as well as in the biomedical and pharmaceutical industries as a result of their excellent barrier properties toward gases and hydrocarbons.[1–7] The structure of EVOH copolymers affects the material's ability to limit gas or hydrocarbon diffusion through a membrane.[8, 9] Unfortunately, the current commercial route to these materials involves the free-radical polymerization of vinyl acetate and ethylene monomers followed by saponification.[10] The overall architecture is impossible to control and EVOH produced in this fashion contains a degree of branching similar to low-density polyethylene (LDPE).[11, 12] Furthermore, while the relative amount of vinyl alcohol can be controlled in the feed ratio of the two monomers, exact placement of alcohol functionality along the polymer backbone cannot be controlled.[9] This has resulted in a poor understanding of structure–property relationships in EVOH.

It has been demonstrated that the incorporation of polar functional groups pendent from a linear polymer backbone can be readily accomplished through ring-

opening metathesis polymerization (ROMP) with functional group-tolerant late transition metal catalysts.[9, 10, 13–17] Polar, substituted cyclic olefins such as alcohol-, ketone- or even halogen-substituted cyclooctenes undergo ROMP to form absolutely linear polymer bearing pendent functional groups.[13] The asymmetric monomer, however, prevents absolute control over the placement of the polar group along the polymer backbone. Head-to-head (HH), head-to-tail (HT), and tail-to-tail (TT) couplings are all possible, leading to a regiorandom distribution of functionality.[13] This problem has been addressed by two different olefin metathesis polymerization techniques, displayed in Figure 8.1.[9, 12, 18]

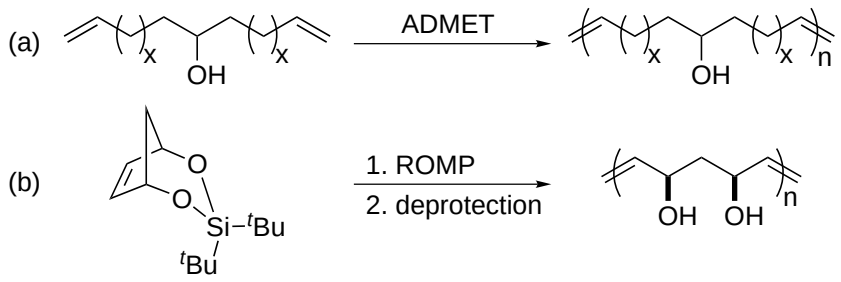
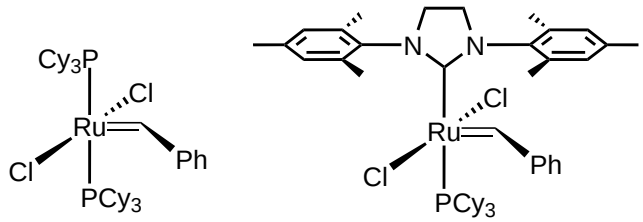


Figure 8.1: (a) ADMET of symmetric alcohol-containing monomer to produce a regioregular EVOH copolymer. (b) ROMP of a temporarily strained, symmetric monomer to produce a regioregular EVOH material with a higher vinyl alcohol content.

Valenti *et al.* reported the acyclic diene metathesis polymerization (ADMET) of a symmetric alcohol-containing monomer (Figure 8.1a).[12] The molecular weights, however, are restricted to $< 3 \times 10^4$ g/mol when employing ADMET and the relatively high hydrocarbon to alcohol ratio limits the overall barrier properties of these EVOH materials.[1, 12] More recently, we illustrated that ROMP of a symmetric monomer could be carried out in high yield to afford a linear EVOH type material (Figure 8.1b) with controlled placement of the alcohol functionality, molecular weight control over a wide range, and a much higher incorporation of alcohol groups.[9] Functional group-tolerant ruthenium catalysts **1**[19] and **2**[20] (Figure 8.2) were necessary to carry out the ROMP of the polar monomer.

While ROMP is capable of producing linear high molecular weight polymer, the amount of ring strain inherent in the cyclic olefin monomer plays a critical role in the

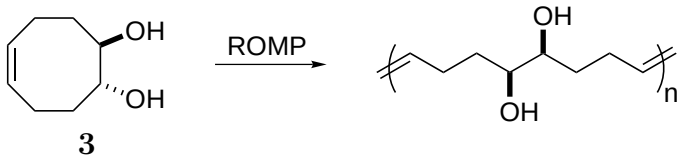


1 **2**

Figure 8.2: Ruthenium olefin metathesis catalysts.

polymerizability of each monomer.[21, 22] The addition of substituents to monocyclic olefins serves to lower the ring strain and can render a monomer non-polymerizable via ROMP.[21] Therefore, we introduced a method to temporarily add ring strain through carefully chosen protecting groups while keeping the monomers symmetric to avoid issues of regiorandom monomer addition.[9] While ROMP of symmetric monomers resolves the problems of branching and regiocontrol of functional groups, the effect of stereochemistry between neighboring alcohols has yet to be addressed. We would like to report our attempts to separately gauge the effect of relative stereocontrol on material properties. This allowed for a more detailed structure–property study with respect to barrier properties of architecture-controlled EVOH materials.

