

Degradable Cyclooctadiene/Acetal Copolymers: Versatile Precursors to 1,4-Hydroxytelechelic Polybutadiene and Hydroxytelechelic Polyethylene[†]

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ABSTRACT: In addition to environmental issues associated with polymers possessing easily cleavable links, the selective degradation of copolymers at one of the monomer units is a convenient route to telechelic polymers. Ring-opening metathesis polymerization (ROMP) initiated by $(\text{Cy}_3\text{P})_2\text{Cl}_2\text{Ru}=\text{CHR}$ (Cy = cyclohexyl; Ph = phenyl; R = CHCPh_2 or Ph) was used for the synthesis of cyclooctadiene (COD)/4,7-dihydro-1,3-dioxepin copolymers. 1,4-Hydroxytelechelic polybutadiene (HTPBD) is obtained upon fragmentation of a copolymer of COD and 4,7-dihydro-2-phenyl-1,3-dioxepin at the benzylidene acetal functionalities by stirring with acids (aqueous HCl/MeOH , aqueous H_2SO_4 , or trifluoroacetic acid (TFAA)/ MeOH in CH_2Cl_2). For the benzylidene acetal the copolymerization reaction may be run in neat monomer with no additional solvent. Reaction quenching, and polymer cleavage, precipitation, and purification may be effected in one step by stirring the viscous reaction product in MeOH containing 10% HCl . A two-step procedure using trifluoroacetic anhydride (TFAA)/acetic acid (AcOH) in CH_2Cl_2 followed by NaOMe/MeOH in THF was employed for the degradation of a COD/4,7-dihydro-1,3-dioxepin copolymer. Acetal incorporation and thus the molecular weights of the resulting telechelics are dependent upon the feed ratios. The percent methylene acetal incorporated into the COD/acetal copolymer is ~60% of the amount of acetal in the feed (e.g., for COD/acetal feed = 2:1, COD/acetal incorporation = ~4:1). For the less reactive benzylidene acetal, incorporation is ~40% of the amount of acetal in the feed. Polydispersities for 1,4-HTPBD prepared from the COD/benzylidene acetal copolymer are typically narrow (~1.1–1.3). It was also demonstrated that the COD/benzylidene acetal copolymer may be simultaneously hydrogenated and degraded in one step using *p*-toluenesulfonohydrazide to produce hydroxytelechelic polyethylene (HTPE).

Introduction

Degradable materials, those which may be fragmented into lower molecular weight segments or component parts, have received increased attention of late both for environmental reasons and for applications in medicine and biotechnology.¹ Polymers which may be cleaved at specific sites along the chains are also of interest, however, as precursors to telechelic polymers.² These polymers bearing functionalities at both termini are useful as macromonomers in condensation polymerizations and as precursors for the preparation of block copolymers, and they have been exploited in network formation, among other applications.³ Hydroxytelechelic polybutadiene (HTPBD), for example, has been used in polyurethane synthesis to impart elastomeric and other desirable properties.⁴ In addition to the chain scission approach,² HTPBD has been prepared by a number of different routes. These include the radical polymerization of butadiene in the presence of H_2O_2 ,⁵ anionic routes,⁶ the use of difunctional nickel allyl initiators for butadiene polymerization with selective end-capping reactions,⁷ metathesis degradation,⁸ and ring-opening metathesis polymerization (ROMP) of cyclooctadiene in the presence of chain-transfer reagents.⁹ Commercial HTPBD, prepared via the radical method, results in mixtures of 1,2 and 1,4 repeat units and at least three different types of hydroxy end groups; some of the latter methods give only 1,4-HTPBD. In this paper we describe a different route to 1,4-hydroxytelechelic polybutadiene which involves the selective

decomposition of degradable copolymers prepared by ROMP.

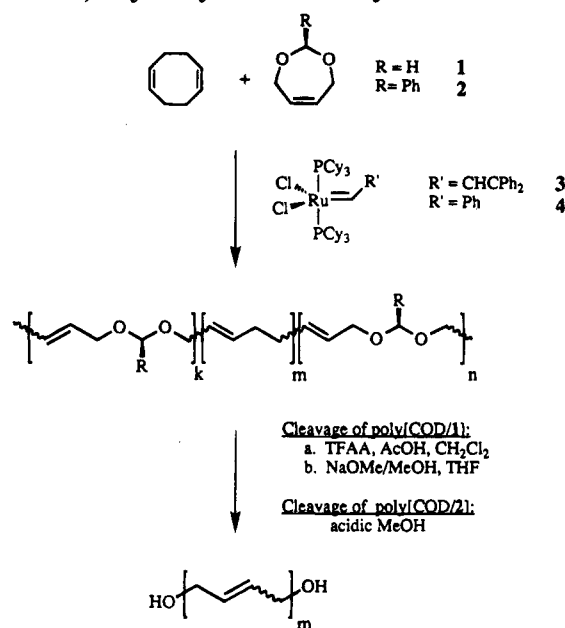
Copolymers of Cyclooctadiene (COD) and 4,7-Dihydro-1,3-dioxepins

