Articles

Controlled Synthesis of High Molecular Weight Telechelic Polybutadienes by Ring-Opening Metathesis Polymerization

Shengxiang Ji,[†] Thomas R. Hoye,*,[†] and Christopher W. Macosko[‡]

Department of Chemistry and Department of Chemical Engineering and Materials Science, University of Minnesota, 207 Pleasant St. S.E., Minneapolis, Minnesota 55455

Received April 8, 2004; Revised Manuscript Received May 24, 2004

ABSTRACT: High molecular weight telechelic [dicyano- and dichloro-] polybutadienes (TPBs) have been synthesized via ring-opening metathesis (ROM) polymerization of 1,5-cyclooctadiene (COD) in the presence of the difunctional chain transfer agents (CTAs), 1,4-dicyano- or 1,4-dichloro-2-butene. To achieve high molecular weights, it was critical that the COD monomer contained very low levels of the contaminating, isomeric 4-vinylcyclohexene (VCH), since the latter serves as a competing CTA. An NMR method for determining the level of VCH was developed as well as “reactive purification” strategy in which the VCH was selectively depleted by its (faster) hydroboration. A “two-stage” protocol for preparation of the TPBs was developed wherein a small portion of the eventual charge of COD and the entire quantity of the CTA were first copolymerized to produce telechelic oligomeric butadiene (TOB) of low viscosity. After all of the CTA had been consumed, the remaining COD was charged. This protocol allowed for better MW control and for higher functionality in the resulting TPBs. Finally, diamino-terminated TPBs were prepared by lithium aluminum hydride reduction of the precursor dicyano-TPBs.

Introduction

α,ω-Difunctional (telechelic) polymers have attracted much interest due to their unique properties and synthetic challenges.[1] These polymers bear functional groups at both termini and have potential applications as, e.g., pressure-sensitive adhesives,[2] compatibilizers for polymer blends,[3] binders for composite materials (e.g., rocket propellant binders),[4] building blocks for segmented block copolymers,[5] and cross-linking agents for polymer networks. Styrene−butadiene−styrene (SBS) block copolymers containing central polybutadiene (PB) blocks of high molecular weight are particularly attractive in their potential for use in pressure-sensitive adhesives. However, premade SBS block copolymers are difficult to process due to their high order−disorder transition temperature and high viscosity. An attractive strategy for approaching this problem would be the use of appropriate reactive coupling reactions in the melt between high molecular weight functional telechelic PBs (TPBs) to generate the SBS block copolymers in situ.[3,6]

Telechelic polybutadienes with different functional groups, such as dihydroxyl (e.g., Krasol LBH and Poly Bd),[7] diamino,[8] dichloro,[9] diepoxy,[10] diacrylate,[10] and dicarboxylic acid,[8c,11] have been synthesized by radical polymerization, anionic polymerization, or ring-opening metathesis (ROM) polymerization. Among these, ROM polymerization is an established and reliable strategy for the synthesis of TPBs having high functionality, especially for linear 1,4-PBs. However, most of the previously reported telechelic polybutadienes prepared by ROM polymerization are of relatively low molecular weight (most <10K with some in the range of 10K−50K), and in some cases it has not been feasible to obtain targeted molecular weights accurately.

Results and Discussion

In this paper we describe the synthesis of some high molecular weight TPBs prepared by ROM polymerization of 1,5-cyclooctadiene (COD, **1**) in the presence of an acyclic 1,*n*-difunctional alkene as a chain transfer agent (CTA). Using a strategy modeled after that developed by the groups of Pinazzi,[12] Chung,[13a] and Grubbs[13b] for the synthesis of TPBs, we have devised a protocol for preparation of TPBs in the 20K−200K MW range that contain two allylic chloride (**3a**) or cyano groups (**3b**) using 1,4-dichloro-2-butene (**2a**) and 1,4-dicyano-2-butene (**2b**), respectively. The cyano groups in **3b** have also been successfully reduced to homoallylic primary amine groups (**3c**), thereby providing a diamino-TPB having high functionality [Fn = % of chain termini bearing the intended functional group(s)] and high MW. Importantly, by carefully dealing with the issues of monomer (COD) purity[14] and CTA reactivity, we have been able to develop a reliable protocol for achieving targeted molecular weights, including those up to 200K.

