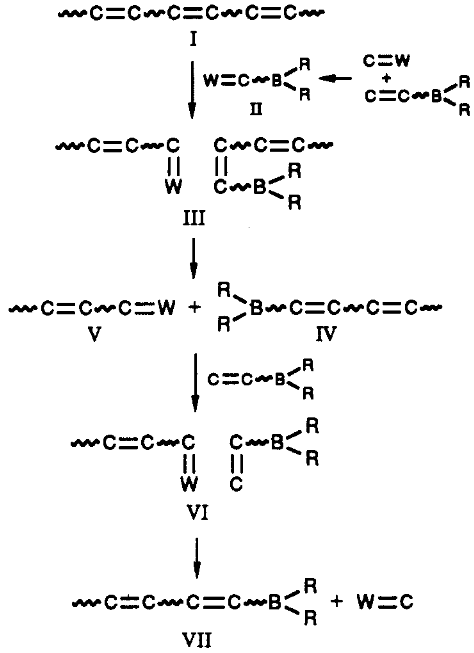
A New Synthetic Route to Telechelic Polymers

Telechelic polymers[1] with functional groups at both chain ends have been a very interesting class of materials. They represent 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 termination of living polymers with suitable reagents and 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, this process is very limited because only a few monomers undergo living propagation. In this paper, we introduce a new method that involves cometathesis reaction of borane monomers and unsaturated polymers.

It is well-known that olefins are interconvertible to other olefins in the metathesis reaction by forming the metallocyclobutane intermediate. Usually, the reaction is fast and reversible. In the case of a polymer,[1] the metathesis reaction taking place in the backbone is corresponding to a polymer chain breaking and re-forming reversible processes. In most cases, the equilibrium conditions can be achieved and the average molecular weights of the polymers become constant.[12] It is certainly very interesting to take the advantage of this dynamic equilibrium, particularly to direct the re-forming process to a functionalization reaction. In other words, the resulting polymer is a telechelic polymer with a molecular weight much lower than the original one. To achieve this goal, the borane monomer, containing both a borane moiety and an olefin group, was investigated in a reversible metathesis reaction between an unsaturated polymer and the tungsten carbene catalyst. This idea is better explained in Scheme I.

During the reversible metathesis reaction between an unsaturated polymer and a tungsten carbene catalyst, one can expect that some tungsten carbene active sites react with α-olefins in borane monomers. The resulting new tungsten carbene molecule (II), with a borane group at one end of molecule, then involves the metathesis degradation process by reacting with the internal double bonds in polymer chains (I). In this reaction, it not only breaks the polymer chain but also introduces a borane group to one of the broken chain ends (IV). The other broken chain end simultaneously generates a new tungsten carbene (V), which can also react with borane monomer. This reaction functionalizes the other half of the broken chain end (VII). Overall, both broken chain ends are functionalized by borane groups in each polymer chain scission reaction. The tungsten carbene catalyst is regenerated at the end of reaction cycle. Therefore, the same degradation and functionalization reactions can continuously take place in the catalytic fashion. As one can expect, the molecular weight of a polymer decreases along with an increase in the functional group concentration. It is important to note that the catalytic cycles are only possible by providing no side reactions to the catalyst, particularly catalyst poison by functional groups. Fortunately, our previous studies[13-15] have demonstrated the good stability of borane groups to a broad range of transition-metal catalysts.