Scheme 8.1: ROMP of *trans*-diol **3**.



3

The direct ROMP of cyclooctene-*trans*-diol (**3**) was afforded by the addition of ruthenium catalyst **1** to monomer **3** as depicted in Scheme 8.1.[3] Unfortunately, this polymerization could only be carried out in neat monomer, as solubility of the unprotected diol **3** in common organic solvents suitable for ROMP was minimal.[3] Moreover, the molecular weight of the resulting ROMP polymer was limited to *ca.* 20000 g/mol due to diffusion in the highly viscous polymerization mixture.[3–5] All attempts to ROMP cyclooctene-*cis*-diol (**4**) failed as **4** is a crystalline solid with a melting point

well above the temperature range useful for catalysts **1** and **2**. Again, the lack of solubility of **4** in organic solvents suitable for ROMP prevented solution polymerization of the unprotected diol monomer. In order to produce perfectly linear EVOH materials that differed only in the relative stereochemistry between the neighboring 1,2-diols along the polymer backbone, protection of the diols was used to enhance the solubility of monomers **3** and **4**.

8.3 Results and Discussion

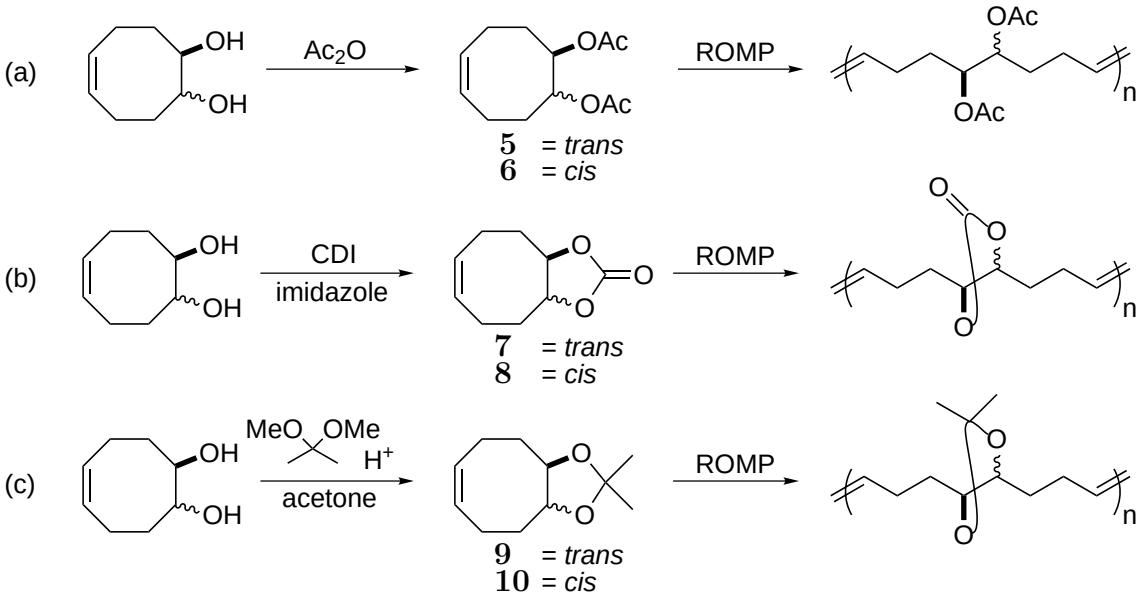
8.3.1 Monomer Design and Synthesis

In order to compare the effect that relative stereochemistry has on EVOH material properties, two monomers differing only in diol stereochemistry were selected: cyclooctene-*trans*-diol **3** and cyclooctene-*cis*-diol **4**. Due to the limited solubility of the diols in organic solvents,[3] the free alcohols were protected prior to polymerization. Considerations of monomer symmetry as well as ring strain were taken into account so that the resulting ROMP polymers would retain regioregular placement of alcohol groups along the polymer backbone and that high yields could be achieved.

