Chapter 7

Synthesis of Well-Defined Poly(vinylalcohol$_2$-*alt*-methylene) via Ring-Opening Metathesis Polymerization

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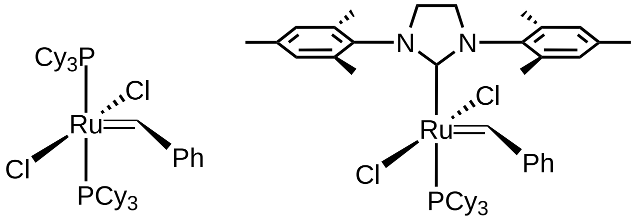
7.1 Abstract

The synthesis of a new methylene-(vinyl alcohol) copolymer, poly((vinyl alcohol)$_2$-*alt*-methylene) (MVOH), by ring-opening metathesis polymerization with ruthenium catalysts is reported. Unsaturated cyclic 1,3-diols were protected with a di-*tert*-butylsilyl group to form strained cyclic olefins. The molecular weights of the polymers were controlled by varying the monomer-to-catalyst ratios or by the addition of a chain transfer agent. Hydrogenation and subsequent deprotection of the ROMP polymers yield the MVOH copolymer structure which was confirmed by ^{1}H NMR and ^{13}C NMR spectroscopies. Thermal properties of the corresponding MVOH copolymer are reported.

7.2 Introduction

Interest in making well-defined linear polymers with alcohol functionalities is spurred by the commercial utility of ethylene-(vinyl alcohol) (EVOH) copolymers. EVOH copolymers are a class of materials that exhibit excellent barrier properties towards gases and hydrocarbons[1] and have found use in the food packaging and in biomedical and pharmaceutical industries.[1, 2] Furthermore, the lack of understanding of the property–structure relationships in these materials has fueled academic interest in the microstructure of EVOH copolymers.[2–5] The most widely employed synthetic route to EVOH copolymers is the free radical polymerization of ethylene and vinyl acetate, followed by saponification.[3] These EVOH copolymers contain a degree of branching, much like low-density polyethylene (LDPE), and have a random distribution of alcohol functionality along the polymer backbone[2, 4] both of which limit the elucidation of the structure–property relationships in these materials.

The direct incorporation of polar functional groups along the backbone of linear polymers made via ring-opening metathesis polymerization (ROMP) is now possible due to the development of functional group tolerant late transition metal olefin metathesis catalysts. Recently, Hillmyer *et al.* reported the ROMP of cyclooctenes bearing an alcohol-, ketone-, halogen-, or acetate substituent with a ruthenium olefin metathesis catalyst.[6] However, the asymmetry of the substituted cyclooctene allowed for head-to-head (HH), head-to-tail (HT), and tail-to-tail (TT) coupling, yielding polymer with regiorandom placement of the functional groups.[6] A similar problem was encountered by Chung *et al.*, who reported the ROMP of a borane-substituted cyclooctene with an early transition metal catalyst followed by oxidation to yield an alcohol functionalized linear polymer.[3] A solution to this regiorandom distribution of functional groups was reported by Valenti *et al.* using the acyclic diene metathesis (ADMET) polymerization of an alcohol-containing symmetric diene.[4, 7] However, the molecular weights of these polymers are restricted to $< 3 \times 10^4$ by ADMET,[4] and their rich hydrocarbon content limits the barrier properties of the final EVOH copolymers.[1]



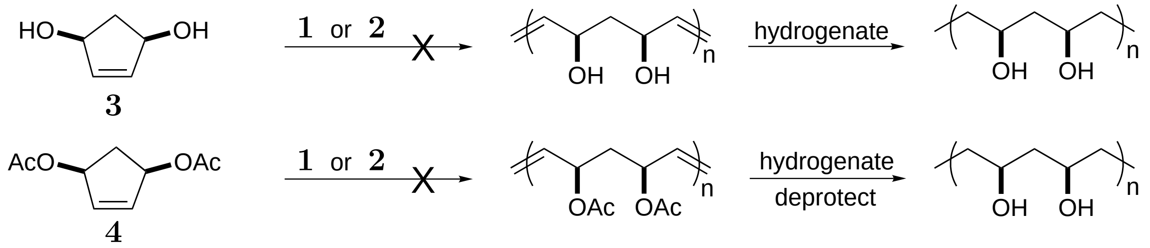
1 **2**

Figure 7.1: Ruthenium olefin metathesis catalysts (Cy=cyclohexyl).

To produce copolymers with a high content of precisely spaced alcohol functionalities, we favor a polymerization scheme involving the ROMP of a symmetric alcohol-containing monomer with functional group tolerant ruthenium catalysts, $(PCy_3)_2(Cl)_2Ru{=}CHPh$ (**1**)[8] and $(IMesH_2)(PCy_3)(Cl)_2Ru{=}CHPh$ (**2**)[9] (Figure 7.1).

Catalysts **1** and **2** have been shown to afford the ROMP of many substituted cyclic olefins.[10–13] Recent development of ruthenium catalysts, such as **2**, coordinated with an N- heterocyclic carbene has allowed for the ROMP of low-strain cyclopentene and substituted cyclopentene.[10] The ROMP of a symmetric cyclopentene yields a regioregular polyalkene as no difference exists between HH, HT, and TT couplings. Hence, the ROMP of alcohol- or acetate-disubstituted cyclopentene monomers was

Scheme 7.1: Attempt to ROMP cyclopentene monomers **3** and **4**.