To demonstrate this degradative method, we targeted the copolymers of COD and commercially available *cis*-4,7-dihydro-1,3-dioxepins, **1** and **2**, which may be subsequently cleaved at the acetal moieties (Scheme 1). Initially, **1** and **2** were probed for their ability to undergo homopolymerization using $(\text{Cy}_3\text{P})_2\text{Cl}_2\text{Ru}=\text{CHR}$ (Cy = cyclohexyl, Ph = phenyl, R = $\text{CH}=\text{CPh}_2$ (**3**), R = Ph (**4**)) as initiators.¹⁰ Poly[**1**] was readily obtained as an opaque white waxy material, but it was not possible to prepare a homopolymer of the benzylidene acetal monomer, **2**, using ruthenium initiators, **3** and **4**. In the presence of COD, however, both monomers ring open to give COD/acetal copolymers (Table 1). Concentrated solutions of the Ru catalyst, **3** or **4**, were introduced to neat monomer mixtures at 25 °C under nitrogen. The reactions became highly viscous after several hours. They were typically run for ~15 h before quenching with ethyl vinyl ether and purification by precipitation from MeOH . Both copolymers are off-white materials, with poly[COD/**1**] being considerably more viscous than poly[COD/**2**] at comparable molecular weights. Yields are reported based on MeOH -insoluble polymer.¹¹ Monomer to catalyst loadings of up to ~5000:1 resulted in the production of high molecular weight polymer in good yield (87%). For higher monomer loadings (~9800:1), longer reaction times or elevated temperatures may be required to drive the reaction to completion as there was evidence of unreacted monomer in the MeOH fractions upon precipitation. Since the benzylidene acetal, **2**, is less reactive than COD and it does not homopolymerize,

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Scheme 1. Preparation and Cleavage of COD/4,7-Dihydro-1,3-dioxepin Copolymers To Give 1,4-Hydroxytelechelic Polybutadiene



in cases of very high loadings of **2**, large amounts of unreacted acetal are recovered at the end of the reaction. Correspondingly, the yields of these reactions are depressed.

The molecular weights and polydispersity indices (PDIs) of the copolymers were estimated by gel permeation chromatography which was calibrated versus polystyrene standards. Poly[COD/1] exhibits broader molecular weight distributions than the copolymer of COD and **2**. This may be attributed in part to the tendency of poly[COD/1] to form gels. The exact mechanism of this side reaction was not determined, although it presumably occurs by cross-linking which could broaden the PDI. No gelation was observed for poly[COD/2]. Relative monomer incorporation, determined from integration of the allylic proton resonances, indicates that COD is slightly more reactive than the acetal monomers, **1** and **2** (Table 1). That is, acetal incorporation is lower than the feed ratios for both monomers: % **1** in poly[COD/1] = 60% **1** in feed; % **2** in poly[COD/2] = ~40% **2** in feed.

The ¹H NMR spectra of poly[COD/1] contain three distinct sets of resonances which correspond to polybutadiene runs, isolated acetal groups in polybutadiene, and a small number of segments with consecutive acetal units. Since **2** does not homopolymerize, consecutive benzylidene acetals appear to be unfavorable. However, from the ¹H NMR spectrum (Figure 1) it is difficult to distinguish between isolated and neighboring benzylidene acetals. The acetal regions of poly[COD/1] and poly[COD/2] are compared in Figure 2. The ¹H and ¹³C NMR spectra indicate that the olefins in the polybutadiene segments of these copolymers are predominantly cis, whereas olefins neighboring acetals are primarily trans. Olefins in the acetal runs of poly[COD/1] and in poly[1] are high trans.¹²

Poly[COD/acetal] Copolymer Cleavage at the Acetal Functionalities: 1,4-HTPBD

The COD/acetal copolymers were degraded to produce 1,4-hydroxytelechelic polybutadiene. Representative results of these investigations are compiled in Table 2.

The benzylidene acetal moieties in poly[COD/2] are readily cleaved to free hydroxyls and benzaldehyde under acidic conditions. A series of trial reactions were run by adding different acids to the copolymer in CH₂Cl₂ solution. Poly[COD/2] is degraded in homogeneous solution by trifluoroacetic acid in the presence of MeOH. Since small amounts of an additional byproduct were observed in the product mixture using these conditions, other acids were also probed. Both 10% aqueous H₂SO₄ and 10% aqueous HCl were also effective in producing 1,4-HTPBD from poly[COD/2]. For 10% HCl, however, the reaction did not go to completion. This may be due to lower solubility of aqueous HCl in the organic reaction mixture; greater separation of reaction components was observed to occur under these conditions. When small amounts of MeOH were added to the 10% HCl reaction mixture to improve miscibility, the copolymer were effectively cleaved. The degradation reaction was also effected in acidic MeOH containing only small amounts of methylene chloride in the reaction medium. This observation led to the development of a simplified one-pot, two-step procedure for the preparation of 1,4-HTPBD from COD and **2**. It was discovered that stirring the crude viscous copolymer reaction mixture with acidic methanol for ~1 day served to quench the reaction, to cleave the copolymer, and to precipitate and purify the resulting hydroxytelechelic product all in one step. These processes occur in a heterogeneous mixture. Dilution with CH₂Cl₂ and quenching with ethyl vinyl ether are unnecessary.

A more rigorous two-step procedure was required for the cleavage of the robust methylene acetals in poly[COD/1]. First the copolymer was reacted with trifluoroacetic anhydride (TFAA) and acetic acid (AcOH) in a methylene chloride solution to produce shorter chains end-capped with ester or acetal-ester groups.¹³ These intermediates were hydrolyzed in a THF solution by addition of NaOMe in MeOH to give 1,4-HTPBD.⁹ The HTPBD product from these reactions is less pure than that prepared from poly[COD/2] as evidenced by its yellow color and a broad impurity observed at ~1–2 ppm in certain ¹H NMR spectra. This, combined with the two steps required for cleavage and the tendency of poly[COD/1] to cross-link, make the methylene acetal **1** a less practical reagent than **2** for the preparation of 1,4-HTPBD.

