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Highly efficient syntheses of acetoxy- and hydroxy-terminated telechelic poly(butadiene)s using ruthenium catalysts containing *N*-heterocyclic ligands

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Abstract

Bis(acetoxy)-terminated telechelic poly(butadiene) (PBD) with molecular weights controllable up to 3.0×10^4 have been prepared via the ring-opening metathesis polymerization (ROMP) of cyclooctadiene when 1,4-bis(acetoxy)-2-butene was included as a chain transfer agent (CTA). The polymerizations were catalyzed by a highly active ruthenium catalyst 1,3-bis(2,4,6-trimethylphenyl)imidazol-2-ylidene) $(PCp_3)(Cl_2Ru = CHCHC(CH_3)_2$ (Cp = cyclopentyl) (**6**) with monomer/catalyst ratios as high as 9.8×10^4. Removal of the acetoxy groups with sodium hydroxide afforded hydroxy end-terminated telechelic PBD (HTPBD). Examination of the telechelic PBDs revealed an exclusive 1,4-PBD microstructure with a predominately *trans* geometry (up to 90%). The high activity and stability of **6** permitted a one-step synthesis of HTPBD using the unprotected free alcohol, 2-butene-1,4-diol, as the CTA.

Keywords: Hydroxy end-terminated telechelic poly(butadiene) (HTPBD); Ring-opening metathesis polymerization (ROMP); Ruthenium

1. Introduction

Telechelic polymers, which contain two reactive functional groups situated at both termini of the polymeric chains, have been employed as key components in the synthesis of block copolymers and polymeric networks, in reaction injection molding applications, and as cross-linking agents to enhance thermal and mechanical properties of other materials [1–3]. Hydroxy-terminated telechelic poly(butadiene) (HTPBD) is a particularly useful telechelic polymer and is of great importance in the polyurethane industry [4]. We previously reported the synthesis of HTPBD via the ring-opening metathesis polymerization (ROMP) of cyclooctadiene (COD) in the presence of *cis*-1,4-bis(acetoxy)-2-butene (**1**), catalyzed by ruthenium catalyst **2** (Scheme 1) [5,6]. The acyclic olefin acts as a chain transfer agent (CTA) that not only aids in regulating molecular weight but also effectively transfers functionality (in this case the acetoxy groups) to the ends of the polymer chains [7]. Using this method, the average number of functional groups per polymer chain (F_n) is close to 2, the molecular weights are controllable up to 10 kDa, and *only* 1,4-linkages are observed in the PBD backbone. In addition, this approach has been recently extended to the synthesis of amino- and carboxyl-terminated PBDs [8]. Other metathetical routes to HTPBDs have also been reported [7–14]. While radical or anionic polymerization methods are often employed, demanding conditions are usually necessary and varying amounts of 1,2-linkages are introduced into the polymer backbone [3,4,15–17]. This not only leads to F_n values that deviate greatly from 2, but also limits the material's elastomeric potential [3].

One drawback of our previously reported route to HTPBD is that it necessitates a post-polymerization deprotection step [5]. When the free alcohol, *cis*-2-butene-1,4-diol (**3**), was used directly, it was found that telechelic PBD obtained contained significant amounts of aldehyde end-groups [5,18,19]. We believe that either ruthenium species **4**, which forms from the cross metathesis of catalyst **2** with **3**, decomposes over the timescale of the polymerization (Eq. (1)), or **2** simply decomposes in the presence of **3**. In either case, the decomposition product, which has been previously suggested to be a ruthenium hydride species,

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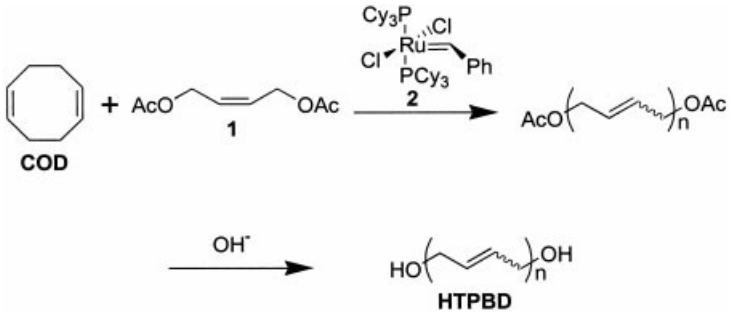
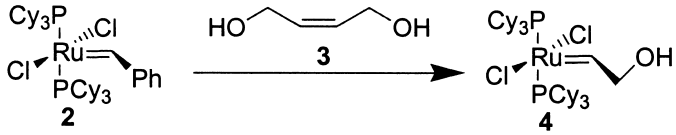


