8662 *Macromolecules* **1995,** *28,* 8662–8667

Chain Transfer in the Ring-Opening Metathesis Polymerization of Cyclooctadiene Using Discrete Metal Alkylidenes[†]

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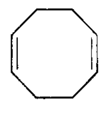
Received May 23, 1995; Revised Manuscript Received September 12, 1995[®]

ABSTRACT: The ring-opening metathesis polymerization of cyclooctadiene (**COD**) in the presence of a difunctional chain transfer agent (CTA) was investigated. The effect of the CTA structure and choice of metathesis catalyst on the overall efficiency of the polymerization reaction is discussed. A separation of the oxygen functionality from the olefin in the CTA by two methylene units significantly enhances the stability of the discrete, tungsten-based metathesis catalyst used for these polymerizations. Furthermore, a more robust well-defined metathesis catalyst based on molybdenum was more effective than the tungsten-based catalyst. The preparation of low-molecular-weight hydroxytelechelic polybutadienes with one type of regiochemistry, number-average functionalities that approach 2.0, and in high yield was accomplished.

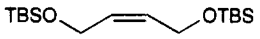
Introduction

Acyclic olefins act as chain transfer agents in the ring-opening metathesis polymerization of cyclic olefins.[1] The use of acyclic olefins bearing functional groups leads to the incorporation of these functional groups at the chain ends of the polyalkenamers produced, and this strategy has been employed for the synthesis of telechelic polymers.[2–10] A particularly useful class of polymers that can be synthesized using this strategy are the telechelic polybutadienes. In addition to ROMP, other routes to telechelic polybutadienes based on metathesis have also been investigated.[11–14]

Recently, we reported the synthesis of hydroxytelechelic polybutadiene (HTPBD) via the ring-opening metathesis polymerization (ROMP) of cyclooctadiene (**COD**) in the presence of a difunctional chain transfer agent (CTA). The system we employed consisted of the well-defined catalyst W(CHAr)(NPh)[OCMe$(CF_3)_2]_2$(THF) (Ar = *o*-methoxyphenyl) (**W**)[15,16] and the bis(*tert*-butyldimethylsilyl) (TBS) ether of *cis*-2-butene-1,4-diol as the CTA (**1**).



COD



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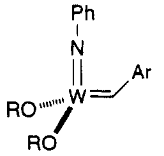


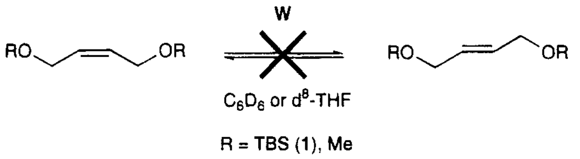
W: R = $(CF_3)_2CH_3C$
Ar = *o*-methoxyphenyl

This system was effective for the production of HTPBD; however, the preparation of low-molecular-weight polymers (using low [**COD**]/[CTA] ratios) resulted in low yields of polymer. It was speculated that premature catalyst decomposition resulted in incomplete conversion of the monomer and the CTA. In this paper, we examine the effect of CTA structure and choice of catalyst on the overall efficiency of the ROMP/CT (ring-opening metathesis polymerization with chain transfer) reaction.

Results and Discussion

The low yields at high [CTA]/[**W**] ratios (or low [**COD**]/[CTA] ratios) in the ROMP/CT system using **1** as the chain transfer agent were attributed to the instability of the alkylidene moiety generated from the metathesis of a propagating (or initiating) alkylidene with **1.**[17] As a test of this, the metathesis isomerization of **1** was attempted in the absence of **COD**. Successful isomerization requires the intermediacy of a β-substituted alkylidene and thus probes the stability of this alkylidene.

Successful metathesis of **1** (>95% cis) should result in equilibration of the cis/trans isomers of **1** (<95% cis).[1] Metathesis isomerization of **1** and its dimethyl ether analog was attempted in benzene and in THF at substrate to catalyst ratios ranging from 3:1 to 300:1. In no case was isomerization of the double bond observed (eq 1).



(1)

Not only was **W** ineffective for the isomerization, but decomposition of the starting alkylidene species was observed in all cases.[18] The instability of **W** is consistent with the reported inactivity of tungsten-based metathesis catalysts with allylic ethers.[19–23] For example, Wagener has shown that a minimum of two methylene groups between the oxygen and the olefin are necessary for successful acyclic diene metathesis polymerization (ADMET) of ether containing dienes employing a similar tungsten-based metathesis catalyst.[22] Coordination of the ether to the metal center when allylic ethers were employed was presumed to deactivate the catalyst. This is in analogy to the coordination of the carbonyl group in the attempted metathesis of methyl acrylate by a tungsten based catalyst reported by Schrock.[24] Also, decomposition of allylic ethers in the presence of the classical metathesis catalyst system $WCl_6/SnMe_4$ to

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[®] Abstract published in *Advance ACS Abstracts,* November 1, 1995.

