Utility of a Ruthenium Metathesis Catalyst for the Preparation of End-Functionalized Polybutadiene

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Received September 4, 1996; Revised Manuscript Received November 27, 1996[⊗]

ABSTRACT: The polymerization of cyclooctadiene (COD) in the presence of an allylic difunctionalized chain transfer agent (**1**) by a ruthenium metathesis catalyst (Ru) was accomplished. Deprotection of the resulting acetate end-functionalized polybutadiene was performed, leading to commercially important 1,4-hydroxytelechelic polybutadiene (HTPBD) with number average functionalities close to 2.0. The polymerizations were performed at high monomer concentrations or in the absence of solvent, and the robust nature of Ru allowed the use of high monomer to catalyst ratios (∼0.01 mol % Ru relative to total olefin). Investigation of the metathesis of olefin alcohols with Ru showed that side reactions may complicate the use of these compounds as chain transfer agents in metathesis polymerizations. The kinetics of this Ru-catalyzed ring-opening metathesis polymerization with added chain transfer agent was also investigated.

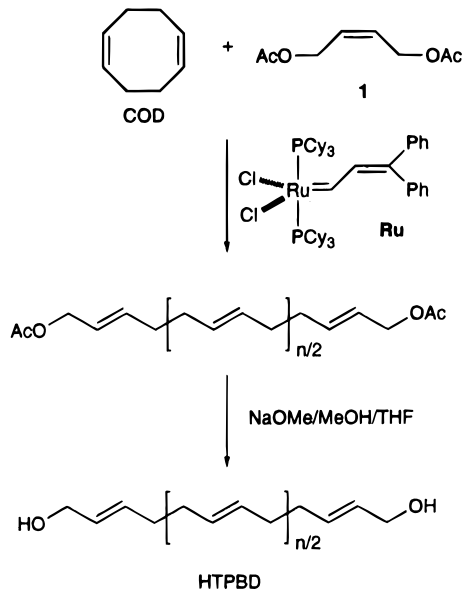
Introduction

Recent advances in ring-opening metathesis polymerization (ROMP),[1] acyclic diene metathesis polymerization (ADMET),[2] and metathesis degradation[3,4] in the presence of an appropriate chain transfer agent (CTA) have been realized for the preparation of end-functionalized polymers. Although each of these metathesis-based methods employs different polymer precursors (i.e. cyclic olefins, dienes, and unsaturated polymers, respectively), the eventual success relies mainly on the stability and activity of the catalytic species during the polymerization/chain transfer reaction. This typically requires the use of hydrocarbon monomers and protection of functional groups in the CTA so that deactivation of the metathesis catalyst through coordination or side reactions are minimized. Also, the judicious choice of the CTA such that metathesis with the CTA does not lead to a substituted alkylidene that is unstable is important to catalyst efficiency. For both molybdenum- and tungsten-based metathesis catalysts, this typically requires the separation of the functional group from the olefin in the CTA to be at least two methylene units.[1,5] The synthesis of CTAs with protected functionalities that are well-removed from the olefin is one limitation in these metathesis techniques for the preparation of end-functionalized polymers.[6] We now report that a neat mixture of cycoloctadiene (COD) and the simple allylic CTA (**1**) can be polymerized using a ruthenium-based metathesis catalyst (Ru)[7] to yield difunctional 1,4-polybutadiene (Scheme 1). The acetate end groups can be removed under mild conditions in high yield to give the commercially important hydroxytelechelic polybutadiene (HTPBD).

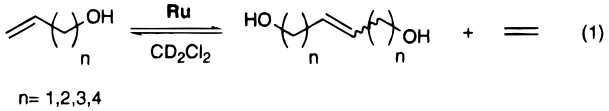
Results and Discussion

Complex Ru has been shown to effect the metathesis of a number of functionalized olefins including allylic alcohol, allylic ether, 3-buten-1-ol, and methyl oleate.[7,8]

