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Poly(5-hydroxyoctenylene) and Its Derivatives: Synthesis via Metathesis Polymerization of an Organoborane Monomer

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ABSTRACT: The synthesis of a new monomer, (5-cyclooctenyl)diethylborane, and its polymerization by ring-opening metathesis are reported. This resultant polyborane rendered a novel polymer, poly(5-hydroxyoctenylene), upon oxidation. The hydroboration/oxidation reactions can be controlled to give polymers with varying amounts of hydroxyl groups on the backbone. The structure of the polyalcohols was confirmed by ^{1}H NMR and ^{13}C NMR spectroscopy. In addition, ^{13}C NMR spectroscopy confirmed the presence of various 1,4-, 1,5-, and 1,6-diol sequences in the completely hydroxylated polymer. The glass transition temperatures of the polymers were fairly low and lie between 10 and 45 °C. The polymers are thermally stable and begin to lose weight only at temperatures above 400 °C, compared to poly(vinyl alcohol), which undergoes weight loss at temperatures as low as 300 °C.

Introduction

The area of functional polymers is receiving greater attention as we develop methods to fine tune both the amount and the location of the functional groups on the polymer backbone. This control of microstructure of the polymer is very important for the complete understanding of its structure–property relationship. Functional polymers have been conventionally prepared mostly by free-radical or anionic polymerizations and, more recently, by group-transfer polymerization. Due to the reactivity of transition-metal catalysts toward a large variety of functional groups, the synthesis of polyolefins with organic functionalities has met with only limited success.[1] We have recently developed organoborane monomers that can be polymerized by both Ziegler–Natta[2] and ring-opening metathesis polymerization.[3] These organoborane polymers can be quantitatively converted to hydroxyl-containing materials under mild conditions.

In our previous paper we reported the synthesis of norbornenyl-9-borabicyclo[3.3.1]nonane and its ring-opening metathesis polymerization to give pure exo-hydroxy polymer after oxidation.[3] In the present paper we report the synthesis of a new cyclooctenylborane monomer, which after polymerization and oxidation gave a novel polymer, poly(5-hydroxyoctenylene). Further derivatization by hydroboration followed by oxidation gave polymers with varying amounts of hydroxyl groups. The detailed spectral characterization and thermal analysis of these polymers are reported.

Experimental Section

Materials. Catecholborane, 9-BBN, and Et_2AlCl were purchased from Aldrich Chemical Co. and used without further purification. Analytical grade toluene and THF were stirred over sodium–benzophenone ketyl, distilled into dry vessels equipped with Teflon needle valve closures, and stored under argon. Analytical grade hexane was distilled over sodium metal and stored similarly under argon. 1,5-Cyclooctadiene (Gold Label, 99+%) was purchased from Aldrich Chemical Co. in a Sure/Seal bottle under nitrogen and used without further purification. NMR solvents, $CDCl_3$ and CD_3OD, were purchased from Aldrich Chemical Co. and used directly.

General Procedures. All manipulations of the organoboranes and the transition-metal catalysts were done in an inert atmosphere, usually in an argon-filled Vacuum Atmospheres drybox. NMR spectra were recorded on a Bruker AM-360 spectrometer. The ^{13}C NMR spectra were recorded with a DEPT (distortionless enhancement by polarization transfer) pulse sequence in order to suppress the solvent ($CDCl_3$) peak, which overlapped with one of the polymer peaks. A nutation angle of 45° was used. The DEPT pulse sequence transfers the proton polarization to the carbon nucleus, and therefore neither deuterated nor quaternary carbons appear in the spectrum. Since these polymers do not contain any quaternary carbons, this pulse sequence rendered their complete spectrum. GPC chromatograms were obtained with a Waters 600E delivery system that was connected to a Waters 410 refractive index detector. A series of three Ultrastyragel columns with pore sizes of 10^3, 10^4, and 10^6 Å were used to effect the separation. The molecular weights are reported with polystyrene as calibration standard. The DSC and TGA analyses were done on a Perkin-Elmer DSC-7 and TGA, respectively. The samples were first heated to ca. 180 °C and quenched rapidly to −110 °C. The reported DSC thermograms were obtained by heating samples treated in the above fashion at a heating rate of 20 °C/min.