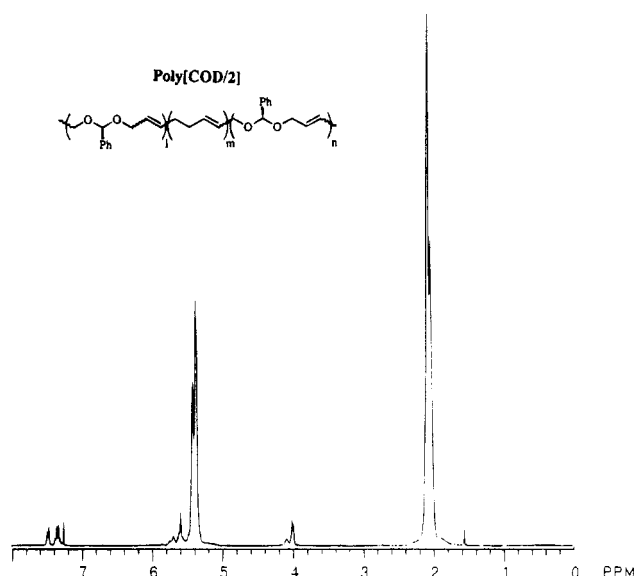
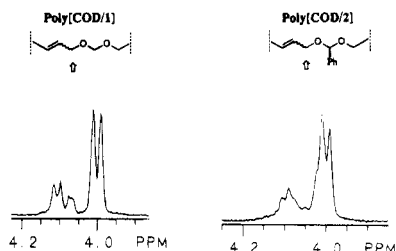
The hydroxytelechelic products of copolymer cleavage were analyzed by NMR and gel permeation chromatography (GPC). A ¹H NMR spectrum of 1,4-HTPBD prepared in a one-pot preparation from poly[COD/2] is shown in Figure 3. Resonances attributable to the polymer end groups are resolved into three cis/trans sets clearly evident at ~1.2 (HOCH₂CH=), ~4.1 (HOCH₂CH=), and ~5.6 ppm (HOCH₂CH=). The larger sets of peaks at ~2.0 and ~5.4 ppm arise from polybutadiene.⁹ The cis/trans ratios of the olefin end groups and polybutadiene runs determined in the copolymerization reaction are conserved in the telechelic products.¹² In contrast to the 1,4-HTPBD prepared using ROMP, **3**, and chain-transfer agents which is predominantly trans,⁹ polymer prepared by this degradative approach has a high cis content.¹² In both preparations the allylic alcohol end groups are predominantly trans.

Comparison of the ¹H NMR integrations of the allylic end-group signals with those arising from polybutadiene allows for the estimation of *M_n* (Table 2). This calculation assumes that all chains are terminated with hydroxyl groups (*F_n* = 2).¹⁴ These values are typically lower than the number-average molecular weights, *M_n*,

Table 1. Copolymerization of Acetal Monomers, 1 and 2, with Cyclooctadiene Using Ruthenium Carbene Initiators, 3 and 4

acetal	feed ratio ^a ([COD]:[acetal]:[Ru])	incorporation ^b (COD:acetal)	$M_n \times 10^{-4}$ ^c	$M_w \times 10^{-4}$ ^c	PDI ^c	yield ^d (%)
1	0:1000:1		1.72	7.65	4.44	70
1	2350:275:1	13:1	8.90	21.5	2.41	73
1	1000:200:1	8.7:1	11.4	18.4	1.62	
1	1100:275:1	6.8:1	6.41	2.22	3.46	72
2	0:1200:1					no reaction
2	0:1300:1 ^e					no reaction
2	1700:140:1	27:1	16.1	31.9	1.98	83
2	4600:500:1	23:1	15.6	28.8	1.85	87 ^f
2	4600:500:1	23:1	15.8 ^g	28.6 ^g	1.81 ^g	
2	8700:1100:1	18:1	5.09	10.0	1.98	51 ^h
2	1625:300:1 ^e	13:1	7.02	12.7	1.80	82
2	2025:560:1	9.3:1	6.43	10.7	1.67	66 ^f
2	2040:190:1	7:1	2.36 ^g	4.20 ^g	1.78 ^g	
2	1100:620:1	4.2:1	6.77	10.9	1.62	65 ^f
2	580:750:1	2.4:1	3.30	4.98	1.51	37 ^f

^a COD = cyclooctadiene; Ru = 3; (Cy₃P)₂Cl₂Ru=CHCPh₂ unless otherwise indicated. Reaction conditions: 15 h, 25 °C. ^b Determined by ¹H NMR. ^c By CH₂Cl₂ GPC vs polystyrene standards. ^d Yields are not corrected for unreacted monomer and low molecular weight oligomers. ^e Ru = 4; (Cy₃P)₂Cl₂Ru=CHPh. ^f Small aliquot removed from a one-pot prep for determination of the copolymer composition prior to treatment with acid. ^g Determined from the entire reaction mixture prior to precipitation from MeOH. ^h Reaction conditions: 24 h, 25 °C. Mass recovery: high molecular weight polymer, 51%; MeOH fraction (mainly unreacted acetal), 16%; volatiles (COD, low molecular weight oligomers), 33%.