Scheme 1. Synthesis of CTA 2

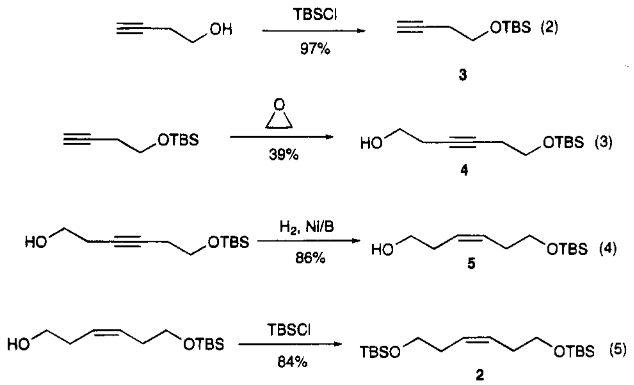


Table 1. Comparison of 1 and 2 as CTAs[a]

CTA	$[\mathbf{COD}]_0/[\mathrm{CTA}]_0$	$[\mathrm{CTA}]_0/[\mathbf{W}]_0$	$\bar{M}_n \times 10^{-3}$ [b]	PDI[b]	yield (%)
1	54	13.5	14.1	3.0	40
1	57	10.5	10.7	2.8	51
2	64	11.9	7.2	2.7	98
2	26	24.6	2.8	2.5	92

[a] Standard polymerization procedure (see Experimental Section). [b] Determined by GPC in methylene chloride vs polystyrene standards.

Table 2. ROMP/CT Employing 2 as the CTA and W as the Catalyst[a]

entry	$[\mathbf{COD}]_0/[\mathbf{2}]_0$	$[\mathbf{COD}]_0/[\mathbf{W}]_0$	$\bar{M}_n$[b]	$\bar{M}_n \times 10^{-3}$ [c]	PDI[c]	yield (%)
1	94	848	7990	14.5	2.3	94
2	37	843	4210	7.4	2.2	96
3	22	841	3490	5.0	2.2	94
4	11	859	2310	3.6	1.9	83

[a] Standard polymerization conditions (see Experimental Section). [b] Determined by VPO. [c] Determined by GPC in toluene vs polystyrene standards.

yield a stable tungsten alkoxide complex has been observed.[21] The inability of **W** to isomerize **1** coupled with its decomposition in the presence of **1** is consistent with prior reports on allylic ether metathesis. However, it is clear from our previous polymerization results that the allylic ether fragment is being incorporated as polymer end groups.[17] Therefore, the reaction of an oxygen-containing alkylidene with either **COD** or the polybutadiene backbone is occurring at a rate that is competitive with decomposition. If **1** were only acting as a chain-terminating species (i.e., the rate of reaction of the oxygen-containing alkylidene with any other olefin was zero), then a number-average functionality ($\bar{F}_n$) close to 1 would be expected. Functionalities close to 2 were observed. In analogy to the ADMET polymerization of bisallylic ethers,[22,25] separation of the oxygen from the olefin by two methylene units should increase the stability of the resultant substituted alkylidene and thus lead to improved polymerization yields at high concentrations of CTA. For the ROMP/CT systems described above, this requires the synthesis of the homoallylic derivative of **1**.

Both cis and trans olefins should be effective CTAs in principle. However, the use of a cis olefin should increase the relative rate of CTA incorporation to **COD** polymerization. In fact, in a preliminary experiment using 1,10-bis(*tert*-butyldimethylsiloxy)-*trans*-5-decene as the CTA in a **COD** polymerization, virtually no molecular weight reduction was seen over the same time period used in typical ROMP/CT reactions. Presumably, this is due to the slower reaction of the trans olefin. It is likely, however, that eventual incorporation of this CTA into the polymer would be observed in analogy to the system employed by Chung where a difunctional *trans*-5-decene was employed as a CTA.[9] Nevertheless, since **1** was predominantly cis (>95%), direct comparison of the homoallylic analog requires the synthesis of 1,6-bis(*tert*-butyldimethylsiloxy)-*cis*-3-hexene (**2**).

The synthesis of **2** is outlined in Scheme 1.[26] Protection of 3-butyn-1-ol as the *tert*-butyldimethylsilyl ether[27] gave compound **3** in 97% yield (eq 2). Ring opening of ethylene oxide by the lithium acetylide derived from **3** was accomplished in liquid ammonia to give **4** in 39% yield (eq 3).[28] Other reaction conditions were investigated (e.g., Lewis acid catalyzed ring opening in THF[29,30]); however, the reaction in liquid ammonia gave the highest yields (~40%) and the best reproducibility. Hydrogenation of **4** using the nickel/sodium borohydride based catalyst described by Brown[31] was employed for the semireduction of the alkyne to give the corresponding cis (>95% cis by NMR and GC) alkene **5** (eq 4). Protection of **5** as the *tert*-butyldimethylsilyl ether[27] gave **2** in 84% yield (eq 5). The overall yield for the four steps was 27%, and all of the steps were carried out on a multigram scale.

