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Poly(*exo*-5-hydroxynorbornene): Structural Characterization and Property Evaluation of Various Cis–Trans Isomer Compositions

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ABSTRACT: Poly(*exo*-5-hydroxynorbornene) was synthesized via ring-opening metathesis polymerization of an organoborane derivative of norbornene. The polyborane was oxidized by using alkaline H_2O_2 to give the hydroxy polymer. With the objective of controlling the spatial orientation of the hydroxyl groups on the polymer backbone, polymers with different cis–trans contents were synthesized by different polymerization catalysts. The structural characterization of these polymers was done by using IR, ^{1}H NMR, and ^{13}C NMR spectroscopy. The molecular structure details will be discussed in terms of sequence distribution of cis–trans and head–tail diads. The thermal properties and molecular orientation of various isomeric structures were evaluated by DSC and two-dimensional surface studies at the air–water interface separately. Surface area measurements show that the polymer backbone with cis structure has significantly higher rigidity than that of the corresponding trans form.

Introduction

The incorporation of functional groups into hydrocarbon polymers represents a useful method for modifying the chemical and physical properties of polymers, such as adhesion to substrates and compatibility with other polymers in polymer blends. Unfortunately, the sensitivity of most organometallic catalysts toward functional monomers with heteroatoms, such as O, N, and X (halides), has often hampered their utilization in the synthesis of functional polymers. We have developed organoborane monomers such as 1-alkenyldialkylboranes[1,2] and cycloalkenyldialkylboranes[3,4] that are stable to organometallic polymerization catalysts. The former compounds were polymerized by using the Ziegler–Natta process, while the latter compounds were subjected to ring-opening metathesis polymerization. Organoboranes are very versatile intermediates and have been transformed into a variety of functional groups.[5-7] Among the various functional groups, the hydroxyl group can be readily obtained under mild oxidation conditions using alkaline H_2O_2. Using this approach, we have synthesized a variety of poly(alcohol)s by Ziegler–Natta polymerization.[1,2] The alcohol content in these polymers may be varied by copolymerization with other 1-alkenes.[8]

In our previous paper, we demonstrated that cycloalkenyldialkylboranes such as norbornenyl-9-borabicyclononane can be polymerized by ring-opening metathesis catalysts.[3] A standard catalyst combination, such as WCl_6/Me_4Sn, was used to give poly(*exo*-5-hydroxynorbornene) upon oxidation. The polymer was found to contain equal amounts of both cis and trans double bonds. The spatial orientation of the hydroxyl group in these polymers is governed by both the exo–endo and cis–trans isomer composition. Because of the polar nature of the hydroxyl group, the different orientations of these functional groups along the polymer backbone would result in interesting differences in some of their interfacial behavior, such as at the air–water interface or oil–water interface. Our approach to the synthesis gives the pure exo form of the borane monomer and, therefore, the pure *exo*-hydroxy polymer. To further control the orientation of the hydroxyl group on the polymer backbone, we have synthesized polymers with different isomer compositions ranging from almost completely cis to high trans. The isomer composition of these polymers was determined by ^{13}C NMR spectroscopy, and the detailed spectral analysis of these polymers is presented in this paper. Preliminary data on the spreading behavior of the different isomers at an air–water interface are also discussed.

Experimental Section

All the manipulations of the organometallic and organoborane compounds were done in an inert atmosphere, either in a drybox or by using Schlenk techniques. Toluene and THF were distilled over sodium benzophenone ketyl, and 2-propanol was distilled first over CaH_2 and then over $SnCl_2$. The solvents were then stored under argon in the drybox. WCl_6, Me_4Sn, norbornadiene, and 9-borabicyclononane (9-BBN) were purchased from Aldrich Chemical Company. Me_4Sn was distilled under argon over CaH_2 and stored in a Schlenk tube. Norbornadiene was degassed by the freeze–pump–thaw technique prior to use. W(CH-*t*-Bu)(NAr)(OCMe[CF_3]$_2$)$_2$ and W(CH-*t*-Bu)(NAr)(O-*t*-Bu)$_2$ (Ar = 2,6-diisopropylphenyl) were provided by Professors K. B. Wagener and R. R. Schrock, respectively.