Acetate protection afforded both the *trans* and *cis* monomers **5** and **6**, respectively (Scheme 8.2a). Both of these monomers underwent ROMP to yield the acetate-protected polymers, although higher monomer concentrations were necessary to achieve reasonable yields of polymer due to a decrease in ring strain relative to un-substituted cyclooctene. Both ROMP polymers, however, formed gels and did not dissolve in common organic solvents. Therefore, another protection strategy was employed. In an attempt to increase polymer yields at low monomer concentrations, carbonate protection was chosen to make bicyclic (8,5-fused) monomers that would retain symmetry as illustrated in Scheme 8.2b. While both the *trans*-carbonate **7** and *cis*-carbonate **8** did undergo ROMP, the resulting ROMP polymers were intractable in CH_2Cl_2, toluene, and THF and were only mildly soluble in DMF. A different bicyclic protection was carried out to form the *trans*-acetonide **9** and *cis*-acetonide **10** as shown

in Scheme 8.2c. The ROMP of these monomers produced polymers that remained soluble in common organic solvents and allowed for subsequent hydrogenation and deprotection steps to arrive at EVOH copolymers differing only in relative stereochemistry between neighboring alcohol functionalities.

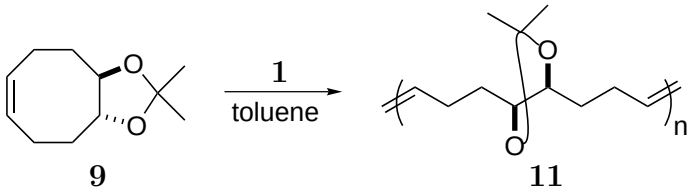
Scheme 8.2: Protection strategies for *trans* and *cis* cyclooctene-diol monomers.



8.3.2 ROMP of Acetonide Monomers with Catalyst 1

It has been previously demonstrated that ROMP of strained cyclic olefins with catalyst **1** occurs in a controlled and living fashion.[23, 24] Therefore, ROMP of monomers **9** and **10** was expected to yield polymers in which the molecular weight could be controlled by setting the monomer to catalyst ratio, $[M]_0/[\mathbf{1}]$. ROMP polymer **11**

Scheme 8.3: ROMP of **9** with catalyst **1** yields acetonide-protected polymer **11**.



forms upon introduction of catalyst **1** to a solution of *trans* monomer **9**, as shown in Scheme 8.3. Product yield, however, greatly depends on the monomer concentration, as shown in Figure 8.3a. Polymer yields are poor when $[M]_0 < 2$ M, although yields are reasonable and MW control is dictated by [M]/[**1**]ratio when the polymerization is carried out at 3 or 4 M (Figure 8.3b). The low yields of polymer produced from polymerizations below $[M]_0 = 2$ M are likely due to low ring strain as a result of the *trans*-8,5-ring fusion in **9**.[21] This has been observed before with *trans*-8,6-ring fusions by Miller *et al.*[25] Miller noted that the ring-closing metathesis (RCM) of acyclic dienes to produce *trans*-8,6-fused bicyclic compounds afforded higher yields than for the corresponding RCM of *cis*-8,6-fused compounds.[25] This suggests that *trans*-8,5 fused materials like **9** might also prefer the ring-closed form while the opposite might be true for *cis*-8,5 fused materials such as **10**. In fact, this trend holds for the ROMP of monomers **9** and **10**, as the ability for these two monomers to undergo ROMP is markedly different.

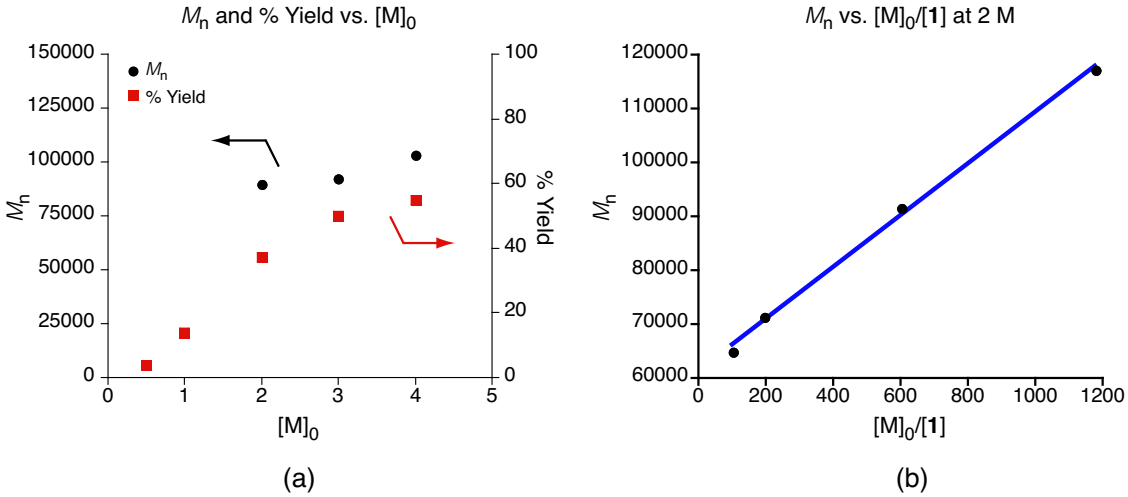
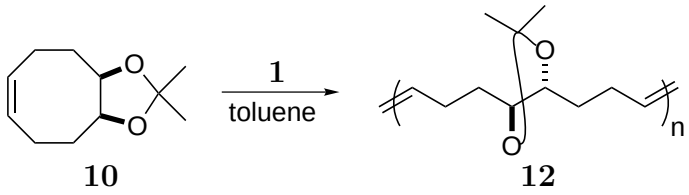