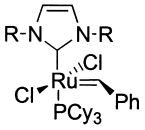
Scheme 1.

then catalyzes the isomerization of the allyl alcohol end-group to an aldehyde [5,19,20].

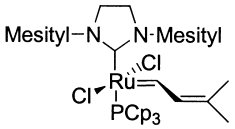


Decomposition (1)

Recently, several new highly active ruthenium catalysts (**5** and **6**), which utilize *N*-heterocyclic carbene ligands, have been reported [21–26]. In particular, catalyst **6**, displays an unsurpassed level of activity and functional group tolerance in ring-closing metathesis (RCM), cross-metathesis (CM) and ROMP when compared to other ruthenium catalysts [21–31]. Herein, we report that the high activities of catalyst **6** have allowed for the preparation of acetoxy-terminated PBDs, using **1** as the CTA, with extremely low catalyst loadings (up to monomer/catalyst = 9.8×10^4). In addition, as described below, these catalysts are stable in the presence of the free alcohol **3**. Thus, we report a *one-step* synthesis of HTPBD via the ROMP of COD using catalyst **6**, *in the presence of the free alcohol* **3**.



5: R=iPr, cyclohexyl (Cy), or mesityl (2,4,6-trimethylphenyl)



6: Mesityl=2,4,6-trimethylphenyl, Cp=cyclopentyl

2. Experimental

2.1. Materials and characterization methods

COD (redistilled, 99 + %) and *cis*-2-butene-1,4-diol were purchased from Aldrich. *cis*-1,4-Bis(acetoxy)-2-butene was purchased from TCI America and distilled from CaH_2 prior to use. The *cis*-2-butene-1,4-diol was distilled prior to use. All monomers, chain transfer agents and solvents were purged with argon prior to use. Catalysts **2** and **6** were prepared as previously reported [6,25,26].

Gel permeation chromatography (GPC) measurements were carried out using an Alltech 510 liquid chromatography pump equipped with a Viscotek refractometer using HPLC grade THF as the eluent. The GPC columns (10 μm linear mixed bed, American Polymer Standards Corp.) were calibrated against monodispersed polystyrene standards (Shodex). All ^1H and ^{13}C NMR spectra were recorded on a GE NMR spectrometer (300 MHz, ^1H; 75 MHz, ^{13}C), and all chemical shifts are given in ppm and were referenced to residual protio solvent. All spectra were obtained in the solvent indicated at 25°C unless otherwise noted.

*2.2. Polymerization of COD using catalyst **6** with **3** as the CTA*

All polymerizations were set-up using standard Schlenk techniques. A small flask equipped with a magnetic stirring bar was de-gassed, backfilled with argon, and then sealed with a rubber septum. A typical example is given as follows. COD (4.7 g, 44 mmol), CTA **3** (190 mg, 2.2 mmol), THF (0.3 ml) and benzene (2.8 ml) were transferred into the flask via syringe. Inside a dry box under nitrogen atmosphere, a small vial was charged ruthenium catalyst **6** (6.9 mg, 8.8 μmol) and dissolved in a minimal amount of benzene. The catalyst solution was removed from the dry box, transferred into a syringe, and injected into the above reaction mixture, which was preheated to 55°C in an oil bath. After 24 h, the reaction mixture was opened to air and poured into rapidly stirring acidic methanol (~0.1 M HCl). Non-solvent was decanted away from the precipitated polymer and the polymer was washed with fresh methanol several times. The

Table 1
Synthesis of bis(acetoxy) telechelic PBD under a variety of conditions (bulk polymerization of COD using catalyst **6**. 1,4-bis(acetoxy)-2-butene was included as a CTA. COD/CTA = 5 in all cases. Theoretical $M_w = 700$, at 100% conversion)