Isomerization of **2** from >95% cis to ~75% trans by **W** in C_6D_6 at relatively low olefin to catalyst ratios (<10) was observed. Unlike the attempted isomerization of **1**, the initial alkylidene species from **W** was stable for up to 3 months in the presence of **2**. Therefore, the use of **2** as a CTA in the polymerization of **COD** should generally lead to higher yields of polymer compared to **1** at similar $[\mathbf{COD}]_0/[\mathrm{CTA}]_0$ ratios. This analysis presumes the decomposition problem is directly related to the choice of CTA and not inherent to the stability of the propagating alkylidene.[32] A comparison of the two CTAs was performed to establish their relative efficiency. These results are shown in Table 1. Clearly, **2** is a much more effective CTA in terms of molecular weight reduction and polymerization yield. Even at more than twice the concentration of CTA relative to **W**, the homologated CTA gave a much higher yield of polymer. In addition, much lower molecular weights were synthesized in more reasonable yields using **2** as the CTA. At this point, it was clear that **2** was the CTA of choice in these polymerizations even though its synthesis is considerably longer.

ROMP/CT reactions similar to the ones reported using **1**[17] were repeated using **2** as the CTA at significantly lower $[\mathbf{COD}]_0/[\mathrm{CTA}]_0$ ratios (11–94 vs 54–654). Similar reaction conditions were employed (the concentration of **COD** in these polymerizations was ~5 M in toluene). The results are given in Table 2. Unlike the ROMP/CT reactions using CTA **1**, no unreacted **COD** was observed in the system using **2** as the CTA. However, unreacted **2** was observed and quantified ($[\mathbf{2}]_t$). The less than quantitative yields in these polymerizations is due to the incomplete conversion of CTA and not to unreacted **COD**.[33] The relationship between the measured $\bar{X}_n$ (VPO) and the ratio of the initial amount of **COD** ($[\mathbf{COD}]_0$) to the total amount of CTA reacted ($[\mathbf{2}]_0 - [\mathbf{2}]_t$) is shown in Figure 1.[34] There is a linear relationship between the $[\mathbf{COD}]_0/([\mathbf{2}]_0 - [\mathbf{2}]_t)$ ratio and the observed $\bar{X}_n$.[35] Using the molecular weights from the VPO measurements, $\bar{F}_n$ values for the four samples were calculated from the calculated $\bar{X}_n$ and the ^{1}H NMR integrations to be 1.3(6), 1.5(4), 1.9(2), and 1.8(6) for entries 1–4, respectively. The $\bar{F}_n$ values calculated for the two higher-molecular-weight samples were disap-

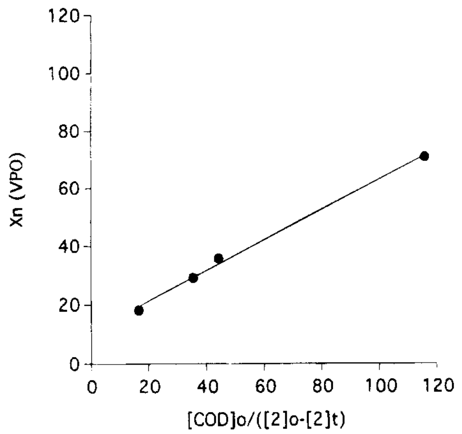


Figure 1. Relationship between the $[\mathbf{COD}]_0/([\mathbf{2}]_0 - [\mathbf{2}]_t)$ ratio and $\bar{X}_n$ from the results shown in Table 2.

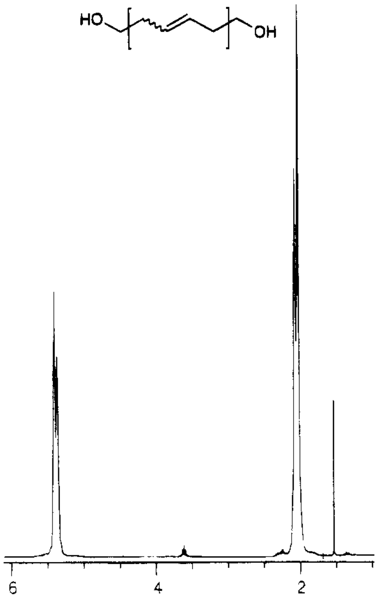


Figure 2. ^{1}H NMR spectrum (300 MHz, $CDCl_3$) of a HTPBD synthesized employing catalyst **W** and CTA **2** (scale is in ppm, the peak at ~1.5 ppm is residual water in the solvent).