Scheme I



In a typical experiment, 1-hexenyl-6-(9-BBN)[13] (2.83 g) was added to 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 $Sn(Me)_4$, 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 of ethylene. The viscosity of a polymer solution decreased significantly during the reaction process. After a certain reaction time, the reaction was terminated by the addition of isopropyl alcohol (2 mL). The solution was then subjected to high vacuum to remove toluene, excess isopropyl alcohol, and unreacted 1-hexenyl-6-(9-BBN). The resulting viscous liquid was redissolved in 30 mL of THF for oxidation reaction. The reaction was carried out by adding 2.5 mL of 6 N NaOH solution and 4.8 mL of 30% H_2O_2 solution. To ensure the complete oxidation, the solution was heated to 45 °C for 3 h. The purification procedure was very dependent on the molecular weight. For high molecular weight cases, the coagulation of a polymer was used by adding 100 mL of isopropyl alcohol to the solution, and then standard solution–desolution cycles were applied to further remove the impurities. On the other hand, in the low molecular weight cases, in which the reactions were performed for more than 15 min, the final polymer solution was washed with brine solution several times. The THF fraction was collected from a separation funnel. After solvent removal, the remaining polymer was a viscous and light brown liquid that was then subjected to standard silica column chromatography to remove the impurities. The elution solvent was started from a complete nonpolar solvent, such as hexane, and then changed to a light polar solvent by mixing hexane with diethyl ether. After solvent removal, all polymer fractions are free of impurities.

Figure 1 shows the GPC curves of the resulting α,ω-hydroxy-1,4-polybutadiene with various metathesis reaction times. The molecular weight of the polymer rapidly decreased while the reaction proceeded. The liquid oligomers were obtained within a half hour reaction time. To be able to measure the molecular weight of the oligomers, a series of columns (two 10^2 Å, one 5×10^2 Å, one 10^3 Å, and one 10^4 Å) were used in GPC measurements. Table I summarizes the results. It is interesting to note that the molecular weight distribution becomes slightly narrower as the molecular weight decreases. This may be due to the statistical preference in the reaction of a high mo-

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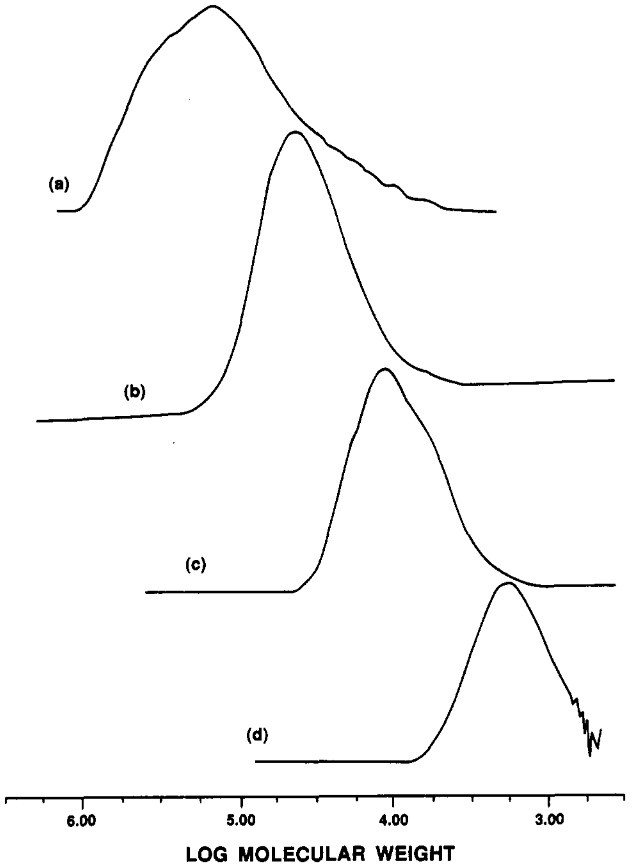


Figure 1. Comparison of GPC curves between (a) *cis*-1,4-polybutadiene and α,ω-hydroxy-1,4-polybutadiene at various reaction times (b) 8 min, (c) 15 min, and (d) 30 min.