Entry	M/C[a]	Temp. (°C)	Time (h)	Yield (%)[b]	M_w, NMR[c]	M_n, GPC[d]	PDI[d]	*trans* (%)[e]
1	10 300	25	12	75	1300	2100	1.6	65
2	10 300	25	24	72	1200	2000	1.5	70
3	10 300	25	12	72	1300	1900	1.5	75
4	10 300	25	24	72	1250	1600	1.5	85
5	10 300	55	12	70	950	1500	1.4	90
6	10 300	55	24	69	1050	1700	1.4	90
7	10 300	55	12	71	950	1500	1.4	90
8	10 300	55	24	68	1100	1700	1.4	90
9	26 100	25	12	62	1650	2600	1.6	80
10	26 100	25	24	69	1550	2400	1.6	75
11	26 100	25	12	69	1600	2400	1.7	80
12	26 100	25	24	69	1450	2100	1.6	60
13	26 100	55	12	73	1050	1600	1.5	70
14	26 100	55	24	68	1150	1800	1.4	70
15	26 100	55	12	74	1150	1700	1.5	50
16	26 100	55	24	68	1250	1900	1.4	50
17	49 200	55	24	66	1100	1900	1.4	90
18	98 300	55	24	74	1250	2000	1.4	70

[a] Monomer (COD) to catalyst **6** ratio.
[b] Isolated yield of polymer.
[c] Molecular weight determined using end-group analysis (^{1}H NMR), assuming $F_n = 2.0$.
[d] Determined using GPC with THF as the eluent. Values reported relative to polystyrene standards.
[e] Percent *trans* olefin in polymer backbone determined using ^{1}H NMR spectroscopy.

polymer was then dried under dynamic high vacuum and characterized by ^{1}H NMR, ^{13}C NMR and GPC. ^{1}H NMR (300 MHz, $CDCl_3$): δ 5.6–5.7 (m, H_a, H_b, *cis* and *trans*), 5.42 (bs, H_c, *trans*), 5.38 (bs, H_c, *cis*), 4.18 (d, H_d, *cis*), 4.09 (d, H_d, *trans*), 2.09 (bs, H_c, *cis*), 2.04 (bs, H_c, *trans*). ^{13}C NMR (75 MHz, $CDCl_3$): 132.70 (C_3, tc), 130.30 (C_3, tt), 130.09 (C1, tc), 129.99 (C1, tt), 129.60 (C_1, cc), 129.42 (C_1, ct), 63.77 (C_4, t), 58.60 (C_4, c), 32.68 (C_2, t), 27.39 (C_2, c). GPC (THF, relative to polystyrene standards): M_n = 3600, PDI = 1.5.

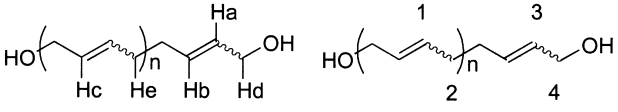


Table 2
Synthesis of telechelic PBDs with a variety of molecular weights (bulk polymerization of COD using catalyst **6**. 1,4-bis(acetoxy)-2-butene was included as a CTA. Reaction time(24 h. Reaction temperature(55°C)

Entry	M/C[a]	COD/CTA	M_w		M_n, GPC[b]	PDI[b]	Yield (%)[c]	*trans* (%)[d]
			Theor[e]	NMR[f]				
1	26 100	5	500	1150	1800	1.4	68	70
2	19 800	10	1200	2150	2600	1.7	88	90
3	23 000	15	1750	2650	3100	1.8	89	90
4	19 600	20	2300	3250	3800	2.0	92	90
5	24 500	60	6600	7900	7200	2,5	91	90
6	24 500	80	8800	9300	107 00	2.1	95	90
7	24 500	100	10 900	10 200	15 200	2.2	89	90
8	49 000	200	21 750	24 500	30 000	2.0	98	90

[a] Monomer (COD) to catalyst **6** ratio.
[b] Determined using GPC with THF as the eluent. Values reported relative to polystyrene standards.
[c] Isolated yield of polymer.
[d] Percent *trans* olefin in polymer backbone determined using ^{1}H NMR spectroscopy.
[e] Theoretical molecular weight((%Yield) × (COD/CTA) × (M_w of COD)((M_w of CTA).
[f] Molecular weight determined using end-group analysis (^{1}H NMR), assuming $F_n = 2.0$.