pointingly low. However, for the lower-molecular-weight samples, the functionalities were close to 2.0. The diminished $\bar{F}_n$ values can be attributed to large macrocycles and to unfunctionalized end groups derived from the catalyst.[35] The estimated error in the $\bar{F}_n$ values is ±0.2 assuming ±15% error in the molecular weight measurement and a ±5% error in the NMR integration.[36]

The HTPBDs prepared using **2** as the CTA were characterized. Deprotection of the HTPBD was accomplished with tetra-*n*-butylammonium fluoride (TBAF) as described in the previous system.[17] Figure 2 shows the ^{1}H NMR spectrum of a representative low-molecular-weight HTPBD synthesized using **2** as the CTA. As in the initial HTPBDs synthesized using CTA **1**, only 1,4 repeat units were observed. The multiplet at δ 3.58 was assigned to the methylene protons adjacent to the oxygen for both cis and trans end groups. Allylic end group protons were observed slightly downfield (~δ 2.25) of the backbone allylic protons, and olefinic end group protons were observed slightly downfield (~δ 5.5) of the backbone allylic protons. Addition of trifluoroacetic anhydride to this sample resulted in the formation of the trifluoroacetate end-capped polymer. The methylene protons adjacent to the oxygen shifted downfield by ~0.75 ppm, the allylic end group protons shifted downfield by ~0.2 ppm, and the olefinic end group protons shifted downfield by ~0.1 ppm. The ^{13}C NMR spectrum of the HTPBD was also consistent with the structure shown in Figure 2. Two equally intense resonances were observed at δ 62.3 and δ 62.7 and assigned to end group carbons adjacent to the oxygen (both cis and trans end groups). Also, the backbone was determined to be 53% trans from the ^{13}C NMR spectrum. Olefinic and allylic carbons adjacent to the end group oxygen were also observed in the ^{13}C NMR spectrum (see the Experimental Section for the complete assignment).

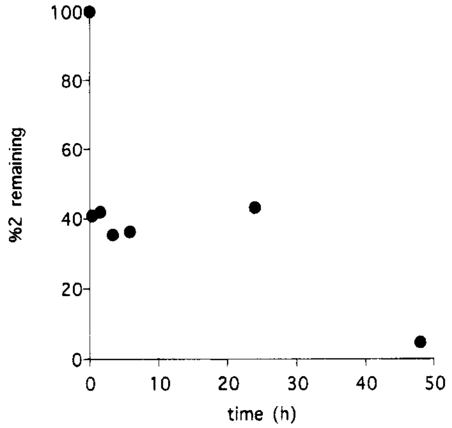


Figure 3. Disappearance of **2** over time in a typical ROMP/CT reaction employing **W** as the catalyst and **COD** as the monomer. A second aliquot of catalyst was added at t = 34.8 h.

Changing the CTA from **1** to **2** resulted in significant increases in the yields of polymer isolated from these ROMP/CT reactions. Lower-molecular-weight polymers ($<10^4$) were synthesized and isolated in good yields. The HTPBDs isolated contained only 1,4 repeat units, and low-molecular-weight polymers had $\bar{F}_n$ values close to 2.0. The end groups on the HTPBD using **2** as the CTA are homoallylic rather than allylic alcohols. Although the synthesis of **2** is more complicated than the synthesis of **1**, it is a superior CTA for the preparation of HTPBD. However, inspection of Table 2 reveals that the yield of polymer drops off at relatively low $[\mathbf{COD}]_0/[\mathbf{2}]_0$ concentrations (entry 4) as a consequence of the incomplete conversion of **2**. Although this diminished yield is not as severe with **1** as the CTA, the progress of a typical ROMP/CT reaction using **2** as the CTA was investigated.

The origin of this low yield was investigated by following the conversion of monomer and CTA in one of these polymerizations using GC. A ROMP/CT experiment similar to entry 4 in Table 2 ($[\mathbf{COD}]_0/[\mathbf{2}]_0 = 11$) was repeated, and aliquots were taken from the polymerization at different times and precipitated into methanol. The precipitated polymer was filtered, and the filtrate was analyzed by GC. After 0.33 h there was no **COD** detected by GC. The disappearance of **2** as a function of reaction time is shown in Figure 3. It appears that the maximum amount of **2** is consumed within the first hour of the reaction. Even after 24 h there is no further decrease in the amount of **2** remaining in the solution. Addition of a second aliquot of **W** (~10 mol % **W** relative to the remaining **2**) resulted in almost complete consumption of **2** (<5% remaining) and a decrease in the viscosity of the polymerization solution. Also, after 48 h two isomers of the cyclic oligomer cyclododecatriene (CDT) were observed by GC (identi-