Figure 8.3: (a) ROMP of **9** with catalyst **1** at 55 °C, $[M]_0$/[**1**]= 400 at varying $[M]_0$. (b) Molecular weight control is achieved by varying $[M]_0$/[**1**]ratio.

As illustrated in Scheme 8.4, when catalyst **1** is introduced to a solution of monomer **10** ROMP polymer **12** is formed in high yield at much lower initial monomer concentrations. Reasonable yields (50-60%) can be achieved at $[M]_0 = 0.25$ M and

Scheme 8.4: ROMP of **10** with catalyst **1** yields acetonide-protected polymer **12**.



10 **12**

yields exceed 75% at $[M]_0 = 1$ M. Figure 8.4 shows excellent molecular weight control over a wide range for the ROMP of **10** with catalyst **1** at 1 M. As indicated by the data in Table 8.1, M_n is directly related to the [monomer]/[catalyst]ratio in a linear manner, and the polymerizations reach high yields within 24 h with relatively narrow PDIs.

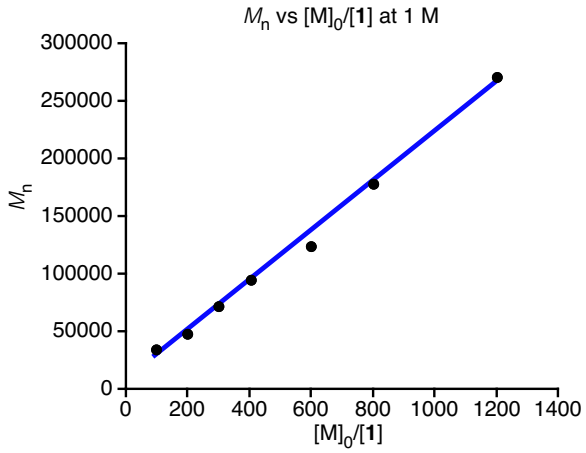


Figure 8.4: ROMP of **10** carried out at 1 M and 55 °C with catalyst **1** to produce polymer **12**; molecular weight control is achieved by varying the $[M]_0$/[**1**]ratio.

8.3.3 ROMP of Acetonide Monomers with Catalyst 2

While controlling the polymer molecular weight by adjusting the monomer to catalyst ratio is straightforward, the amount of catalyst employed directly affects the polymer produced. In an effort to reduce the amount of catalyst necessary to carry out the ROMP of monomers **9** and **10**, the use of highly active catalyst **2** was investigated.[14] It has been shown previously that the use of catalyst **2** with an acyclic chain transfer agent (CTA) affords telechelic polymers of controlled molecular

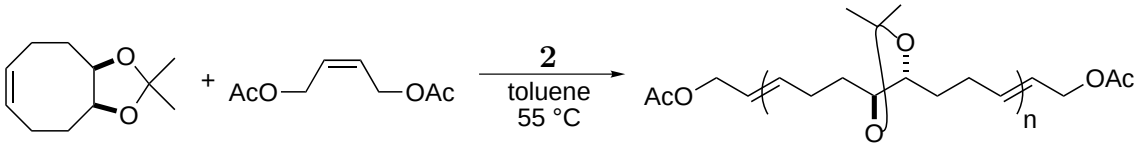
Table 8.1: ROMP of **10** ($[M]_0$=1 M) with **1** at 55 °C for 24 h.