**Figure 1.** ¹H NMR spectrum (300 MHz, CDCl₃) of poly[COD/2].**Figure 2.** Comparison of the allylic acetal regions of the ¹H NMR spectra (300 MHz, CDCl₃) of poly[COD/1] and poly[COD/2] (downfield, cis; upfield, trans; central signal in the spectrum of poly[COD/1], consecutive acetals).

determined by GPC (CH₂Cl₂) versus polystyrene standards. Vapor pressure osmometry indicated a molecular weight similar to that determined by ¹H NMR for a particular hydroxytelechelic product (VPO, M_n = 1750; NMR, M_n = 2272). The copolymer cleavage products are fractionated upon precipitation of the reaction solutions in methanol. In some cases data for both methanol-insoluble higher molecular weight HTPBD and the less pure lower molecular weight MeOH-soluble

fraction are given. As is expected, cleavage of copolymers with higher acetal content results in larger amounts of low molecular weight MeOH-soluble HTPBD product. (See yields for cleavage of poly[COD/2].) For very high loading of 2 (poly[COD/2] composition: 2.4:1) no high molecular weight polymer precipitated from MeOH solution. In this case the entire unpurified reaction mixture was analyzed by NMR and GPC. Similar analysis of the entire reaction mixture prior to precipitation was conducted for the cleavage reaction using H₂SO₄ for comparison with the polymer product after precipitation. The PDI is somewhat broader, and M_n is slightly lower for the whole reaction, as is expected. On the whole, these results show that the molecular weight of the telechelic product correlates with the amount of acetal in the copolymer and, thus, in the initial feed.¹⁵ It may also be noted that the polydispersities of the telechelic polymers prepared by this ROMP-cleavage method are narrower than what were observed for telechelics prepared by ROMP-chain transfer.⁹

Hydrogenation of Poly[COD/2]: Hydroxytelechelic Polyethylene

The COD/acetal copolymers are also of interest since they allow entry into derivatives of polyethylene. For example, selective hydrogenation of the olefins of acetal-containing copolymers would result in a degradable polyethylene, that is, polyethylene with acetal moieties distributed along the backbone. Other methods which target both the olefins and the acetals could produce hydroxytelechelic polyethylene in one step. This was tested by reacting poly[COD/2] with *p*-toluenesulfonohydrazide in the presence of tripropylamine in refluxing *o*-xylene.¹⁶ After cooling, the reaction mixture was added to ethanol to precipitate the polymer product, which was further purified by successive washes with ethanol and acetone. This approach results in simultaneous olefin hydrogenation and fragmentation at the benzylidene acetals links to give hydroxytelechelic polyethylene. By high-temperature NMR (100 °C) in a C₆D₅Cl solution both the internal and terminal methylene protons are observable (Figure 4). Other acetals or ketals which are less susceptible to attack during hydrogenation could allow for the preparation of acid-sensitive degradable polyethylenes.

Table 2. COD/Acetal Copolymer Degradation to 1,4-Hydroxytelechelic Polybutadiene

copolymer	acetal	composition (COD:acetal)	reaction conditions ^a	$M_n \times 10^{-3}$ ^b	$M_w \times 10^{-3}$ ^b	PDI ^b	M_n ^c	yield (%)
1		6.8:1	i. TFAA, AcOH ii. NaOMe, MeOH ^d	10.2	11.5	1.13	1711	38 ^e
1		13:1	i. TFAA, AcOH ii. NaOMe, MeOH ^d	9.7, ^e 2.3 ^f	18.0, ^e 3.4 ^f	1.86, ^e 1.51 ^f	3009	40, ^e 50 ^f
2		13:1	TFA, MeOH, 1 day	11.5	13.8	1.20	2522	56 ^e
2		13:1	10% H ₂ SO ₄ , 5 h	6.5 ^g	9.2 ^g	1.41 ^g	1674 ^g	
2		13:1	10% H ₂ SO ₄ , 5 h	7.8 ^e	9.4 ^e	1.21 ^e		
2		13:1	10% HCl, 1 day					partial rxn
2		13:1	10% HCl/MeOH, 1 day	10.0	12.4	1.24	2202	53 ^e
2		23:1	10% HCl/MeOH, 6 h ^h	16.4	21.4	1.30	3117	56 ^e
2		9.3:1	10% HCl/MeOH, 6 h ^h	7.65, ^e 2.57 ^{f,i}	9.73, ^e 2.87 ^{f,i}	1.27, ^e 1.16 ^{f,i}	2467 ^j	47, ^e 32 ^f
2		8.4:1 ^k	10% HCl/MeOH, 1 day ^l	5.15	7.80	1.52	2143	40 ^e
2		7:1	10% HCl/MeOH, 15 h ^{h,m}	4.80	5.78	1.20	1603	
2		7:1	10% HCl/MeOH, 15 h ^{h,n}	3.08	3.82	1.24	1603	
2		4.2:1	10% HCl/MeOH, 6 h ^h	6.09, ^e 3.21 ^{f,i}	6.81, ^e 3.56 ^{f,i}	1.12, ^e 1.11 ^{f,i}	1675	24, ^e 64 ^f
2		2.4:1	10% HCl/MeOH, 6 h ^h	3.03 ^{f,i}	3.50 ^{f,i}	1.16 ^{f,i}	364 ^g	94 ^{f,g}