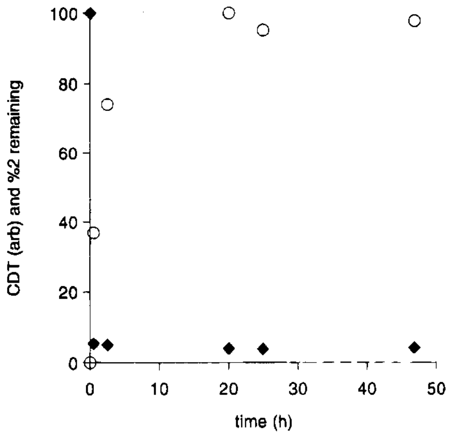
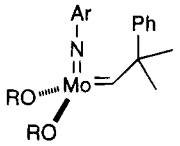


Figure 4. Disappearance of **2** over time (%, ♦) and the appearance of CDT over time (arbitrary units, ○) in a typical ROMP/CT employing **Mo** as the catalyst and **COD** as the monomer.

fied by GC/MS). This cyclic was not observed in the first seven aliquots. From these results it appears that both polymerization and chain transfer are fast. However, the catalyst decomposes before complete conversion of the CTA (**2**). If the catalyst were still active, a steady decrease in **2** should have been observed as well as the formation of cyclic oligomers. Moreover, the catalyst appears to have completely decomposed within the first hour of the reaction. Significant improvements in the yield and monomer conversion are achieved using **2** as the CTA as compared to the initial systems using **1** as the CTA, but there still exists a problem with catalyst decomposition and thus incomplete conversion of CTA.

In an effort to further increase the yield of polymerization (conversion of the CTA), the more robust molybdenum-based metathesis catalyst $Mo(CHMe_2Ph)(NAr)(OCMe(CF_3)_2)_2$ (Ar = 2,6-(i-Pr)C_6H_3),[37-39] **Mo**, was investigated.



Mo: R = $(CF_3)_2CH_3C$
Ar = 2,6-diisopropylphenyl

Wagener showed that complex **Mo** was more suited for the ADMET of ether-containing dienes as compared to tungsten-based catalysts.[25] Like **W**, complex **Mo** also effected the cis–trans isomerization of **2**. Complex **Mo** was employed in a ROMP/CT experiment similar to entry 4 in Table 2 ($[\mathbf{COD}]_0/[\mathbf{2}]_0 = 10$). Again, the progress of the reaction was followed by GC. After 0.5 h no **COD**, ~5% of the initial **2**, and CDT were observed. The reaction was followed over 2 days. The results are shown in Figure 4. The amount of CDT was not quantified; however, a steady increase in its relative concentration was observed over the first 20 h of the reaction. The concentration of CDT leveled off after 20 h. Larger oligomers were also seen in the GC, but it was not determined if they were linear or cyclic in nature. The residual **2** did not drop below 3% of its original concentration ($[\mathbf{2}]_0$) over 2 days.

From the results presented above, it is clear that for the most successful ROMP/CT polymerizations (in terms of incorporation of CTA and robust nature of the catalyst) the combination of **2** and **Mo** as the chain transfer agent and catalyst respectively should be employed. The HTPBDs synthesized using **W** or **Mo** as the catalyst were spectroscopically indistinguishable, although the backbone stereochemistry of the HTPBDs synthesized using **Mo** was generally higher trans. This is consistent with the observed longevity of the active species in these polymerizations. In addition, for **Mo**-catalyzed polymerizations, significantly higher $[\mathbf{COD}]_0/[\text{catalyst}]_0$ ratios could be used without significant decreases in yield. For example, two polymerizations were performed at $[\mathbf{COD}]_0/[\mathbf{Mo}]_0$ ratios ≈ 1200 and $[\mathbf{COD}]_0/[\mathbf{2}]_0$ ratios of 23 and 80. The yields of isolated polymer were 94 and 98%, respectively. As a consequence of the higher $[\mathbf{COD}]_0/[\mathbf{Mo}]_0$ ratios, negative contributions to the $\bar{F}_n$ from the catalyst can be minimized. In a subsequent ROMP/CT experiment employing catalyst **Mo** and CTA **2** ($[\mathbf{COD}]_0/[\mathbf{Mo}]_0 = 2400$ and $[\mathbf{COD}]_0/[\mathbf{2}]_0 = 16$), a low-molecular-weight HTPBD was synthesized with an $\bar{F}_n$ value of 1.94 (calculated from the VPO molecular weight, $\bar{M}_n = 3250$, and ^{1}H NMR integration). Using the increased $[\mathbf{COD}]_0/[\mathbf{Mo}]_0$ ratio, the polymerization mixture contained 83.5% **COD**, 16.3% **2**, and only 0.2% **Mo** by weight.