Scheme 1. Ru-Catalyzed Preparation of HTPBD



(In addition, ruthenium-based metathesis catalysts are particularly effective in the ring-closing metathesis of highly functionalized dienes.[9]) The difunctional derivatives of these olefins should act as CTAs in the ROMP of cyclic olefins. Preliminary experiments[10] showed that both *cis*-2-butene-1,4-diol and *cis*-3-hexene-1,6-diol were effective CTAs in the polymerization of COD by Ru. However, side reactions, incomplete conversion of COD, and slow reaction rates were undesirable features. In a more complete study, the efficiency of Ru for the metathesis of olefin alcohols was investigated. The metathesis coupling of four olefin alcohols was investigated in CD_2Cl_2 (eq 1). The corresponding olefin diol



n= 1,2,3,4

was observed in all cases; however, the yields decreased with decreasing separation of the hydroxyl group and the olefin. The results are summarized in Table 1. In addition, aldehyde byproducts were observed by ^1H

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[⊗] Abstract published in *Advance ACS Abstracts,* February 1, 1997.

S0024-9297(96)01316-2 CCC: $14.00

Table 1. Metathesis of Terminal Olefin Alcohols by Ru[a]

entry	olefin alcohols	[ROH]/[Ru]	time (h)[b]	yield (%)[c]
1	CH_2=$CHCH_2OH$	68	2.5	21
2	CH_2=$CHCH_2CH_2OH$	54	2.5	27
3	CH_2=$CH(CH_2)_2CH_2OH$	45	4.5	55
4	CH_2=$CH(CH_2)_3CH_2OH$	39	4.5	55

[a] 9.6 mM solution in CD_2Cl_2. [b] At room temperature. [c] Determined by ^{1}H NMR spectroscopy.

NMR spectroscopy in some of the reactions with lower alcohols. This suggests that a side reaction involving isomerization of the olefin down the alkyl chain to give the corresponding enol (aldehyde) is occurring. This type of behavior has been observed in the aqueous Ru(II) isomerization of allylic ethers and alcohols and has been attributed to the in situ formation of ruthenium hydride species.[11] A similar reaction appears to be occurring in the Ru/olefin alcohol reactions studied here. This isomerization reaction cannot be tolerated in a metathesis/chain transfer polymerization since this side reaction decreases catalyst efficiency and number average functionality, $\bar{F}_n$, in the resulting telechelics.

Although the use of unprotected alcohols as CTAs is not completely compatible with the current Ru-catalyzed metathesis/chain transfer system, the clean metathesis of other allylic-functionalized molecules by Ru was promising for the preparation of telechelics. Earlier studies using tungsten- and molybdenum-based metathesis catalysts and allylic CTAs (or allylic-functionalized monomers[5]) showed that catalyst decomposition was a limiting side reaction.[1,12] In this study we chose to focus on a protected CTA that was both easily synthesized and highly compatible with Ru. The bis(acetate) of *cis*-2-butene-1,4-diol (**1**) can be prepared in large quantities and in high yield. In addition, the acetate protecting groups can easily be removed at the end of the polymerization.[13] The compatibility of **1** with Ru was established through the cis−trans metathesis isomerization of **1** (>95% cis) in a C_6D_6 solution at 45 °C ([**1**] ∼ 0.5 M, [**1**]/[Ru] ∼ 56). The isomerization of **1** was followed by ^{1}H NMR spectroscopy measuring the accumulation of *trans*-**1** over time. The amount of trans isomer leveled off at 70% after 15 h. A second aliquot of **1** was added to decrease the relative amount of trans isomer to 42% ([**1**]/[Ru] ∼ 95). Again, isomerization back to a mixture that contained 70% of the trans isomer of **1** was observed. A final aliquot of **1** was added, and further isomerization was observed. Metathesis activity was observed for over 2 days at 45 °C, and no side products were observed in the ^{1}H NMR spectrum. Similar behavior was observed for the Ru isomerization of a related CTA, 1,4-bis(benzyloxy)-*cis*-2-butene. In contrast, the molybdenum metathesis catalyst, $Mo(CHCMe_2Ph)(NAr)(OCMe(CF_3)_2)_2$ (Ar = 2,6-(*i*-Pr)C_6H_3), does not effect the isomerization of **1**, and only decomposition of the catalyst was observed under similar conditions. These results combined with earlier catalyst stability studies are in accord with the now well-established reactivities of ruthenium, molybdenum, and tungsten metathesis catalysts.[14]