Preparation of (5-Cyclooctenyl)diethylborane. 1,5-Cyclooctadiene (25 g, 0.231 mol) and catecholborane (4.3 g, 0.036 mol) were placed in a Schlenk flask fitted with a Teflon needle valve and heated in an oil bath at 100 °C for ca. 20 h. The unreacted diene was removed by cryogenic distillation in a high-vacuum line. The remaining oil was dissolved in dry deoxygenated hexane (150 mL); Et_2AlCl (6.4 g, 0.036 mol) in hexane (100 mL) was added to the solution dropwise with stirring. The reaction was allowed to proceed for ca. 16 h. The dialkoxyaluminum chloride that precipitated out was removed by filtration. The hexane was then removed cryogenically from the filtrate, and the residual oil was subjected to fractional vacuum distillation. The second fraction collected at 50 °C (at 0.02 mmHg) yielded ca. 1.5 g of the required product to give a 25% yield. The ^{1}H NMR spectrum of the product was in agreement with the expected structure.

Polymerization and Oxidation. $W(CH\text{-}t\text{-}Bu)(NAr)(OCMe[CF_3]_2)_2$ (11 mg, 0.014 mmol) was dissolved in 1 mL of toluene in the drybox. (5-Cyclooctenyl)diethylborane (500 mg, 2.81 mmol) was added to the catalyst solution and stirred. Instantaneous polymerization resulted, causing the solution to gel. The polymerization was terminated by the addition of an excess of 2-propanol. The precipitated polymer was washed thoroughly and redissolved in ca. 10 mL of THF. The subsequent oxidation was carried out in a 50-mL Schlenk flask, outside of the drybox. NaOH solution (6 N, 0.61 mL, 3.66 mmol) was degassed by bubbling dry argon through it and added to the polymer solution under a flow of argon. H_2O_2 solution (30%, 1.25 mL,

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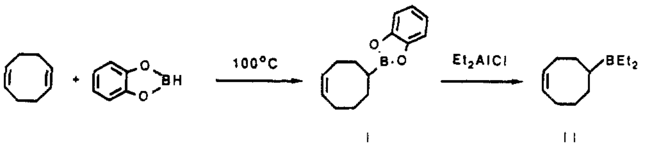
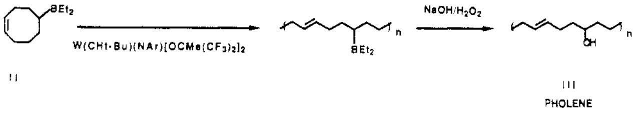
Scheme I



Scheme II



10.9 mol) was then added dropwise to the polymer solution, which was cooled with an ice–water bath. After the addition was complete, the solution was heated in an oil bath at 40–50 °C for 12–16 h. The polymer was precipitated in water, washed, and redissolved in THF. A small amount of insoluble material was removed by centrifugation; the supernatant solution was then reprecipitated in water. The polymer was dried in a vacuum oven at 50 °C. The yield after oxidation was 210 mg, corresponding to a 60% yield.

Hydroboration of the Unsaturated Polyborane. The polymerization was carried out as described above. After the polymerization, only a few drops of 2-propanol were added to cause the termination,[4] and ca. 10 mL of THF was added to dissolve the gel. 9-BBN (2-fold excess) was then added to the polymer solution and allowed to react for ca. 16 h. The oxidation and purification of the polymer were done similarly as described above. A smaller mole ratio of 9-BBN was used to effect a smaller extent of hydroboration.

