produced polymers with narrow MWDs irrespective of the length of the alkyl group ($\bar{M}_w/\bar{M}_n$ = 1.2–1.4). In contrast, the MWD of poly(1-chloro-2-phenylacetylene) was not so narrow; this might be due to the steric effect of phenyl group. Other substituted acetylenes except *tert*-butylacetylene also yielded polymers with broad MWDs. Thus, it is worth noting that the MWD of polymers greatly depends on the kind of monomers.

Conclusions

The $MoCl_5$–*n*-Bu_4Sn–EtOH catalyst system effected living polymerization of 1-chloro-1-alkynes to give polymers with narrow MWDs ($\bar{M}_w/\bar{M}_n$ = 1.1–1.4). Though the present living polymerization is yet imperfect with respect to the [P*]/[Cat] ratio and the "monomer-addition" experiment, it is the first clear example of living polymerization of acetylenic monomers. Elucidation of the propagating species, improvement of the catalyst system to induce more perfect living polymerization,[12] and exploitation of other monomers that undergo living polymerization are under progress.

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Registry No. $MoCl_5$, 10241-05-1; *n*-Bu_4Sn, 1461-25-2; EtOH, 64-17-5; Et_3SiH, 617-86-7; Ph_3SiH, 789-25-3; Ph_3Sb, 603-36-1; H_3CCO_2H, 64-19-7; H_3CCO_2-*n*-Bu, 123-86-4; H_2O, 7732-18-5; Me_4S_7, 594-27-4; 1-chloro-1-octyne (homopolymer), 100858-77-3; acetone, 67-64-1; 1-chloro-1-hexyne (homopolymer), 100858-76-2; 1-chloro-1-decyne (homopolymer), 100858-79-5; 1-chloro-1-hexadecyne (homopolymer), 108711-62-2; 1-chloro-2-phenylethyne (homopolymer), 81953-16-4; 1,6-dibromo-1-hexyne (homopolymer), 89298-41-9; 2-octyne (homopolymer), 80652-33-1; phenylethyne (homopolymer), 25038-69-1; 3,3-dimethyl-1-butyne (homopolymer), 51730-68-8; 3-trimethylsilyl-1-octyne (homopolymer), 100858-80-8.

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Synthesis of Functional Hydrocarbon Polymers with Well-Defined Molecular Structures

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ABSTRACT: The paper describes the preparation of well-defined functional polymers with narrow molecular weight distributions and functional groups homogeneously distributed along the polymer chains. The chemistry involves the hydroboration of polydienes. Since both thermodynamics and kinetics are favorable for this reaction, a completely homogeneous modification is obtained. The hydroborated polymers are valuable intermediates that can be converted to a variety of functional polymers. Polyalcohol is one of the examples that will be discussed in detail in this paper. To retain the narrow molecular weight distribution, several experimental methods, including vacuum techniques, low reaction temperatures, and boric acid removal, were employed during the reaction. The resulting functional polymers have molecular weight distributions of 1.07. In the paper, we also compare the hydroboration reactivities of various unsaturated polymers. The steric effect in the hydroboration of polymers is quite similar to that of simple organic compounds.

Introduction

The area of functional polymers is becoming one of the most active in polymer science.[1-4] Many desirable properties, such as permeability, compatibility, adhesiveness, etc., can be influenced by adding specific functional groups to conventional hydrocarbon polymers.

It has been a long-time goal of synthetic polymer chemists to prepare well-defined functional polymers (including ion-containing polymers) with narrow molecular weight distributions and functional groups homogeneously distributed along the polymer chains. However, there are very few such model compounds available today. Most of the model compounds are telechelic polymers[5-8] that contain functional groups at either one or both ends of polymer chains.

This paper describes an improved method for the preparation of homogeneously functional polymers with narrow molecular weight distribution (M_w/M_n = 1.07).