The ROMP of COD by Ru in the presence **1** was examined. A polymerization reaction was carried out in toluene ([COD] ∼ 5 M, [COD]/[Ru] = 4700, [COD]/[**1**] = 30) under an argon atmosphere at 45 °C for 28 h. A low-molecular-weight (∼4k) polybutadiene oil was isolated in 88% yield by precipitation in methanol. The ^{1}H NMR spectrum was consistent with the expected acetate end-functionalized polybutadiene. The acetate end groups could be removed by treatment of a THF solution of the polymer with 0.7 M sodium methoxide in methanol at 0 °C. The resulting HTPBD was isolated by repeated precipitations and washings in methanol. The colorless, clear oil was fully characterized by ^{1}H NMR, ^{13}C NMR, and IR spectroscopies, and the structure was found to be consistent with perfect 1,4-HTPBD containing allylic alcohol end groups.

This polymerization procedure was repeated several times, and the results are collected in Table 2. With adequate stirring and control of reaction temperature, these polymerizations can be performed in the absence of solvent and on a large scale with similar results.[15] Also, the robust nature of this system allows the use of approximately 0.01 mol % of Ru relative to the total olefin concentration without significantly affecting the yield. A decrease in the fraction of catalyst in *any* metathesis-based system used in the synthesis of end-functionalized polymers reduces the number of unfunctionalized end groups arising from initiation or termination thus maximizing $\bar{F}_n$. The functionalities for these polymers were close to 2.0, as determined by VPO and end group titration (Table 2).

The robust nature of Ru was further confirmed by following the reduction in molecular weight of the polybutadiene as a function of time by ^{1}H NMR spectroscopy. Aliquots were taken from a polymerization (entry 5, Table 2) and were isolated by precipitation in methanol. The ratio of end group resonances to backbone resonances gives an estimate of the number average degree of polymerization, $\bar{X}_n$, assuming a perfectly difunctional chain (see experimental section). The molecular weight of the polybutadiene decreased rapidly in the beginning of the reaction and decreased slowly thereafter (Figure 1). A continuous reduction in molecular weight was observed over approximately 1 day.

The repeated isomerization of **1**, the effectiveness of extremely low catalyst loadings, and the observed reduction in molecular weight over long periods of time verify the robust nature of the catalytically active species in this type of metathesis/chain transfer reaction. To further understand the reaction pathway, the progress of a polymerization was followed in-situ by ^{1}H NMR spectroscopy. A neat sample of Ru, COD, and **1** ([COD]/[Ru] = 1450, [**1**]/[Ru] = 167) was heated to 50 °C in the probe of an NMR spectrometer. COD, **1**, end group, and repeat unit resonances were all well-resolved in the ^{1}H NMR spectrum. From integration intensities relative to an internal standard (in a sealed capillary inside the NMR tube) three values were calculated: the percentage of COD polymerized, the percentage of **1** incorporated into the polymer as end groups, and the percentage of trans repeat units in the polybutadiene. The results are shown in Figure 2. After 2.75 h ∼98% of the COD had been polymerized, and ∼71% of **1** had been incorporated as end groups. Over the next 15 h a steady increase in the concentration of end groups was observed. This is in accord with the above experiment where the majority of the molecular weight reduction was observed in the beginning of the reaction. After 15 h at 50 °C ∼90% of **1** had been incorporated as polymer end groups. An increase in the percentage of trans repeat units was also observed during the course of the reaction. This is consistent with interchain metathesis and thus prolonged activity of the catalytic species.

From these experiments it is clear that molecular weight reduction and end group incorporation occurs

Table 2. Polymerization Results Employing Ru, 1, and COD for the Preparation of HTPBD

entry	[COD]/ [Ru]	[COD]/ [**1**]	[COD] (M)[a]	scale (g)[b]	yield[c]	$10^{-3}\bar{M}_n$[d]	PDI[d]	$\bar{M}_n$[e]	$\bar{F}_n$[f]	trans (%)[h]	*t* (h)	*T* (°C)
1	3000	15	~5	25	60	5.0	1.3	2830	1.9	65	16	45
2	4700	44	~5	26	80	10.1	1.6	6490	2.05	50	20	45
3	4900	43	neat	135	88			6430	1.81	40	6	45
4	3700	14	~5	115	71	4.3	1.5	2920[g]	(2.0)	60	20	45
5	4600	11	neat	127	88			2040[g]	(2.0)	45	22	48
6	4700	30	>5	19	88[i]			4240[g]	(2.0)	60	28	45