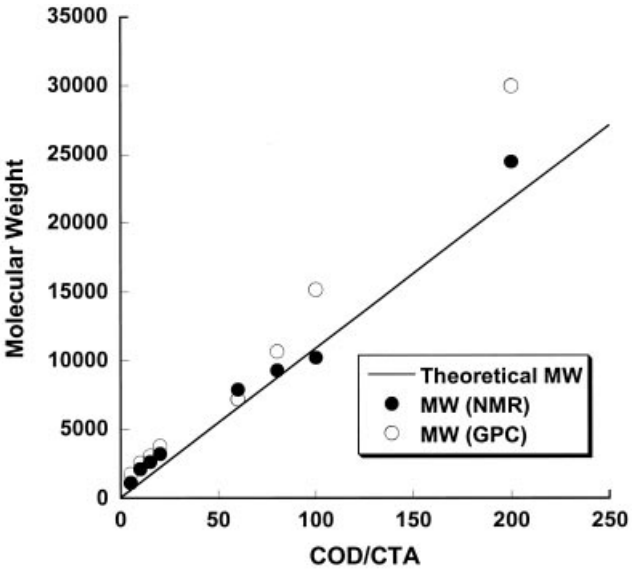


Fig. 1. Dependence of PBD molecular weight on COD/CTA.

3. Results and discussion

3.1. Preparation of bis(acetoxy)-terminated telechelic poly(butadiene)s

Previously, while exploring the preparation of telechelic PBDs via the ROMP of COD in the presence of CTA **1** and catalyst **2**, we reported the maximum monomer/catalyst ratio that could be employed was 1.0×10^4 [5,19]. At lower catalyst loadings, **2** began to lose activity over the timescale of the polymerization and led to reduced yields of polymer and CTA incorporation. However, as shown in Table 1, when catalyst **6** was employed bis(acetoxy)-terminated telechelic PBDs were prepared with monomer/catalyst ratios up to 9.8×10^4. We attribute the ability to use lower catalyst loadings to the increased stability and higher activity of catalyst **6** over **2**. Isolated yields of telechelic polymer ranged between 62 and 75%, and the microstructure of the PBD backbone was found to contain predominately *trans* geometry. In all cases, ^{1}H NMR and ^{13}C NMR analysis supported an F_n near 2. Molecular weights obtained by ^{1}H NMR analysis were in excellent agreement with their theoretical values (based on yield). Molecular weights obtained by GPC were higher than predicted and may be explained by the differences in hydrodynamic volume of PBD and the polystyrene standards used for calibration. In all cases the acetoxy groups were easily cleaved using a methanolic solution of sodium hydroxide to afford the corresponding HTPBDs [5].

Such low monomer/catalyst loadings permitted the synthesis of much higher molecular weight telechelic PBDs. It is important to remember that non-functional end-groups (which cause deviations in F_n from 2) come predominately from the catalyst (e.g. the dimethylvinyl carbene group on **6**