We initially studied the preparation of relatively low molecular weight TPBs using the dinitrile **2b** in order to gain insight about the reactivity of this new CTA. Specifically, polymer **3b** having a MW of 21.6K was targeted. When living polymerizations involving chain transfer events proceed to 100% conversion, the MW is

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[†] Department of Chemistry.
[‡] Department of Chemical Engineering and Materials Science.
* Corresponding author: e-mail hoye@chem.umn.edu.

10.1021/ma0493067 CCC: $27.50

a function of the monomer:CTA molar ratio; therefore, we used a 200:1 ratio of **1**:**2b**. ROM polymerization of a methylene chloride solution of these reactants in the presence of the dihydroimidazolylidene-containing ruthenium carbene complex **G2** (2 mol % based upon the amount of CTA) was carried out at 40 °C. After ~2 h none of **1** remained, but approximately half of the CTA **2b** was still present. Precipitation by slow addition into methanol provided the product **3b**. GPC analysis indicated an M_n of ~38K. This higher than expected M_n is consistent with incomplete consumption of the CTA (observable by ^{1}H NMR spectroscopy of the crude product mixture). This suggested that the rate of monomer propagation was faster than the chain-transfer interruption by the bis-nitrile **2b**. We attempted to overcome this problem by increasing the reaction time. For example, in an experiment to produce **3b** having 10.8K MW, a 100:1 ratio of **1**:**2b** was used. After ~6 h both of **1** and **2b** were completely consumed. The M_n of **3b** was 8.6K−10.7K (over five experiments). However, when longer reaction times were used in attempts to produce higher MW samples of **3b** (21.6K again with a 200:1 ratio of COD/CTA), incomplete consumption of **2b** was again observed. A significant difference in experiments designed to produce higher MW material is that the reaction mixtures become substantially more viscous, which exacerbates the incomplete conversion. Further extension of the reaction time is limited by the finite lifetime of the catalytic species derived from **G2**.[15]

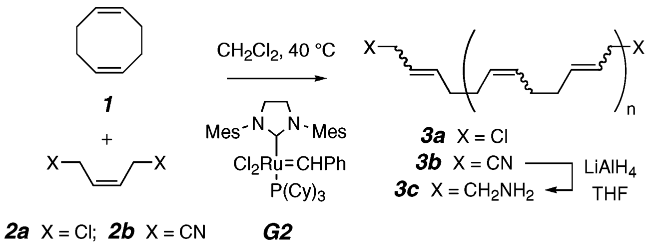
We hypothesized that initial incubation of a small amount of the COD monomer (**1**) with the full charge of the slowly reacting CTA **2b** would provide a fully converted set of oligomeric CTAs (**3b** where *n* is a small number) in a living environment. Subsequent addition and ROM polymerization of the remainder of monomer **1** might then result in higher MW samples of **3b**, since the oligomeric CTAs should be more reactive than dicyanobutene (**2b**) itself. This reactivity difference is to be expected since the internal alkenes in oligo-**3b** are more electron rich (and more numerous) than the double bond in dicyanobutene (**2b**). To test this plan, a 20:1 ratio of **1**:**2b** (in CH_2Cl_2) was incubated with 2 mol % **G2** for ~1 h. Both COD and the CTA were fully consumed (and the solution was only slightly viscous). Introduction of an additional 180 parts of COD (**1**) and continued heating at 40 °C for ~6 h resulted in complete consumption of the additional **1** and a sample of **3b** having an M_n of ~15 K. Thus, full conversion of both **1** and **2b** was achieved using this "two-stage" modification, but the targeted M_n or 21.6K was not achieved (for reasons discussed below).