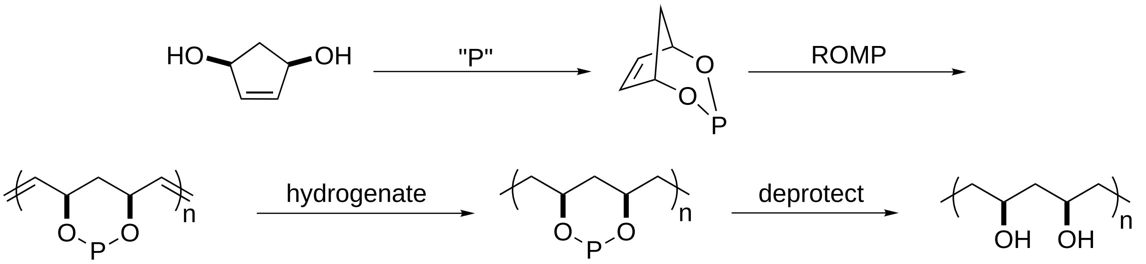


attempted (Scheme 7.1).

Unfortunately, neither catalyst **1** nor the more active **2** could afford the ROMP of these cyclopentene monomers, most likely due to their low ring strain. In addition, the oxygen-containing substituents may coordinate to the olefin metathesis catalysts or sterically inhibit catalyst coordination with the olefin. Therefore, a different protection strategy was employed in an effort to maintain the 1,3-substituted cyclopentene structure while temporarily increasing monomer ring strain and moving the oxygen functionalities further from the olefin to facilitate ROMP.

A general synthetic route to a linear polymer with precisely-spaced alcohol functionalities is displayed in Scheme 7.2. In this paper, we describe a method to produce a new vinyl alchol copolymer, poly((vinyl alcohol)$_2$-*alt*-methylene) (MVOH). This alternating MVOH copolymer has a high content of precisely-spaced vinyl alcohol functionalities which are *cis* within each monomer repeat unit and, depending upon the relative orientation between adjacent monomer units, may provide for tacticity in the MVOH material.

Scheme 7.2: A bicyclic protection strategy enroute to MVOH through a temporarily strained, symmetric monomer.

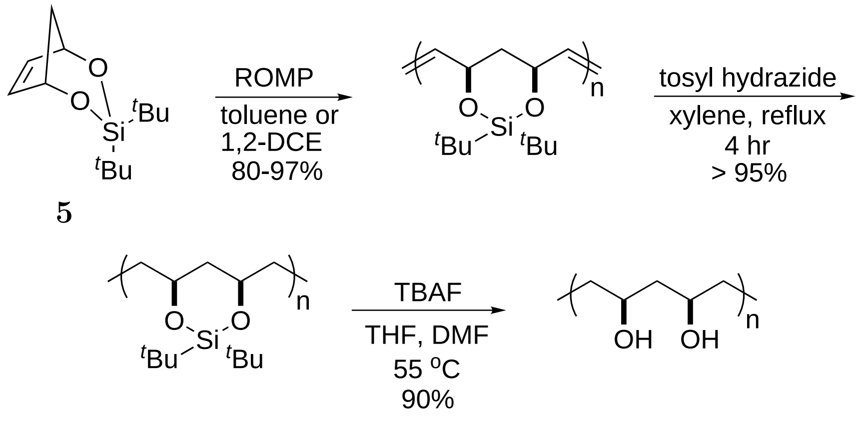


7.3 Results and Discussion

7.3.1 Monomer Design and Synthesis

We believe the ROMP of monomers **3** and **4** was not successful due to low ring strain,[10] to possible heteroatom coordination with catalysts **1** and **2**, or by steric hinderance of the olefin. Hence, a highly strained, bicyclic monomer, 3,3-di-*tert*-butyl-2,4-dioxa-3-sila-bicyclo[3.2.1]oct-6-ene, (**5**) was readily synthesized[14] to overcome these problems. Monomer **5** maintains symmetry and a 1,3-diol relationship that, upon hydrogenation and silane deprotection, ensures an alternating copolymer with two successive vinyl alcohol units followed by a methylene unit (Scheme 7.3). Also, the symmetry of a five-member ring with 1,3-substitution dictates a regioregular polymer as head-to-head and head-to-tail connections are equivalent. Furthermore, by tying up the heteroatoms with the silane, a *cis* relationship in each repeat unit between the vinyl alcohols is maintained. Depending on the *cis*/*trans* ratio of the ROMP polymer, tacticity in the final MVOH copolymer may be affected.[12, 13]

Scheme 7.3: Synthetic route to MVOH through a temporarily strained, symmetric bicyclic monomer.



7.3.2 ROMP of Bicyclic Silicon-Protected Diol with 1

Previous results have demonstrated that the ROMP of norbornene and oxanorbornenes with **1** is a controlled polymerization.[15, 16] It is therefore reasonable to believe that the ROMP of **5** with catalyst **1** might also be a controlled polymerization.

Upon exposure to catalyst **1**, monomer **5** undergoes ROMP and gels quickly (Figure 7.2). Therefore, polymerizations were carried out in solution (1:1 vol) with either toluene or 1,2-dichloroethane (1,2-DCE) to ensure a homogeneous polymerization. Monomer **5** was polymerized with varying amounts of **1** at 55 °C (Table 7.1). All polymerizations reached high conversion ($\geq$ 80%) in approximately 1 day and were fully characterized by ^{1}H/^{13}C NMR (Figure 7.5a and c) and MALLS/SEC. Over the molecular weight range 2 x 10^4–2.2 x 10^5 g/mol, PDI values were relatively low and constant for polymers produced in both chlorinated and aromatic solvents. Also, it is evident that the [**5**]/[**1**]ratio is reflected in the M_n of each polymer in a linear fashion.

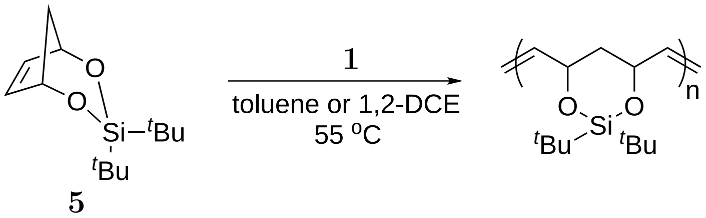


Figure 7.2: ROMP of monomer **5** with catalyst **1**.

