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Synthesis of Telechelic 1,4-Polybutadiene by Metathesis Reactions and Borane Monomers

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ABSTRACT: This paper describes a novel method for preparing telechelic 1,4-polybutadiene polymers which have functional groups, such as hydroxy and iodo groups, located at both ends of the polymer chains. The chemistry is based on borane-terminated 1,4-polybutadiene intermediates, in which the borane groups can be quantitatively converted to other functional groups under mild reaction conditions. The preparation of borane-terminated 1,4-polybutadiene involves two metathesis reactions, one being ring-opening metathesis polymerization of 1,5-cycooctadiene in conjunction with a borane monomer as the chain-transfer agent, the other involving the metathesis degradation of 1,4-polybutadine with the simultaneous functionalization of the broken chain end by borane monomer. Due to the good stability of borane moieties to transition-metal catalysts and good solubility of borane-containing polymers in hydrocarbon solution, both metathesis reactions are very effective in providing telechelic polymers with not only a high degree of functionalization but also controllable molecular weight.

Introduction

Telechelic polymers[1] with functional groups at both chain ends are a very interesting class of materials. They have several potential uses, including both theoretical (e.g. model network[2]) and commercial (e.g. liquid rubber[3]) applications. In the past, this type of polymer was mostly prepared by terminating living polymers with suitable reagents in conjunction with the use of difunctional initiators[4,5] or functionally substituted initiators.[6] The anionic,[7] cationic,[8] and recently metathesis[9,10] living polymerizations are particularly preferred because these routes provide well-defined polymers with a high degree of functional groups at both ends of the polymer chain. However, these processes are limited because only a few monomers undergo living propagation.

It is well-known that metal–carbene metathesis catalysts react rapidly and reversibly with olefins by forming metallocyclobutane[11] intermediates. This reaction mechanism has been successfully applied to ring-opening metathesis polymerization (ROMP) and olefin-exchange reactions. The recent development of Lewis acid-free alkylidene complexes[12] with well-characterized molecular structures, such as $W(CHtBu)(NAr)(OCCH_3(CF_3)_2)_2$, has significantly broadened the understanding of the overall chemistry as well as facilitating the preparation of well-defined polymer structures. In addition, chain-transfer reaction in ROMP has also been reported. For example, styrene and 1,3-dienes are effective chain-transfer agents[13] in norbornene polymerization using $Mo(CHtBu)(NAr)(OtBu)_2$ catalyst. On the other hand, the dynamic equilibrium of olefin-exchange reactions has also been applied to the degradation[14,15] of polymer chains by mixing an unsaturated polymer with a small olefin molecule. The resulting products are low molecular weight polymers with some cyclic compounds. The chemistry was further extended by incorporating this metathesis exchange reaction into the metathesis ring-opening polymerization. With the use of organic silicon-containing olefins[16] in ring-opening polymerization of a cyclic olefin, a polymer with a terminal silicon group was obtained. However, the yield was generally quite low and the product usually contained some insoluble gel due to side reactions. Moreover, the silyl end group is not a versatile intermediate. It is difficult to convert the silyl polymer to other functional polymers under simple mild chemical reactions.

In general, transition-metal catalysts, including olefin metathesis catalysts, possess only limited stability[17,18] toward functional groups that contain heteroatoms such as O, S, and N. This has hampered their use for the polymerization of monomers that contain such functionalities. Our approach to functional polymers has been to develop borane monomers[19] that do not destroy the activity of transition-metal catalysts and are quantitatively converted to functional polymers following polymerization. This approach allows us to employ a much wider range of highly reactive catalysts that are usually very susceptible to functional groups. A broad range of new functionalized polymers prepared by metathesis[20,21] and Ziegler–Natta[22] catalysts has been obtained. The advantages of this chemistry are (a) the stability of the borane moiety to transition-metal catalysts, (b) the solubility of borane compounds in hydrocarbon solvents (hexane and toluene) used in transition-metal polymerizations, and (c) the versatility of borane groups, which can be transformed to a remarkable variety of functionalities under mild reaction conditions.

Results and Discussion

In this paper, the advantages of borane monomers and metathesis catalysts are extended to the preparation of telechelic 1,4-polybutadiene which has functional groups at both ends of the polymer chain. The chemistry is based on the synthesis of α,ω-bis(borane)-1,4-polybutadiene which can then be quantitatively converted to the corresponding telechelic 1,4-polybutadiene polymers with various functional groups. Two processes have been found to be very effective in introducing a borane group to the chain ends of 1,4-polybutadiene. One involves ring-opening metathesis polymerization (ROMP) of 1,5-cyclooctadiene with the use of a chain-transfer agent which contains a borane group, while the other is the metathesis degradation of 1,4-polybutadiene with simultaneous introduction of borane groups at the broken chain ends.

ROMP of 1,5-Cyclooctadiene and Borane Monomer Containing α,ω-Bis(borane) and an Internal Double Bond. To achieve the preparation of telechelic polymers,

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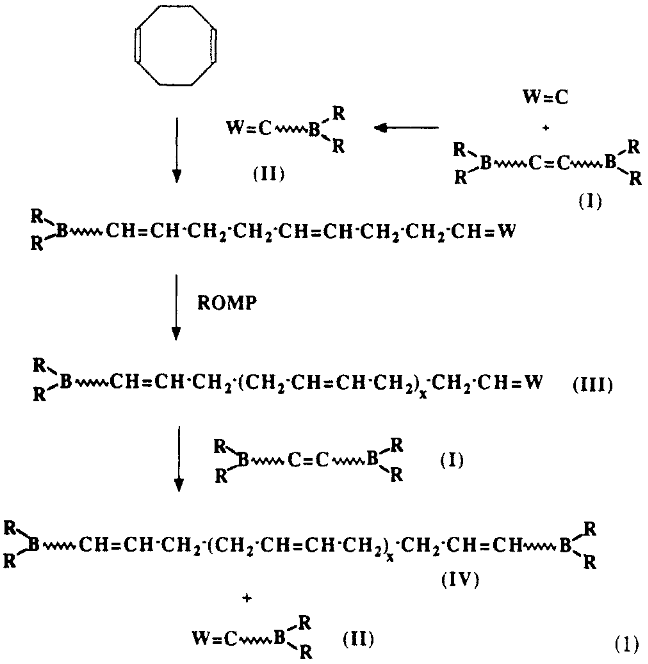
some borane-containing olefins were investigated. A borane monomer containing one internal double bond and substituted with two α,ω borane groups, such as 1,10-bis(9-BBN)-5-decene, is the preferred choice. This reagent was obtained by dihydroboration of 1,5,9-decatriene with 2 equiv of dialkylborane such as 9-borabicyclononane (9-BBN), which has good hydroboration selectivity toward α-olefins. The ^{1}H NMR spectrum of the resulting 1,10-bis(9-BBN)-5-decene shows only one peak in the olefin region (at 5.4 ppm), corresponding to an internal double bond, with no detectable signal for α-olefin.