Table 1. Dicyano (3b) and Dichloro (3a) Telechelic Polybutadienes (TPBs) Produced by Two-Stage (See Text) ROM Polymerization of 1,5-Cyclooctadiene (1) and the Chain Transfer Agent 2b or 2a, Respectively (Scheme 1)

entry	monomer:CTA ratio [COD (1)]/[CTA (2)]	theor M_n (K)	obsd M_n[c] (K)	corrected[g] theor M_n (K)
1	100:1[a]	10.8	8.6−10.7[d]	9.8
2	200:1[a]	21.6	14.6−16.5[e]	18.0
3	1000:1[b]	108	46.0[f]	54.0

[a] 1,4-Dicyano-2-butene (**2b**) as CTA, 2 mol % **G2**. [b] 1,4-Dichloro-2-butene (**2a**) as CTA, 4 mol % **G2**. [c] Measured by GPC using a PS standard and THF elution (universal calibration). [d] Five separate experiments. [e] Eight separate experiments. [f] One experiment. [g] Assuming 0.1 mol % VCH impurity as an additional CTA.

Scheme 1



Using the two-stage method, we prepared the set of polymers described in Table 1. The target (or theoretical) MW was determined by varying the ratio of monomer to CTA. We noticed that the observed M_n was consistently low in every experiment. Moreover, the higher the targeted MW the greater the deviation between theory and actual M_n. Polymerization had proceeded essentially to complete conversion (100% for all cases in entries 1 and 2 and ~98% for entry 3) as determined by monitoring the disappearance of COD (**1**) by ^{1}H NMR analysis. At this juncture[16] we recalled observing small amounts of resonances in the ^{1}H NMR spectra for terminal olefins (i.e., P−C*H*=C*H*$_2$) in a series of low-MW, oligomeric (~0.35K−5K) telechelics made by the usual one-step method. We hypothesized that the presence of these terminal alkenes and our inability to reach target MWs in polymerization reactions were related. Namely, if the COD monomer (or solvent) purity was compromised by the presence of acyclic, vinyl-containing species, these would act as competing CTAs, thereby increasing the number of chain termini while simultaneously introducing P−CH=CH_2 units. COD was analyzed carefully by ^{1}H NMR spectroscopy. As shown in Figure 1A, the COD was observed to contain 4-vinylcyclohexene (VCH), an isomer formed in the production of COD from butadiene, which constitutes an acyclic contaminant. COD purity and its impact on ROM polymerization synthesis of PBs[17a] and cyclic PBs[17b] have been described as a complicating factor in the context of preparation of higher MW polymers.

The amount of VCH in our samples was quantified either by comparative integration in the ^{1}H NMR spectrum of (i) the carbon-13 satellite peaks of the COD −C*H*= resonance vs the VCH vinylic proton resonances or (ii) the methine proton of cumene, a precisely known amount of which was added as an internal standard. Each ^{13}C*H*= satellite peak is 0.55 mol % of the four equivalent hydrogens (^{12}C*H*=) in COD. The spectrum in Figure 1A ($CDCl_3$ solution) is of a sample of commercial "redistilled" COD as received and specified as having a level of VCH of "0.4% max". By measuring the relative intensity of the ^{13}C satellite resonances at 5.42 and 5.73 ppm (vs TMS) vs the VCH resonances at 4.94 (RCH=C$H_a$$H_b$), 5.02 (RCH=C$H_a$$H_b$), and 5.84 (RC*H*=C$H_a$$H_b$),[18] we estimated that this sample contained about 0.1 mol % (~1000 ppm) of VCH relative to COD (i.e., [COD]/[VCH] ≈ 1000).[19] Considering this level of VCH and the fact that it would serve as an undesired CTA, we recalculated the "corrected theoretical" M_ns that are listed in the final column in Table 1. These agree well with the experimental results, supporting the hypothesis that COD purity is a critical issue.[17b]

Strategies to reduce the amount of VCH impurity from the monomer COD were examined. Atmospheric boiling points are ca. 131 and 150 °C. Careful fractional distillation (through a 50 cm Vigreaux column) removed ≤50% (i.e., still >500 ppm) of the VCH, so yet more