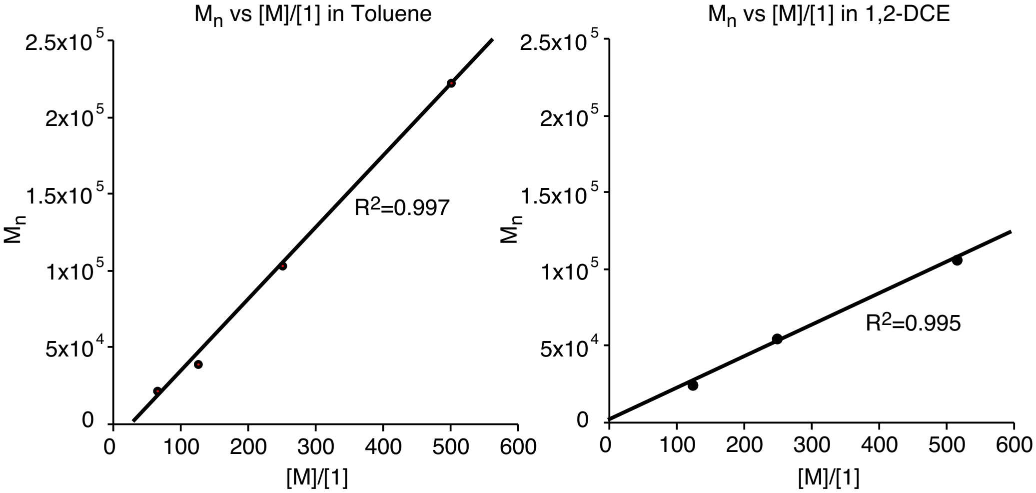


Figure 7.3: Graphs of M_n vs [monomer]/[catalyst]ratio for the ROMP of **5** with **1** in toluene and 1,2-DCE.

The graphs in Figure 7.3 display the molecular weight vs [monomer]/[catalyst]ratios for the series **P1–4**, carried out in toluene, and **P5–7**, carried out in 1,2-DCE. The slopes of the graphs in Figure 7.3 differ by a factor of approximately 2, which indicates a difference in the initiation rates of catalyst **1** in toluene and 1,2-DCE. Catalyst **1** appears to be initiating more readily in 1,2-DCE (**P5–7**), as the slope of roughly 1 is obtained when plotting DP vs. [monomer]/[catalyst].[17] A difference in initiation rates for **1** has been previously observed by Sanford *et al.*,[11] and these data are consistent with faster initiation in chlorinated vs aromatic solvents. Low PDI's and the linear relationship between molecular weight vs [monomer]/[catalyst]are characteristic of a controlled polymerization.

Table 7.1: ROMP of **5** with **1**

Polymer	[**5**]/[**1**]	time (h)	% yield	M_n ($\times10^{-3}$) GPC[a]	M_w ($\times10^{-3}$) GPC[a]	PDI
P1[b]	63	21	90	21.8	28.4	1.3
P2[b]	130	17	97	39.3	51.7	1.3
P3[b]	250	24	95	103.4	139.2	1.3
P4[b]	510	18	95	222.3	309.1	1.4
P5[c]	120	21	84	24.2	33.7	1.4
P6[c]	250	27.5	77	55.3	73.9	1.3
P7[c]	510	27.5	80	105.8	131.6	1.2

[a] Samples run in THF; molecular weight values obtained using MALLS with an average dn/dc value of 0.108 mL/g. [b] Polymerizations run in toluene. [c] Polymerizations run in 1,2-DCE.

7.3.3 ROMP of Bicyclic Silicon-Protected Diol with 2 and a Chain Transfer Agent

Telechelic polymers can be made readily via ROMP of a cylic olefin with a symmetric chain transfer agent (CTA).[18–21] With the more active catalyst **1**, the molecular weight of the resulting polymer is controlled solely by the [monomer]/[CTA]ratio at thermodynamic equilibrium; furthermore, much lower catalyst loadings can be employed, thereby reducing costs considerably. When the ROMP of **5** with CTA **6** is carried out in toluene (Figure 7.4), the M_n is controlled by the ratio of [**5**]/[**6**], and high conversions are obtained with a catalyst loading up to 4 x 10^4.

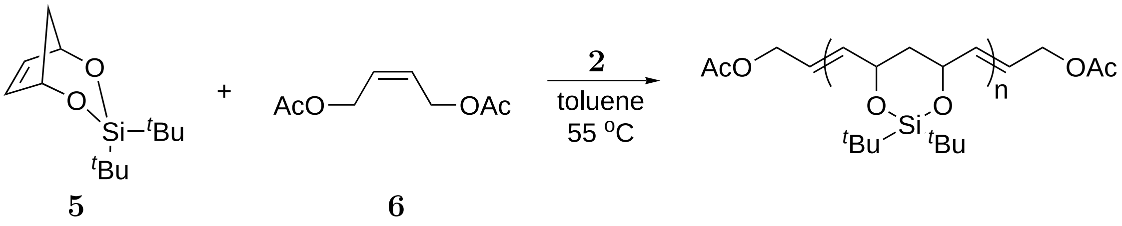


Figure 7.4: ROMP of monomer **5** with catalyst **2** and chain transfer agent **6**.

Entries **P8–10** in Table 7.2 indicate that thermodynamic equilibrium is reached within 24 h, after which the molecular weight and conversion remain constant. As expected, as the [monomer]/[CTA]ratio is doubled, the M_n increases by a factor of two (**P8** & **P11**).