The borane monomer I, 1,10-bis(9-BBN)-5-decene, was then employed in the ROMP polymerization of 1,5-cyclooctadiene, as shown in eq 1. In this reaction, the conventional tungsten carbene catalyst (W=C) was prepared from WCl_6 and Me_4Sn reagents before charging into the reaction mixture of 1,5-cyclooctadiene and 1,10-bis(9-BBN)-5-decene. One can expect that some tungsten carbene active sites react with borane monomer I to yield a new tungsten carbene molecule (II) which contains a borane group as part of the alkylidene ligand. The catalyst (II) then initiates ROMP of 1,5-cyclooctadiene to give 1,4-polybutadiene (III) which has one terminal borane group and a tungsten carbene at the other chain end. Further metathesis reaction between polymer III and borane monomer I will result in a telechelic polymer (IV) by introducing another borane group to the chain end. The tungsten carbene catalyst (II) with a terminal borane group is regenerated at the end of the reaction cycle. Therefore, the same ROMP and functionalization reactions can continuously take place in a catalytic fashion. It is certainly possible to write an alternative reaction path, in which the W=C catalyst reacts with 1,5-cyclooctadiene at the beginning of the reaction cycle. In this route, the first polymer generated has one imperfect chain end which is an α-olefin. To minimize this defect, one can use a minimum amount of catalyst; in this work the monomer/catalyst mole ratio was usually 500/1. In addition, the further equilibrium reaction between α-olefin, which is much more reactive than an internal double bond, and tungsten carbene catalyst (II) can complete the chain end with a borane group.



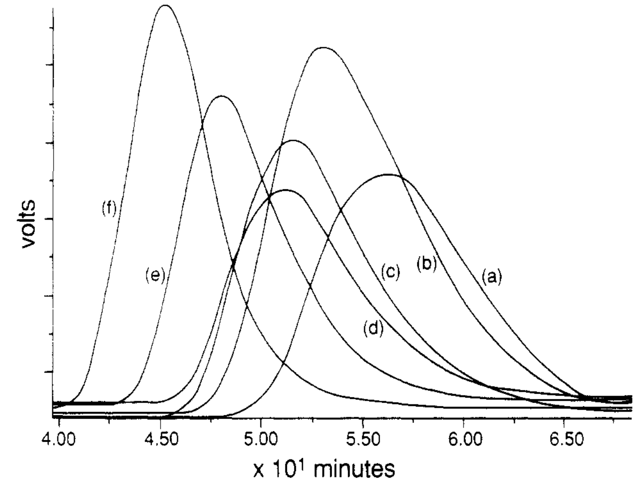


Figure 1. GPC curves of borane groups terminated 1,4-polybutadiene prepared by ROMP of 1,5-cyclooctadiene (COD) and 1,10-bis(9-BBN)-5-decene (I) with various molar ratios: (a) 10/1, (b) 20/1, (c) 35/1, (d) 50/1, (e) 100/1, and (f) 100/0.

Table I
Properties of α,ω-Dihydroxy-1,4-polybutadiene Prepared by ROMP Reaction, Followed by Oxidation

sample[a]	COD/diborane[b]	M_n	M_w	M_w/M_n	yield (%)
I-A	10/1	6 900	14 300	2.1	70
I-B	20/1	12 600	25 400	2.0	67
I-C	35/1	18 700	37 800	2.0	75
I-D	50/1	21 000	42 700	2.1	72
I-E	100/1	51 050	92 700	1.8	75
I-F	100/0	122 200	245 000	2.0	72

[a] ROMP catalyst, WCl_6/Me_4Sn, COD/W = 500/1; 2-h reaction time. [b] Diborane, 1,10-bis(9-BBN)-5-decene; COD, 1,5-cyclooctadiene.

A series of polymerizations were carried out at room temperature by varying the mole ratio of monomer and chain-transfer agent. In general, the average molecular weight of polymer reached a maximum within 1 h, then decreasing to an equilibrium value. On the other hand, the maximum yields (70–80%) were obtained after 2 h. Figure 1 shows GPC curves of resulting telechelic polymers by varying the mole ratio of 1,5-cyclooctadiene and 1,10-bis(9-BBN)-5-decene; each reaction was performed for 2 h. As one might expect, the molecular weight of each polymer chain is dependent on the molar ratio of 1,5-cyclooctadiene and chain-transfer agent, 1,10-bis(9-BBN)-5-decene. The higher the concentration of chain-transfer agent used, the lower the molecular weight of resulting polymer obtained. Due to the very high susceptibility of alkylboranes to air oxidation, the borane group terminated 1,4-polybutadiene was not structurally characterized but was instead quantitatively oxidized under mild conditions, using alkaline H_2O_2, to yield α,ω-dihydroxy-1,4-polybutadiene. Table I summarizes the experimental results. Overall, the molecular weights of telechelic polymers were higher than the theoretical value after 2-h reaction time. In sample I-A, we would expect each polymer chain to have 20 repeat units of 1,4-butadiene, instead of the more than 120 units as the experiment suggests. The chain-transfer reaction to the internal double bond in the borane monomer is significantly slower than the metathesis reaction of the internal double bonds in 1,5-cyclooctadiene (see below). The ring strain of 1,5-cyclooctadiene obviously contributes to the difference. The molecular weight of polymer continuously decreased to an equilibrium value which was usually more than twice the theoretical value. On the other hand, about 70% yield was obtained within 2-h reaction time in all cases, despite the significant difference in the concentration of 1,10-bis(9-BBN)-5-decene chain-transfer agent. This indicates ROMP was