Table 2. Synthesis of Telechelic Polybutadienes 3 Using Purified COD (1) and 1,4-Dicyano- (2b) or 1,4-Dichloro-2-butene (2a) by Two-Stage ROM Polymerization

CTA	monomer:CTA ratio [COD (**1**)]/[CTA (**2**)]	initiator (mol %)[a]	COD conv (%)	CTA conv (%)	calcd M_n[b] (K)	obsd M_n[c] (K)	PDI
2b	200:1	2	100	100	21.6	20.3	1.97
2b	400:1	3	100	100	43.2	39.8	1.57
2b	600:1	3	92.0	100	59.6	54.0	1.59
2b	800:1	4	92.7	100	80.0	74.5	1.80
2b	1000:1	4	88.5	100	95.6	90.3	1.79
2a	2000:1	5	87.8	100	190	196	1.37

[a] Based on CTA. [b] Theoretical $M_n \times$ COD % conversion. [c] Measured by GPC using a PS standard and THF elution (universal calibration).

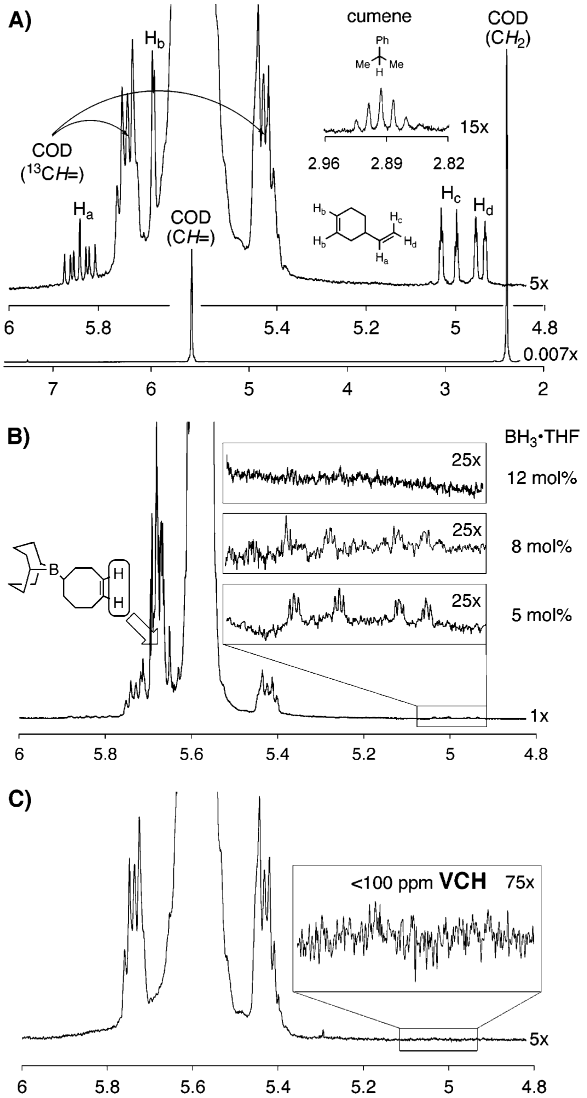
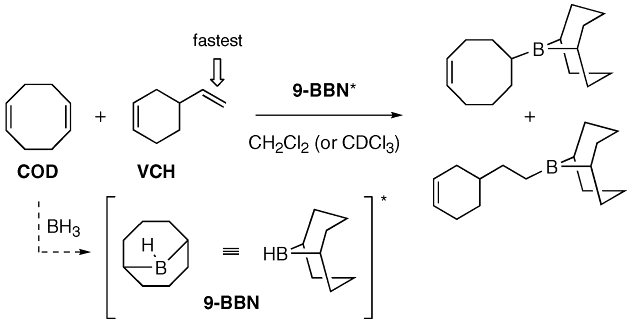


Figure 1. ¹H NMR spectra of (A) commercial COD, containing ~1000 ppm VCH, (B) commercial COD following treatment with increasing amounts of H_3B·THF, and (C) purified COD (<100 ppm VCH) following H_3B·THF treatment and distillation.