Results and Discussion

One of the most straightforward approaches for the synthesis of alkenyl- and cycloalkenylboranes[5] is by controlled monohydroboration of diolefinic hydrocarbons using an excess of the olefin to suppress the formation of the bis-hydroboration product. Among the various dialkylboranes (R_2BH) available for such reactions, only the ones with very bulky R groups are stable and isolable. Examples of such boranes are 9-borabicyclo[3.3.1]nonane (9-BBN) and diisopinocamphenylborane (Ipc_2BH).[6] 9-BBN has been used for the synthesis of a variety of alkenylboranes: $CH_2{=}CH(CH_2)_nCH_2\text{-}BBN$ with $n = 2, 3,$ and 5[1] and also cycloolefinic boranes such as norbornenyl-9-BBN.[2] However, the synthesis and isolation of the analogous cyclooctenyl-9-BBN monomer were difficult. The molecular weight of cyclooctenyl-9-BBN being large, its distillation proved to be very difficult even under high-vacuum conditions. Therefore, the synthesis of a lower molecular weight and lower boiling derivative, cyclooctenyldiethylborane (II), was undertaken. The synthesis of the diethyl derivative was achieved in two steps (Scheme I). In the first step 1,5-cyclooctadiene was heated to 100 °C with catecholborane in the absence of solvent. Formation of the bis-hydroboration product was minimized by employing a large excess of the diene. By running the reaction neat, we could easily recover the excess diene by distillation. The residual product mixture containing cyclooctenylcatecholborane (I) was treated with diethylaluminum chloride to give the required monomer, which was easily purified by distillation. Among the various ethylaluminum compounds, diethylaluminum chloride gave the best results, as the dialkoxyaluminum chloride formed precipitated out and was easily removed by filtration. Use of triethylaluminum, on the other hand, leads to the formation of a viscous reaction mixture, making the isolation of the required product difficult. Triethylaluminum is also more reactive than diethylaluminum chloride and was shown to undergo alkyl-exchange reaction with the product, trialkylborane II, and catalyze the scrambling of the alkyl groups in the borane.[7]

The monomer II was polymerized with a Lewis acid free metathesis catalyst, $W(CH\text{-}t\text{-}Bu)(NAr)(OCMe[OCF_3]_2)_2$.[8] The polymerization occurred very rapidly; the resulting polymer was oxidized with alkaline H_2O_2 to give poly(5-hydroxyoctenylene) (PHOLENE) (III) (Scheme II). The ^1H NMR spectrum of PHOLENE is shown in Figure 1a. The relative integral intensities of the various protons (vinylic protons at 5.4 ppm, C*H*OH at 3.6 ppm, and the saturated methylene protons at 2.0–2.2 and 1.3–1.6 ppm) are in accordance with the expected structure III. PHOLENE (III) can be described as a terpolymer of butadiene, ethylene, and vinyl alcohol. The unique feature of the structure lies in the fact that arrangement of the monomer units on the backbone is exactly controlled, leading to a regular terpolymer. A variation in the arrangement, however, can occur due to the presence of various head to head, head to tail, and tail to tail sequences.

The ^{13}C NMR spectrum of PHOLENE is shown in Figure 2a. This spectrum indicates that mainly trans double bonds are formed during the polymerization.[9] The assignment of the various peaks in the spectrum was made based on the measured chemical shift values of unsubstituted poly(1-octenylene) (POLENE).[10] Upon substitution of one of the hydrogens in POLENE with an OH group, the chemical shifts of all its carbons are shifted. The extent by which the various α to ϵ carbon atoms are shifted upon such a substitution in a linear secondary alcohol has been established.[11] Using these OH shift parameters, we calculated the expected carbon chemical shifts of poly(5-hydroxyoctenylene); these calculated values are compared to those obtained experimentally in Table I. The table indicates good agreement between the calculated and observed values. The small discrepancy between the observed and calculated values of the α-carbon may indicate that the α-OH shift parameter in the polymer is smaller than that observed in linear secondary alcohols.

The borane polymer can be further modified by hydroboration with 9-BBN prior to oxidation. By controlling the stoichiometry of the hydroborating agent, one can get either partially or completely hydroborated polymer, which upon oxidation gives polyalcohols (PHOLENE-OHp and PHOLENE-OH, respectively) (Scheme III). Complete hydroboration–oxidation results in structure V, which can be described as an alternating copolymer of ethylene and vinyl alcohol. The ^1H NMR spectra of IV and V are shown in Figure 1b,c, and their ^{13}C NMR spectra in Figure 2a,b. The extent of oxidation was calculated from the relative intensity of the vinyl protons. Upon partial oxidation, the ^{13}C NMR spectrum becomes more complicated, and the peak due to the C-5 carbon (Figure 2b) splits into three peaks corresponding to the different environments that are generated.