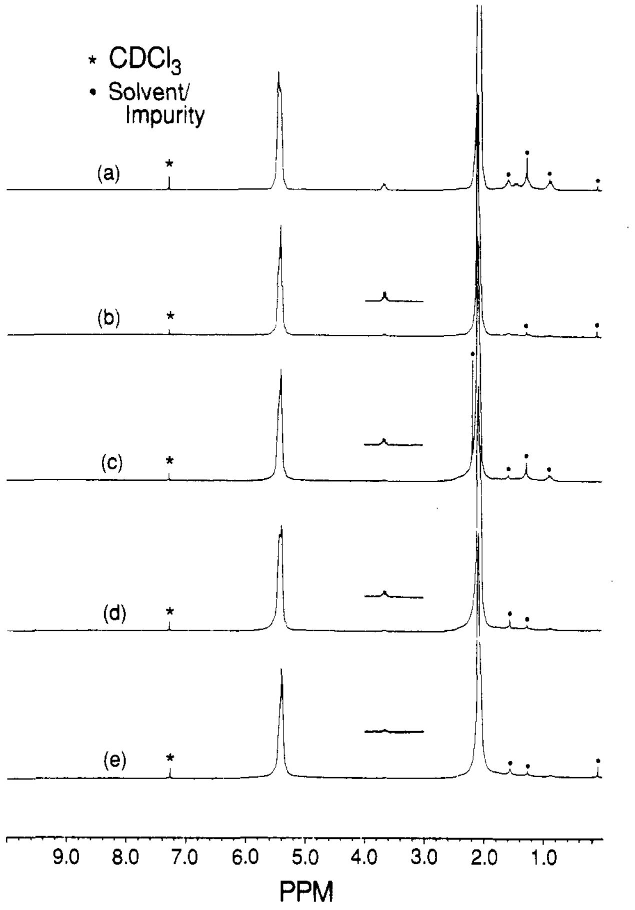
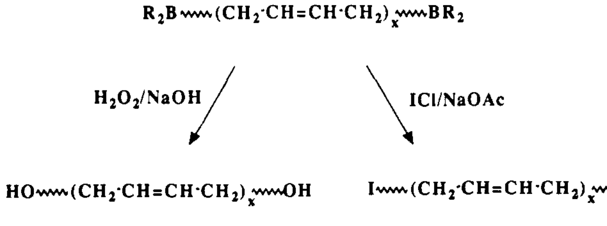


Figure 2. ^{1}H NMR spectra of α,ω-dihydroxy-1,4-polybutadiene polymers: (a) sample I-A, (b) sample I-B, (c) sample I-C, (d) sample I-D, and (e) sample I-E.

not significantly interrupted by the chain-transfer reaction, the rates of polymerization for both tungsten carbene species in II and III are almost identical. It is also interesting to note that the molecular weight distribution of telechelic polymers is very close to 2, the same as 1,4-polybutadiene in pure ROMP polymerization.

Telechelic 1,4-Polybutadiene with Hydroxy and Iodine Terminal Groups. One of the important advantages of the borane functional group is its versatility. The quantitative interconversion of borane to a broad range of functional groups can be achieved under mild reaction conditions. Due to the good solubility of borane-containing polymers, the interconversion reactions in polymeric cases are very similar to those in the corresponding small molecules. Equation 2 shows two reactions for the preparation of α,ω-dihydroxy-1,4-polybutadiene and α,ω-diiodo-1,4-polybutadiene from α,ω-bis(9-BBN)-1,4-polybutadiene.



(2)

Figure 2 compares the ^{1}H NMR spectra of α,ω-dihydroxy-1,4-polybutadiene shown in Table I. The new peak at $\delta = 3.6$ ppm is attributed to that of methylene unit bearing a primary hydroxy group. With the combination of GPC and ^{1}H NMR results, one can theoretically calculate the functionality number, the average number of functional groups in each polymer chain. This calculation is reasonably accurate for sample I-A, with relatively lower molecular weight and higher functional group concentration. The peak intensity corresponds to that of telechelic 1,4-polybutadiene with two primary hydroxy groups. There is no peak corresponding to α-olefin (5–5.9 ppm) which would represent unfunctionalized chain ends.

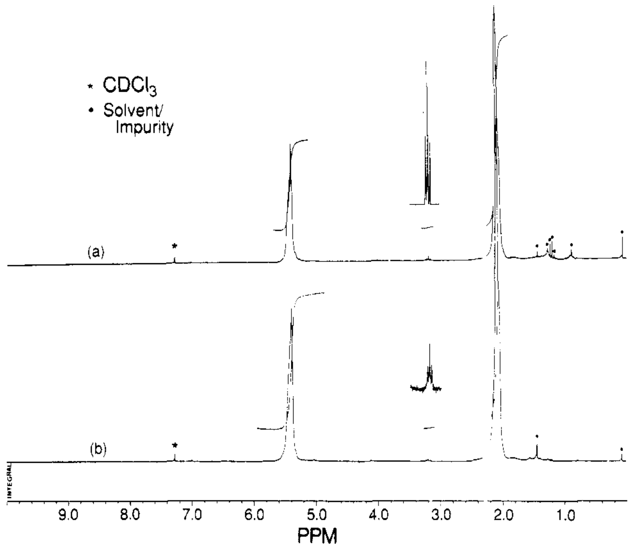


Figure 3. ^{1}H NMR spectra of two α,ω-diiodo-1,4-polybutadienes prepared by ROMP of 1,5-cyclooctadiene and 1,10-bis(9-BBN)-5-decene with molar ratios of COD/(I) of (a) 10/1, (b) 20/1.