Table 7.2: ROMP of **5** with **2** and CTA **6**

Polymer^b	[**5**]/[**2**]	[**5**]/[**6**]	time (h)	% yield	M_n ($\times 10^{-3}$) GPC^a	M_w ($\times 10^{-3}$) GPC^a	PDI
P8	20000	100	23	84	57.4	57.4	2.5
P9	20000	100	70	82	58.3	58.3	2.3
P10	20000	100	113	80	57.1	151.1	2.6
P11	40000	200	22	87	120.2	278.7	2.3

^{a}Samples run in THF; molecular weight values obtained using MALLS with an average dn/dc value of 0.110 mL/g. ^{b}All polymerizations run in toluene.

7.3.4 Hydrogenation of Polymers

Hydrogenation of the polymer backbone was carried out in high yield by tosyl hydrazide reduction in refluxing xylenes.[22–26] The saturated polymers were fluffy white solids and were characterized by ^{1}H and ^{13}C NMR as well as MALLS/SEC. Figure 7.5a displays the ^{13}C NMR spectrum of the unsaturated polymer backbone made with catalyst **1**. Upon hydrogenation, the loss of olefinic carbons is clearly evident in Figure 7.5b as the carbon, 1, in the sp^2 region at 131–132 ppm has disappeared and a new carbon, 1’, appears in the sp^3 region at 34 ppm. Figure 7.5c displays the ^{1}H NMR spectrum prior to saturation of the backbone. The four peaks between 4 and 6 ppm in Figure 7.5c represent the two sets of *cis* and *trans* olefin protons, H_a, and methine protons, H_b. For polymers made with catalyst **1** (**P1–7**), integration is consistent between the two sets with a 1.4/0.6 *trans*/*cis* ratio or 70% *trans* olefins along the polymer backbone, while the polymers made with catalyst **2** (**P8–11**) consisted of 50% *trans* olefins.[27] These sets of peaks disappear (Figure 7.5d) upon hydrogenation as the *cis* and *trans* methine protons collapse to a singe peak, H_f, at 4 ppm and new methylene protons, $H_e + H_{g/h}$, appear between 1.4 and 1.6 ppm.

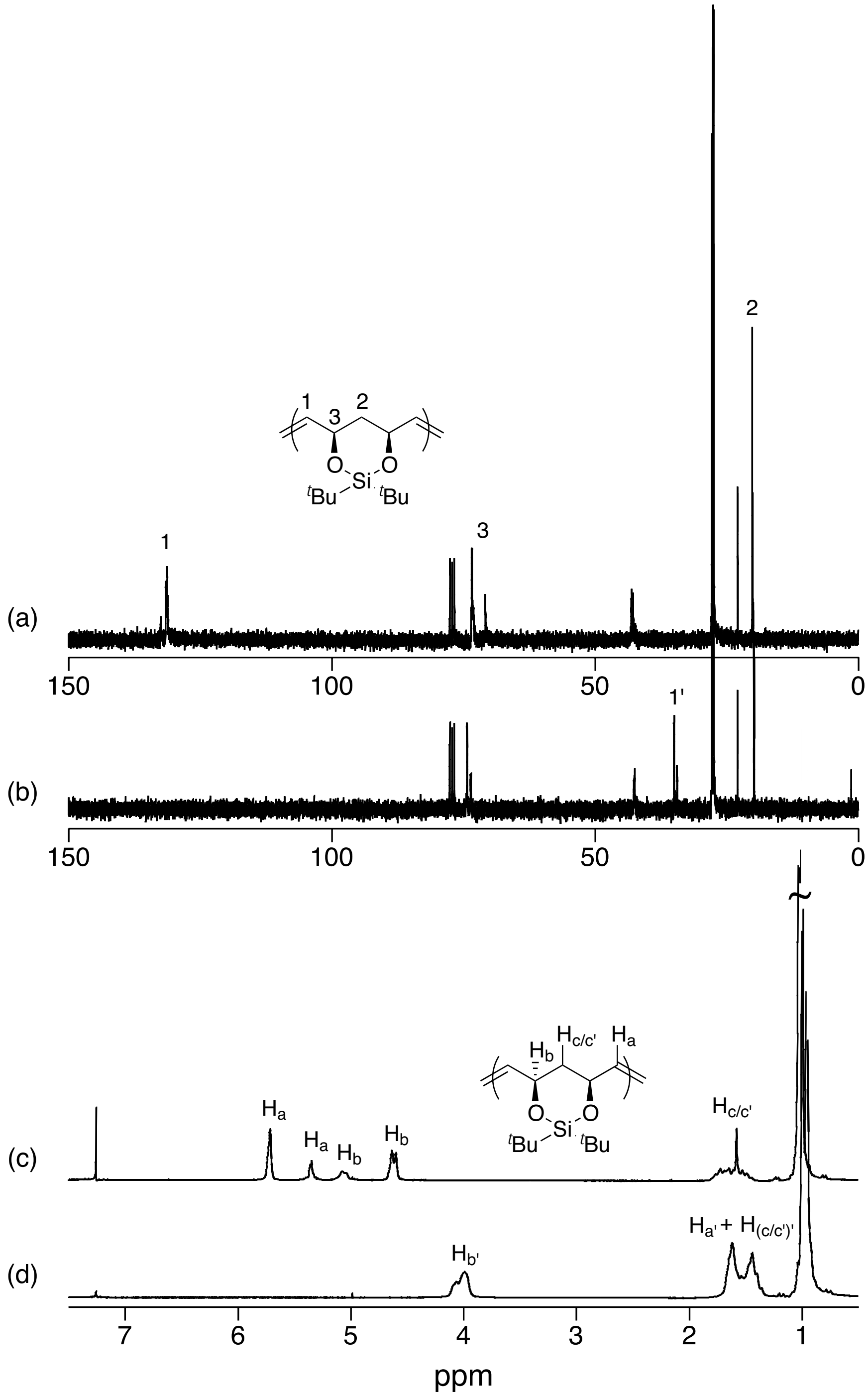


Figure 7.5: (a) ^{13}C NMR spectrum of ROMP polymer from monomer **5** with catalyst **1**. (b) ^{13}C NMR spectrum of polymer after hydrogenation. (c) ^{1}H NMR spectrum of ROMP polymer from monomer **5** with catalyst **1**. (d) ^{1}H NMR spectrum of polymer after hydrogenation.