The three possible arrangements, i.e., head to head, head to tail, and tail to tail, in PHOLENE are shown in Scheme IV. Upon oxidation these sequences would generate three kinds of diol segments: 1,4-, 1,5-, and 1,6-diols. The dashed lines in Scheme IV indicate the alternative position for the hydroboration of the double bond. The 1,4-diol would generate two kinds of carbons, C_α and C_β, while the 1,5- and 1,6-diols would generate three kinds of carbons, C_α, C_β, and C_γ (Table II). One can calculate the expected chemical shifts for these sequences, as done previously, using the various α to ϵ chemical shift constants for a linear secondary alcohol (Table I). These shift constants were applied to the various carbon chemical shifts of the completely hydroborated and oxidized poly(1-octe-

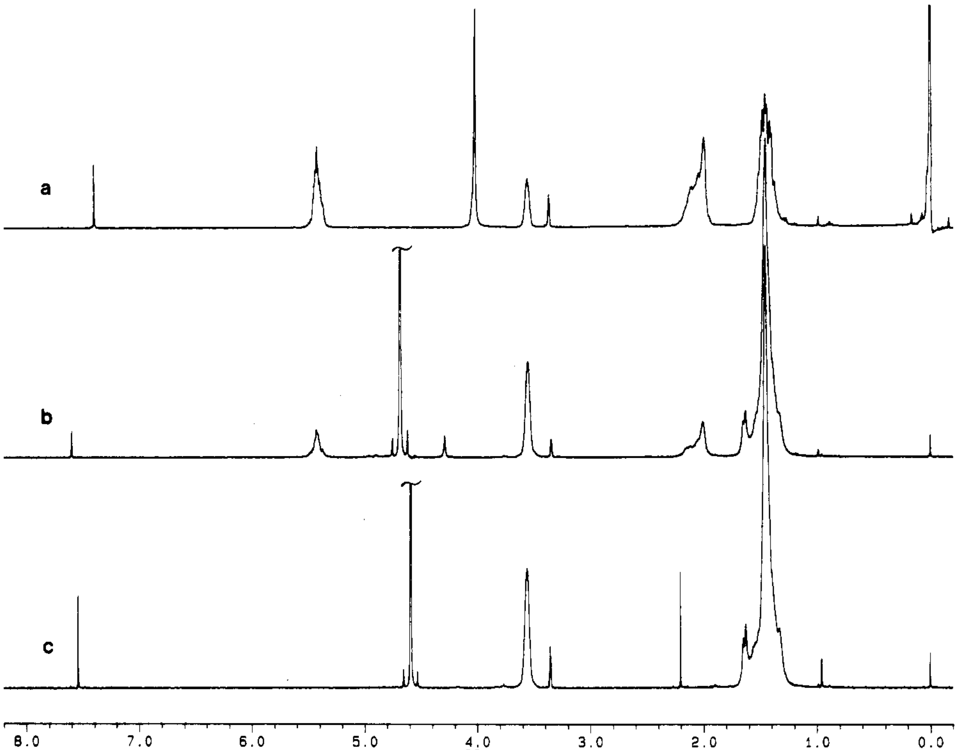


Figure 1. ^{1}H NMR spectra of poly(5-hydroxyoctenylene) (PHOLENE) (a) before oxidation, (b) after partial oxidation, and (c) after complete oxidation (PHOLENE-OH).