^a Reactions were run in CH₂Cl₂ solution unless otherwise indicated. See, the Experimental Section for detailed procedures. ^b Determined by CH₂Cl₂ GPC. ^c Determined from ¹H NMR integrations on MeOH-insoluble telechelic product assuming $F_n = 2$. ^d Reaction in THF. ^e MeOH-insoluble fraction. ^f MeOH-soluble fraction. ^g Determined from the entire reaction mixture prior to MeOH precipitation. ^h One-pot preparation. The copolymer reaction was diluted with CH₂Cl₂ and quenched with ethyl vinyl ether but was not isolated prior to scission. Copolymer composition was determined by removal of an aliquot prior to acid treatment. ⁱ Low-MW HTPBD coelutes with methanol-soluble UV-active reaction byproducts. Data were calculated from an extrapolated GPC curve. ^j For entire sample prior to MeOH precipitation, $M_n = 1459$. ^k Estimated based on feed. ^l One-pot prep without dilution with CH₂Cl₂ and quenching with ethyl vinyl ether. Reaction was added directly to MeOH containing 10% HCl. ^m Quenched reaction was added directly to MeOH containing 10% HCl and a small amount of additional CH₂Cl₂. ⁿ Quenched reaction was added to MeOH containing 10% HCl but no additional CH₂Cl₂.

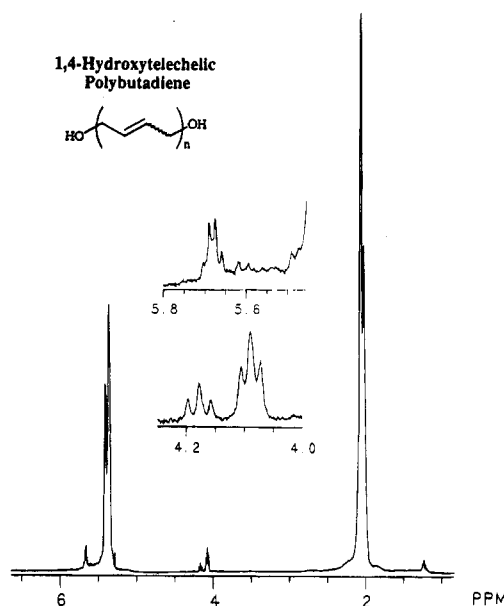


Figure 3. ¹H NMR spectrum (300 MHz, CDCl₃) of 1,4-hydroxytelechelic polybutadiene. The polymer was prepared from poly[COD/2] by cleavage with 10% HCl/MeOH in CH₂Cl₂.

Conclusion

We have demonstrated that a benzylidene acetal/COD copolymer prepared by ROMP using ruthenium carbene initiators is a versatile precursor to a variety of important polymeric materials. Perfectly 1,4-hydroxytelechelic polybutadiene is conveniently accessed via a one-pot procedure which involves the fragmentation of poly[COD/benzylidene acetal] by hydrolysis in acidic methanol. The more stable poly[COD/methylene acetal] is not amenable to this synthetic route but instead requires a more laborious two-step procedure for cleavage. It has also been shown that the benzylidene acetal copolymer is a useful precursor to unbranched hydroxytelechelic polyethylene. This is produced in one step from poly[COD/benzylidene acetal] by hydrogenation with *p*-toluenesulfonylhydrazide.

Hydroxytelechelic Polyethylene

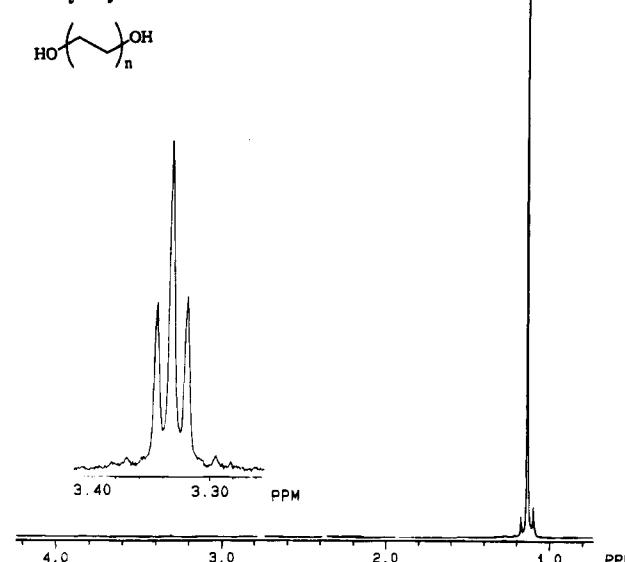


Figure 4. ¹H NMR spectrum (500 MHz, C₆D₆Cl, 100 °C) of hydroxytelechelic polyethylene prepared from poly[COD/2] using *p*-toluenesulfonylhydrazide.