Norbornenyl-9-borabicyclononane (I). 9-BBN (12.2 g, 0.1 mol) was dissolved in 150 mL of THF, placed in an addition funnel, and added dropwise to a stirred solution of norbornadiene (36.86 g, 0.4 mol) in 50 mL of THF. After about 16 h, the solvent and the excess of norbornadiene were removed under vacuum. The remaining viscous oil was subjected to fractional vacuum distillation. The center cut was collected at a temperature of 90–97 °C under vacuum of 0.01 Torr to give 13.2 g (62% based on 9-BBN). The ^{1}H NMR spectrum of the product was found to be in agreement with that expected for the exo form.[9] This hydroboration reaction is very selective, occurring by cis addition from the less hindered side of the double bond.

Polymerization of I. The polymerization reactions were carried out in the drybox at room temperature. Toluene was used as the solvent with a 2 M monomer concentration. Typically, WCl_6 (18.64 mg, 0.047 mmol) was dissolved in 2.4 mL of toluene in the drybox, and Me_4Sn (13 μL, 0.094 mmol) was added to it with stirring. The catalyst solution was allowed to age for 5 min

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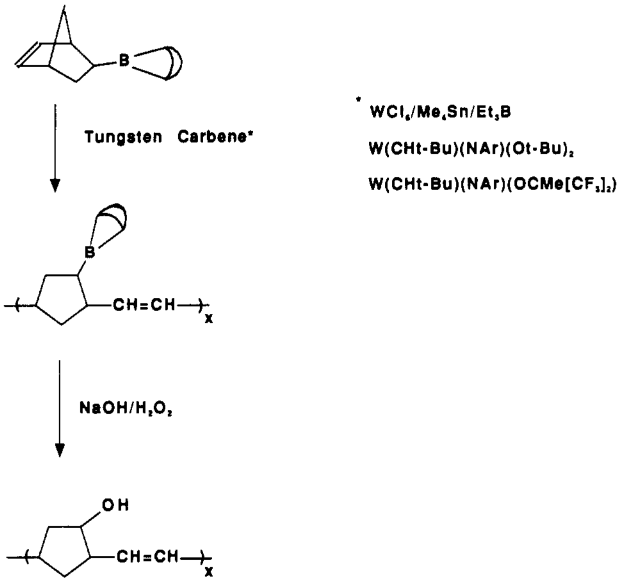
Scheme I



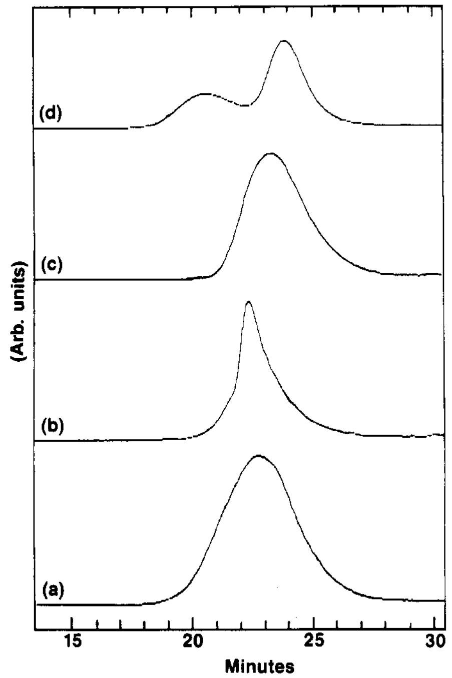


Figure 1. GPC profiles of PNBEOH polymers using (a) WCl$_6$/Me$_4$Sn, (b) W(CH-*t*-Bu)(NAr)(O-*t*-Bu)$_2$, (c) W(CH-*t*-Bu)(NAr)(OCMe[CF$_3$]$_2$)$_2$ (60 h), and (d) W(CH-*t*-Bu)(NAr)(OCMe[CF$_3$]$_2$)$_2$ (2 h).