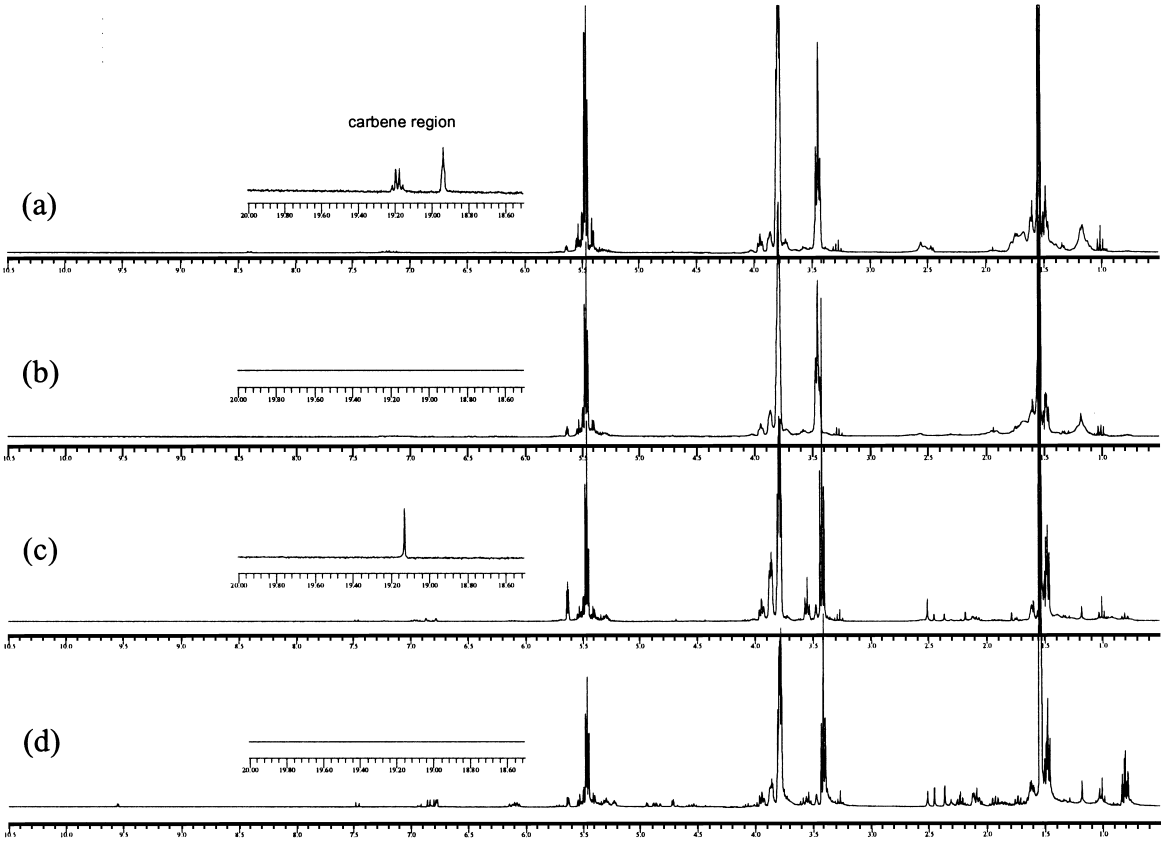


Fig. 2. ^{1}H NMR spectra of crotyl alcohol in the presence of ruthenium catalysts **2** and **6**, solvent = THF-d_8: (a) catalyst **2**, 20 min; (b) catalyst **2**, 7 h; (c) catalyst **6**, 20 min; and (d) catalyst **6**, 21 h.

Table 3
One-step synthesis of HTPBD (ROMP of COD using catalyst **6**. Monomer/catalyst(5000 in all entries. *cis*-2-Butene-1,4-diol (**3**) was included as a CTA)

Entry	Solvent system[a]	COD/CTA[b]	Yield (%)[c]	M_w, NMR[d]	M_n, GPC[e]	PDI[e]	*trans* (%)[f]
1	A	15	29	2250	3900	1.7	40
2	B	10	36	1280[g]	2380	2.8	25
3	C	5	26	390[g]	1340	1.7	25
4	D	20	45	2400	3600	1.5	45

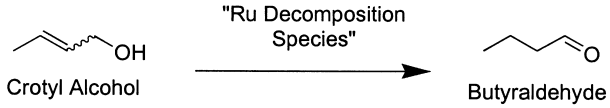
[a] A: THF. B: benzene. C: CH_2Cl_2. D: benzene/THF (9/1 v/v).
[b] Monomer (COD) to CTA **3** ratio.
[c] Isolated yield of polymer.
[d] Molecular weight determined using end-group analysis (^{1}H NMR), assuming $F_n = 2.0$.
[e] Determined using GPC with THF as the eluent. Values reported relative to polystyrene standards.
[f] Percent *trans* olefin in polymer backbone determined using ^{1}H NMR spectroscopy.
[g] Aldehyde resonances were observed in the ^{1}H and ^{13}C NMR spectra.

or the benzylidene group on **2**) [7,19]. Thus, to prepare a telechelic PBD with an $F_n > 1.99$, a CTA/catalyst ratio of >200 must be employed [19]. Since $M_w \sim$ COD/CTA, the maximum M_w is ~5500 for a catalyst with maximum COD/catalyst $= 1.0 \times 10^4$. As shown in Table 2, by varying the COD/CTA ratio and adjusting the COD/catalyst ratio, telechelic PBD with M_ws controllable up to 3.0×10^4 have been prepared when using **6**. A linear relationship between the COD/CTA and the M_w of the isolated telechelic polymer was observed (Fig. 1). Molecular weights determined by end-group analysis using ^{1}H NMR spectroscopy and GPC were in good agreement with their theoretical values.