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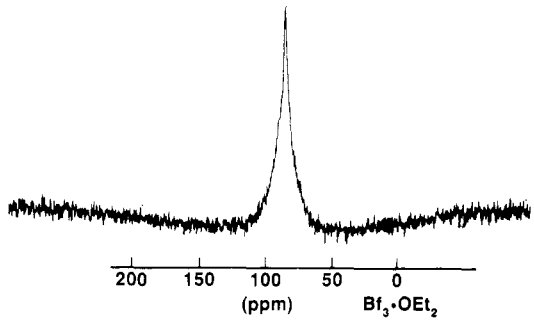
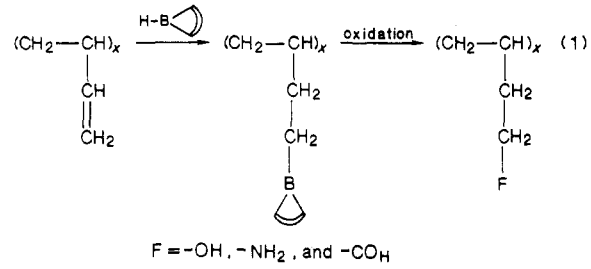


Figure 1. ^{11}B NMR spectrum of hydroborated 1,2-polybutadiene.

This method involves hydroboration of polydiene, particularly 1,2-polybutadiene, as shown in eq 1. The hydroborated polymers become valuable intermediates that can be converted to a whole host polymers, e.g., –OH, $-NH_2$, –COH, etc. Although similar polydiene chemistry was mentioned without details some years ago[9] and more recently with EPDM,[10] such polymer modifications have been plagued by chain scission and/or gelation side reactions.[11-13]



(1)

Results and Discussion

In general, the application of organic chemistry to polymer backbones is not straightforward. While thermodynamic reactivities may be the same, kinetic ones may be quite different. Often, the reagents used to modify hydrocarbon polymers are polar in nature. During the reaction, it is difficult to prevent micelle formation or even phase separation, which limits the collisions between active sites in polymers and reagents. The end result is inhomogeneous modification or incomplete reactions.

Hydroboration is one of the most active reactions in olefin chemistry.[14] In many cases, the reaction can be completed under mild conditions with quantitative yield. Moreoever, alkylboranes are hydrophobic in nature with the carbon–borane bond showing covalent character.[15] All reagents, including starting materials, intermediate compounds formed during the reactions, and final products, are hydrocarbon soluble. Thus, homogeneous reaction is assured.

Hydroboration and Oxidation of 1,2-Polybutadiene. The nonfunctional polymer precursors 1,2-polybutadiene, 1,4-polybutadiene, and polyisoprene were prepared by standard anionic polymerization. A typical molecular weight distribution (M_w/M_n) for such polymer is about 1.1. The structure of each polymer was characterized by ^{13}C NMR and is summarized in the Experimental Section.

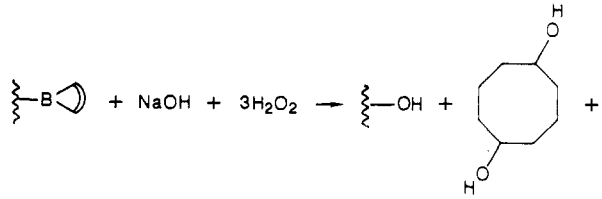
The hydroboration of 1,2-polybutadiene was performed under vacuum at –10 °C for 1 h. The degree of modification was controlled by varying the borane charge. To prevent gel formation, it is necessary to use a monofunctional dialkylborane, such as 9-borabicyclo[3.3.1]nonane (9-BBN). After hydroboration, the modified polymer was analyzed by ^{11}B NMR. As shown in Figure 1, the single resonance at 87.5 ppm (vs BF_3·OEt_2), characteristic of trialkylborane,[16] indicates that the reaction is complete and no side reactions have occurred during the hydroboration process. It should be noted that a complete oxygen-free environment is also essential in order to prevent side reactions. As is well-known, the trialkylborane is very reactive toward oxygen and the free radical formed during the oxidation process. In the case of polymer, free radicals can cause cross-linking and molecular weight broadening. In fact, a solution of polyborane will gel upon exposure to air.