[a] As a toluene solution. [b] Grams of COD + grams of **1**. [c] Isolated yield of deprotected polymer. [d] As determined by GPC in methylene chloride. [e] As determined by VPO. [f] $\bar{M}_n$ determined by VPO and hydroxyl equivalent weight determined by titration value. [g] By ^{1}H NMR spectroscopy assuming $\bar{F}_n = 2.0$. [h] Estimated from the ^{1}H NMR or ^{13}C NMR spectrum. [i] Calculated before deprotection.

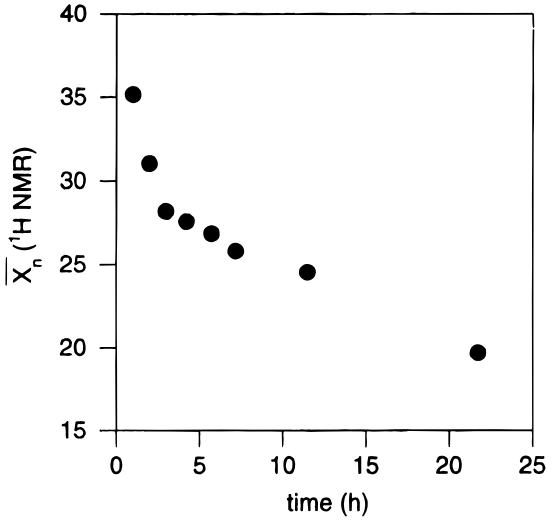


Figure 1. Number average degree of polymerization $\bar{X}_n$, as a function of time for entry 5 in Table 2.

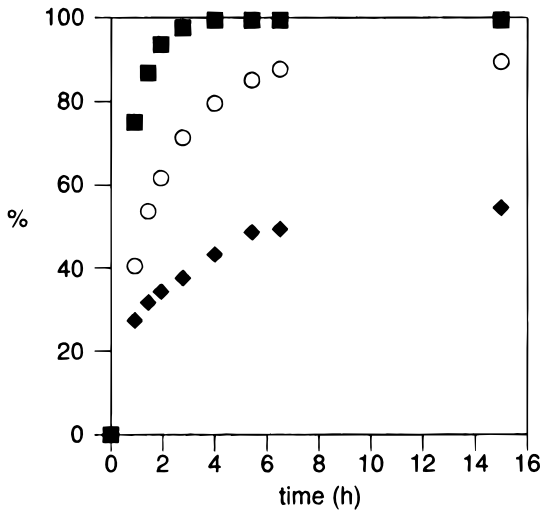


Figure 2. Progress of a polymerization reaction employing COD, **1**, and Ru followed by ^{1}H NMR spectroscopy: percentage COD polymerized (squares); percentage **1** incorporated as end groups (open circles); percentage trans repeat units in the polymer backbone (diamonds).

through termination of active chains by **1** (incorporation of **1** as polymer end groups at early reaction times), reinitiation by the functionally substituted ruthenium species (continued molecular weight reduction after 1 equiv of **1** had reacted and established activity of the functionalized ruthenium alkylidenes with other olefins), and by incorporation of **1** into preexisting polybutadiene chains (reduction of molecular weight after near complete conversion of COD). Therefore, the combination of **1** and Ru should be effective for all three metathesis-based polymerization schemes for the preparation of end-functionalized polymers.

Of the presently available metathesis routes to HTPBD, we believe this polymerization scheme has many advantageous features over other methods. First, **1** is readily available and the acetate protecting groups in the polybutadiene precursor can easily be removed by treatment with base. Second, the robust nature of Ru allows for the use of very low catalyst loadings and for large scale preparations. Third, the polymerization can easily be performed in the absence of solvent.