The strategy described herein for the synthesis of 1,4-HTPBD involving selective copolymer degradation could be extended to other cyclic olefin monomers. A variety of polymeric materials bearing a whole range of different end functionalities including commercially important amines or acids, for example, could be generated provided that certain criteria are met. First, cyclic olefin monomers containing cleavable functionalities must be screened to determine whether they undergo ring-opening metathesis in copolymerization reactions. Second, the degradable group must be distributed along the copolymer backbone and must not be prone to form blocky materials. This could be achieved in the original ring-opening reactions if the reactivities of the two monomers are roughly comparable. Both relief of ring strain upon opening and the probability of monomer addition to the growing chain end are important factors.¹⁷ Or, the cleavage sites could be distributed after

polymerization by chain-transfer reactions if the reaction is allowed to reach equilibrium and randomization is energetically more favorable than blockiness. Other cleavable monomers and copolymer systems are under investigation to determine whether this synthetic approach using ROMP might be extended to the synthesis of different telechelic polymers and new degradable materials.

Experimental Section

General Considerations. Argon was purified by passage through columns containing BASF R3-11 catalyst (Chemalog) and 4 Å molecular sieves (Linde). Ambient-temperature NMR spectra were recorded on a GE QE-300 spectrometer (300.01 MHz ^1H ; 75.49 MHz ^{13}C). High-temperature NMR spectra were obtained using a Bruker 500 AM spectrometer (500.138 MHz ^1H). Gel permeation chromatographs were obtained with methylene chloride as the eluent (flow rate: 1.0 mL/min) using an HPLC system equipped with an Altex Model 110A pump, a Rheodyne Model 7125 injector, a 100- μL injection loop, an American Polymer Standards 10- μm mixed-bed column, and a Knauer differential refractometer. Molecular weights, M_w and M_n , and polydispersities were calculated from the chromatographs relative to monodisperse polystyrene standards, or they were determined by ^1H NMR as indicated. Vapor pressure osmometry was conducted using a Jupiter Model 233 instrument in toluene at 47 °C using sucrose octaacetate for calibration. The melting point of hydroxytelechelic polyethylene was obtained by DSC using a Perkin-Elmer 7 (scan rate: 10 °C/min) and is reported as the peak temperature. FTIR spectra were recorded on polymer films using a Perkin-Elmer 1600 series instrument. Elemental analyses were performed at the California Institute of Technology Elemental Analysis Facility.

Materials. The monomers cyclooctadiene, *cis*-4,7-dihydro-1,3 dioxepin (**1**) and *cis*-4,7-dihydro-2-phenyl-1,3 dioxepin (**2**) were used as received from Aldrich and were degassed by repeated freeze-pump-thaw cycles prior to use. The ruthenium carbene catalysts, **3** and **4**, were prepared as previously described.¹⁰ Methylene chloride was either distilled from CaH_2 followed by degassing by repeated freeze-pump-thaw cycles or it was passed through solvent purification columns.¹⁸ All other solvents and chemicals were reagent grade and were used without further purification.

Polymer Synthesis. Poly[1]. A CH_2Cl_2 solution (0.21 mL) of **3** (10.3 mg) was added to **1** (1.1 g) in a vial equipped with a Teflon-lined cap in the drybox. After 1 h at 25 °C the reaction solidified. After 4 h the reaction was removed from the box and was diluted with additional CH_2Cl_2 (7 mL), and ethyl vinyl ether (100 μL) and BHT were added to quench the reaction and to stabilize the polymer product, respectively. The polymer was purified by precipitation from MeOH (2 \times) to give a white, waxy solid. Yield: 70%. ^1H NMR (CDCl_3 , 300 MHz): δ 4.08 (d, $J = \sim 1$ Hz, 4H; $-\text{OCH}_2\text{CH}=\text{CH}-$, trans); 4.15 (d, $J = 4.6$ Hz, 4H; $-\text{OCH}_2\text{CH}=\text{CH}-$, cis); 4.69 (s, 2H; $-\text{OCH}_2\text{O}-$, cis); 4.70 (s, 2H; $-\text{OCH}_2\text{O}-$, trans); 5.72 (t, $J = 4.0$ Hz, 2H; $-\text{CH}=\text{CH}-$, cis); 5.82 (br s, 2H; $-\text{CH}=\text{CH}-$, trans). Cis:trans ratio = $\sim 1:6$. ^{13}C NMR (CDCl_3 , 300 MHz): δ 63.48 ($-\text{OCH}_2\text{CH}=\text{CH}-$, cis); 67.68 ($-\text{OCH}_2\text{CH}=\text{CH}-$, trans); 94.20 ($-\text{OCH}_2\text{O}-$); 129.50 ($-\text{CH}=\text{CH}-$). IR (cm^{-1}): 3030 (sh), 2947, 2866, 1466, 1383, 1290, 1212, 1174, 1108, 1032, 984, 962, 932.

Poly[COD/1]. A typical run is described below. A CH_2Cl_2 solution (0.43 mL) of **3** (8.1 mg) was added to a mixture of COD (1.04 g) and **1** (0.24 g) in a vial equipped with a Teflon-lined cap in the drybox. After 2 h the reaction had set. After 15 h, the reaction was removed from the box and was diluted with CH_2Cl_2 (~ 3 mL), and ethyl vinyl ether (~ 100 μL) and BHT were added. After 3 h, the mixture was precipitated in MeOH (2 \times). The polymer was collected and then dried in vacuo. Yield: 72%. ^1H NMR (CDCl_3 , 300 MHz): δ 2.04 (s, trans), 2.08 (s, cis), 2.11 (s, 8H; $=\text{CHCH}_2\text{CH}_2\text{CH}=\text{CH}-$); 4.02 (d, $J = 6.1$ Hz, 4H; $-\text{OCH}_2\text{CH}=\text{CHCH}_2\text{CH}_2-$, trans); 4.10 (br, 4H; $-\text{OCH}_2\text{CH}=\text{CHCH}_2\text{CH}_2-$); 4.13 (d, $J = 5.3$ Hz, 4H; $-\text{OCH}_2\text{CH}=\text{CHCH}_2\text{CH}_2-$, cis); 4.69 (s, 2H; $-\text{OCH}_2\text{O}-$, cis); 4.70 (s, 2H; $-\text{OCH}_2\text{O}-$, trans); 5.38 (s, 4H; $-\text{CH}_2\text{CH}_2\text{CH}=\text{CHCH}_2\text{CH}_2-$, cis); 5.42 (m, 4H; $-\text{CH}_2\text{CH}_2\text{CH}=\text{CHCH}_2\text{CH}_2-$, trans);