7.3.5 Deprotection of Polymers

Deprotection of the saturated polymer was accomplished with tetrabutylammonium fluoride (TBAF) in (3:1 v/v) THF:DMF to produce the new alternating MVOH copolymer. It was necessary to use DMF as a cosolvent in the deprotection step so that the polymeric material would remain soluble throughout the entire reaction. Reactions carried out solely in THF resulted in incomplete deprotection. MVOH copolymers could then be obtained as a whitish, stringy solid by precipitation from the THF/DMF solution into a MeOH:CH_2Cl_2 (1:1 v/v) solution. Once dried, the MVOH copolymers were readily soluble in DMSO (at room temperature), but not in DMF, water, THF, or MeOH. MALLS/SEC characterization was not carried out on the final product due to the insolubility of MVOH copolymer in THF.

Only three sets of carbon resonances are observed in the ^{13}C NMR spectrum of poly((vinyl alcohol)$_2$-*alt*-methylene) (originating from the ROMP polymer produced with catalyst **1**) in DMSO-d_6, as shown in Figure 7.7a. The peaks labeled 1 and 3 in Figure 7.7a consist of two peaks as shown in the insets. Recent research has elucidated the tacticity of poly(vinyl alcohol) (PVA) homopolymer with high field NMR spectrometers.[28, 29] Nagara *et al.* report that the chemical shift data for the methine carbon (carbon 3 in Figure 7.7a) follows the trend for triads: $\delta_{mm} > \delta_{rm/rm} > \delta_{rr}$.[29] By analogy, the methine region in Figure 7.7a is suggestive of a higher m dyad tacticity for MVOH produced with catalyst **1**. In contrast, the equal intensities of these peaks in the material produced with catalyst **2** suggest equal m and r dyad distributions; the m and r dyads are shown in (Figure 7.6). The carbon assigned as 2 can only exist in one local environment as the two alcohol functionalities that surround it must always be in a *cis* relationship.

The ^1H NMR spectra in Figure 7.7b shows complete removal of the silane protect-

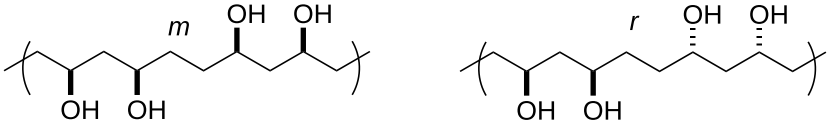


Figure 7.6: Structures of the m and r dyads in the MVOH polymer.

ing group, as no signals are present around 1.0 ppm. The peak at 4.5 ppm, H_d, was assigned to the alcohol protons as it disappeared upon addition of D_2O, leaving the peak at 3.6 ppm, H_a, to be assigned to the methine protons. The remaining peaks between 1.2 and 1.6 ppm, $H_{b/b'}$ + $H_{c/c'}$, are assigned as the 6 methylene protons. All of these assignments are in good agreement with the similar EVOH copolymers previously prepared,[2, 30] and the ^{1}H NMR spectra for MVOH made with catalysts **1** and **2** are the same.