Experimental Section

General Considerations. Argon was purified by passage through columns of BASF R3-11 catalyst (Chemalog) and 4 Å molecular sieves (Linde). NMR spectra were recorded on a JEOL GX-400 spectrometer (399.65 MHz 1H, 100.40 MHz 13C) or a GE QE-300 Plus (300.10 MHz ^{1}H; 75.49 MHz ^{13}C) spectrometer. Chemical shifts are reported in ppm (δ) downfield from tetramethylsilane and referenced to residual protio solvent. Coupling constants are reported in hertz (Hz). IR spectra were recorded on a Perkin-Elmer 1600 series FT-IR spectrometer. GPC analyses in methylene chloride were obtained on an HPLC system utilizing an Altex Model 110A pump, a Rheodyne model 7125 injector with a 100 μL injection loop, two American Polymer Standards 10 μm mixed bed columns, and a Knauer differential refractometer. The molecular weights and polydispersities are reported versus monodisperse polystyrene standards. VPO was carried out using a Jupiter model 233 in toluene at 60 °C using sucrose octaacetate for calibration. The calibration was confirmed using a low-molecular-weight polybutadiene standard (Polysciences, MW 2760, PDI = 1.08). Elemental analysis was performed at the California Institute of Technology Elemental Analysis Facility. Hydroxyl end group titrations were performed at Thiokol Corp. The hydroxyl groups were capped with toluenesulfonyl isocyanate. The resulting sufonyl carbamate is acidic in a nonaqueous system and can be titrated directly with tetrabutylammonium hydroxide after unreacted toluenesulfonyl isocyanate has been destroyed with water.

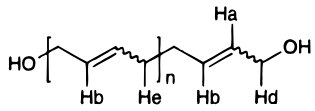
Materials. Toluene (Baker HPLC grade) was distilled from CaH_2 under argon and degassed. Methylene chloride-d_2 (CD_2Cl_2) was dried over CaH_2, vacuum-transferred, and then degassed by three continuous freeze−pump−thaw cycles before being transferred into the drybox for use in the NMR experiments. Benzene (and C_6D_6) was distilled from a purple Na/benzophenone ketyl solution prior to use. *cis*-2-Butene-1,4-diol (Aldrich) was distilled from $CaSO_4$ under vacuum prior to use. COD (Aldrich) was filtered through neutral alumina before use. All the olefin alcohols were obtained from Aldrich Chemical Co., passed through a plug of activated neutral alumina, and then degassed by three continuous freeze−pump−thaw cycles before being transferred into the drybox for use in the NMR spectroscopy experiments. Solid Ru catalyst was prepared by published procedures[7] and manipulated in a nitrogen-filled drybox. All other solvents, salts, and commodity chemicals were reagent grade and used without further purification.

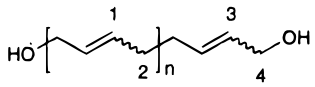
Metathesis of Terminal Olefin Alcohols by Ru. In a typical experiment, 0.45 mL of the catalyst solution (9.6 mM in CD_2Cl_2) was added to a 5 mm NMR tube inside a nitrogen-filled drybox. The olefin alcohol was then added via a microliter syringe. The tube was capped with a rubber

septum, shaked vigorously, and taken out of the drybox. The reaction was monitored by ^{1}H NMR spectroscopy at room temperature.

Preparation of $AcOCH_2CH{=}CHCH_2OAc$ (1). Acetic anhydride (108 g, 100 mL, 1.06 mol, 2.5 equiv) was added dropwise to a stirring methylene chloride/chloroform (~400 mL, 1:1 v/v) solution of *cis*-2-butene-1,4-diol (37.3 g, 0.42 mol, 1 equiv) and triethylamine (107 g, 148 mL, 1.06 mol, 2.5 equiv) at 0 °C over ~1 h. The solution was allowed to slowly warm to room temperature and stirred overnight (or followed by TLC). The orange solution was washed with water (3 × 300 mL) and concentrated on a rotovap. The resultant orange oil was distilled under reduced pressure (~0.05 mmHg), and the middle fraction was collected at ~54 °C. The distillate was stirred over calcium hydride at room temperature, overnight, under vacuum (~0.05 mmHg). This was then redistilled under reduced pressure (as above ~54 °C) and collected in a flask which was sealed under argon. The isolated yield was ~58 g (80%). GC 100% pure, >97% cis. ^{1}H NMR ($CDCl_3$): δ 5.73 (m, 2H), 4.65 (d, J = 5Hz, 4H), 2.05 (s, 6H). ^{1}H NMR (C_6D_6): (cis) δ 5.50 (m), 4.48 (d), 1.62 (s), (trans) δ 5.52 (m), 4.32 (d), 1.63 (s). ^{13}C NMR ($CDCl_3$): δ 170.2, 127.8, 59.6 (trans, 63.5), 20.5 (trans, 25.0). Anal. Calcd for $C_8H_{12}O_4$: C, 55.81; H, 7.02. Found: C, 55.29; H, 7.08.