before the addition of monomer I (1 g, 4.7 mmol), corresponding to a 1/100 catalyst-to-monomer ratio. The solution was stirred at room temperature. The polymerization was very rapid and caused an immediately observable increase in the viscosity of the reaction mixture. After 2 h, the polymerization was terminated by addition of an excess of 2-propanol. The precipitated polymer was washed thoroughly and redissolved in THF for oxidation. The typical yield of polyborane was about 84%. In both "Lewis acid free" catalyst cases, similar reaction conditions were used except the catalyst-to-monomer ratio was changed to 1/300 and the termination agent was benzaldehyde. The high *cis*-polyborane was obtained by using W(CH-*t*-Bu)(NAr)(OCMe[CF$_3$]$_2$)$_2$ as the catalyst. The isomer content was almost independent of the reaction time. On the other hand, the high trans polymer was prepared by W(CH-*t*-Bu)(NAr)(O-*t*-Bu)$_2$ catalyst. The isolated yield in both cases were very high, over 95% after 2 h reaction time.

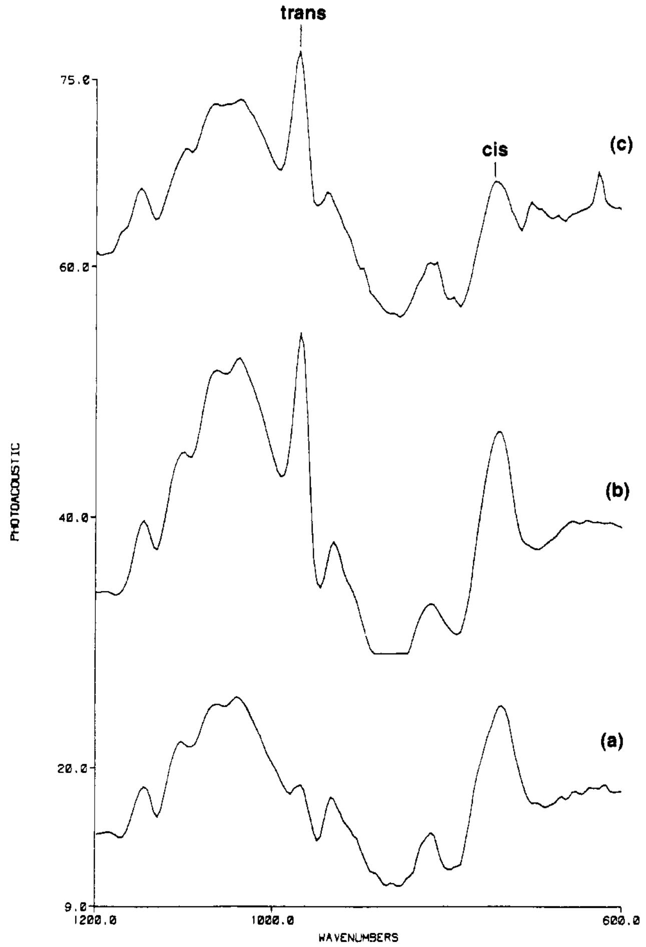


Figure 2. IR spectra of PNBEOH. (a) 93% cis, (b) 48% cis, and (c) 24% cis.

Oxidation of Polyborane. The polyborane was dissolved in THF, in a Schlenk flask, and removed from the drybox. Aqueous NaOH solution (6 M, 1.3 M excess) was degassed by bubbling argon and added to the solution of polyborane, which was cooled in an ice-water bath. H$_2$O$_2$ (30% solution, 3.9 M excess) was then added dropwise with stirring to the cool polymer solution. The solution was allowed to warm to room temperature and then heated at 40 °C for 12-16 h. The resulting poly(*exo*-5-hydroxynorbornene) was isolated by precipitating in an excess of water, washed thoroughly with acetone, and dried. Poly(*exo*-5-hydroxynorbornene) with various isomers was found to be insoluble in common organic solvents such as chloroform, THF, toluene, etc. However, it was readily soluble in the presence of varying amounts of methanol as a cosolvent, for example, in CHCl$_3$/MeOH or THF/MeOH.