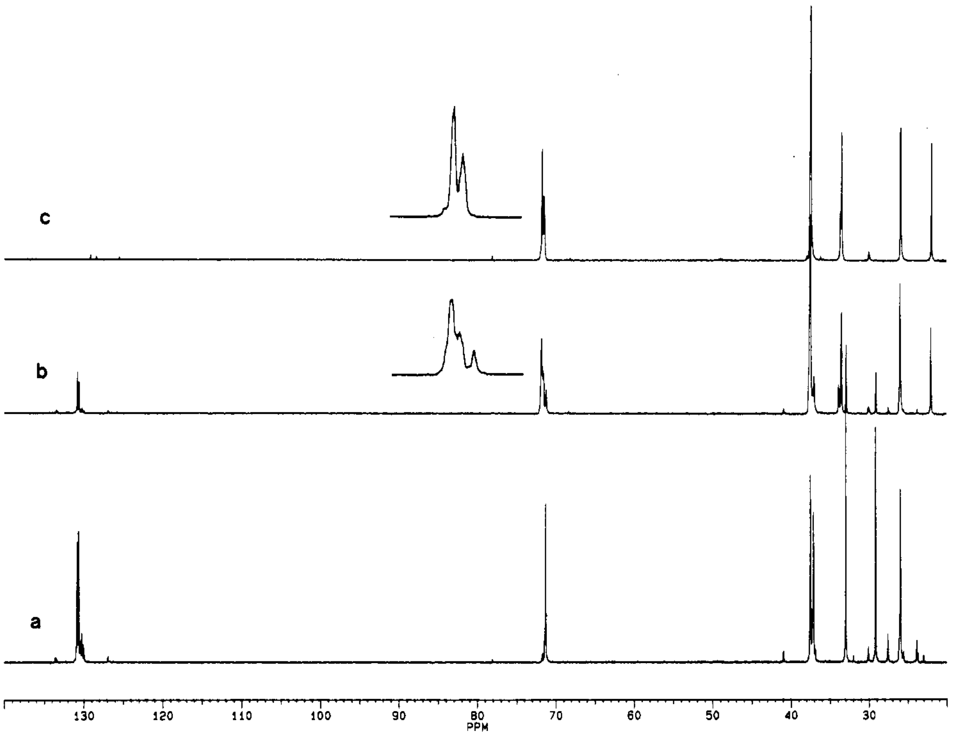


Figure 2. ^{13}C NMR spectra of PHOLENE (a) before oxidation, (b) after partial oxidation, and (c) after complete oxidation (PHOLENE-OH).

nylene) (POLENE-OH) (Table II). On the basis of these calculations, the various peaks of PHOLENE-OH were assigned. These calculated values along with the observed ones are listed in Table II. The calculation yields two different values depending on the carbon whose chemical shift one uses for the calculation. For example, in the case of the $C_\alpha(1,4)$, a value of 71.35 ppm is obtained if one uses the C_α (71.15 ppm) chemical shift of POLENE-OH and the δ or ϵ shift constants (+0.2 ppm), while a value of 73.83 ppm is obtained if either the C_δ or C_ϵ (29.33 ppm) chemical shift and the α-shift constant (+44.5 ppm) were used.

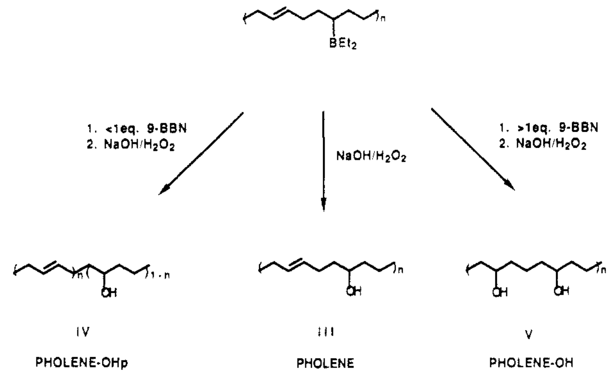
Although the absolute calculated values using the various substitution parameters are slightly different from the observed ones, the assignment of the various carbons can be made with confidence, because the order (downfield to upfield) is correctly predicted. Thus, the C_β methylene carbon of both 1,5- and 1,6-diols appears at 36.5 ppm, while that of the 1,4-diol appears at 32.6 ppm. On the other hand, the C_γ methylenes of the 1,5- and 1,6-diols appear at 21.1 and 25 ppm, respectively. One further confirmation comes from the fact that the differences in chemical shifts, $[C_\beta(1,5) - C_\beta(1,4)]$ and $[C_\gamma(1,6) - C_\gamma(1,5)]$, are found to be

Table I

sample		chem shift, ppm							
		C1	C2	C3	C4	C5	C6	C7	C8
POLENE									
trans		130.37	130.37	36.62	29.65	29.09	29.09	29.65	32.62
cis		12.989	129.89	27.27	2..78	29.26	29.26	29.78	27.27
PHOLENE									
trans	obsd	130.46	130.66	28.99	37.32	71.13	36.91	25.82	32.80
	calcd[a]	130.37	130.57	29.32	37.05	73.59	36.49	26.35	32.82
cis	obsd	129.94	130.17	23.75		71.30		25.95	27.45
	calcd[a]	129.89	130.09	23.97	37.18	73.76	36.66	26.48	27.27

[a] Calculated by using chemical shift parameters for secondary alcohols: $\alpha = +44.5$, $\beta = +7.4$, $\gamma = -3.3$, $\delta = +0.2$, $\epsilon = +0.2$.