Scheme 2



efficient distillation would be required. We then studied selective reaction of the contaminating VCH as a means to its removal. Since hydroboration of terminal (monosubstituted) alkenes is known to proceed much faster than that of internal (1,2-disubstituted) alkenes, we first chose the bulky borane, 9-borabicyclononane (9-BBN; 1-hexene and cyclooctene are hydroborated by 9-BBN with a rate ratio of 14:1[20]). Reaction of COD with 5 mol % 9-BBN (Scheme 2 and Experimental Section) provided a sample of COD that still contained a detectable level of VCH. Increasing the 9-BBN load to 10 mol % provided COD in which the VCH could no longer be observed [estimated limit of detectability of VCH in COD by this NMR analysis was 100 ppm (i.e., [COD]/[VCH] ≥ 10 000)].

This approach, while effective, could ultimately be limited in scale by the expense of 9-BBN. Ironically, 9-BBN is prepared by hydroboration of COD by borane (BH_3) (Scheme 2).[21] We capitalized on that fact by treating the COD/VCH crude monomer directly with a solution of the (cheaper) borane·tetrahydrofuran complex (BH_3·THF) in THF (1 M). In the insets in Figure 1B are shown a series of spectra of samples of COD treated with increasing amounts of BH_3·THF. The full spectrum (4.8−6.0 ppm) and the expansion in the bottom inset (4.9−5.1 ppm) show the extent of VCH depletion following reaction with 5 mol % BH_3·THF. The spectra in the additional insets in Figure 1B show the continued reduction in VCH levels following reaction with 8 and 12 mol % BH_3·THF, respectively. The amount of VCH in each of these samples was best estimated by comparison of peak intensities of the terminal vinyl protons with those of the cumene methine proton [PhC*H*Me$_2$; the septet of that single proton in a sample containing 140 ppm (160 μM) of cumene is shown in the inset of Figure 1A[22]]. Following the treatment with 12 mol % borane, the COD was distilled directly from the reaction vessel to provide highly purified COD, the spectrum of which is shown in Figure 1C.

Using this source of “pure” COD, we reexamined the synthesis of telechelic dichloro- and dicyano-PBs (**3a** and **3b**) by ROM polymerization. The series of polymers shown in Table 2, having M_ns ranging from 20K to 200K, was prepared by the two-stage strategy. In the higher molecular weight cases the rate of conversion slowed since the reaction mixtures became quite viscous. Active carbene lifetime eventually became the limiting factor. Nonetheless, as the last two entries demonstrate, fairly high conversion (DP) was achieved using a 1000:1 (or 2000:1) [monomer]:[CTA] ratio using only 4 (or 5) mol % (based on [CTA]) of **G2**. The targeted M_n of 108K (or 216K) should have provided 95.6K (or 190K) PB (calcd M_n) at the observed 88.5% (or 87.8%) conversion. The observed (measured) M_n of 90.3K (or 196K) is in good agreement.

Finally, reduction of the terminal cyano groups to primary amines by lithium aluminum hydride ($LiAlH_4$) was studied. The reaction was first examined for low molecular weight TPBs (**3b**, 2K, 5K, and 10K). Excess $LiAlH_4$ was added to a THF solution of **3b**, and the mixture was stirred for 12 h at ambient temperature. Following workup and isolation (see Experimental Section), the ^1H NMR spectrum of the precipitated polymer indicated complete reduction. Namely, the chemical shift of the $\mathrm{C}H_2\mathrm{C{\equiv}N}$ adjacent to the cyano group (δ 3.09 ppm) in the starting polymer was absent, and a new resonance for the $\mathrm{C}H_2\mathrm{NH_2}$ methylene protons at δ 2.65–2.75 ppm (broad) had appeared. The resulting diamino-TPBs were examined by GPC, and no coupling byproducts were observable. While we are not yet in a position to assign with confidence a precise value to the functionality of these diamino-TPBs, there is not doubt but that it is “high”. Additionally, we have not fully assessed the efficiency of this nitrile to amine reduction for the higher MW TPBs. We are exploring various NMR-based strategies for reliably quantifying amine functionality at very low concentrations.