Table I
Elemental Analysis Results of Hydroxylated 1,2-Polybutadiene Polymers

hydroxylated poly-1,2-butadiene		C	H	O	total (%)
100% MODIFICATION	THEOR.	66.66	11.11	22.23	100
	EXP.	66.60	11.14	22.24	99.98
30% MODIFICATION	THEOR.	80.80	11.11	8.08	100
	EXP.	80.64	11.19	8.19	100.02

In some ways, the borane moieties on polymers behave quite similarly to those of low molecular weight organic compounds. Both can be converted to various organic functionalities by various procedures, e.g., oxidation, described by H. C. Brown.[14] However, the production of well-defined polymers requires additional care. For example, partially hydroborated polymers contain not only borane groups but also residual double bonds. The latter groups can also react with strong oxidation reagents to produce gelled products. Consequently, the oxidation procedure is carried out under vacuum at very low temperature (–25 °C), using only a stoichiometric amount of oxidation reagent ($NaOH/H_2O_2$).

Purification of Polyalcohols. The polymer isolation step is another potential source of cross-linking during the preparation of functional polymers via hydroboration because of the presence of trace amounts of boric acid. As expected, the oxidation of hydroborated polymer by $NaOH/H_2O_2$ yields not only polyalcohol but also some low molecular weight impurities, e.g. boric acid, cyclic alcohols, etc., as shown in eq. 2. Standard precipitation methods can be used to remove most of the low molecular weight impurities. However, residual boric acid still remains after such treatment. Unfortunately, boric acid reacts slowly at room temperature with alcohol groups to form trialkoxyborane[17] that can act as a cross-linking center between polymer chains. In fact, a high molecular weight shoulder in GPC trace of hydroxyl polymer was observed when the boric acid was not removed. In order to maintain a narrow polymer molecular weight distribution, it is necessary to remove boric acid from polyalcohol. This fact was not fully appreciated by previous workers.[9-13]



(2)

Fortunately, boric acid and methanol form a complex that has an azeotrope at 58 °C, even lower than that of methanol (65 °C). A multiple-stage distillation process was, therefore, carried out to separate the boric acid—methanol complex from the polyalcohol solution. The collected distillate had a NMR resonance at 20 pm (vs BF_3·OEt_2), exactly the same as that of boric acid itself.[18] The final polymer was isolated and dried in a vacuum oven overnight. Elemental analysis for hydroxylated polymers

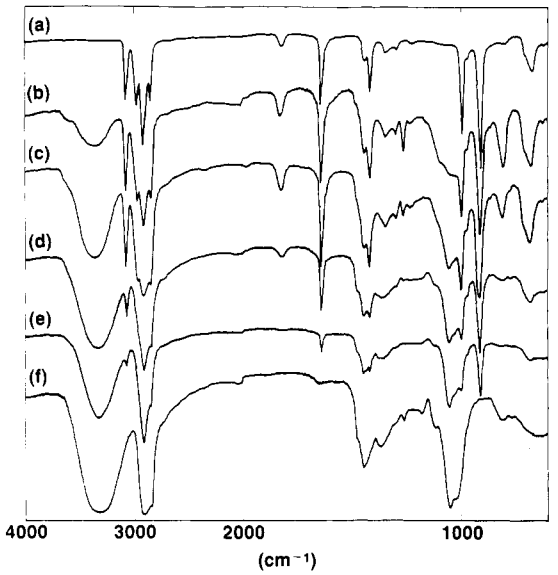


Figure 2. IR Spectra of hydroxylated 1,2-polybutadiene, the degree of hydroxylation: (a) none, (b) 10%, (c) 25%, (d) 50%, (e) 70%, (f) 100%.

with 30% and 100% modifications show close agreement with the theoretical values (Table I).

Infrared Spectral Studies. A series of IR spectra of hydroxylated 1,2-polybutadiene of varying degrees of modification is shown in Figure 2. Two strong absorption bands for hydroxyl groups, peaks at ν(OH) = 3340 cm^{-1} and ν(CO) = 1050 cm^{-1}, increase, while all absorption peaks for vinyl groups at 3065, 1820, 1635, 990, and 905 cm^{-1} decrease. Complete conversion from vinyl to hydroxyl groups can be obtained under mild conditions, and the degree of modification can be controlled by controlling the reagent stoichiometry. Also such absorption bands are quite broad for the 100% modified polymer. This may be due to mixed morphologies, i.e., crystalline and glassy states. Differences in tacticity for the polyalcohol are also expected to contribute to different sets of absorption bands in the IR spectrum. Slight shifts between equivalent vibrational modes broaden the absorption bands. In fact, X-ray results show partial crystallinity in this material. The main ordering, peak at 20.33° (α = 4.36 Å), corresponds to the spacing between two side groups, which is almost the same as that in isotactic polyolefins with long side chain groups. In addition, there is an additional weak peak at 40.22° (d = 2.24 Å), relating to additional side chain ordering in this molecule which may result from the fact that atactic polydiene starting materials were used.[18] Moreover, no detectable ordering between the polymer chains was observed, which also reflects the disordered nature of the polymer.