3.2. ^{1}H NMR analysis of **2** and **6** in the presence of allylic alcohols

As previously mentioned, when HTPBD was prepared from the ROMP of COD in the presence of CTA **3**, aldehyde end-groups were observed indicating that the allylic functionality isomerized over the timescale of the polymerization. To help gain a better understanding of this drawback, the stability and metathetical activity of catalysts **2** and **6** in the presence of the free diol **3** (~500 equivalents, 95 + % *cis*) were examined by ^{1}H NMR spectroscopy in CD_2Cl_2 (25°C). Over 15 min, catalyst **2** isomerized the predominately *cis* olefin (95 + %) to its *trans* isomer (70%), while **6** afforded 95% *trans* olefin over the same timescale. In addition, formation of [Ru] = $CHCH_2OH$ from cross metathesis of the starting catalyst ([Ru] = CHPh **2** or [Ru] = $CHCHC(CH_3)_2$ **6**) with **3** was observed. No catalyst decomposition or aldehyde formation was observed in either case (**2** or **6**).

The lack of ruthenium hydride species or aldehyde substrates does not rule out the possibility that olefin migration (followed by tautomerization) occurs *after* the CTA has been incorporated into the polymer chains. Using crotyl alcohol as a model compound for the termini of the HTPBD, the isomerization of crotyl alcohol to butyraldehyde (Eq. (2)) in the presence of **2** and **6** was examined in a variety of solvents. In benzene-d_6 or CD_2Cl_2, alcohol isomerization was observed within minutes, regardless of which catalyst (**2** or **6**) was used (Eq. (2)). It has been previously proposed that the decomposition products contain ruthenium hydride species that can isomerize allylic alcohols to aldehydes [5,20]. While complete decomposition was observed for both catalysts (complete loss of carbene proton signals) within a few hours, no ruthenium hydride species were observed.



(2)

Surprisingly different results were obtained in THF-d_8. In the presence of ~250 equivalents of crotyl alcohol, extremely small amounts ($\ll$ 1%) of butyraldehyde were observed after 24 h, when either catalyst was employed. However, decomposition of **2** occurred rapidly (<2 h) while **6** was more robust and appeared active for over 6 h. Complete decomposition of **6** was observed after 21 h. Representative ^{1}H NMR spectra summarizing these results are shown in Fig. 2. In addition, no ruthenium hydride species (for either catalyst) were observed.

It has been previously observed that well-defined ruthenium catalysts exhibit lower metathesis activity in THF relative to solvents such as benzene or CH_2Cl_2 [32,33]. While THF may reduce activity, catalyst lifetimes seem to be extended. The mechanism of olefin metathesis using well-defined ruthenium catalysts appears to be predominately dissociative in nature [34]. In addition, catalyst decomposition also appears to be bimolecular and dependent on phosphine concentration (higher phosphine concentrations give longer catalyst lifetimes) [35]. As shown in Eq. (3), THF may coordinate to the ruthenium center after

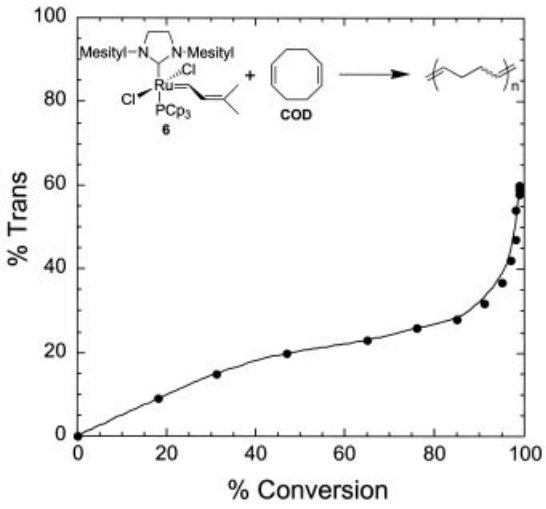
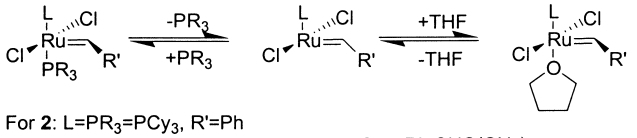