Conclusions

Ring-opening metathesis (ROM) polymerization of cyclooctadiene (COD) can be used to synthesize high molecular weight polybutadienes (PBs). As previously demonstrated, use of a difunctional, acyclic chain transfer agent (CTA) allows the preparation of telechelic PBs (TPBs). A limiting feature in using this strategy for production of high molecular weight TPBs is the monomer purity. That is, low levels of 4-vinylcyclohexene (VCH) impurity present in commercial samples of COD act as an additional CTA and interfere with achieving high molecular weight targets. Reaction purification of COD with borane agents and subsequent distillation effectively removes the VCH impurity to provide highly purified COD monomer. Because COD enters into ROM polymerization faster than the CTAs, not all CTA is consumed in some of these viscosity-limited preparations if the full charge of COD is present from the outset. Therefore, a two-stage approach was used: (i) a relatively low (20–40:1) molar ratio mixture of COD to CTA was initially copolymerized to full conversion, during which time the viscosity remained low; (ii) the remaining COD was then introduced to the living metathesis system to drive the TPBs to high molecular weights. The combined use of highly pure COD (≤100 ppm VCH) and this two-stage approach allows reproducible preparation of high and controlled molecular weight telechelic polybutadienes.

Experimental Section

Purification of COD Monomer by Hydroboration with 9-BBN Dimer. 9-BBN dimer (5.0 g of white solid, 0.041 mol) was dissolved in 50 mL of CH_2Cl_2 in a dry 250 mL flask under a N_2 atmosphere at ambient temperature. Commercial “redistilled” COD (50 mL, 44.1 g, 0.41 mol) was added by syringe over ~3 min. There was no indication of an exotherm. The mixture was stirred at ambient temperature for 12 h. The reaction progress was monitored by ^1H NMR spectroscopy. The vinyl peaks of VCH at 4.95, 5.01, and 5.85 ppm disappeared, indicating substantial consumption of the vinyl group in the VCH. CH_2Cl_2 was removed under reduced pressure. COD was vacuum-distilled (bp, 23–26 °C, ~0.5 mmHg) directly from the reaction pot through a 50 cm Vigreaux column to give 33.0 g (75.0%) of purified COD. Reanalysis by ^1H NMR spectroscopy showed a nondetectable level of VCH. Quantification by addition to the NMR sample of known amounts of cumene as an internal standard suggested that the level of detectability of the VCH was ca. 100 ppm (vs COD).

Purification of COD Monomer by Hydroboration with $H_3B{\cdot}THF$. COD (50 mL, 0.41 mol) was added to a dry 250 mL flask under a N_2 atmosphere, and 50 mL of a 1 M $H_3B{\cdot}THF$ solution (0.044 mol, 12 mol %) was added slowly via a syringe at 0 °C over 30 min. The mixture was stirred at ambient temperature for 1 h. THF was removed under reduced pressure. The COD was vacuum-distilled (bp, 26 °C, ~0.75 mmHg) through a 50 cm Vigreaux column. This sample contained 0.3% THF. The sample was redistilled (bp, 25–26 °C, ~0.65 mmHg) to give 26.5 g (60.1%) of COD, the purity of which was indistinguishable from that described above.