[**10**]/[**1**]	M_n ($\times 10^{-3}$) GPC[a]	PDI	% yield
100	34.4	1.3	79
200	47.7	1.7	81
300	72.4	1.6	78
400	94.7	1.6	80
600	124	1.5	76
800	178	1.5	72
1200	271	1.3	73

[a]Samples run in THF; molecular weight values obtained using MALLS.

weight.[9, 26–29] The addition of a CTA such as **13** to the ROMP of **10** yielded telechelic polymer **14** as depicted in Scheme 8.5.

Scheme 8.5: ROMP of **10** with catalyst **2** in the presence of chain transfer agent **13** to yield telechelic acetonide-protected polymer **14**.



10 **13** **14**

Polymers **12** and **14** differ only by the functional groups at the termini of the latter. Moreover, the molecular weight of **14** can be easily controlled by the ratio of monomer to CTA, [**10**]/[**13**],[9, 27–29] thereby reducing the amount of catalyst needed for polymerization and simultaneously removing effect of catalyst in determining polymer molecular weight.[26]

Through the use of catalyst **2** and a CTA, much higher monomer-to-catalyst ratios can be employed allowing access to a large range of polymer molecular weights. The plot in Figure 8.5 and the data in Table 8.2 show excellent molecular weight control for the ROMP of **10** with CTA **13** at 1 M with $[M]_0$/[**2**]ratio of 5000.

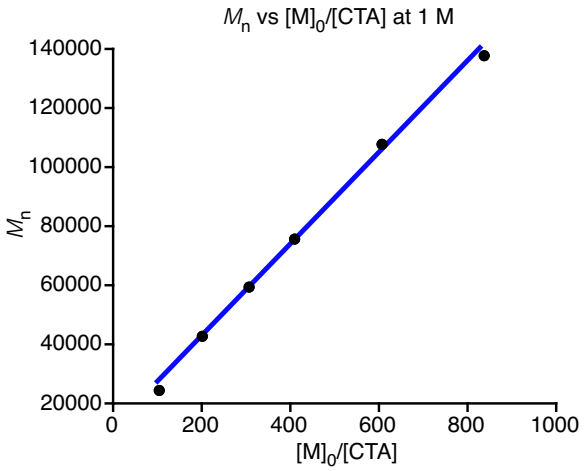


Figure 8.5: ROMP of **10** carried out at 1 M and 55 °C with catalyst **2** and CTA **13** to produce telechelic polymer **14**; molecular weight control is achieved by varying the $[M]_0/[CTA]$ratio.

8.3.4 Hydrogenation of Acetonide-Protected ROMP Polymers

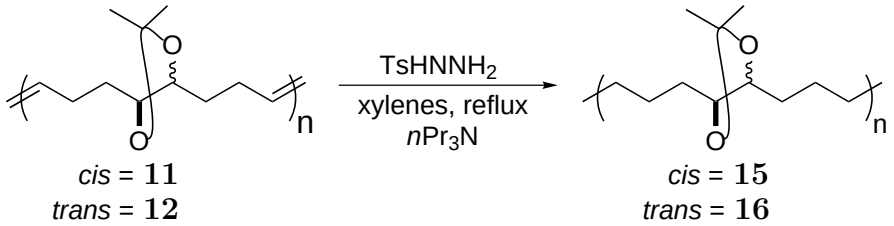
While polymers resulting from the ROMP of monomers **5**–**8** led to gelled or intractable materials, polymers **11** and **12** were soluble in common organic solvents, allowing for mild hydrogenations to be carried out. Direct formation of diimide in situ[9, 30–34] afforded complete hydrogenation of the olefins without removing the acetonide protecting group as depicted in Scheme 8.6. After 5–6 h in refluxing xylenes, hydrogenation of the ROMP polymers was complete as evidenced by the lack of olefin signals in both the ^{1}H and ^{13}C NMR spectra. The hydrogenation reaction was carried out with 1 equiv of tri-propylamine (per tosylhydrazide) in order to keep the acetonides from catalytically deprotecting with the formation of tosic acid.[9] Saturated polymers **15** and **16** remained soluble in organic solvents, allowing for characterization by ^{1}H and ^{13}C NMR, gel permeation chromatography (GPC), as well as thermal analysis by differential scanning calorimetry (DSC).

Table 8.2: ROMP of **10** ($[M]_0$=1 M) with **2** at 55 °C for 24 h, [**10**]/[**2**]=5000.

[**10**]/[**13**]	M_n ($\times 10^{-3}$) GPC[a]	PDI	% yield
100	24.5	1.9	70
200	43.0	1.6	74
300	59.8	1.6	74
400	75.7	1.6	75
600	108	1.6	76
800	138	1.5	76

[a]Samples run in THF; molecular weight values obtained using MALLS.