5.59 (m, 2H; $-\text{OCH}_2\text{CH}=\text{CHCH}_2\text{CH}_2-$, cis); 5.71 (br t, 2H; $-\text{OCH}_2\text{CH}=\text{CHCH}_2\text{CH}_2-$, cis); 5.76 (m, 2H; $-\text{OCH}_2\text{CH}=\text{CHCH}_2\text{CH}_2-$, trans); 5.84 (br t, 2H; $-\text{OCH}_2\text{CH}=\text{CHCH}_2\text{CH}_2-$, trans). ^{13}C NMR (CDCl_3 , 300 MHz): δ 26.80, 27.37, 32.37, 32.78, 62.93, 67.99, 93.31, 93.48, 126.12, 128.99, 129.17, 129.40, 129.57, 129.73, 129.97, 130.08, 134.34. IR (cm^{-1}): 3005, 2918, 2845, 1654, 1447, 1403, 1378, 1312, 1239, 1162, 1109, 1037, 967, 731. Anal. Calcd for $\text{C}_{89}\text{H}_{137.6}\text{O}_4$: C, 84.19; H, 10.81. Found: C, 84.12; H, 10.73. (Polymer composition, as determined by ^1H NMR: COD:1:H $_2\text{O}$ = 10.3:1.5:1.)

Poly[COD/2]. The copolymers were prepared as described above for poly[COD/1] with the following exception. The acetal monomer, followed by COD, was added to methylene chloride solutions of the Ru catalyst, **3** or **4**. ^1H NMR (CDCl_3 , 300 MHz): δ 2.02 (br s, 8H; $=\text{CHCH}_2\text{CH}_2-$, trans); 2.06 (br s, 8H; $=\text{CHCH}_2\text{CH}_2-$, cis); 3.98 (d, $J = 5.4$ Hz, 4H; $=\text{CHCH}_2\text{O}-$, trans); 4.07 (m, 4H; $=\text{CHCH}_2\text{O}-$, cis); 5.36 (br s, 4H; $-\text{CH}_2\text{CH}_2\text{CH}=\text{CHCH}_2\text{CH}_2-$, cis); 5.40 (br s, 4H; $-\text{CH}_2\text{CH}_2\text{CH}=\text{CHCH}_2\text{CH}_2-$, cis); 5.57 (m, 2H; $-\text{OCH}_2\text{CH}=\text{CHCH}_2\text{CH}_2-$, trans); 5.64 (m, 2H; $-\text{OCH}_2\text{CH}=\text{CHCH}_2\text{CH}_2-$, cis); 7.33 (m, 3H; phenyl); 7.46 (m, 2H; phenyl). The acetal resonance ($-\text{OCHPhO}-$) is obscured by the olefin signals. ^{13}C NMR (CDCl_3 , 300 MHz): δ 26.80, 27.13, 27.35, 27.59, 32.11, 32.37, 32.65, 60.74, 65.92, 65.99, 100.10, 100.22, 126.09, 126.18, 126.29, 126.70, 128.12, 128.29, 128.86, 129.01, 129.19, 129.38, 129.55, 129.69, 129.94, 130.05, 130.23, 133.92, 134.00, 138.56, 138.62. IR (cm^{-1}): 3005, 2916, 2844, 1654, 1449, 1402, 1350, 1309, 1239, 1206, 1028, 966, 700.

Copolymer Scission. Preparation of 1,4-HTPBD from Poly[COD/2]. Trial Reactions: (see Table 2 for molecular weight data). **A. TFA/MeOH.** Poly[COD/2] (13:1) (0.5 g) was dissolved in CH_2Cl_2 (5 mL). MeOH (200 μL) and CF_3COOH (200 μL) were added. The reaction solution was stirred under Ar for 1 day and then was added to MeOH to precipitate water white telechelic product: 0.26 g (56%). **B. 10% HCl.** Poly[COD/2] (13:1) (0.15 g) was dissolved in CH_2Cl_2 (3 mL). 10% HCl (100 μL) was added. The suspension was stirred vigorously for 1 day after which time NMR analysis indicated incomplete reaction. (Note: This reaction may have been retarded by incomplete mixing of the reagents, as some of the reaction components beaded up on the walls of the flask during the course of the reaction.) **C. 10% H_2SO_4 .** Poly[COD/2] (13:1) (80 mg) was dissolved in CH_2Cl_2 (2 mL), and 10% H_2SO_4 (100 μL) was added. The suspension was stirred vigorously for 5 h, after which time NMR analysis indicated complete reaction. This product was analyzed both before and after MeOH precipitation. **D. 10% HCl/MeOH/ CH_2Cl_2 .** Poly[COD/2] (13:1) (0.15 g) was dissolved in CH_2Cl_2 (3 mL), and MeOH (0.55 mL) followed by 10% HCl (100 μL) was added. The suspension was stirred vigorously for 1 day after which time NMR analysis indicated complete reaction. Water white 1,4-HTPBD product was obtained after precipitation from MeOH: 76 mg (53%). **E. 10% HCl/MeOH/ CH_2Cl_2 .** Many other runs were conducted analogous to "D" but with decreasing amounts of CH_2Cl_2 and increasing amounts of MeOH present. These were performed both on isolated copolymer and in one-pot preparations in which the crude copolymer was submitted to cleavage conditions without isolation by precipitation. These trial reactions culminated in a simplified one-pot synthesis with no added CH_2Cl_2 which is described below.