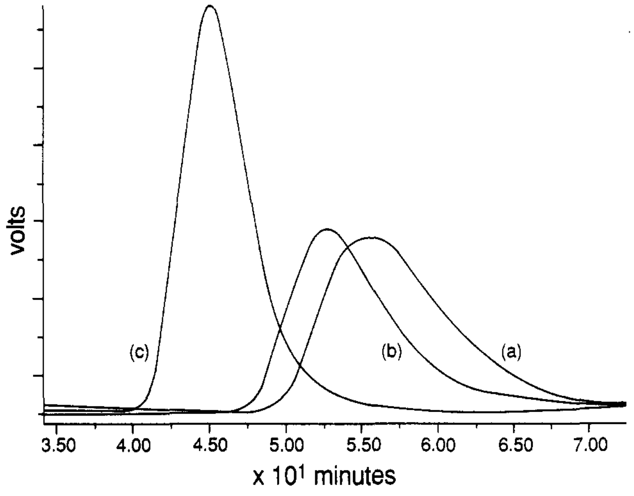


Figure 4. (a, b) Comparison of GPC curves between two α,ω-diiodo-1,4-polybutadienes. (c) Pure 1,4-polybutadiene prepared by ROMP of 1,5-cyclooctadiene.

The borane groups in α,ω-bis(9-BBN)-1,4-polybutadiene also react readily with iodide ion in the presence of mild oxidizing agents. The iodine monochloride[23] is usually generated in situ by reacting sodium iodide and methanolic chloramine-T. As is known, the primary alkyl group reacts preferentially to yield primary alkyl iodide. The use of the conveniently prepared α,ω-bis(9-BBN)-1,4-polybutadiene offers the advantages of selective iodination[23] with quantitative yield. Figure 3 shows the ^{1}H NMR spectra of two α,ω-diiodo-1,4-polybutadiene polymers which were obtained from the interconversion of sample I-A and I-B, respectively. The triplet peak at 3.2 ppm is clear evidence of primary alkyl iodide groups and the peak intensity also indicates two functional groups per polymer chain. The GPC curves of two iodo terminal 1,4-polybutadienes are shown in Figure 4. Similar molecular weight distribution ($M_w/M_n \sim 2$) was obtained as for the hydroxy group terminated polymer cases. It is interesting to compare

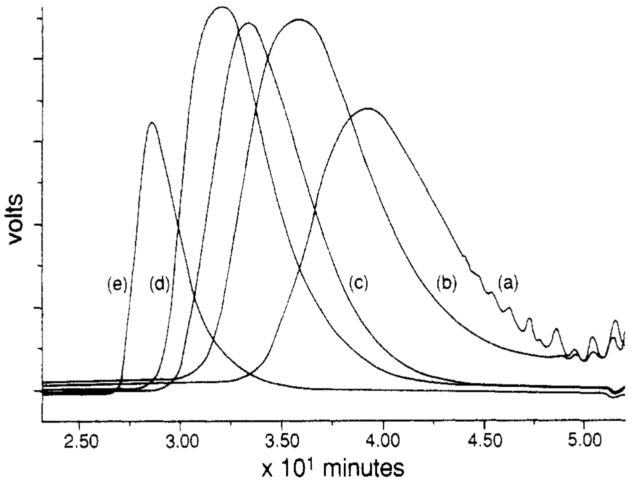


Figure 5. GPC curves of telechelic 1,4-polybutadiene prepared by ROMP of 1,5-cyclooctadiene and 6-(9-BBN)-1-hexene with various molar ratios: (a) 20/1, (b) 35/1, (c) 50/1, (d) 100/1, and (e) 100/0.

Table II
Summary of Hydroxy Group Terminated 1,4-Polybutadiene Prepared by ROMP and Oxidation Reactions

sample	COD/ borane[b]	M_n	M_w	M_w/M_n	yield (%)
II-A	20/1	2 200	4 500	2.0	65
II-B	35/1	4 900	11 600	2.3	65
II-C	50/1	12 200	23 720	1.9	72
II-D	100/1	18 300	37 100	2.0	73
II-E	100/0	122 200	245 000	2.0	72

[a] ROMP catalyst, WCl_6/Me_4Sn and COD/W = 500/1; 2-h reaction time. [b] Borane, 6-(9-BBN)-1-hexene; COD, 1,5-cyclooctadiene.

the GPC curves between Figure 1a and Figure 4a, both converted from the same α,ω-bis(9-BBN)-1,4-polybutadiene (sample I-A). Two curves are almost identical, which implies the "clean" interconversion reaction of the borane (alkyl-9-borabicyclononane) group.[24,25] The average molecular structure of this telechelic 1,4-polybutadiene is

$$F\text{-}(CH_2)_3\text{-}(CH_2\text{-}CH{=}CH\text{-}CH_2)_{120}\text{-}(CH_2)_3\text{-}F$$

F: -OH, -I

which contains about 120 repeat units of 1,4-butadiene and two primary functional groups, hydroxy or iodo groups, located at each polymer chain end. A telechelic polymer with a molecular weight in this range is a very useful material, for example, as the building block (soft segment) for the preparation of multiple block copolymers and three-dimensional rubber networks.