Scheme III



Scheme IV

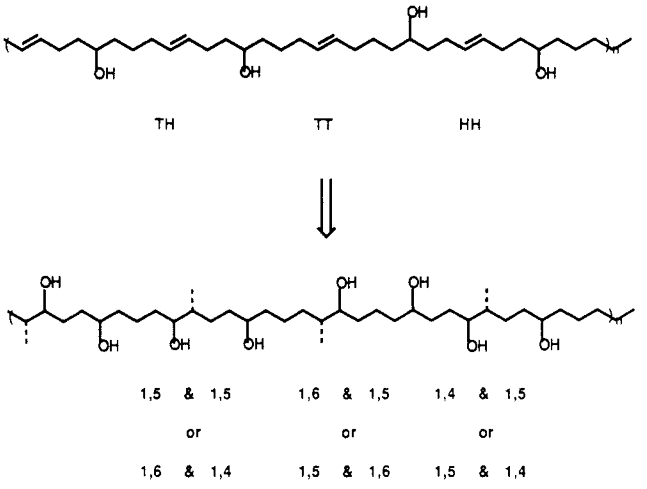
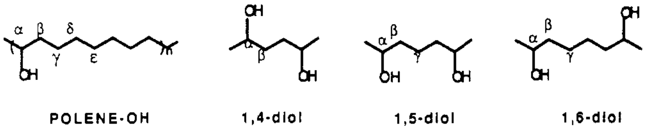


Table II



POLENE-OH		PHOLENE-OH		
		chem shift, ppm		
chem shift, ppm	assignt	obsd	calcd[a]	assignt
71.15	C_α	70.77	71.35 (73.83)	C_α (1,4); C_α (1,5)
36.81	C_β	70.54	71.15 (73.63)	C_α (1,6)
25.21	C_γ	36.49	37.00 (36.73)	C_β (1,5); C_β (1,6)
29.33	C_δ, C_ϵ	32.73	33.50 (32.61)	C_β (1,4)
		32.56		
		25.03	25.41 (26.03)	C_γ (1,6)
		25.00		
		21.06	21.91	C_γ (1,5)

[a] The two values are obtained by using the various OH-group shift constants on the chemical shift values observed for POLENE-OH.

Table III

sample	mol % of 1,4-diol	mol % of 1,5-diol	mol % of 1,6-diol
PHOLENE-OH	32.8 30.6[a]	36.6	30.6
PB-OH	27.4 25.2[a]	44.8	27.8

[a] Mole percent calculated from an alternate method using the 1,4-diol peak at 32.6 ppm and the single peak due to both the 1,5- and 1,6-diols at 36.5 ppm.

equal and have a value of 3.9 ppm. On the basis of our assignment, this difference should correspond to $-(\delta - \gamma)$, where δ is a small positive value and γ is a larger negative value. The C_β(1,4) and C_γ(1,6) peaks appear as doublets, suggesting the presence of two different local environments. The exact nature of this splitting eludes explanation, although it may be due to intramolecular hydrogen bonding between the adjacent OH groups of different sequences.

The amounts of the various diol segments present in the polymer can be calculated from the relative intensities of these peaks.[12] Since the C_γ carbon peak of the 1,5-diol segment (21.1 ppm) represents only one carbon, while all the other peaks represent two carbons in each segment, the intensity of the former peak is doubled prior to their comparison. The mole percent of the 1,4-diol segment can be calculated by comparing the intensity of the 32.5 ppm peak with either that of the 36.5 ppm peak or those of the peaks at 25 and 21.1 ppm. The mole percents of the various diol segments thus obtained are listed in Table III. The close agreement between the values obtained from both these calculations reaffirms our peak assignments.

The completely oxidized polymer structure V can also be obtained by the complete oxidation of pure poly(1,4-butadiene). Pure poly(1,4-butadiene) was obtained by ring-opening metathesis polymerization of 1,5,9-cyclododecatriene.[13] Complete hydroboration–oxidation of poly(1,4-butadiene) gave PB-OH, an alternating copolymer of ethylene and vinyl alcohol. The ^{13}C NMR spectrum of PB-OH is compared with that of PHOLENE-OH in Figure 3. The spectra indicate that the structures of the two polymers are similar, but the relative intensities of the various peaks are different. The amounts of the various diol segments were calculated as in the case of PHOLENE-OH and are given in Table III. The mole percent of 1,5-diol segment in the PB-OH case is significantly higher than in the case of PHOLENE-OH. If the hydroboration of polybutadiene were statistically random, one would expect