General Polymerization and Deprotection Procedure Employing COD, 1, and Ru. A three-neck, 250 mL, round bottom flask equipped with a mechanical stirrer, was charged with 1,5-cyclooctadiene (131 g, 1.22 mol, 4880 equiv). The chain transfer agent (**1**) (4.9 g, 0.029 mol, 114 equiv) was added to the reaction flask via pipet. The two open necks of the flask were capped with septa. The mixture was purged with a vigorous stream of argon through a needle (the outlet going to a oil bubbler) for 30 min. With a continual purge of argon, Ru (0.23 g, 2.5×10^{-4} mol, 1 equiv) was added as a methylene chloride solution (~1.2 mL) via syringe (Ru is very soluble in the COD/**1** mixture and can be added as solid). The reaction was kept under a slow purge of argon, the mechanical stirrer was started, and the flask was immersed in an oil bath at 45–50 °C. The dark red-orange reaction mixture was stirred for 6 h. The resulting light orange reaction mixture was allowed to cool to room temperature and was poured into ~500 mL of slightly acidic methanol (add 15 mL of 1 M HCl to 500 mL of methanol). The polymer that precipitated became white, and the methanol solution turned yellow. The methanol was decanted, and the methanol wash was repeated three times. The polymer was then dissolved in ~600 mL of tetrahydrofuran and cooled to 0 °C. A 100 mL aliquot of 0.7 M sodium methoxide in methanol was added to the THF solution (a slight volume of THF was added because the polymer started to precipitate). This was stirred for 5.5 h at 0 °C. The reaction mixture was poured into 1 L of slightly acidic methanol and stirred overnight at room temperature. The mixture was decanted, and the polymer was washed three times with methanol/HCl, methanol/water, and pure methanol successively. Care must be taken in these purification steps since very-low-molecular-weight telechelics are slightly soluble in THF/methanol mixtures. After the final wash the polymer was dissolved in 1 L of methylene chloride (reagent grade) and isolated by rotary evaporation and subjected to high vacuum at ~40 °C overnight to yield ~120 g (~88%) of a clear, viscous liquid. IR (neat): 3320, 2914, 1655, 1435, 1352, 1312, 1081, 965, 726 cm^{-1}. The ^{1}H NMR and ^{13}C NMR spectra were assigned as follows: ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.6–5.7 (m, Ha and Hb, cis and trans), 5.40 (bs, Hc trans), 5.35 (bs, Hc cis), 4.16 (d, J = 7 Hz, Hd cis), 4.06 (d, J = 5 Hz, Hd trans), 2.06 (bs, He cis), 2.01 (bs, He trans); ^{13}C NMR (100 MHz, $CDCl_3$) δ 132.8 (C3, tc), 130.5 (C3, tt), 130.2 (C1, tc), 130.1 (C1, tt), 129.7 (C1, cc), 129.5 (C1, ct), 63.8 (C4, t), 58.6 (C4, c), 32.8 (C2, t), 27.5 (C2, c).





Acknowledgment. Funding for this research was provided by the NSF, Thiokol Corp., and Bayer. M.A.H. thanks IBM for a graduate fellowship. S.T.N. thanks the Department of Defense, Office of Army Research, for an NDSEG Predoctoral Fellowship and the California Institute of Technology for an Institute Fellowship. We are grateful to Dr. Lou Cannizzo at Thiokol Corp. for titration analysis of the HTPBD hydroxyl end groups.

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MA961316N