Typical Two-Stage Polymerization Procedure. In the first stage, second-generation Grubbs precatalyst (**G2**, 2.08 mg, 2.44 μmol) and 1,4-dicyano-2-butene (**2**, 8.65 mg, 0.082 mmol) were dissolved in CH_2Cl_2 (2 mL) in a 100 mL round-bottom flask under a N_2 atmosphere. COD (**1**, 0.4 mL, 3.26 mmol) was added at room temperature, and another 1 mL of CH_2Cl_2 was added. The resulting mixture was warmed to 40 °C and stirred for ~1 h.[23] Once complete consumption of **2** was verified, the remaining portion of neat COD (3.6 mL, 28 mmol) was added followed by additional CH_2Cl_2 (7 mL). This mixture was stirred at 40 °C for another 6 h. Additional CH_2Cl_2 (~30 mL) was added, the solution was poured into methanol (~0 °C), and the precipitated polymer was isolated by decantation and drying. ^1H NMR ($CDCl_3$): 5.41 (br, *trans*-$\mathrm{C}H{=}$), 5.36 (br, *cis*-$\mathrm{C}H{=}$), 3.06 (br, $-\mathrm{C}H_2\mathrm{CN}$), 2.08 (br, *cis*-$\mathrm{C}H_2-$), and 2.03 (br, *trans*-$\mathrm{C}H_2-$). ^{13}C NMR [$CDCl_3$ containing 0.1 M $Cr(acac)_3$]: 129.8 [$={C}_{\mathrm{trans}}\mathrm{H(CH_2)_2C_{cis}H}=$], 129.7 [$=C_{\mathrm{trans}}\mathrm{H(CH_2)_2}C_{\mathrm{trans}}\mathrm{H}=$], 129.3 [$=C_{\mathrm{cis}}\mathrm{H(CH_2)_2}C_{\mathrm{cis}}\mathrm{H}=$], 129.1 [$=C_{\mathrm{cis}}\mathrm{H(CH_2)_2C_{trans}H}=$], 117.8 (*cis*-$C\mathrm{N}$), 117.4 (*trans*-$C\mathrm{N}$), 32.92 [$=\mathrm{C_{trans}H}C\mathrm{H_2}-C\mathrm{H_2C_{trans}H}=$], 32.89 [$=\mathrm{C_{cis}H}C\mathrm{H_2-CH_2C_sH}=$], and 27.6 ($=\mathrm{C_{cis}H}C\mathrm{H_2}$).

Typical $LiAlH_4$ Reduction Procedure. In a 500 mL flask 20K cyano-terminated TPB **3b** (1.6 g, 0.08 mmol) was dissolved in 200 mL of dry THF under a N_2 atmosphere. Lithium aluminum hydride powder (121.6 mg, 3.2 mmol) was added in small portions over 15 min under a N_2 atmosphere. The reaction mixture was stirred at room temperature for 12 h and quenched by the sequential addition of water (0.12 mL), aqueous sodium hydroxide (0.12 mL, 15% NaOH), and water (0.36 mL). Filtration of the resulting slurry of pale gray solid through a plug of silica gel and washing of the column with additional THF gave a pale solution. Partial solvent removal, precipitation into cold methanol, and decantation of solvent gave the amino-terminated telechelic PB **3c**. ^1H NMR ($CDCl_3$): 5.41 (br, *trans*-$\mathrm{C}H{=}$), 5.36 (br, *cis*-$\mathrm{C}H{=}$), 2.75 (br, $-\mathrm{C}H_2\mathrm{NH_2}$), 2.08 (br, *cis*-$\mathrm{C}H_2-$), and 2.03 (br, *trans*-$\mathrm{C}H_2-$). ^{13}C NMR ($CDCl_3$): 130.4 [$=C_{\mathrm{trans}}\mathrm{H(CH_2)_2C_{cis}H}=$], 130.2 [$=C_{\mathrm{trans}}\mathrm{H(CH_2)_2}C_{\mathrm{trans}}\mathrm{H}=$], 129.8 [$=C_{\mathrm{cis}}\mathrm{H(CH_2)_2}C_{\mathrm{cis}}\mathrm{H}=$], 129.6 [$=C_{\mathrm{cis}}\mathrm{H(CH_2)_2C_{trans}H}=$], 42.2 ($C\mathrm{H_2NH_2}$), 32.93 [$=\mathrm{C_{trans}H}C\mathrm{H_2}-C\mathrm{H_2C_{trans}H}=$], 32.88 [$=\mathrm{C_{cis}H}C\mathrm{H_2-CH_2C_sH}=$], and 27.6 ($=\mathrm{C_{cis}H}C\mathrm{H_2}$).