Fig. 3. %*trans* olefin in PBD backbone vs. %conversion of COD to polymer using catalyst **6**. Polymerization monitored using ^{1}H NMR spectroscopy. Solvent = CD_2Cl_2.Temp = 25°C. $[\mathbf{6}]_0$ = 0.5 mM. COD/**6** = 300.

phosphine dissociation suppressing metathetical activity and attenuating bimolecular decomposition pathways.



(3)

3.3. Synthesis of HTPBD

In order to prepare HTPBD with F_n values that approach 2 using the free diol **3**, any alcohol isomerization to aldehyde functionality must be minimized. The stability of **6** in the presence of the free diol **3** and crotyl alcohol poised us to prepare HTPBD via the ROMP of COD using the unprotected diol **3** as the CTA. As shown in Table 3, when THF was used as solvent, HTPBD was obtained in a modest yield of 29%. THF solutions of low molecular weight PBD are difficult to precipitate in methanol, which may account for the low yield. However, ^{1}H and ^{13}C NMR supported an F_n near 2 and no aldehyde resonances were observed. In accordance with the model study of crotyl alcohol, when non-coordinating solvents such as 1,2-dichloroethane or benzene were employed, isomerization of the allylic alcohol end-groups occurred as aldehyde end-groups were observed in the isolated polymer. Interestingly, when a mixture of benzene/THF (9/1 v/v) was employed, an increased yield (45%) of telechelic polymer was obtained without compromising any structural integrity of the allyl alcohol end-group. Attempts at preparing HTPBD under similar conditions using catalyst **2** afforded no polymer, which was in accord with the results obtained above that indicate **2** decomposes rapidly in the presence of the free diol **3**.

Close examination of the HTPBD prepared via this one-step method revealed that relatively high amounts (~60%) of *cis* olefin were present in the PBD backbone. This was an unexpected result as generally high *trans* PBD is observed in the ROMP of COD with **1** and **6** (Tables 1 and 2) and stems from secondary metathesis reactions that form the more thermally stable olefin isomer [7]. In the absence of secondary metathesis reactions, the ROMP of COD should yield at least 50% *cis* olefin in the resulting PBD backbone. Fig. 3 suggests that **6** may kinetically favor the formation of the *cis* isomer as at up to an 80% conversion of COD to PBD, a very high *cis* content (>75%) is observed in the polymer. Thus, our results (high amounts of *cis* olefin, low yields and F_n values near 2) may be explained by a relatively high rate of CTA incorporation countered with catalyst decomposition occurring over the timescale of the polymerization, limiting secondary metathesis reactions.

4. Conclusions

Highly active ruthenium catalyst **6** has allowed the preparation of bis(acetoxy)-terminated telechelic PBDs with molecular weights controllable up to 3.0×10^4. The polymers were obtained via the ROMP of COD in the presence of an acetoxy functionalized CTA using monomer/catalyst ratios as high as 9.8×10^4. The acetoxy groups were easily cleaved with methanolic solutions of sodium hydroxide to afford high yields of HTPBD. ^{1}H NMR spectroscopy studies in CD_2Cl_2 or benzene-d_6 using crotyl alcohol as a model for the HTPBD termini suggest that 1,3-bis(2,4,6-trimethylphenyl)imidazol-2-ylidene) $(PCp_3)(Cl_2Ru=CHCHC(CH_3)_2$ (Cp = cyclopentyl) (**6**) and $(PCy_3)_2RuCl_2(CHPh)$ (**2**) decompose in the presence of allylic alcohols and their decomposition products isomerize allylic alcohols to aldehydes. While no isomerization was observed in THF-d_8, the stability of **2** still appeared limited. In contrast, the stability and activity of **6** did not diminish and led to the successful one-step preparation of HTPBD using the unprotected 2-butene-1,4-diol (**3**) as the CTA.