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

sample	reaction time, min	M_w	M_n	polydispersity
PB	0	436 362	172 136	2.53
PB-OH-A	8	82 594	39 673	2.08
PB-OH-B	15	14 070	8 073	1.74
PB-OH-C	30	1 896	1 026	1.85

[a] Molecular weight calculation was based on the calibration curve of polybutadiene (35% cis, 55% trans, and 10% 1,2-isomers).

lecular weight polymer in the beginning of the reaction. The reaction was very effective even under mild reaction conditions. The molecular weight of 1,4-polybutadiene decreased from 200 000 to 1000 within a half hour. In other words, every polymer chain on average was degraded about 200 times. To ensure the understanding of the reagents involved in this reaction, two control reactions were also performed. One was done under the same metathesis reaction conditions without borane monomer. Only a slight change in the molecular weight was observed even after a long reaction time; the equilibrium state was reached at a molecular weight of about 70 000. The other experiment was carried out by replacing 1-hexenyl-6-(9-BBN) by 1-hexene. The same molecular weight decreasing pattern was observed without a functionalization reaction. These comparisons clearly demonstrate the unique features of borane monomers and polymers, not only no detectable catalyst poison in the metathesis reaction but also the good solubility in hydrocarbon solvents, which ensures an effective and homogeneous reaction under mild reaction conditions.

Figure 2 shows the ^{1}H NMR spectra of α,ω-hydroxy-1,4-polybutadiene with various metathesis reaction times. A new triplet peak at 3.5 ppm, corresponding to methylene unit next to primary hydroxyl group, was observed in all cases. The peak intensity increases along with the reaction time and is inversely proportional to the molecular weight of the polymer. The same results were concluded from IR studies; two new absorption peaks at 3300 cm^{-1} (ν_{OH}) and 1050 cm^{-1} (ν_{CO}) are due to the hydroxyl groups in the functionalized polymer. With 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 the sample PB-OH-C, with relatively lower molecular weight and higher functional group concentration. The functionality number is slightly below 2 in all cases. In other words, some of polymer chains have only one or no functional groups. The column chromatography with a gradient solvent polarity was used to fractionalize the polymer mixtures. This technique is suitable for low molecular weight (<2000) polymers. Table II shows the fractionization results of

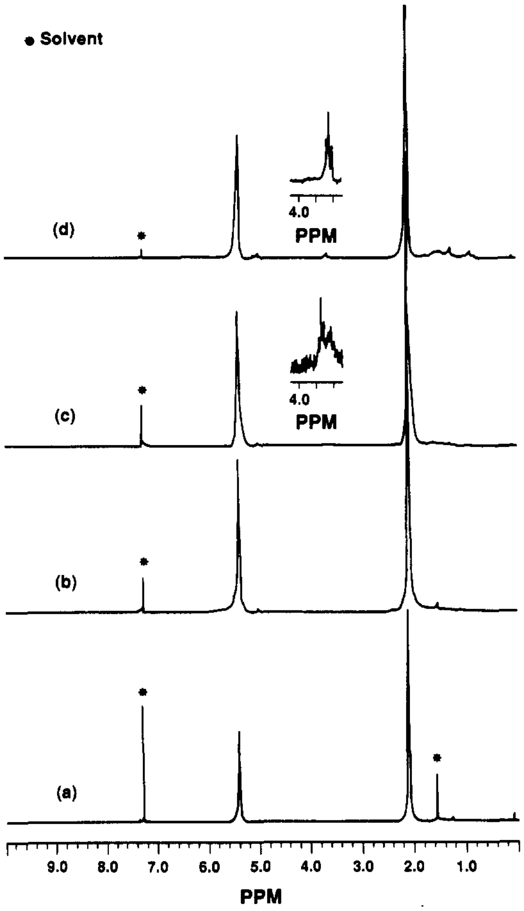


Figure 2. Comparison of ^{1}H NMR spectra between (a) *cis*-1,4-polybutadiene and α,ω-hydroxy-1,4-polybutadiene at various reaction times (b) 8 min, (c) 15 min, and (d) 30 min.