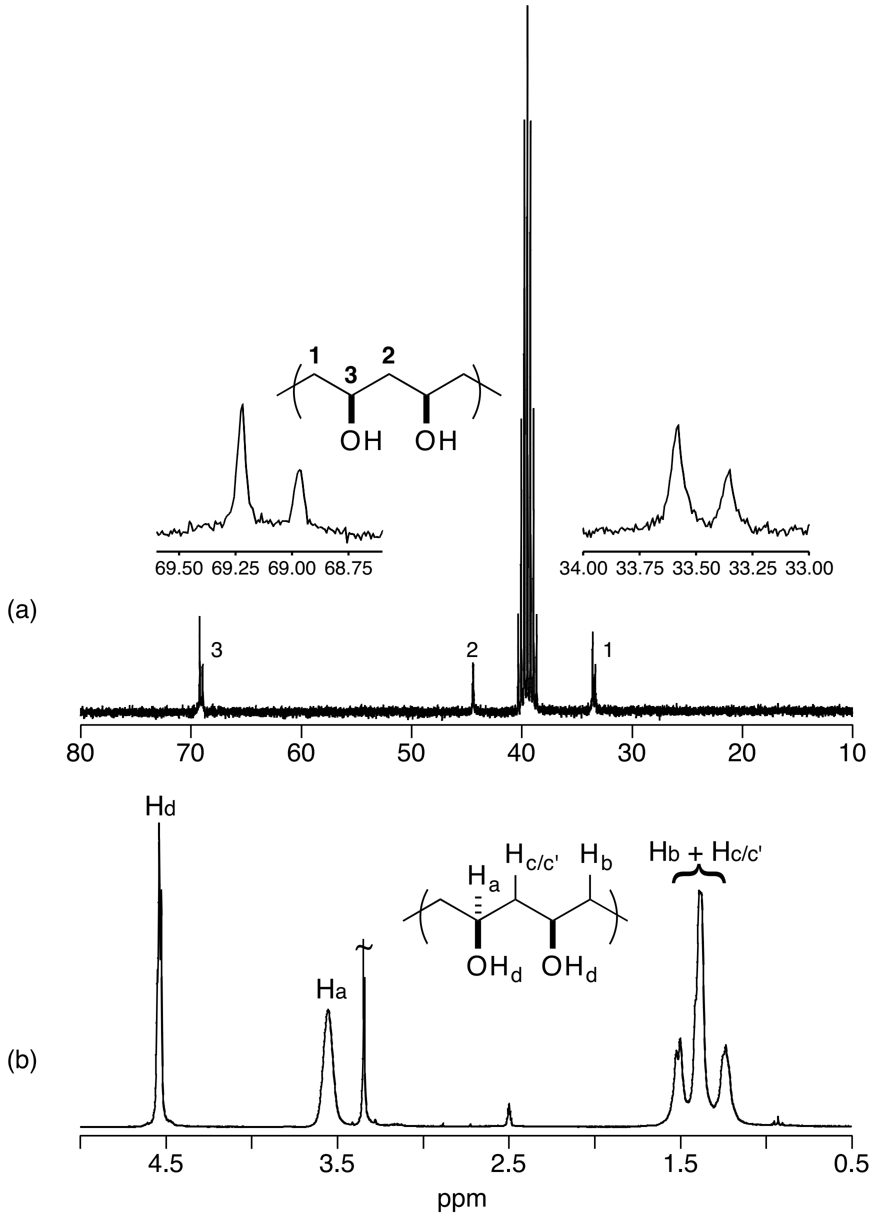


Figure 7.7: ^{13}C NMR spectrum (a) ^{1}H NMR spectrum (b) of unprotected MVOH polymer (originating from the ROMP of monomer **5** with catalyst **1**.

7.3.6 Thermal Analysis

Figure 7.8a shows the DSC thermogram of the MVOH copolymer, originating from catalyst **1**, with a clear melting transition at 193 °C (peak, 180 °C onset; a T_{m} of 180 °C was observed for the MVOH originating from catalyst **2**). This high T_{m} is consistent with a higher vinyl alcohol content in the copolymer as Mori *et al.* have shown that the T_{m} of EVOH copolymers varies over the range of ca.120–200 °C with increasing vinyl alcohol content.[30] The TGA curve displayed in Figure 7.8b shows an onset to decomposition at 360 °C. The thermal stability of the MVOH copolymer is substantially better than PVA homopolymer which displays thermal weight loss slightly below 300 °C.[3] A small decrease in weight is observed in the TGA curve around 60 °C and coincides with a large peak in the DSC thermogram. This is consistent with elimination of methanol, likely trapped in the MVOH copolymer upon precipitation. The melting temperature and increased thermal stability relative to PVA are comparable with structurally similar EVOH materials.[3, 30–32]

7.4 Conclusions

The successful ROMP of temporarily strained cyclopentene derivatives with ruthenium olefin metathesis catalysts **1** and **2** has been demonstrated. The symmetry of the monomer allowed for the placement of precisely defined alcohol functionality along the polymer backbone. Hydrogenation of the polymers followed by silane deprotection allowed for the synthesis of a new methylene-(vinyl alcohol) polymer which is similar to EVOH copolymers in structure and properties. Polymers were isolated in high yield and characterized by ^{1}H and ^{13}C NMR spectroscopies. Molecular weight of the polymers could be controlled over a large range by varying the monomer-to-catalyst ratio as well as by addition of chain transfer agents to the polymerization. Thermal properties of the new copolymer was determined by DSC and TGA analysis and showed a higher thermal stability than PVA. To our knowledge, these MVOH copolymers represent the first vinyl alcohol–hydrocarbon materials that can be syn-

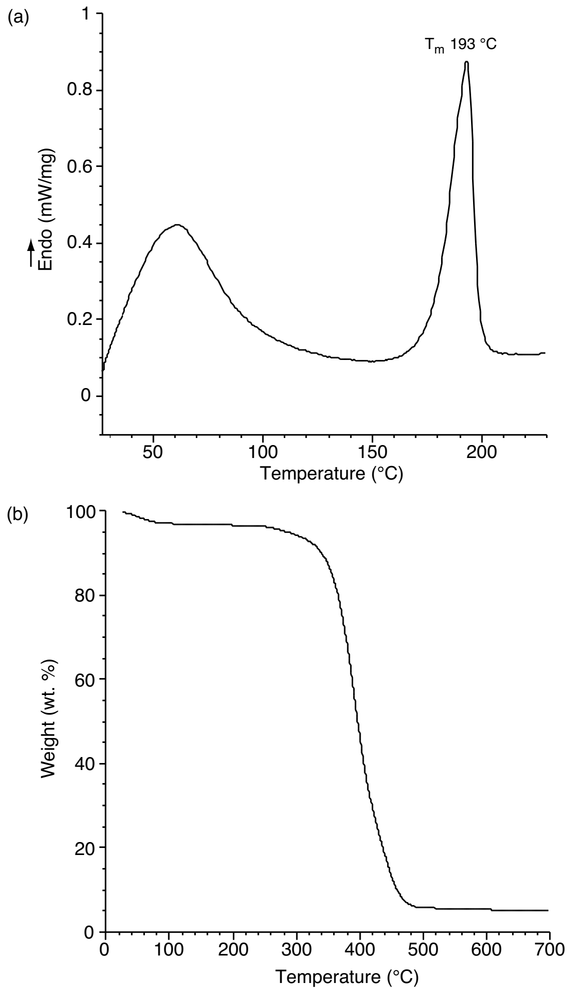


Figure 7.8: (a) DSC heating scan of deprotected MVOH polymer at a scan rate of 10 °C/min. (b) Thermogravimetric analysis of deprotected MVOH polymer at a scan rate of 10 °C/min under N_2 purge.

thesized in a controlled fashion over a large molecular weight range, are completely regioregular, and contain a desirable high alcohol percentage. This should allow for a more detailed understanding of the structure–property relationship in EVOH-type materials and aid in studies of grafting materials such as lactic acid[33] and/or functional groups[5] from the alcohol functionalities. Finally, this methodology is currently being applied toward other heteroatom-containing, temporarily strained cycloolefin monomers.