ROMP of 1,5-Cyclooctadiene and Borane Monomers Containing α-Olefin. It can also be predicted that similar ROMP of 1,5-cyclooctadiene and chain-transfer reaction would take place when other borane monomers, such as ω-borane-α-olefin, are employed. These monomers were generally prepared by monohydroboration of α,ω-dienes with dialkylboranes. Usually, excess diene was used to minimize the dihydroboration products. Preferred dienes are 1,4-pentadiene, 1,5-hexadiene, and 1,7-octadiene. Figure 5 shows the GPC curves of resulting 1,4-polybutadiene with various concentrations of chain-transfer agent, 6-(9-BBN)-1-hexene. The reaction was carried out under the same reaction conditions as the previous cases, using WCl_6/Me_4Sn catalyst, a 1,5-cyclooctadiene/tungsten mole ratio of 500/1, and 2-h reaction time at room temperature. Table II summarizes the details of experimental results. In general, the molecular weight of the borane group terminated 1,4-polybutadiene is significantly lower in 6-(9-BBN)-1-hexene cases, compared with the same reaction conditions using 1,10-bis(9-BBN)-5-decene. In fact, some oligomer peaks shown in Figure 6a indicate effective chain-transfer reaction during the polymerization. On the basis of the resulting molecular weight, the selectivity of metathesis reactions between 1,5-cyclooctadiene and 6-(9-BBN)-1-hexene is quite small. It is interesting to estimate the reactivity difference between α-olefin and internal olefin in two chain-transfer agents. As shown in eq 3, the propagating site can either continue the propagation reaction or react with chain-transfer agent to stop the polymer chain growth. Obviously, the depolymerization reaction is also involved during these reactions. In a qualitative calculation, it is reasonable to assume that the effect of depolymerization on the molecular weight of polymer is similar in all cases, independent of the chain-transfer agent. Without considering depolymerization, the degree of polymerization (X_n) of polymer is governed by $1/X_n = 1/(X_n)_0 + C_{tr}[CT]/[M]$, where [CT]/[M] is the mole ratio of borane monomer to 1,5-cyclooctadiene. $(X_n)_0$ represents the degree of polymerization without chain-transfer reaction and C_{tr} (k_{tr}/k_p) is the chain-transfer constant. $(X_n)_0$ is about 1130, which is calculated from sample F in Table I. For a qualitative evaluation of the chain-transfer constants for each reaction, one could simplify calculations by assuming constant [CT]/[M] during each reaction. Figure 6 is a plot of $1/X_n$ vs [CT]/[M] for the different reactions. The slope of the straight line gives a rough estimation of C_{tr}. By no means are the lines perfect, but nevertheless they are useful as references. C_{tr1} (k_{tr1}/k_p) is in the range 0.05–0.07 and $C_{tr2}(k_{tr2}/k_p)$ is in the range 0.4–0.8. It is quite obvious the order of rate constant of reactions is $k_p \gtrsim k_{tr2} \gg k_{tr1}$. It is not surprising to see that the metathesis reaction is about 1 order of magnitude more favorable for α-olefin than for internal olefin in acyclic olefins. However, the ring strain in 1,5-cyclooctadiene still offers greater metathesis reactivity compared to acyclic cases.

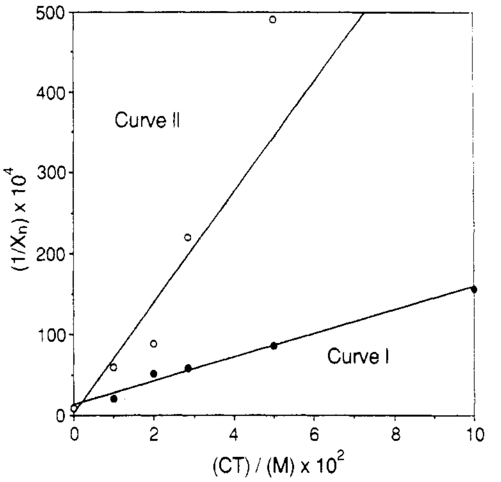
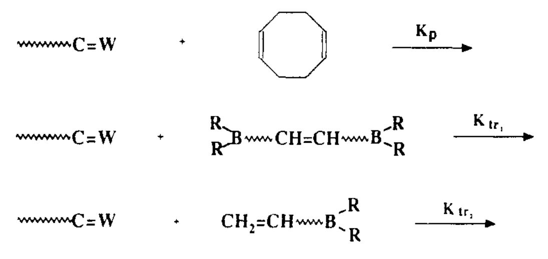


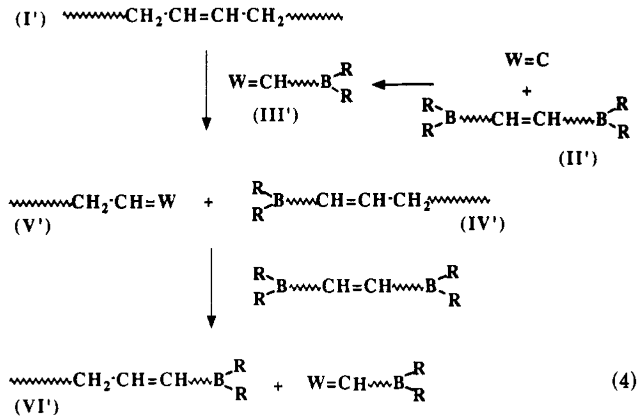
Figure 6. Plot of $1/X_n$ vs [CT]/[M], the slope of the straight line is C_{tr}.



(3)

Figure 7 shows the ^{1}H NMR spectra of the resulting hydroxy-terminated 1,4-polybutadienes which are from the same samples as in Table II. The same peak at 3.6 ppm, corresponding to the methylene unit bearing a primary hydroxy group, is shown in all samples. However, two peaks centered at 5 and 5.9 ppm, corresponding to α-olefins, are also present. The peak intensity ratio between the peaks at 5 and 3.6 ppm was used to calculate the ratio of α-olefins and hydroxy groups at the polymer chain ends. A significant number of unfunctionalized chain ends exist in all polymers in Table II. The undesirable side reaction, resulting in α-olefin chain ends as well as the product fractionations, will be discussed later.

Metathesis Degradation of 1,4-Polybutadiene Using Borane Monomers Containing α,ω-Bis(borane) and an Internal Double Bond. The other approach to preparing borane group terminated 1,4-polybutadiene is by the metathesis degradation of 1,4-polybutadiene and consequent functionalization of the broken chain ends with borane groups. The overall reaction mechanism is an olefin-exchange reaction between 1,4-polybutadiene and a borane monomer, such as 1,10-bis(9-BBN)-5-decene. The detailed steps are illustrated in eq 4.



(4)

During the reversible metathesis reaction between 1,4-polybutadiene and tungsten carbene catalyst, one can expect that some tungsten carbene active sites react with borane monomers II′ to result in the new tungsten carbene molecule III′ which contains a borane group as the alkylidene ligand. The catalyst (III′) then undergoes the metathesis reaction with the internal double bonds in 1,4-polybutadiene (I′). In this metathesis reaction, not only is the polymer chain broken but a borane group is also introduced to one of the broken chain ends (IV′). The other broken chain end simultaneously generates a new tungsten carbene (V′) which can subsequently react with borane monomer II′. This reaction functionalizes the other half of the broken chain ends (VI′). Overall, both broken chain ends are functionalized by borane groups in each polymer chain scission reaction. The tungsten carbene catalyst (III′), containing the borane group, is regenerated at the end of the reaction cycle. Therefore, the same degradation and functionalization reactions can continuously take place in catalytic fashion. As one can expect, each polymer chain has two borane-terminated chain ends and the molecular weight of the polymer decreases during the reaction.