Instrumentation. NMR spectra were recorded on a Bruker AM-360 spectrometer. The ^{13}C NMR spectra were recorded by using the DEPT (distortionless enhancement by polarization transfer) pulse sequence due to the overlap of one of the carbon peaks with the solvent (CDCl$_3$) peak. The DEPT pulse sequence transfers the proton polarization to the carbon nucleus, and therefore, both the deuterated and quaternary carbons do not appear in the spectrum. Since the polymers do not contain any quaternary carbons, this pulse sequence yielded their complete spectra. The IR spectra were recorded on a Digilab FTS40 spectrometer, using an MTEC 100 photoacoustic cell. GPC chromatograms were obtained by using 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 was used to effect the separation. The molecular weights are reported using polystyrene as the calibration standard. The DSC analysis was done by using a Perkin-Elmer DSC-7. The samples were first heated to about 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. The air-water interface studies were done by the usual Langmuir surface balance technique,[10] which measures the actual surface force between a clean surface and a monolayer

Table I
Summary of Poly(*exo*-5-hydroxynorbornene) Prepared by Three Tungsten Catalysts

sample/catalyst	reaction time, h	yield, %	cis content, %	M_n	M_w/M_n
PNBEOH-A/W(CH-*t*-Bu)(NAr)(OCMe[CF$_3$]$_2$)$_2$	2	95	93	270 204 34 833	bimodal
PNBEOH-B/WCl_6/Me_4Sn	2	84	48	58 198	2.3
PNBEOH-C/W(CH-*t*-Bu)(NAr)(O-*t*-Bu)$_2$	2	95	26	63 211	1.6
PNBEOH-D/W(CH-*t*-Bu)(NAr)(OCMe[CF$_3$]$_2$)$_2$	60	80	90	36 535	1.8