GPC Studies. The efficacy of hydroboration, oxidation, and isolation processes are seriously tested by the GPC studies. If there are no side reactions, polymer molecular weight distributions should be the same before and after modification. Indeed, this is the case, as shown in Figure 3 (M_w/M_n = 1.07). Additionally, the molecular weight of parent material increases to the expected molecular weight for modified sample. However, such excellent results can only be obtained by using a high vacuum techniques, low reaction temperatures for both hydroboration and oxidation reactions, and removal of trace amounts of boric acid from the final polymer.

Molecular Structure and Reactivity. The reaction of an α-olefin and dialkylborane is essentially instantaneous in THF solvent at room temperature.[20] The same reaction of a hindred olefin is much slower.[21] In order to

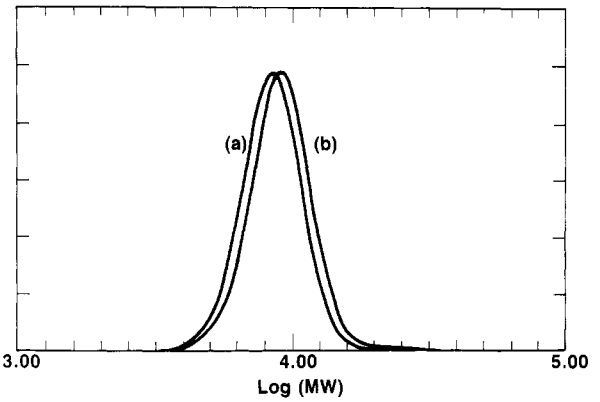


Figure 3. GPC traces of (a) pure 1,2-polybutadiene and (b) 25% hydroxylated 1,2-polybutadiene.

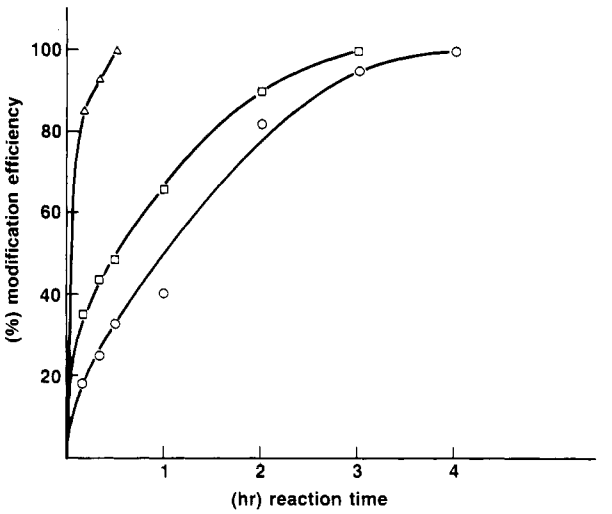
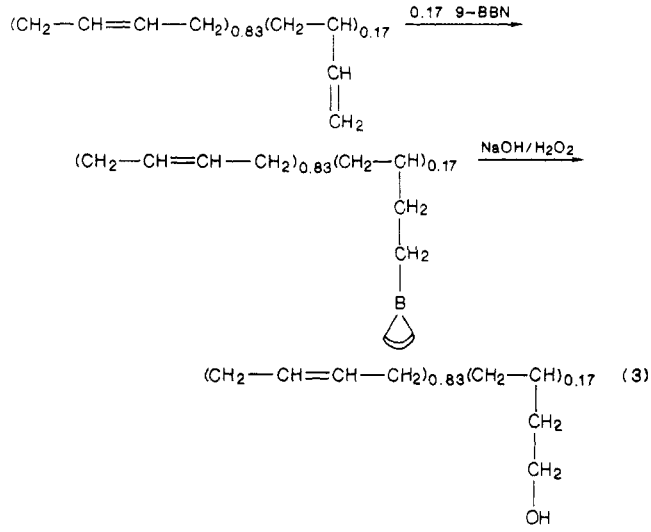