7.5 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 $CDCl_3$ or DMSO-d_6 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.

Materials. Toluene was dried by passage through solvent purification columns.[34] *cis*-4-Cyclopentene-1,3-diol (> 99%) was obtained from Fluka and used as received. *cis*-1,4-Diacetoxy-2-butene (95+%) (**6**) was obtained from TCI America and degassed by an argon purge prior to use. *N*,*N*-Dimethylformamide (anhydrous) (DMF), 1,2-dichloroethane (anhydrous), 2,6-lutidine (99+%, redistilled) and di-*tert*-butylsilyl-bis(trifluoromethanesulfonate) (97%) were obtained from Aldrich and used as received. $(PCy_3)_2(Cl)_2Ru{=}CHPh$ (**1**),[8] $(IMesH_2)(PCy_3)(Cl)_2Ru{=}CHPh$ (**2**),[35] and 3,3-di-*tert*-butyl-2,4-dioxa-3-sila-bicyclo[3.2.1]oct-6-ene[14] (**5**) were synthesized according to the literature.

Polymerization of 3,3-Di-*tert*-butyl-2,4-dioxa-3-sila-bicyclo[3.2.1]oct-6-ene (5) via ROMP with Catalyst 1. In a typical experiment, a small vial was charged with 0.25 g (1.0 mmol) of monomer and a stirbar. The monomer was degassed by three freeze–pump–thaw cycles. 3.4 mg (4.13×10^{-6} mol) of catalyst **1** was added as a solution in 1,2-dichloroethane or toluene (1 mL of solvent). The vial was placed in a 55 °C aluminium heating block stirring under argon for approximately 20 h. The reaction mixture was dissolved in 3 mL dichloromethane and precipitated into 50 mL of stirring MeOH. The white polymer precipitate was washed several times with MeOH and dried in vacuo overnight; yield (77–95%). See Table 7.1 for molecular weight data. ^{1}H NMR (300 MHz, CDCl$_3$): 5.75 *trans* (bs, 2H), 5.38 *cis* (d, $J = 4.0$ Hz, 2H), 5.08 *cis* (d, $J = 8.8$ Hz, 2H), 4.62 *trans* (d, $J = 10.2$ Hz, 2H), 1.4–1.8 (m, 2H), 1.0 (18H). ^{13}C NMR (75 MHz, CDCl$_3$): 132.3, 131.4, 131.1, 73.3, 70.7, 42.9, 42.6, 27.6, 27.5, 27.3, 22.8, 20.0,19.9.

Polymerization of 3,3-Di-*tert*-butyl-2,4-dioxa-3-sila-bicyclo[3.2.1]oct-6-ene (5) with CTA 6 via ROMP with Catalyst 2. In a typical experiment, a small vial was charged with 0.25 g (1.0 mmol) of monomer and a stirbar. The monomer was degassed by three freeze–pump–thaw cycles. Under an argon atmosphere, 0.25 mL (1.0 x 10^{-2} mmol) of a 6.90 mg/mL CTA in toluene solution was added via a syringe. Then 0.75 mL (5.3 x 10^{-5} mmol) of a 0.0595 mg/mL solution of **2** in toluene was added via a syringe. The vial was placed in a 55 °C heating apparatus and left stirring under argon for 23–113 h. The reaction mixture was dissolved in 2 mL of dichloromethane and precipitated into 50 mL of stirring MeOH. The white polymer precipitate was washed several times with MeOH and dried in vacuo overnight; yield (82–90%). See Table 7.2 for molecular weight data. ^{1}H NMR (300 MHz, CDCl$_3$): 5.73 *trans* (m, 2H), 5.35 *cis* (m, 2H), 5.06 *cis* (m, 2H), 4.62 *trans* (d, $J = 10.2$ Hz, 2H), 1.4–1.8 (m, 2H), 1.0 (18H). ^{13}C NMR (75 MHz, CDCl$_3$): 131.6, 131.3, 73.5, 43.2, 27.7, 27.6, 23.0, 20.2, 20.1.

Hydrogenation of Polymers after ROMP. In a typical experiment, a dry flask was charged with 0.35 g of polymer (M_n = 80360 g/mol, PDI = 1.3), 1.80 g of tosyl hydrazide (9.4 mmol, 6.5 equiv per double bond), 15 mL of xylenes, and a trace of BHT. The mixture was degassed by three freeze–pump–thaw cycles, and a reflux condenser was attached to the flask under argon. The reaction was heated to reflux for 4 h. The solution was cooled to room temperature and then precipitated into 125 mL of stirring MeOH. The white polymer precipitate was washed several times with MeOH and then dried in vacuo overnight; yield 0.34 g (99%). M_n = 75140 g/mol, PDI = 1.2, dn/dc = 0.076. ^{1}H NMR (300 MHz, CDCl$_3$): 3.9–4.1 (2H), 1.4–1.7 (6H), 1.0 (18H). $_{13}$C NMR (75 MHz, CDCl$_3$): 74.1, 73.5, 73.4, 42.4, 42.3, 34.8, 34.3, 27.8, 27.7, 27.3, 22.8, 19.7.