Table II
Summary of Hydroxylated Polybutadiene after Column Fractionation

fraction	solvent hexane/ether	yield, g	M_n	M_w/M_n	functionality
1	100/0	0.25	399	1.32	<0.1
2	99/1	0.568	990	1.63	0.3
3	98/2	0.251	1135	1.86	∼1
4	95/5	0.911	1646	1.29	∼1
5	90/10	0.768	877	1.21	1.6
6	70/30	1.12	877	1.88	∼2
7	0/100	0.56	1048	1.87	∼2

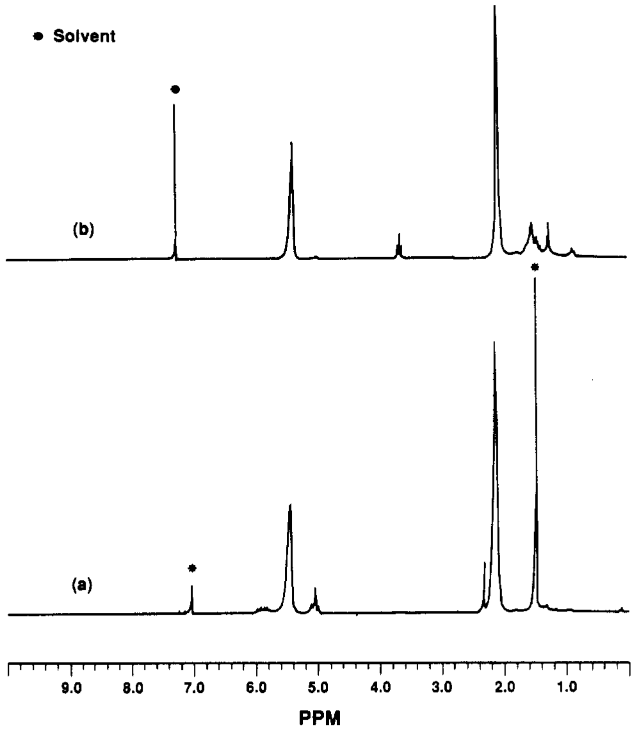


Figure 3. Comparison of ¹H NMR spectra between (a) fraction 1 and (b) fraction 6.

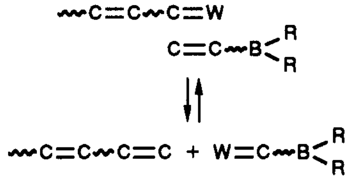
sample PB-OH-C, which was separated by hexane/ether mixed solvent. Overall, the molecular weight is not much different between each fraction, and the molecular weight distribution is slightly reduced from that of the original mixture. On the other hand, the functionality number increases with an increase of the solvent polarity. Only a small portion of polymer (18%, fractions 1 and 2) has almost no functional group. The middle portions (26%, fractions 3 and 4) have a functionality close to 1. The major portion (56%, the sum of fractions 5–7) of polymer has a functionality number of about 2. The average molecular structure of this α,ω-hydroxy-1,4-polybutadiene is

$$HO(CH_2)_3(CH_2CH{=}CHCH_2)_{20}(CH_2)_3OH$$

which contains 20 repeat units of 1,4-butadiene and two primary alcohol groups in each polymer chain end. The telechelic polymer with a molecular weight in this range (1000–2000) is a very useful material, for example, as the building block for the preparation of multiple-block copolymers and three-dimensional polymer networks.

It is certainly very important to know the molecular structure of the less perfect fractions (fractions 1–4). Figure 3 compares the ¹H NMR spectra of fractions 6 and 1. Two new chemical shifts around 5 and 5.9 ppm in fraction 1 are strong evidence for the existence of α-olefin groups at unfunctionalized chain ends. The α-olefin groups may result from the reaction between compound V and a borane monomer, with the undesirable coupling direction as shown in Scheme II. The overall chemistry is obviously not yet perfect. To further improve the yield of α,ω-hydroxy-1,4-polybutadiene, a new borane monomer is currently under investigation.

Scheme II



In conclusion, this paper presents a new approach to the preparation of telechelic polymers. The combination of metathesis reaction and a borane monomer offers a unique reaction condition, not only breaking the polymer chain but also functionalizing the broken chain ends. This chemistry is possible because of three important advantages in borane monomers, mainly (a) the stability of borane groups to tungsten carbene catalysts, (b) the solubility of borane monomers and polymers in the 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. This chemistry can certainly be applied to other polyolefin systems that are otherwise very difficult to obtain in telechelic forms by the existing methods. The overall scope and limitations of this chemistry will be reported in a complete paper.

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