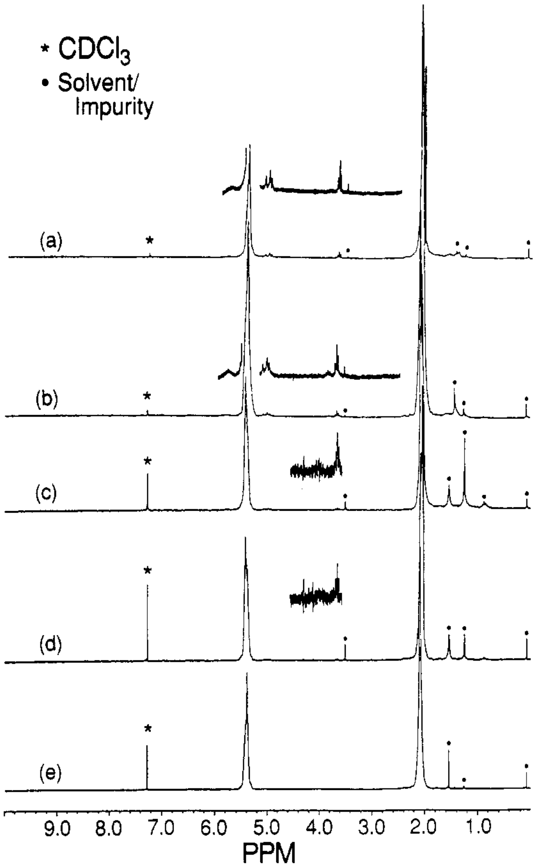


Figure 7. ^{1}H NMR spectra the hydroxy group terminated 1,4-polybutadienes: (a) sample II-A, (b) sample II-B, (c) sample II-C, (d) sample II-D, and (e) sample II-E.

Table III
Summary of α,ω-Dihydroxy-1,4-polybutadiene Prepared by Metathesis Degradation under Various Reaction Conditions

sample[a]	butadiene[b]/ catalyst[a]	butadiene[b]/ monomer[c]	M_n	M_w/M_n
III-A	100/1	6/1	1000	1.7
III-B	100/1	10/1	1200	2.2
III-C	100/1	20/1	1200	2.4
III-D	250/1	6/1	4300	2.1
III-E	250/1	10/1	7900	2.1

[a] The reaction time for all samples is 0.5 h using WCl_6/Me_4Sn as catalyst. [b] Butadiene units in 1,4-polybutadiene which has molecular weights of M_w = 436 000 and M_n = 172 000. [c] Monomer is 1,10-bis(9-BBN)-5-decene.

As expected, the borane group terminated 1,4-polybutadiene can be interconverted to α,ω-dihydroxy-1,4-polybutadiene or α,ω-diiodo-1,4-polybutadiene. Table III summarizes the experimental results of the olefin-exchange reaction between 1,4-polybutadiene, with $M_n \sim 170\,000$, and 1,10-bis(9-BBN)-5-decene as the borane monomer. The reaction was very effective even under mild reaction conditions. In most cases, the molecular weight of 1,4-polybutadiene rapidly decreased to a few thousand, yielding liquid oligomers within a 0.5-h reaction time. For example in sample III-A, the molecular weight of 1,4-polybutadiene decreased from nearly 200 000 to about 1000 in 0.5 h. In other words, every polymer chain on average was degraded about 200 times. To ensure an understanding of the reaction, two control reactions were simultaneously performed. One was done under the same metathesis reaction conditions without borane monomer. Only a slight change in molecular weight was observed even after a long reaction time, the equilibrium state was reached at a molecular weight (M_n) of about 70 000. The other experiment was carried out by replacing 1,10-bis(9-BBN)-5-decene with 1-hexene. The same molecular weight reduction pattern was observed without the functionalization reaction. These comparisons clearly demonstrate the unique features of borane monomers and polymers, not only no catalyst deactivation in the me-

Table IV
Summary of Molecular Weight Changes during Metathesis Degradation[a] of *cis*-1,4-Polybutadiene

sample	reaction time (min)	M_w[b]	M_n	polydispersity
IV-A	0	436 300	172 100	2.5
IV-B	8	82 500	39 600	2.1
IV-C	15	14 000	8 000	1.7
IV-D	30	1 900	1 000	1.9

[a] Reaction conditions: catalyst, WCl_6/Me_4Sn; butadiene units/W = 100/1; butadiene units/6-(9-BBN)-1-hexene = 6/1. [b] Molecular weight calculation was based on the calibration curve of polybutadiene (35% cis, 55% trans, and 10% 1,2-isomers).

tathesis reaction but also good solubility in hydrocarbon solvents, which ensures effective and homogeneous reaction under mild reaction conditions.

The resulting α,ω-dihydroxy-1,4-polybutadiene were characterized by ^1H NMR spectra which are almost the same as those in Figure 2, with a peak at $\delta = 3.6$ ppm, corresponding to methylene unit bearing a primary hydroxyl group. The peak intensity is inversely proportional to the molecular weight of the polymer. No peaks corresponding to α-olefin can be detected. The combination of GPC and ^1H NMR results allow one to calculate the functionality number of each polymer chain, which is about 2 in all cases. However, it is believed that a very low concentration of unfunctionalized chain ends may still exist in the final product, which arises from the chain ends of the original 1,4-polybutadiene. In sample III-A, this defect is estimated to be below 0.5 mol %.

Metathesis Degradation of 1,4-Polybutadiene Using Borane Monomers Containing α-Olefin and Terminal Borane Groups. Using other borane monomers containing α-olefin, such as 6-(9-BBN)-1-hexene, the same polymer degradation[26] with a rapid decrease in polymer molecular weight was observed, as shown in Table IV. Figure 8 shows ^1H NMR spectra of hydroxyl group terminated 1,4-polybutadiene. A peak at $\delta = 3.6$ ppm, corresponding to the primary hydroxyl group, increases in intensity along with the reaction time and is inversely proportional to the molecular weight of polymer. However, the peaks centered at 5 and 5.9 ppm, corresponding to α-olefins, are also shown in all spectra. In general, the spectra are very similar to those in Figure 6. Some polymer chains have only one or no functional group.