Scheme 8.6: Hydrogenation of ROMP polymers by *in situ* diimide formation.



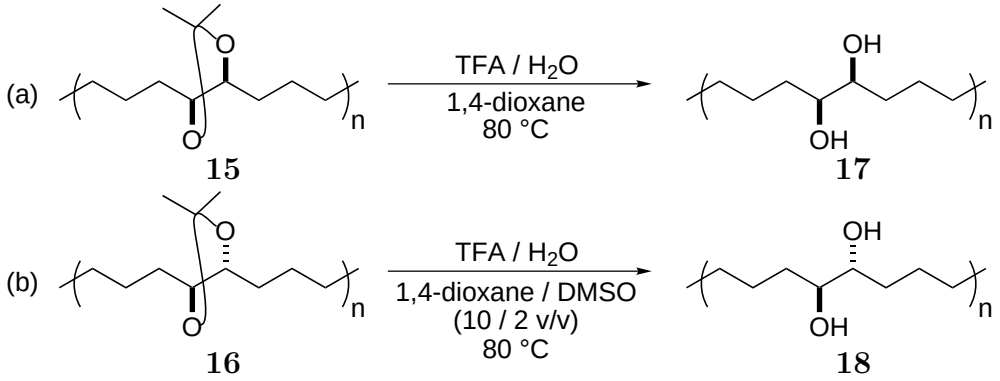
cis = **11**
trans = **12**

cis = **15**
trans = **16**

8.3.5 Deprotection of Acetonide Groups

In order to arrive at the final EVOH structure, deprotection of the acetonide groups was necessary. As shown in Scheme 8.7, removal of the acetonides was accomplished by extended heating at 80 °C in 1,4-dioxane with a catalytic amount of trifluoroacetic acid (TFA) and water. This reaction proved quite challenging as polymers **15** and **16** are hydrophobic and possess a very different solubility profile than the hydrophilic EVOH copolymers **17** and **18**.[9] While the formation of EVOH **17** occurred readily, the transformation of **16** to **18** required 10–20% DMSO as a co-solvent in order to keep the polymer soluble throughout the entire reaction.[9] In the absence of DMSO, the reaction resulted in incomplete deprotection and undesired product which precipitated from solution.

Scheme 8.7: Deprotection of acetonides.



8.3.6 Thermal Analysis of ROMP, Hydrogenated, and Deprotected Polymers

Thermal analysis was carried out on polymers **11** and **12** and **15**–**18** by DSC. Glass transition temperatures, T_g, as well as the relevant melting transition temperatures, T_m, are listed in Table 8.3. Only glass transitions are observed for the amorphous

Table 8.3: Thermal analysis of ROMP, hydrogenated, and deprotected EVOH polymers.

Polymer	T_g, onset (°C)	T_m, onset (°C)
11	-12.4	—
12	-6.6	—
15	-14.1	—
16	-2.7	—
17	34.4	111
18	50	157

acetonide-protected ROMP polymers **11** and **12**. While both T_g values are sub-ambient, they differ by nearly 6 °C, suggesting that the syn and anti diols impose a slightly different packing in the solid state. This difference is even more pronounced (11.4 °C) in the hydrogenated forms, **15** and **16**. Finally, the fully deprotected EVOH copolymers **17** and **18** show a clear difference in both the T_g and T_m values with a nearly 40 °C increase in the melting transition temperature between the syn and anti 1,2-diols. Moreover, the ΔH for the melting transition observed for the syn 1,2-diol

EVOH **17** was 21.17 J/g, while the ΔH for the anti 1,2-diol EVOH **18** nearly doubled, with a value of 42.12 J/g. This indicates that the anti stereochemical relationship between the diols along the polymer backbone allowed for more crystalline regions in the EVOH material relative to the syn stereochemical relationship. In addition, the T_g for **17** was much easier to observe in the DSC trace relative to **18**. Previously, it has been observed that higher melting transitions in EVOH copolymers arise from higher alcohol content.[9, 35] The dramatic increase in T_m between **17** and **18**, however, suggests that the relative stereochemistry between the pendent alcohol groups can also have a remarkable effect on material morphology and crystalline packing of the polymer chains.