Figure 4. Modification efficiency of hydroxyl polymers: (△) 1,2-polybutadiene, (□) 1,4-polybutadiene; (○) polyisoprene.

understand polymer backbone structure and reactivity relationships, a series of kinetics experiments was carried out (Figure 4). The relative reactivity of the various polydienes is 1,2-polybutadiene > 1,4-polybutadiene > 1,4-polyisoprene in ratios of 1:0.167:0.125. This order parallels what is expected from the corresponding small molecule organic models, suggesting that steric hindrance about the olefin is the dominant factor. Such results are opposite to the structure-reactivity relationship for azoester modification[19] of polybutadienes. The latter process is more facile for the 1,4-backbone than for the 1,2-substrate because the 1,4-backbone has more reactive allylic hydrogens. In contrast, hydroboration involves a four-center cycloaddition, which is governed by steric effects.

Another way to demonstrate the structure-reactivity relationships for the hydroboration of polydienes is to use a backbone containing both 1,4- and 1,2-microstructures. Small molecule organic diene, such as 1,4-hexadiene,[21] containing one terminal double bond and one internal double bond can be selectively hydroborated at the terminal position, especially when 9-BBN is used as hydroboration reagent.[17] A similar result is observed for mixed microstructure polybutadienes. The treatment of 1,4-polybutadiene, containing 17 mol % of 1,2-isomer, with 1 equiv of 9-BBN (vs 1,2-isomer) proceeds predominantly to form the monoadduct 1,4-polybutadiene-*co*-hydroxylated-1,2-polybutadiene. The reaction is shown in eq 3. A ^{13}C NMR spectral comparison of the unmodified and modified polymers is shown in Figure 5. The 1,2 units, with resonances between 131.17 and 128.25 ppm, completely disappear, while a new resonance at 59.27 ppm,



expected for primary alcohol, appears.

Thermal Characterization of Hydroxyl Polymers. The thermal properties of the hydroxyl polymers were examined by using DSC and TGA techniques. Figure 6 shows the DSC thermograms of the hydroxyl polyisoprene copolymers. It can be seen that a single exothermic peak continuously moves to higher temperatures with an increase in hydroxyl group concentration. The increase in polymer T_g is expected because of an increase in inter- and intrahydrogen bonding. Similar trends are observed for 1,2-polybutadiene and 1,4-polybutadiene. The absence of two transition temperatures in the partially modified polymers suggests a nonblocky or homogeneous modification.

The fully functionalized polydiene polymers are partially crystalline solids that melt sharply between 48 and 58 °C, as shown in Table II. The detection of crystallinity via DSC confirms X-ray diffraction results (vide supra).

TGA measurements indicate that the fully modified 1,2-polybutadiene is highly stable, showing the onset of decomposition at about 450 °C similar to that of polyoctenol.[23,24] On the other hand, fully modified polyisoprene is less thermally stable (decomposition temperature <300 °C). Presumably the secondary alcohols of the modified polyisoprene are more prone to thermal dehydration[25] than the primary alcohols of the modified 1,2-polybutadiene.

Experimental Section

Materials and Equipment. All dienes (Wiley) were dried by $Al(Et)_3$ at low temperature and were directly vacuum-distilled into the polymerization vessel before reaction. Analytical grade THF was stirred with sodium naphthalide to remove traces of water and oxygen and then was distilled into the reactor by the same manner. 9-Borabicyclo[3.3.1]nonane (9-BBN) (Alrich) was used as received.

IR spectra were obtained with a Perkin-Elmer 298 infrared spectrophotometer. The IR samples were prepared on a KBr window by film casting techniques. Both ^{13}C and ^{11}B NMR spectra were carried out by using JEOL FX902 spectrometer. Molecular weight distributions were determined on a Waters GPC 150 at room temperature, elution speed 1.2 mL/min with THF as solvent. A polybutadiene calibration was used.