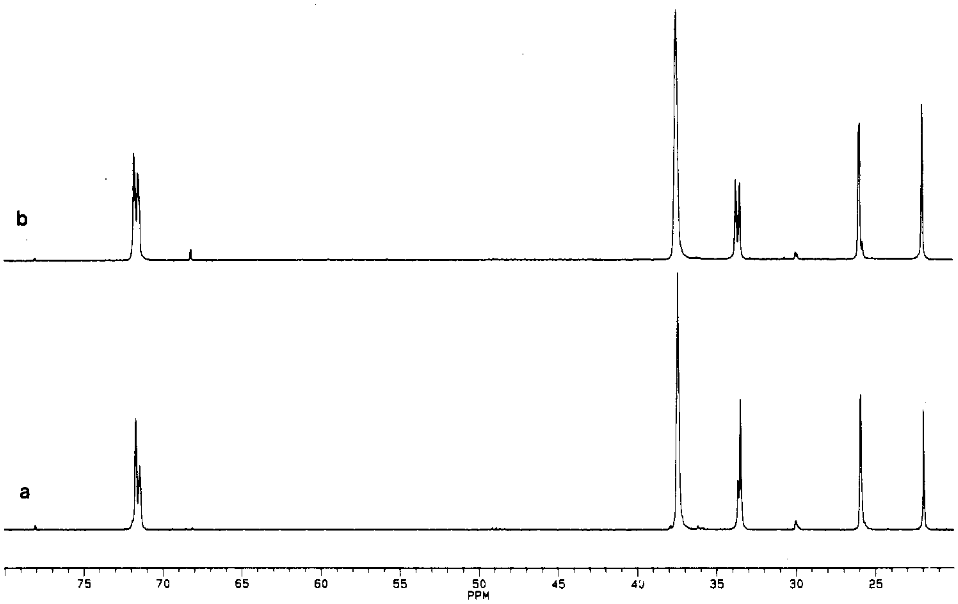


Figure 3. ^{13}C NMR spectra of (a) PHOLENE-OH and (b) PB-OH.

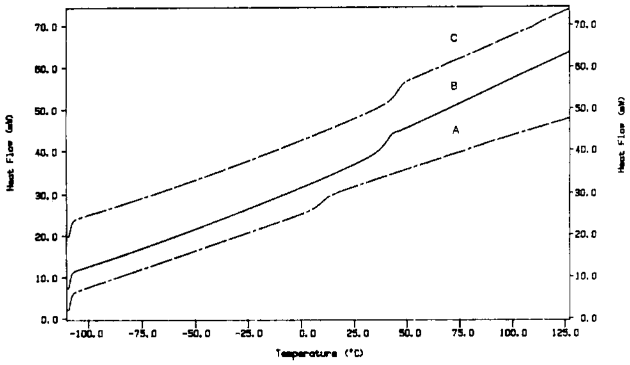


Figure 4. DSC thermograms of PHOLENE (a) before oxidation, (b) after partial oxidation, and (c) after complete oxidation (PHOLENE-OH).

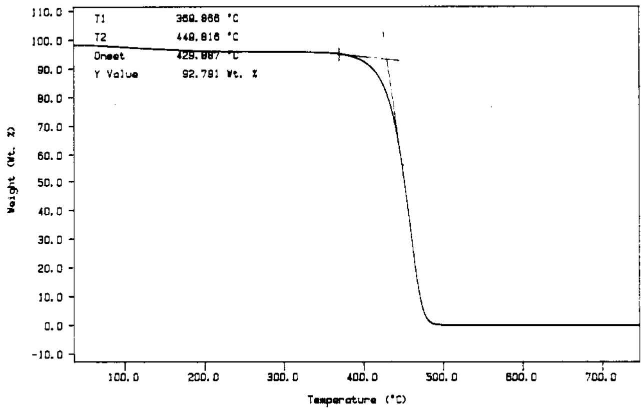


Figure 5. TGA curve of PHOLENE.

the amount of 1,5-diol segment (50%) to be twice that of the 1,6- and 1,4-diol segments (25% each). In the case of PB-OH the observed values are close to the expected ones, suggesting a fairly random hydroboration, whereas in the case of PHOLENE-OH the deviation is much larger.