8.4 Conclusions

The successful ROMP of symmetric cyclooctene diol monomers that differ only in the relative stereochemistry between the alcohols has been demonstrated with the functional group-tolerant ruthenium catalysts **1** and **2**. In order to obtain molecular weight control over the polymers, a protection strategy was needed due to the lack of solubility of cyclooctene diol in common organic solvents. Acetonide protection for the diols provided the necessary solubility as well as enhanced ring strain for the *cis* diol (**4**) in the form of a bicyclic 8,5-fused system while keeping the symmetry of the monomer. Hydrogenation and subsequent deprotection afforded regioregular EVOH copolymers with 1,2-diols along the polymer backbone differing only in a syn and anti relationship. This allowed for direct probing of the effect of relative stereochemistry on EVOH copolymer properties. Thermal analysis indicated that a mere change in the relative stereochemistry greatly affects both the glass and melting transitions of the EVOH materials without requiring an increase in overall alcohol content. The ability to modify the properties of a material by simply imposing regularity on the structure of a polymer chain is evident. Finally, the use of ROMP with late transition metal ruthenium catalysts combined with rational monomer design has allowed us to elucidate the effects of polymer architecture on the material properties of EVOH

copolymers.

8.5 Experimental Section

General Procedures. NMR spectra were recorded on a Varian Mercury 300 (300 MHz for ^{1}H and 74.5 MHz for ^{13}C). All NMR spectra were recorded in $CDCl_3$, DMSO-d_6, or 1,4-Dioxane-d_8 and referenced to residual proteo species. Gel permeation chromatography (GPC) was carried out on two PLgel 5 μm mixed-C columns (Polymer Labs) connected in series with a DAWN EOS multi angle laser light scattering (MALLS) detector and an Optilab DSP differential refractometer (both from Wyatt Technology). No calibration standards were used, and dn/dc values were obtained for each injection assuming 100% mass elution from the columns. Differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) was carried out simultaneously on a Netzsch STA 449C under a flow of N_2 at a heating rate of 10 °C/min or on a Perkin Elmer Pyris1 under a flow of He at a heating rate of 10 °C/min.

Materials. Toluene and CH_2Cl_2 were dried by passage through solvent purification columns.[36] *cis*-1,4-Diacetoxy-2-butene (95+%) (**13**) was obtained from TCI America and degassed by an argon purge prior to use. 1,5-Cyclooctadiene (redistilled, 99+%), 9-Oxabicyclo[6.1.0]non-4-ene (95%), *N,N*-Dimethylformamide (anhydrous, 99.8%) (DMF), 1,1'-Carbonyldiimidazole, *p*-Toluene sulfonhydrazide (97%), Pyridinium *p*-toluene sulfonate (98%), Tripropylamine (99+%), 1,4-Dioxane (99+%), Xylenes (98.5+%), Trifluoroacetic acid (99+%), Acetic anhydride (99+%), and 2,2'-Dimethoxypropane (98%) were obtained from Aldrich as used as received. Potassium osmate (VI) dihydrate (99%) was obtained from Strem and used as received. Dimethylsulfoxide was obtained from ACROS Organics and used as received. Imidazole (99%) was obtained from EM Science and used as received. Acetone (technical grade) was dried over calcium sulfate and filtered prior to use as a solvent. Ruthenium catalysts $(PCy_2)(Cl)_2Ru{=}CHPh$ (**1**)[19] and $(H_2IMes)(PCy_2)(Cl)_2Ru{=}CHPh$ (**2**)[37] as well as organic compounds Cyclooctene-*trans*-diol (**3**),[38] Cyclooctene-*cis*-diol (**4**),[39]

Cyclooctene-*trans*-diacetate (**5**),[40, 41] Cyclooctene-*cis*-diacetate (**6**),[40, 41] Cyclooctene-*trans*-carbonate (**7**),[40] Cyclooctene-*cis*-carbonate (**8**),[40] Cyclooctene-*trans*-acetonide (**9**),[42] and Cyclooctene-*cis*-acetonide (**10**)[43] were all synthesized according to literature procedures.

Polymerization procedure for acetonide-protected monomers with catalyst 1. In a typical experiment, a small vial was charged with 0.185 g (1.0 mmol) of monomer **10** and a stirbar. Under an argon atmosphere, 0.6 mL of degassed toluene was added via syringe. In a separate vial, a 21.2 mg/mL catalyst **1** solution in toluene was prepared. 0.4 mL of the catalyst solution was then added to the monomer solution via syringe under argon. The reaction vial was placed in a 55 °C aluminum heating block stirring under argon for 24 h. The reaction mixture was then quenched with 0.1 mL ethyl vinyl ether and then dissolved in 1 mL CH_2Cl_2 and precipitated into 50 mL of stirring MeOH. A light brown ppt. was washed several times with MeOH and dried in vacuo overnight; yield (79%). See Table 8.1 for molecular weight data. ^{1}H NMR (300 MHz, $CDCl_3$): 5.5 *trans* 5.4 *cis* (two br s, 2H), 4.05 (br s, 2H), 1.95–2.35 (m, 4H), 1.3–1.65 (m, 10H). ^{13}C NMR (75 MHz, $CDCl_3$): 130.2, 129.8, 107.6, 77.5, 30.1, 29.9, 29.4, 29.0, 26.4, 24.2.