Column chromatography with gradient solvent polarity was used to fractionate the polymer mixtures. This technique is suitable for low molecular weight (<2000) polymers. Table V shows the fractionation results of sample IV-D which was separated by hexane/ether mixed solvent. As expected, the molecular weight distribution in each fraction is significantly reduced from that of the original mixture. In general, the functionality number increases with an increase in solvent polarity. Only a small portion of polymer (18%, fractions 1 and 2) has almost no functional group. The middle portions (44%, fractions 3 to 5) have functionalities between 1 and 2. The final portion (38%, the sum of fractions 6 and 7) of polymer has a functionality number of about 2, which contains on average 20 repeat units of 1,4-butadiene and one primary alcohol group at each polymer chain end.

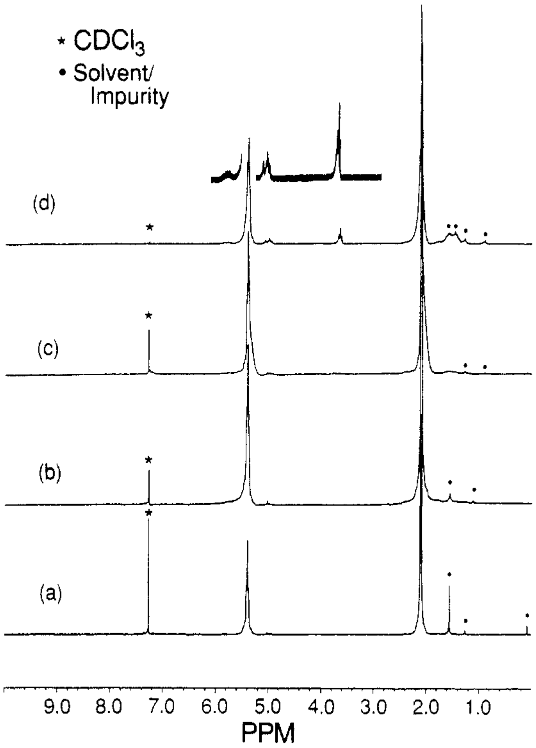
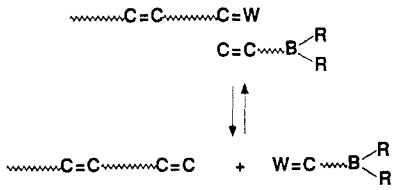


Figure 8. Comparison of ^1H NMR spectra between (a) *cis*-1,4-polybutadiene and hydroxy group terminated 1,4-polybutadiene with various metathesis degradation times: (b) 8 min, (c) 15 min, and (d) 30 min.

Table V
Summary of Column Fractionation of Sample IV-D

fraction	solvent (hexane/ether)	yield (g)	M_n	M_w/M_n	functionality
1	100/0	0.25	400	1.3	<0.1
2	99/1	0.568	990	1.6	0.3
3	98/2	0.251	1130	1.9	~1
4	95/5	0.911	1640	1.3	~1
5	90/10	0.768	870	1.2	1.6
6	70/30	1.12	870	1.9	~2
7	0/100	0.56	1040	1.9	~2

It is certainly very important to know the molecular structure of the imperfect fractions (fractions 1–5) which have unfunctionalized chain ends. It is very interesting to note the unfunctionalized chain ends are α-olefin groups. They are clearly shown in Figure 9, a comparison of ^1H NMR spectra between fraction 6 and fraction 1. Figure 9b is almost identical with Figure 2a, indicating perfect α,ω-dihydroxy-1,4-polybutadiene for fraction 6. On the other hand, the ^1H NMR spectrum of fraction 1 shows no peak indicative of a primary hydroxy group and two new chemical shifts around 5 and 5.9 ppm for α-olefin groups at unfunctionalized chain ends. The α-olefin groups may result from the reaction between tungsten carbene at the polymer chain end and α-olefin in the borane monomer with the undesirable coupling reaction, as shown in eq 5.



(5)

Although this side reaction can be precluded to some extent by causing the dimerization of the α-olefin species, 6-(9-BBN)-1-hexene, by constantly removing the byproduct ethylene and subsequent addition to the polymer solution, the final telechelic polymer never reached acceptable functionality levels without fractionation.

Experimental Section

Materials and Instruments. The 9-borabicyclononane (9-BBN) crystal was used as received from Aldrich. HPLC grade

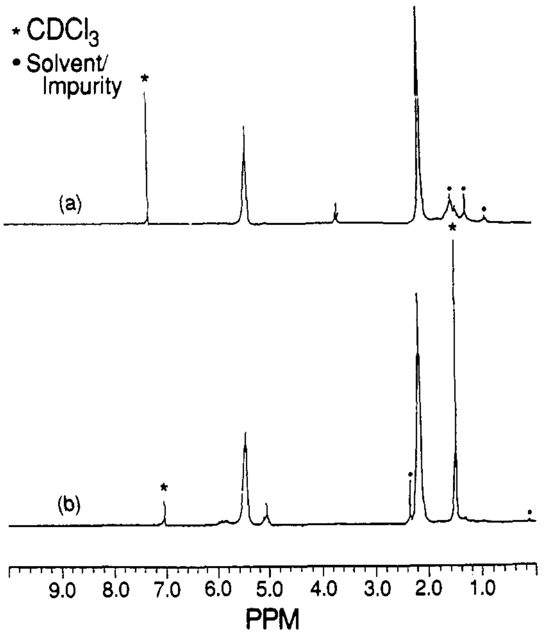


Figure 9. Comparison of ^{1}H NMR spectra between (a) fraction 1 and (b) fraction 6.

toluene and THF were distilled from sodium anthracenide. 2-Propanol, 1,5-cyclooctadiene, and 1,5-hexadiene were dried with CaH_2 and distilled under N_2. All the metathesis reactions were carried out in an inert atmosphere glovebox or on a Schlenk line. The molecular weight of the polybutadiene was determined using a Waters GPC. The columns used were Phenomenex Phenogel of 10^5, 10^4, 10^3, 500, and 100 Å. A flow rate of 0.7 mL/min was used, and the mobile phase was THF. Narrow molecular weight polystyrene samples were used as standards. All the solution NMR's were done on a Bruker WP 200 machine.