This deviation in the relative diol concentrations can arise from two factors: one due to the nonrandom formation of the various HH, HT, and TT sequences in PHOLENE, and the second due to regioselective hydroboration of the parent polyborane. If one looks at Scheme IV, it is clear that a TH or HT sequence would generate twice as many 1,5-diol segments as 1,4- and 1,6-diols, provided the hydroboration of the double bond is random. On the other hand, due to the symmetric placement of the double bonds in the HH and TT segments, a TT sequence would generate equal amounts of 1,6- and 1,5-diols, and a HH sequence would generate equal amounts of 1,4- and 1,5-diols, irrespective of the regiochemistry of the hydroboration. Since the concentrations of the 1,4- and 1,6-diols are found to be equal in PHOLENE-OH, it is apparent that the amounts of HH and TT sequences, if present, are equal. It would also follow that equal amounts of HH and TT segments, together, would result in the same diol distribution as in the case of a HT or a TH segment. Therefore, it would be difficult to comment on the true concentration of the various HH, HT, and TT sequences from these final diol distributions.

Since the concentrations of HH and TT segments in PHOLENE-OH, if present, are equal, the lower concentration of the 1,5-diol (being only slightly higher than that of the 1,4- and 1,6-diols, as opposed to the expected twofold value) can be attributed to the regioselective hydroboration of the HT segment in the polyborane. A preferential attack from the less hindered side in an extended all-trans HT segment (Scheme IV) would lead to the formation of 1,4- and 1,6-diols and result in the observed lowering of the 1,5-diol concentration. This is not an unreasonable explanation considering the bulky nature of the hydroborating agent used, namely, 9-BBN.

The polyalcohols were soluble only in mixed solvents such as THF/methanol and chloroform/methanol. The parent polymer III after acetylation was soluble in pure THF, and hence its molecular weight after acetylation was determined by GPC using THF as the solvent. Its molecular weight was found to be 122 000, with a polydispersity of 2.8. The molecular weight distribution was rather broad as expected for metathesis polymerizations of such unstrained cycloolefins.

The DSC thermograms of the polymers are shown in Figure 4. The glass transition temperature of the parent polymer III was found to be ca. 11 °C and increased to ca. 45 °C upon complete oxidation to give poly(ethylene-*alt*-vinyl alcohol) (V). The T_g of the partially oxidized polymer, was found to be in between the two extremes, as expected. The thermal stability of the parent polymer III and its derivatives IV and V was also found to be significantly better than that of poly(vinyl alcohol). The TGA curve of polymer III is shown in Figure 5. The polymer begins to lose weight at 430 °C, which is ca. 130 °C higher than the value for poly(vinyl alcohol), which begins to lose weight at ca. 300 °C. Derivatives IV and V also have very similar TGA curves. This higher thermal stability of these polyalcohols is noteworthy, as all these polymers have a structure very similar to that of PVOH and yet degrade at much higher temperatures.

In conclusion, we have established a novel route to the synthesis of poly(5-hydroxyoctenylene) (PHOLENE), a regular terpolymer of butadiene, ethylene, and vinyl alcohol. Further use of hydroboration chemistry gave access to polymers with different hydroxyl content. Upon complete hydroboration followed by oxidation, an alternating copolymer of ethylene and vinyl alcohol (PHOLENE-OH) was obtained. The presence of various 1,4-, 1,5-, and 1,6-diol segments in PHOLENE-OH was established by ^{13}C NMR spectroscopy. The relative concentration of the various diol segments in the polymer suggests a regioselective hydroboration of the precursor polyborane, using 9-BBN as the hydroborating agent. The glass transition temperature of the polymers increased with the hydroxyl content. All the polyalcohols had higher thermal stability as compared to poly(vinyl alcohol), which is also a secondary alcohol.

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(4) 9-BBN reacts with alcohol very rapidly to form alkoxy-9-BBN, and hence an excess of alcohol was not used in the termination step.

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(8) The catalyst was provided by Professors K. B. Wagener and J. M. Boncella of the University of Florida, Gainesville.

(9) The trans content was found to be around 80% from the integral intensities of the vinylic carbons.

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(11) Stothers, J. B. *Carbon-13 NMR Spectroscopy*; Academic Press: New York, 1972.

(12) Although a DEPT pulse sequence was used to record the spectra, the intensities of the peaks can be taken to represent the concentration, provided the carbons under consideration are attached to the same number of hydrogens.

(13) A high *trans*-poly(1,4-butadiene) content (>80%) was obtained with $W(CH^tBu)(NAr)(OCMe[OCF_3]_2)_2$ as the catalyst.

Registry No. (5-Cyclooctenyl)diethylborane, 129064-30-8; 1,5-cyclooctadiene, 111-78-4; catecholborane, 274-07-7.