Thermal properties of the polyalcohol were evaluated by Perkin-Elmer TGS-2 thermogrammeric analyzer and DSC-2 differential scanning calorimeter. The DSC measurements were done under a N_2 atmosphere at a heating rate of 20 °C/min. The TGA analysis was carried out in an O_2 or Ar atmosphere (flow rate = 100 cm^3/min) with a sample size of ~10 mg and a heating rate of 10 °C/min. The X-ray patterns were recorded on a Simens D-500 diffractometer. The polyalcohol polymers employed for X-ray study were a polymer solid right after preparation without any further physical treatment.

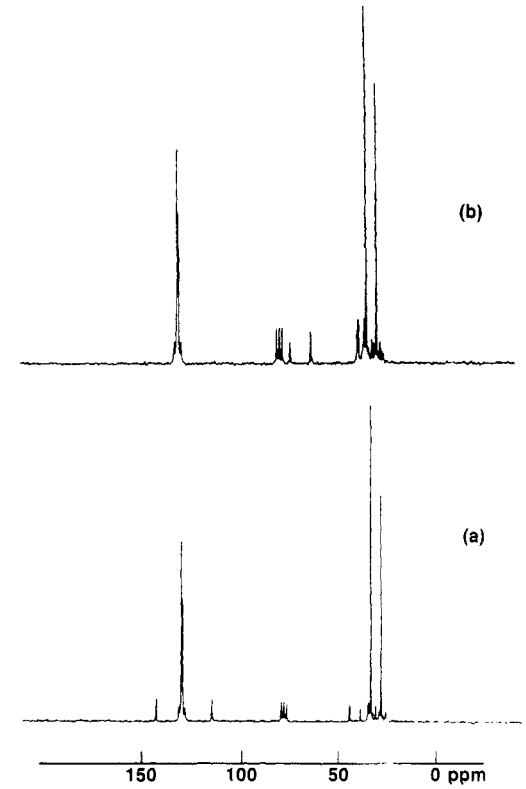


Figure 5. ^{13}C NMR spectra (a) (mixed 1,4 and 1,2)-polybutadiene and (b) 1,4-polybutadiene-*co*-hydroxylated 1,2-polybutadiene.

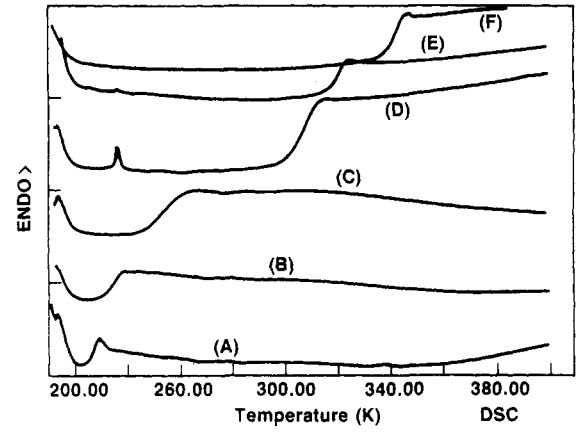


Figure 6. DSC results of hydroxyl polyisoprene with various modification efficiency: (a) 10%, (b) 28%, (c) 35%, (d) 80%, (e) 93%, (f) 100%.

Table II
T_m Value of Hydroxyl Polymers 1,2-Polybutadiene (1,2-PB-OH), 1,4-Polybutadiene (1,4-PB-OH), and Polyisoprene (PI-OH)

sample	1,2-PB-OH	1,4-PB-OH	PI-OH
T_M (°C)	49	48	58

The 1,2-polybutadiene was prepared according to the method of Halasa,[26] which produces polymers with the highest known vinyl contents (>95%) and narrow molecular weight distributions; for example, $M_w/M_n = 1.07$. Both 1,4-polybutadiene and polyisoprene (>90%, 1,4-addition) were prepared by standard anionic polymerization techniques[27] in hexane solvent using *n*-BuLi as the initiator. The mixed microstructural polybutadiene, containing 17% 1,2-isomers and a mixture of cis and trans isomers in 1,4-isomers, was obtained from the Firestone Tire and Rubber Co.