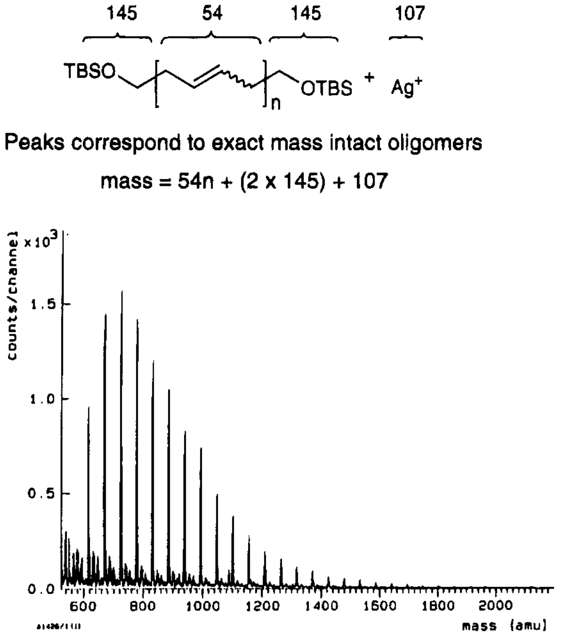


Figure 5. TOF-SIMS spectrum of a low-molecular-weight, TBS-protected HTPBD.

In an effort to verify that the $\bar{F}_n$ was close to 2.0 for these HTPBDs synthesized by this type of ROMP/CT reaction, a low-molecular-weight, TBS-protected HTPBD synthesized using **Mo**, **2**, and **COD** was analyzed by time-of-flight secondary ion mass spectrometry (TOF-SIMS).[40-42] This technique has been successfully employed in the analysis of end-functionalized polystyrenes.[43] For polystyrene, quantification of the degree of functionalization can be obtained. In the case of HTPBD, the polymer was desorbed from a silver substrate, and therefore silver is also desorbed to stabilize and cationize the polymer. The mass spectrum is shown in Figure 5. Each peak corresponds to an intact polymer with exactly two end groups. No other species were observed. From the ^{1}H NMR spectrum, assuming perfect difunctionality, the $\bar{M}_n$ for this polymer was calculated to be 1780. From the TOF-SIMS spectra a $\bar{M}_n$ of 734 was calculated. The discrepancy in the two molecular weights could be due to a number of factors such as sputter yield, extent of fragmentation, and ionization probability for this telechelic. Although a complete, quantitative analysis of this polymer (and unfunctionalized derivatives) was not carried out, it is clear that the species which were desorbed and detected were perfectly difunctional.

Conclusions

In conclusion, ROMP/CT systems employing well-defined metathesis catalysts based on molybdenum or tungsten are effective for the preparation of end-functionalized polybutadiene. Protected hydroxyl end groups were deprotected to give HTPBD. The isolated HTPBDs had one type of alcohol end group (allylic, **1**, or homoallylic, **2**) and one type of regiochemistry in the repeat unit (1,4). The HTPBDs produced by **W** were generally higher cis than the ones produced by **Mo**. The molecular weights of the HTPBDs produced were controlled by the $[\mathbf{COD}]_0/[\mathrm{CTA}]_0$ ratio. $\bar{F}_n$ values close to 2.0 were calculated for low-molecular-weight samples ($\bar{M}_n \leq 4.0 \times 10^3$). For early transition metal catalysts, **2** was a superior CTA compared to **1**. Separation of the oxygen from the metal center by at least two methylene units significantly enhances the longevity of the active species. Also, complex **Mo** outperformed complex **W** in terms of stability. This is in accord with the reported relative stabilities of tungsten- and molybdenum-based metathesis catalysts.[25,37,44,45]

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 ^{1}H, 100.40 MHz ^{13}C) or a GE QE-300 Plus spectrometer (300.10 MHz ^{1}H, 75.49 MHz ^{13}C). 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. Gas chromatographic analyses were performed on a HP-5890 Series II gas chromatograph with an SE-30 capillary column. GPC analyses in methylene chloride were obtained on a HPLC system utilizing an Altex Model 110A pump, a Rheodyne model 7125 injector with a 100 μL injection loop, through 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, 2760 g/mol, PDI = 1.08). GPC analyses in toluene were performed on a Waters Model 150C at 60 °C. The molecular weights and polydispersities are reported versus monodisperse polystyrene standards. Elemental analysis was performed at the California Institute of Technology Elemental Analysis Facility.