Desilation of Saturated Polymers. In a typical experiment, a dry flask was charged with 0.1952 g of polymer and a stirbar. A reflux condenser was attached and the system was purged with argon. 20 mL of dry THF was added followed by 10 mL of dry DMF, at which point the solution became cloudy white. 8 mL of tetrabutylammonium fluoride (TBAF) 1.0 M in THF was added via a syringe. The reaction was brought to reflux (75 °C) for 40 h. It was then cooled to room temperature and precipitated into 400 mL of 1:1 MeOH:CH_2Cl_2 stirring at room temperature. A stringy precipitate was observed; it was vacuum filtered and washed with copious amounts of both MeOH and CH_2Cl_2 and dried under dynamic high vacuum overnight; yield 0.0713 g (87%). ^{1}H NMR (300 MHz, DMSO-d_6): 4.53 (s, 2H), 3.56 (bs, 2H), 1.2–1.6 (6H). ^{13}C NMR (75 MHz, DMSO-d_6): 69.3, 69.0, 44.4, 33.6, 33.3.

7.6 Acknowledgment

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References Cited

[1] Lagaron, J. M.; Powell, A. K.; Bonner, G. *Polym. Testing* **2001,** *20,* 569–577.

[2] Ramakrishnan, S. *Macromolecules* **1991,** *24,* 3753–3759.

[3] Ramakrishnan, S.; Chung, T. C. *Macromolecules* **1990,** *23,* 4519–4524.

[4] Valenti, D. J.; Wagener, K. B. *Macromolecules* **1998,** *31,* 2764–2773.

[5] Bruzaud, S.; Levesque, G. *Macromol. Chem. Phys.* **2000,** *201,* 1758–1764.

[6] Hillmyer, M. A.; Laredo, W. R.; Grubbs, R. H. *Macromolecules* **1995,** *28,* 6311–6316.

[7] Schellekens, M. A. J.; Klumperman, B. *J. Macromol. Sci., Rev. Macromol. Chem. Phys.* **2000,** *C40,* 167–192.

[8] Schwab, P.; Grubbs, R. H.; Ziller, J. W. *J. Am. Chem. Soc.* **1996,** *118,* 100–110.

[9] Scholl, M.; Ding, S.; Lee, C. W.; Grubbs, R. H. *Org. Lett.* **1999,** *1,* 953–956.

[10] Bielawski, C. W.; Grubbs, R. H. *Angew. Chem., Int. Ed.* **2000,** *39,* 2903–2906.

[11] Sanford, M. S.; Love, J. A.; Grubbs, R. H. *J. Am. Chem. Soc.* **2001,** *123,* 6543–6554.

[12] Amir-Ebrahimi, V.; Corry, D. A.; Hamilton, J. G.; Thompson, J. M.; Rooney, J. J. *Macromolecules* **2000,** *33,* 717–724.

[13] Hamilton, J. G.; Frenzel, U.; Kohl, F. J.; Weskamp, T.; Rooney, J. J.; Herrmann, W. A.; Nuyken, O. *J. Organomet. Chem.* **2000,** *606,* 8–12.

[14] Lang, H.; Moser, H. E. *Helv. Chim. Acta* **1994,** *77,* 1527–1540.

[15] Lynn, D. M.; Kanaoka, S.; Grubbs, R. H. *J. Am. Chem. Soc.* **1996,** *118,* 784–790.

[16] Lynn, D. M.; Mohr, B.; Grubbs, R. H. *J. Am. Chem. Soc.* **1998,** *120,* 1627–1628.

[17] The molecular weight of the monomer is 240.41 g/mol. Dividing the M_{n} values by 240.41 g/mol yields a slope of 2.0 in toluene and 0.9 in 1,2-DCE.

[18] Hillmyer, M. A.; Grubbs, R. H. *Macromolecules* **1993,** *26,* 872–874.

[19] Hillmyer, M. A.; Grubbs, R. H. *Macromolecules* **1995,** *28,* 8662–8667.

[20] Hillmyer, M. A.; Nguyen, S. T.; Grubbs, R. H. *Macromolecules* **1997,** *30,* 718–721.

[21] Bielawski, C. W.; Scherman, O. A.; Grubbs, R. H. *Polymer* **2001,** *42,* 4939–4945.

[22] Wu, Z.; Grubbs, R. H. *Macromolecules* **1994,** *27,* 6700–6703.

[23] Hahn, S. F. *J. Polym. Sci., Part A: Polym. Chem.* **1992,** *30,* 397–408.

[24] Harwood, H. J.; Russell, D. B.; Verthe, J. J. A.; Zymonas, J. *Makromol. Chem.* **1973,** *163,* 1–12.

[25] Mango, L. A.; Lenz, R. W. *Makromol. Chem.* **1973,** *163,* 13–36.

[26] Nakagawa, T.; Okawara, M. *J. Polym. Sci., Part A-1* **1968,** *6*, 1795–1807.
[27] The *trans* and *cis* peaks were determined by coupling constants.
[28] Katsuraya, K.; Hatanaka, K.; Matsuzaki, K.; Amiya, S. *Polymer* **2001,** *42,* 9855–9858.
[29] Nagara, Y.; Nakano, T.; Okamoto, Y.; Gotoh, Y.; Nagura, M. *Polymer* **2001,** *42,* 9679–9686.
[30] Mori, Y.; Sumi, H.; Hirabayashi, T.; Inai, Y.; Yokota, K. *Macromolecules* **1994,** *27,* 1051–1056.
[31] Lommerts, B. J.; Sikkema, D. J. *Macromolecules* **2000,** *33,* 7950–7954.
[32] Yokota, K. *Prog. Polym. Sci.* **1999,** *24,* 517–563.
[33] Carlotti, S. J.; Giani-Beaune, O.; Schue, F. *J. Appl. Polym. Sci.* **2001,** *80,* 142–147.
[34] Pangborn, A. B.; Giardello, M. A.; Grubbs, R. H.; Rosen, R. K.; Timmers, F. J. *Organometallics* **1996,** *15,* 1518–1520.
[35] Sanford, M. S.; Ulman, M.; Grubbs, R. H. *J. Am. Chem. Soc.* **2001,** *123,* 749–750.