Acknowledgements

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References

[1] Goethals EJ. Telechelic polymers: synthesis and applications. Boca Raton, FL: CRC Press, 1989.
[2] Van Caeter P, Goethals EJ. TRIP 1995;3:227.
[3] Odian G. Principles of polymerizations. 3rd ed. New York: Wiley, 1991.
[4] Brosse JC, Derouet D, Epaillard F, Soutif JC, Legeay G, Dusek K. Adv Polym Sci 1987;81:167.

[5] Hillmyer MA, Nguyen ST, Grubbs RH. Macromolecules 1997;30:718.
[6] Schwab P, Grubbs RH, Ziller JW. J Am Chem Soc 1996;118:100.
[7] Ivin KJ, Mol JC. Olefin metathesis. London: Academic Press, 1997.
[8] Morita T, Maughon BR, Bielawski CW, Grubbs RH. Macromolecules 2000;33:6621.
[9] Hummel K. Pure Appl Chem 1982;54:351.
[10] Chung TC, Chasmawala M. Macromolecules 1992;25:5137.
[11] Wagener KB, Marmo JC. Macromol Rapid Commun 1995;16:557.
[12] Tamura H, Maeda N, Matsumoto R, Nakayama A, Hayashi H, Ikushima K, Kuraya M. J. Macromol Sci, Pure Appl Chem A 1999;361:1153.
[13] Cramail H, Fontanille M, Soum A. J Mol Catal 1991;65:193.
[14] Hillmyer MA, Grubbs RH. Macromolecules 1993;26:872.
[15] Schnecko G, Degler H, Dongowski R, Caspary G, Angerer S, Ng T. Angew Makromol Chem 1978;70:9.
[16] Kanakavel M. Makromol Chem 1987;188:845.
[17] Xu J, Dimonie VL, Sudol ED, El-Aasser MS. J Polym Sci A-1 1995;33:1353.
[18] Hillmyer MA, Grubbs RH. Polym Prepr (Am Chem Soc Div Poly Chem) 1994;34:388.
[19] Hillmyer MA. PhD thesis, California Institute of Technology, 1995.
[20] McGrath DV, Grubbs RH. Organometallics 1994;13:224.
[21] Weskamp T, Shattenmann WC, Spiegler M, Hermann WA. Angew Chem Int Ed 1998;37:2490.
[22] Huang J, Stevens ED, Nolan SP, Peterson JL. J Am Chem Soc 1999;121:2674.
[23] Scholl M, Trnka TM, Morgan JP, Grubbs RH. Tetrahedron Lett 1999;40:2247.
[24] Weskamp T, Kohl FJ, Hieringer W, Gleich D, Herrmann WA. Angew Chem Int Ed 1999;38:2416.
[25] Scholl M, Ding S, Lee CW, Grubbs RH. Org Lett 1999;1:953.
[26] Chatterjee AK, Morgan JP, Scholl M, Grubbs RH. J Am Chem Soc 2000;122:3783.
[27] Chatterjee AK, Grubbs RH. Org Lett 1999;1:1751.
[28] Ackermann L, Fustner A, Weskamp T, Kohl FJ, Herrmann WA. Tetrahedron Lett 1999;40:4787.
[29] Herrmann WA. Angew Chem Int Ed 1999;38:262.
[30] Frenzel U, Weskamp T, Kohl FJ, Schattenmann WC, Nuyken O, Herrmann WA. J Organomet Chem 1999;586:263.
[31] Bielawski CB, Grubbs RH. Angew Chem Int Ed 2000;39:2903.
[32] Nguyen ST, Johnson LK, Grubbs RH. J Am Chem Soc 1992;114:3974.
[33] Nguyen ST. PhD thesis, California Institute of Technology, 1995.
[34] Dias EL, Nguyen ST, Grubbs RH. J Am Chem Soc 1997;119:3887.
[35] Ulman M, Grubbs RH. J Org Chem 1999;64:7202.