One-Pot Preparation of 1,4-HTPBD from COD and 2. Poly[COD/2] was prepared as described above (COD, 0.927 g, 8.57 mmol; acetal, **2**, 0.447 g, 2.54 mmol; Ru catalyst, **3**, 2.7 mg, feed (COD:2) = 3.4:1). The viscous crude copolymer product was added to MeOH (30 mL) containing 10% HCl (1 mL) without quenching with ethyl vinyl ether. Over time, the insoluble tan copolymer product broke up into smaller, less viscous clear beads suspended in the MeOH solution. After 1 day the heterogeneous mixture was subjected to centrifugation to collect the hydroxytelechelic product, which was further purified by stirring with fresh MeOH (2 \times). (All of the color arising from the catalyst remained in the MeOH fraction.) The high molecular weight fraction was collected and dried under high vacuum for ~ 15 h: 0.462 g (40%). ^1H NMR (CDCl_3 , 300 MHz): δ ~ 1.21 (m, 2H; $-\text{OH}$, cis); 1.24 (m, 2H; $-\text{OH}$, trans); 2.02 (br s, 4H; $=\text{CHCH}_2-$, trans); 2.06 (br s, 4H; $=\text{CHCH}_2-$, cis); 4.07 (m, 2H; $\text{HOCH}_2\text{CH}=\text{CH}-$, trans); 4.16 (m, 2H; $\text{HOCH}_2\text{CH}=\text{CH}-$, cis).

CH=, cis); 5.36 (s 2H; $-CH=CH-$, cis); 5.40 (d, $J = 2.9$ Hz, 2H; $-CH=CH-$, trans); ~ 5.60 (m, 2H; $HOCH_2CH=$, cis); 5.66 (m, 2H; $HOCH_2CH=$, trans). IR (cm^{-1}): 3381 (br), 3005, 2917, 2845, 1654, 1438, 966.

Preparation of 1,4-HTPBD from Poly[COD/1]. Poly[COD/1] (6.75:1 sample) (0.26 g) was dissolved in CH_2Cl_2 (5 mL). The reaction was cooled to 0 °C, and then TFAA (1 mL) followed by AcOH (0.42 mL) was added. After stirring for ~ 15 h at 25 °C, the reaction was again cooled to 0 °C before quenching by slow addition of excess solid K_2CO_3 . After filtration, the solution was concentrated in vacuo. The resulting residue was dissolved in THF (5 mL) and was cooled to 0 °C before addition of 0.7 M NaOMe in MeOH (1 mL). After stirring at 25 °C for 3 h, the reaction was concentrated to a minimal volume (~ 0.5 mL) and then was added to MeOH to precipitate the high molecular weight fraction of 1,4-HTPBD: 99 mg (38%). A lower molecular weight fraction was obtained by concentration of the MeOH fraction.

Preparation of Hydroxytelechelic Polyethylene. To poly[COD/2] (composition 17.5:1) (0.57 g) were added tripropylamine (1.45 mL) and *o*-xylene (20 mL).¹⁶ The mixture was heated to ~ 100 °C, toluenesulfonohydrazide (3.5 g) was added, and then the reaction was heated to reflux for ~ 1 day. Over time the reaction became dark reddish-brown in color. The mixture was cooled and then was added to ethanol. After stirring in EtOH for ~ 15 h, the precipitated polymer was collected and repeatedly triturated and washed with additional ethanol and acetone ($\sim 5\times$). A slightly off-white powdery product was obtained: 0.33 g (60%). Mp (DCS): 123 °C. 1H NMR (C_6D_5Cl , 500 MHz, 100 °C): δ 1.56 (s, 960H; $-CH_2-$); 3.73 (t, $J = 6.5$ Hz, 4H; $-CH_2OH$). By NMR $M_n = 6771$ (assuming $F_n = 2$).

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- (12) Poly[COD/1] (composition: 6.8/1) has $\sim 66\%$ cis olefins in the polybutadiene runs and $\sim 77\%$ trans olefins neighboring acetals. Poly[1] is $\sim 83\%$ trans. Poly[COD/2] (composition: 13/1) is $\sim 63\%$ cis in polybutadiene segments and is comprised of $\sim 70\%$ trans olefins proximal to benzylidene acetals.
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- (14) It should be noted that this telechelic synthesis also produces a small number of polymer chains with 1,1-diphenylbutadiene termini arising from the vinylcarbene initiator or with end groups due to the ethyl vinyl ether quenching reagent. However, signals attributable to these latter end groups were not observable by 1H NMR. These end fragments may remain in the methanol fraction after precipitation.
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