Synthesis of 6-(9-BBN)-1-hexene and 1,10-Bis(9-BBN)-5-decene. This reaction is based on the monohydroboration of 1,5-hexadiene. In an argon-filled drybox, 15.092 g (0.124 mol) of 9-BBN (9-borabicyclononane) dimer crystals was dissolved in 100 mL of dry, degassed THF, and the solution was added dropwise over 2 h to 44.515 g (0.542 mol) of 1,5-hexadiene. The solution was stirred at room temperature for 5 h before any unreacted diene and the THF were removed under vacuum. Another 10.754 g (0.088 mol) of 9-BBN was added to the isolated hexadiene and THF solution as before. Again, after 5 h the unreacted diene and the THF were removed under vacuum and the remaining clear oil fractions were combined and distilled under vacuum. The second fraction collected at 68 °C at 11 μmHg was a clear and slightly viscous liquid which proved to be pure hexenyl-9-borabicyclononane by ^{1}H and ^{11}B NMR. A total of 36.01g was collected for a 73.1% yield.

To enhance the selectivity[27] of hydroboration for α-olefin, the hydroboration reaction of 1,5,9-decatriene was performed at low temperature. Under inert atmosphere, 9-BBN (5.5 g, 45.1 mmol) dissolved in 70 mL of THF solvent was added dropwise to 1,5,9-decatriene (2.837 g, 20.8 mmol) at -10 °C. The reaction mixture was stirred at -10 °C for 10 h and then slowly warmed to room temperature. To ensure the complete consumption of 9-BBN, the reaction was continued at room temperature for another 2 h. After the THF solvent was removed by vacuum distillation, the product was filtered through glass fibers in the drybox to yield 7.51 g (95%) of viscous liquid. The ^{1}H NMR study of the product shows only one chemical shift at 5.7 ppm, corresponding to an internal double bond, in the olefin region with a broad band between 2.25 and 1.05 ppm, corresponding to hydrogens located on saturated carbons. On the basis of the peak intensity ratio between them, the product was a mixture which consisted of 82.75% 1,10-bis(9-BBN)-5-decene, with the remainder being trihydroborated product.

ROMP of 1,5-Cycooctadiene and Borane Monomers. In all ROMP reactions, the metathesis catalyst was prepared by dissolving 20 mg (0.05 mmol) of WCl_6 in 1.5 g of toluene and then adding 18 mg (0.01 mmol) of Me_4Sn to this solution. The catalyst mixture was aged for 5 min before polymerization. In one typical example, this catalyst solution was added to a reaction flask containing 2.723 g (25 mmol) of 1,5-cyclooctadiene, 478 mg (1.3 mmol) of 1,10-bis(9-BBN)-dec-5-ene and 1.5 g of toluene. The reaction was allowed to proceed for 2 h, after which it was terminated by the addition of 6 mL of 2-propanol. Toluene and 2-propanol were then evaporated under reduced pressure, and the polymer was redissolved in THF. The resulting borane-containing polymer was usually not isolated. Instead, the polymer solution in THF was directly used in the following functionalization reactions.

Oxidation and Iodination Reactions. In the oxidation reaction, the polymer solution was placed in an ice bath under inert atmosphere and 2 mL of degassed 6 N NaOH and 2 mL of 30% H_2O_2 solution were added to it sequentially via a cannula. The reaction was then permitted to proceed for 5 h with stirring at 45 °C, after which the flask was exposed to the atmosphere. The procedure to purify the resulting hydroxy polymers was very dependent on their molecular weight. In this example, with relatively low molecular weight polymer, the polymer solution was then washed with 20 mL of concentrated NaOH solution three times and the organic phase was collected. The aqueous phase was washed with 10 mL of THF, and the organic phases were combined and concentrated. This solution was then diluted with THF, $MgSO_4$ was added to it, and the mixture stirred for 1 h. After removal of the solids by centrifugation, the solution was concentrated. To this concentrated solution was added MeOH. The mixture was stirred for 1 h to dissolve 1,10-dec-5-enediol and 1,5-cyclooctanediol that might have been generated from unreacted acyclic olefin. The supernatent liquid was then decanted and the liquidlike viscous polymer dried overnight at 50 °C by the application of high vacuum to yield 2.086 g of product. For high molecular weight cases, the coagulation of polymer was caused by adding 2-propanol to the solution; then standard solution–precipitation cycles were applied to further remove the impurities.

Metathesis Degradation of 1,4-Polybutadiene with Borane Monomers. In a typical experiment, 6-(9-BBN)-1-hexene (2.83 g) was mixed with a solution containing *cis*-1,4-polybutadiene (4.5 g) and toluene (20 mL). The metathesis reaction was started by the addition of 0.33 g of WCl_6 and 0.298 g of Me_4Sn which were premixed and aged for 5 min in 5 mL of toluene. The reaction solution was then continuously stirred at room temperature with a mild vacuum (25 mmHg) to remove the byproduct ethylene. The viscosity of the polymer solution decreased significantly during the reaction process. After a certain reaction time, the reaction was terminated by the addition of 2-propanol (2 mL). The solution was then subjected to high vacuum to remove toluene, excess 2-propanol, and unreacted 1-hexenyl-6-(9-BBN). The resulting viscous liquid was redissolved in 30 mL of THF for the oxidation reaction.

Conclusion

The combination of metathesis reactions and borane monomers offers a unique route to prepare telechelic polymers. This chemistry is possible because of three important advantages of borane monomers, mainly (a) the stability of borane groups to tungsten carbene catalysts, (b) the solubility of borane monomers and polymers in hydrocarbon solvents, such as toluene, and (c) the versatility of borane groups which can be transformed to a remarkably fruitful variety of functionalities under mild reaction conditions. Overall, this synthetic route is very general, and provides not only a simple method to prepare existing telechelic polymers but also to produce new ones which are otherwise very difficult to obtain. A wide range of telechelic polymers with different polymer backbones and functionalities, and their applications to prepare multiple block copolymers, are currently under investigation.

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Registry No. 9-BBN, 280-64-8; 1,10-bis(9-BBN)-5-decene, 143038-17-9; 1,5-hexadiene, 592-42-7; 1,5,9-decatriene, 13393-64-1; 1-hexenyl-9-borabicyclononane, 112741-05-6.