Modification Process. The modification of polydienes was carried out in a high vacuum apparatus. The system consists of two 1-L flasks (A and B), which are separated by a Teflon stopcock. The other stopcock connected to flask A was used to

Table III
A Summary of the Quantity of Reagents for Various Degrees of Modification in Poly-1,2-Butadiene

degree of modificatn	poly-1,2-butadiene	9-BBN	6 N NaOH	30% H_2O_2
10%	3.24 G	0.73 G	1 ML	2 ML
20%	3.24 G	1.46 G	2 ML	4 ML
30%	3.24 G	2.19 G	3 ML	6 ML
50%	3.24 G	3.66 G	5 ML	10 ML
70%	3.24 G	5.11 G	7 ML	14 ML
100%	3.24 G	7.32 G	10 ML	20 ML

control vacuum and nitrogen flow.

After the apparatus was dried in an oven for over 12 h, it was immediately put into the drybox. The 9-borabicyclo[3.3.1]nonane (9-BBN) and polydiene, such as 1,2-polybutadiene, were separately charged to flasks A and B. The amount of the reagent used determines the degree of modification as shown in Table III. The system was then degassed on a vacuum line for 2 h before vacuum distillation. Dry THF solvent (150 mL) over Na^+NAPH^- was added to both flasks. When both sides were dissolved, the polymer solution was cooled to −10 °C, and the 9-BBN solution was added into flask B. The reaction solution in flask B was constantly stirred at this temperature for 1–2 h to complete the reaction. However, to ensure no residual hydride in polymer solution, 1 mL of pure methanol was vacuum-distilled into flask A and added to flask B to react with any 9-BBN left after hydroboration.

The oxidation of the hydroborated polymer to hydroxylated polymer was also carried out in the same high vacuum apparatus. Stoichiometric amounts of $NaOH/H_2O_2$ (as shown in Table III) and low reaction temperatures were needed to prevent side reaction between residual double bonds in partially modified polymers and the hydrogen peroxide. The 6 N NaOH solution was charged to flask A under a strong nitrogen flow and then degassed to high vacuum before adding into flask B. A similar procedure was applied to introduce 30% H_2O_2 solution except adding very slowly, and low reaction temperature (−25 °C) was maintained during the whole process. After the reaction mixture was stirred at this temperature for 1 h, the solution was gradually warmed to 40 °C to ensure complete reaction. The hydroborated polymer was precipitated from the THF solution with water. The polymer was washed three times with distilled water to remove impurities.

Boric acid, a byproduct of the oxidation, is not effectively removed by washing with water. Consequently, the boric acid was removed by complexation and distillation with methanol. The polymer was dissolved in methanol (polymers that had less than 30% modification did not dissolve in methanol—they were simply stirred in methanol) and the solution distilled. The boric acid/methanol complex boils at 58 °C. The distillation was performed slowly, with care at 60 °C or less. When no further distillate could be collected below 65 °C, it was assumed that all of the boric acid had been removed. To further facilitate the precipitation of the polymer, some of the methanol was distilled prior to adding the nonsolvent. In all cases but the 100% modified polymer, the product was precipitated out of methanol by the addition of a very small amount of water. Diethyl ether was used for the 100% modified polymer. after precipitation, the polymers were put into a Teflon pan and dried under a vacuum at 50 °C.

Conclusions

Hydroboration is one of the most selective reactions in olefin chemistry. Hydroboration of polydienes is also thermodynamically and kinetically favorable. Moreover, the hydroborated polymers are valuable intermediate compounds that can be converted to a wide variety of functional polymers. Yet, this polymer modification involves some potential side reactions that will result in scission and/or gelation.[12,13] This paper describes improved experimental techniques for the preparation of gel-free well-defined functional polymers with narrow molecular weight distributions. These improved techniques include methanol complexation of boric acid impurities.

Structure-reactivity studies indicate that the order of hydroboration activity is 1,2-polybutadiene > 1,4-polybutadiene > 1,4-polyisoprene. The 1,2-microstructure can be selectively hydroborated in the presence of the 1,4-microstructures.

Thermal analysis shows single-phase morphology for partially modified hydroxyl polydienes, which indicates the hydroboration is a nonblocky modification process. Sharp melting points between 48 and 60 °C were observed in fully functionalized polymers, hydroxylated 1,2-polybutadiene, 1,4-polybutadiene, and polyisoprene. The hydroxylated 1,2-polybutadiene is more thermally stable than the hydroxylated 1,4-polybutadiene adduct.

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