Materials. Toluene (Baker HPLC grade) was distilled from CaH_2 under argon and degasssed. Benzene (and C_6D_6) was distilled from Na/bezophenone ketyl prior to use. 3-Butyn-1-ol, butyllithium, and TBAF were purchased from Aldrich and used without further purification. *cis*-2-Butene-1,4-diol (Aldrich) was distilled from $CaSO_4$ under vacuum prior to use. Pivalaldehyde (Aldrich) was distilled from CaH_2 prior to use. **COD** (Aldrich) and filtered through neutral alumina before use. Ethylene oxide was purchased from Fluka, and TBSCl was purchased from Petrarch. All other solvents, salts, and other commodity chemicals were reagent grade and used without further purification. Complex **W** was graciously provided by Dr. Lynda K. Johnson. Initial quantities of complex **Mo** were graciously provided by Dr. Greg C. Fu. Complex **Mo** was also synthesized in large scale according to the procedure of Schrock.[37]

Preparation of $HCCCH_2CH_2OTBS$ (3). 3-Butyn-1-ol (25 g, 357 mmol) was added dropwise to a stirred DMF solution (250 mL) of *tert*-butyldimethylsilyl chloride (65 g, 431 mmol) and imidazole (61 g, 896 mmol) at 0 °C over 5 min. The solution was allowed to warm to room temperature over 15 min and heated to 40 °C for 45 min. The solution was removed from the heat, and water (200 mL) was added. The resulting solution was extracted with hexane. The extracts were combined, washed with saturated LiCl, dried over $MgSO_4$, and concentrated to give 64 g (97%) of a clear oil. IR (neat): 3314, 1257, 1109, 838, 777; ^{1}H NMR ($CDCl_3$): δ 3.71 (t, J = 7.2 Hz, 2H), 2.37 (m, 2H), 1.93 (t, J = 2.7 Hz, 1H), 0.87 (s, 9H), 0.04 (s, 6H); ^{13}C NMR ($CDCl_3$): δ 81.7, 69.3, 62.0, 26.0, 23.1, 18.4, −5.2.

Preparation of $HOCH_2CH_2CCCH_2CH_2OTBS$ (4). Anhydrous ammonia (500 mL) was condensed under argon at −40 °C into a 1 L 3-neck flask equipped with a dry ice/acetone condenser. Butyllithium (96 mL, 2.5 M in hexane, 240 mmol) was added via syringe to the reaction flask at −40 °C, and the solution was stirred for 30 min. To this solution was added **3** (44 g, 239 mmol) via syringe. Ethylene oxide (15 mL, 300 mmol), which was precondensed at −78 °C, was then added via cannula to the solution over 30 min. The reaction was stirred at −40 to −30 °C for 72 h with the dry ice/acetone condenser kept at −78 °C, after which time the ammonia was allowed to evaporate. Water (200 mL) was added to the residue and then extracted with ether. The ether was concentrated and the yellow oil was distilled under reduced pressure (97−99 °C, 0.01 mmHg) to yield 21.2 g (39%) of a clear oil. IR (neat): 3354, 1256, 1105, 1050, 837; ^{1}H NMR ($CDCl_3$): δ 3.68 (m, 4H), 2.38 (m, 4H), 1.74 (bs, 1H), 0.88 (s, 9H), 0.05 (s, 6H); ^{13}C NMR ($CDCl_3$): δ 79.5, 77.7, 62.1, 61.2, 26.8, 23.1, 18.3, −5.3. Only eight peaks were observed in the ^{13}C NMR spectrum. The two propargyllic carbons are presumably overlapped. In **5** the two allylic carbons are only separated by 0.1 ppm.

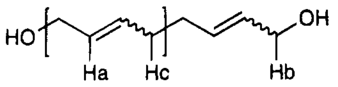
Preparation of $HOCH_2CH_2CHCHCH_2CH_2OTBS$ (5). Following the procedure desribed by Brown,[31] **4** (10 g, 44 mmol, in 100 mL of EtOH) was added to a solution of $Ni(OAc)_2{\cdot}4H_2O$ (11.5 g, 46 mmol), $NaBH_4$ (1.75 g, 46 mmol), and ethylenediamine (3.3 mL, 50 mmol) in EtOH (200 mL). H_2 was slowly bubbled through the solution until the reaction was complete by ^{1}H NMR spectroscopy (1−2 h). EtOAc:hexane (200 mL, 1:1 v/v) was added to the solution, which was subsequently filtered through silica gel and concentrated. The resulting light green jelly was dissolved in EtOAc:hexane (200 mL, 1:1) and filtered through silica gel again to yield 8.7 g (86%) of a clear oil. IR (neat): 3333, 3011, 1256, 1097, 836; ^{1}H NMR ($CDCl_3$): δ 5.51 (m, 2H), 3.62 (m, 4H), 2.56 (m, 4H), 1.80 (bs, 1H), 0.87 (s, 9H), 0.03 (s, 6H); ^{13}C NMR ($CDCl_3$): δ 129.4, 127.3, 62.8, 62.0, 30.9, 30.8, 25.9, 18.4, −5.4.