Acknowledgment. This research was supported in part by the IPRIME (Industrial Partnership for Research in Interfacial and Materials Engineering) program at the University of Minnesota and in part by a grant awarded by the National Institutes of Health (CA-76497). We thank Mr. Jianbin Zhang and Dr. Qiwei Lu for help with GPC analyses.

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(14) There are other studies of ROM polymerization with COD in which the presence of 4-vinylcyclohexene (VCH) impurity may have limited the ultimate molecular weights (refs 13a and 13b).

(15) While we routinely assess the presence of carbene-containing species in olefin metathesis reactions by examining the region of the proton NMR spectrum where $L_nRu{=}CHR$ protons resonate (δ = 19.14 and 17.78 ppm for R = Ph and H, respectively, in $CDCl_3$), the concentrations used in these ROM polymerization experiments are too low for NMR analysis to be useful in the work described here.

(16) A linear regression analysis of the M_n data presented in Table 1 gave the first indication of an additional source of CTA. A plot of $1/M_n$ vs $1/M_n'$ gave a nonzero intercept that indicated the presence of a second CTA. $M_n = [\mathrm{COD}]/([\mathrm{CTA}] + [\mathrm{impurity}]) \times M_0 = 1/([\mathrm{CTA}]/[\mathrm{COD}] + [\mathrm{impurity}]/[\mathrm{COD}]) \times M_0 = 1/\{1/M_n' + [\mathrm{impurity}]/([\mathrm{COD}] \times M_0)\}$. $1/M_n = 1/M_n' + [\mathrm{impurity}]/([\mathrm{COD}] \times M_0)$, where M_n is the measured MW, M_n' is the theoretical MW, and M_0 is the MW of COD.

(17) (a) Nubel, P. O.; Yokelson, H. B.; Lutman, C. A.; Bouslag, W. G.; Behrends, R. T.; Runge, K. D. *J. Mol. Catal. A: Chem.* **1997**, *115*, 43−50. (b) Bielawski, C. W.; Benitez, D.; Grubbs, R. H. *J. Am. Chem. Soc.* **2003**, *125*, 8424−8425. In both of these studies VCH was identified and quantified by gas chromatography. Attempts to remove VCH from COD by careful distillation were not fully successful. In the latter study the monomer was changed to the trimeric 1,5,9-*cis*-*trans*-*trans*-cyclododecatriene (CDT), which is "free" of VCH.

(18) The resonance at 5.66 ppm due to the cyclic alkene protons in VCH is not reliable for quantification because of its partial overlap with the large resonance for the COD vinylic protons; see Figure 1A.

(19) We also observed a less intense (∼0.1 the size of the VCH), broad resonance at δ 2.79 attributable to the C(3) methine proton in 3-vinylcyclohexene.

(20) Brown, H. C.; Liotta, R.; Scouten, C. G. *J. Am. Chem. Soc.* **1976**, *98*, 5297−5301.

(21) Brown, H. C.; Prasad, J. V. N. V.; Zaidlewicz, M. *J. Org. Chem.* **1988**, *53*, 2911−2916.

(22) Notice that the outermost lines of the septet for the cumene methine proton shown in the Figure 1A inset are just discernible above the background noise, suggesting that the limit of detectability of a one-proton singlet under the conditions used to collect this spectrum would be ca. 2 ppm.

(23) The disappearance of 1,4-dicyano-2-butene (**2b**) was monitored by ^1H NMR spectroscopy. Complete consumption is especially important for synthesis of high molecular weight TPBs due to the small mole percent of metathesis precatalyst **G2** used. When the CTA was consumed, oligomers (**3b**) with molecular weight of ca. 4K were formed.

MA0493067