Polymerization procedure for acetonide-protected monomers with catalyst 2 and CTA 13. In a typical experiment, a small vial was charged with 0.185 g (1.0 mmol) of monomer **10** and a stirbar. Under an argon atmosphere, 0.8 mL of a 2.2 mg/mL solution of **13** in toluene was added. Next 0.2 mL of a 0.9 mg/mL solution of catalyst **2** in toluene was added via syringe. The reaction vial was placed in a 55 °C aluminum heating block stirring under argon for 24 h. The reaction mixture was then dissolved in 1 mL CH_2Cl_2 and precipitated into 50 mL of stirring MeOH. A white ppt. was washed several times with MeOH and dried in vacuo overnight; yield (75%). See Table 8.2 for molecular weight data. ^{1}H NMR (300 MHz, $CDCl_3$): 5.5 *trans* 5.4 *cis* (two br s, 2H), 4.05 (br s, 2H), 1.95–2.35 (m, 4H), 1.3–1.65 (m, 10H). ^{13}C NMR (75 MHz, $CDCl_3$): 130.1, 129.7, 107.5, 77.6, 30.1, 29.9, 29.4, 28.9, 26.3, 24.2.

Hydrogenation procedure for acetonide-protected polymers. In a typical

experiment, an oven-dried 500 mL round bottom flask was charged with a stirbar, 1.0 g of polymer **15**, 6.83 g of tosyl hydrazide (35.6 mmol, 6.5 equiv per double bond) 125 mL of xylenes, and a trace of BHT. The mixture was degassed by pulling high vacuum on the solution for about 45 s. Under an argon atmosphere, a flask was fitted with a reflux condenser. The reaction was heated to reflux for 7 h. It was then cooled to room temperature and then precipitated into 700 mL of stirring ice-cold stirring MeOH. The white ppt. was washed several times with MeOH and then dried in vacuo overnight; yield 1.01 g (99%). ^{1}H NMR (300 MHz, $CDCl_3$): 3.58 (br s, 2H), 1.25–1.6 (m, 18 H). ^{13}C NMR (75 MHz, $CDCl_3$): 107.9, 81.2, 33.3, 30.0, 27.7, 26.5.

Deprotection of 15. In a typical experiment, a 25 mL round bottom flask was charged with a stirbar and 0.25 g polymer. The polymer was then dissolved in 10 mL of 1,4-dioxane. A reflux condenser was attached to the flask and the reaction was stirred at 80 °C for 10 min under argon. 1 mL of H_2O and 1 mL of TFA were added via syringe and the reaction was allowed to stir at 80 °C under argon. An additional 2.5 mL of H_2O was added to the reaction over the course of 72 h, after which the reaction was allowed to cool to room temperature and precipitated into 200 mL of acetone stirring at room temperature. A fluffy white solid was obtained through several centrifugation, decant, rinse cycles and dried under vacuum overnight; yield 0.19 g (99%). ^{1}H NMR (300 MHz, DMSO-d_6, 85 °C): 3.55 (br s, 2H), 1.22–1.62 (br m, 12H). ^{13}C NMR (75 MHz, DMSO-d_6, 85 °C): 76.0, 32.9, 29.2, 25.4.

Deprotection of 16. In a typical experiment, a 25 mL round bottom was charged with a stirbar and 255.9 mg of polymer. It was first dissolved in 8 mL of 1,4-dioxane and then under an argon atmosphere 1 mL of DMSO was slowly added to the solution over the course of 30 min. A reflux condenser was attached and the reaction was heated to 80 °C for 2 h. Next 0.2 mL of TFA was added and the reaction was stirred overnight under argon at 80 °C. After 24 h, an additional 0.2 mL of TFA and 1 mL of DMSO were added and the reaction was kept at 80 °C. After 72 h, an additional 1 mL of DMSO and 0.1 mL TFA and 0.2 mL H_2O were added to the reaction. 1 mL of DMSO was also added after 96 h as well as 0.2 mL TFA. Finally, after 144 h, the reaction was stopped and precipitated into 100 mL of acetone stirring at room

temperature. A whitish ppt. was obtained through several centrifugation, decant, rinse cycles and dried under vacuum overnight; yield 200.0 mg (99%). ^{1}H NMR (300 MHz, DMSO-d_6, 85 °C): 3.18 (br s, 2H), 1.05–1.58 (br m, 12H).

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