Preparation of $TBSOCH_2CH_2CHCHCH_2CH_2OTBS$ (2). **5** (2.25 g, 9.8 mmol) was protected with TBSCl by the procedure described above for **3** to yield 3.37 g (84%) of a clear oil. The oil was further purified by distillation from CaH_2 under reduced pressure (90−92 °C, 0.005 mmHg). GC 99.4% pure, >95% cis; IR (neat): 3013, 2955, 2929, 2895, 1472, 1463, 1382, 1099, 937, 834, 737; ^{1}H NMR ($CDCl_3$): δ 5.44 (m, 2H), 3.58 (t, J = 7 Hz, 4H), 2.25 (m, 4H), 0.87 (s, 9H), 0.03 (s, 6H); ^{13}C NMR ($CDCl_3$): δ 127.6, 62.9, 31.3, 26.0, 18.4, −5.4. Anal. Calcd for $C_{18}H_{40}O_2Si_2$: C, 62.72; H, 11.70. Found: C, 62.83; H, 11.32.

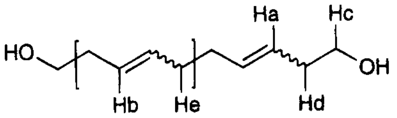
General Polymerization Procedure Employing COD, 1 or 2, and W or Mo. In a nitrogen-filled glovebox, **COD** and the CTA (**1** or **2**) were mixed in a glass vial at room temperature. The monomer/CTA mixture can also be diluted with either toluene or benzene. This dilution facilitates mixing in the case of high-molecular-weight samples. In a separate vial, the catalyst (**W** or **Mo**) was dissolved in a small volume of dry, degassed benzene. The typical scale of these reactions was 1−5 g. See Tables 1 and 2 for typical molar ratios. The contents of the two vials were combined and the reaction mixture was stirred in the glovebox for 2 h. After 2 h the polymerization mixture was terminated with pivalaldehyde, benzaldehyde, or methanol. The polymerization mixture was allowed to stir overnight in the glovebox. The mixture was precipitated into 35 mL of methanol, and the polymer was isolated. The resultant polymer was dried under vacuum overnight.

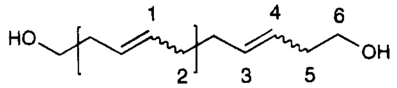
General Deprotection of TBS-End-Capped HTPBD. Deprotections were generally carried out in THF using a 5-fold excess of TBAF relative to TBS (as calculated from the intial amount of CTA added to the polymerization solution) at room temperature under argon. The polymer was precipitated in at least a 5-fold volume excess of methanol. Isolation of HTPBD was generally accomplished by centrifugation or decanting. Further purification of the light yellow oils can be accomplished by filtration of a benzene solution of the HTPBD through neutral alumina.

NMR Characterization. The ^{1}H NMR spectrum of HTPBDs synthesized using CTA **1** was assigned as follows:



^{1}H NMR (400 MHz, CD_2Cl_2): δ 5.38 (bs, Ha cis), 5.43 (bs, Ha trans), 4.14 (m, Hb cis), 4.04 (m, Hb trans), 2.09 (bs, Hc cis), 2.02 (bs, Hc trans). Olefinic protons adjacent to the end group were not observed in the polymers isolated using this procedure and were presumably buried under the backbone olefinic protons. The ^{1}H NMR and ^{13}C NMR spectra of HTPBDs synthesized using CTA **2** were assigned as follows:





^{1}H NMR (500 MHz, $CDCl_3$): δ 5.5 (m, Ha cis and trans), 5.40 (m, Hb trans), 5.35 (m, Hb cis), 3.58 (m, Hc cis and trans), 2.25 (m, Hd cis and trans), 2.08 (m, He cis), 2.03; ^{13}C NMR (75 MHz, $CDCl_3$): δ 134.10 (C4, tc), 134.01 (C4, tt), 133.14 (C4, cc), 133.11 (C4, ct), 130.50 (C1, tc), 130.37 (C1, tt), 129.98 (C1, cc), 129.81 (C1, ct), 126.64 (C3, tc), 126.52 (C3, tt), 125.92 (C3, cc), 125.71 (C3, ct), 62.65 (C6, t), 62.28 (C6, c), 36.35 (C5, t), 33.09 (C2, t), 31.25 (C5, c), 27.79 (C2, c).

Acknowledgment. Funding for this research was provided by the National Science Foundation, Thiokol Corp., and Miles Inc. M.A.H. is the recipient of a graduate fellowship from IBM, for which he is grateful. We would like to thank Professor J. M. DeSimone, Professor R. W. Linton, and Anna Belu at the University of North Carolina for performing the TOF-SIMS analysis. Neftali Morales, a participant in the Minority Undergraduate Research Fellowship (MURF) program at Caltech, provided technical assistance in the preparation of the chain transfer agents described within.

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(34) The molecular weight of the chain transfer agent was subtracted from the VPO molecular weight of the polymer (assuming a perfectly difunctional chain) and the X_n was calculated based on the eight-carbon **COD** repeat unit.

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MA950701U