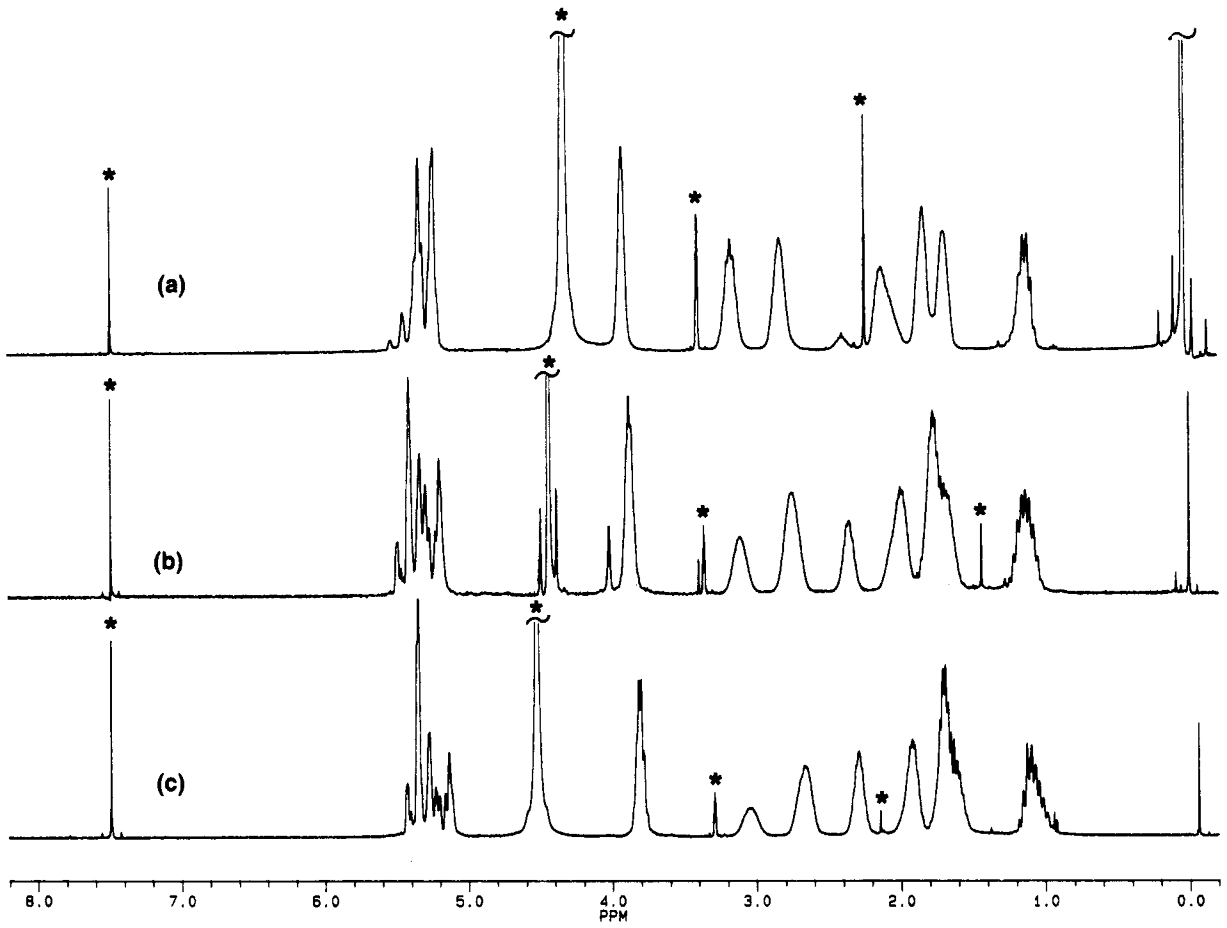


Figure 3. ^1H NMR spectra of PNBEOH. (a) 93% cis, (b) 48% cis, and (c) 24% cis (* peaks are due to solvents).

surface using a force-sting gauge. The polymer was first dissolved in a good solvent (THF/MeOH) and then was spread on the water surface. By compressing and expanding the monolayers at least two times, it was found that the isotherms were extremely stable and reversible.

Results and Discussion

The polymerization of norbornenyl-9-borabicyclononane was carried out by using three different catalysts, shown in Scheme I, to give polymers with different cis–trans compositions. Oxidation of the polyboranes using alkaline–H_2O_2 gave the corresponding poly(*exo*-5-hydroxynorbornene)s. The yields and isomer compositions of these polymers are given in Table I.

WCl_6/Me_4Sn gave a polymer with almost equal amounts of cis and trans double bonds. Conventional catalysts such as $ReCl_5$, which has been used to synthesize *cis*-polynorbornene, failed to polymerize the borane monomer. However, the polymerization was successfully achieved by using a Lewis acid free catalyst, such as W(CH-*t*-Bu)(NAr)(OCMe[CF$_3$]$_2$)$_2$,[11] which yielded a high cis polymer. On the other hand, when the less reactive W(CH-*t*-Bu)(NAr)(O-*t*-Bu)$_2$ was used, a high trans (76%) polymer was formed. Oxidation of these borane polymers yielded *exo*-poly(5-hydroxynorbornene)s with different cis–trans isomer compositions.

Molecular Structure Characterization. The molecular weights of these polymers were determined by GPC of the acetylated (% acetylation[12] > 90) derivatives, as the poly(alcohol)s were insoluble in any single solvent. The GPC curves of the different polymers are shown in Figure 1, and the molecular weights using polystyrene as the calibration standard are given in Table I. The more reactive W(CH-*t*-Bu)(NAr)(OCMe[CF$_3$]$_2$)$_2$ catalyst gave a polymer having a bimodal distribution. However, upon increasing the polymerization time (60 h), the higher molecular weight peak disappears, and the distribution becomes unimodal. This is probably due to the secondary metathesis of the double bonds on the polymer backbone, leading to chain scission. It is interesting to note that, despite this reduction in molecular weight, the cis content in the polymer remains essentially unchanged. This is unlike in the case norbornene polymerization, where it was observed that W(CH-*t*-Bu)(NAr)(OCMe[CF$_3$]$_2$)$_2$ gave high cis polymer at low temperatures (−40 to −20 °C) but upon retaining the polymer at 25 °C for several days, a high trans polymer was obtained.[13] This suggests that, in the case of 9-BBN substituted polymer, the catalyst retains the same stereospecificity during its reaction with the double bonds on the polymer backbone as with that on the norbornenyl-9-borabicyclononane monomer. This is

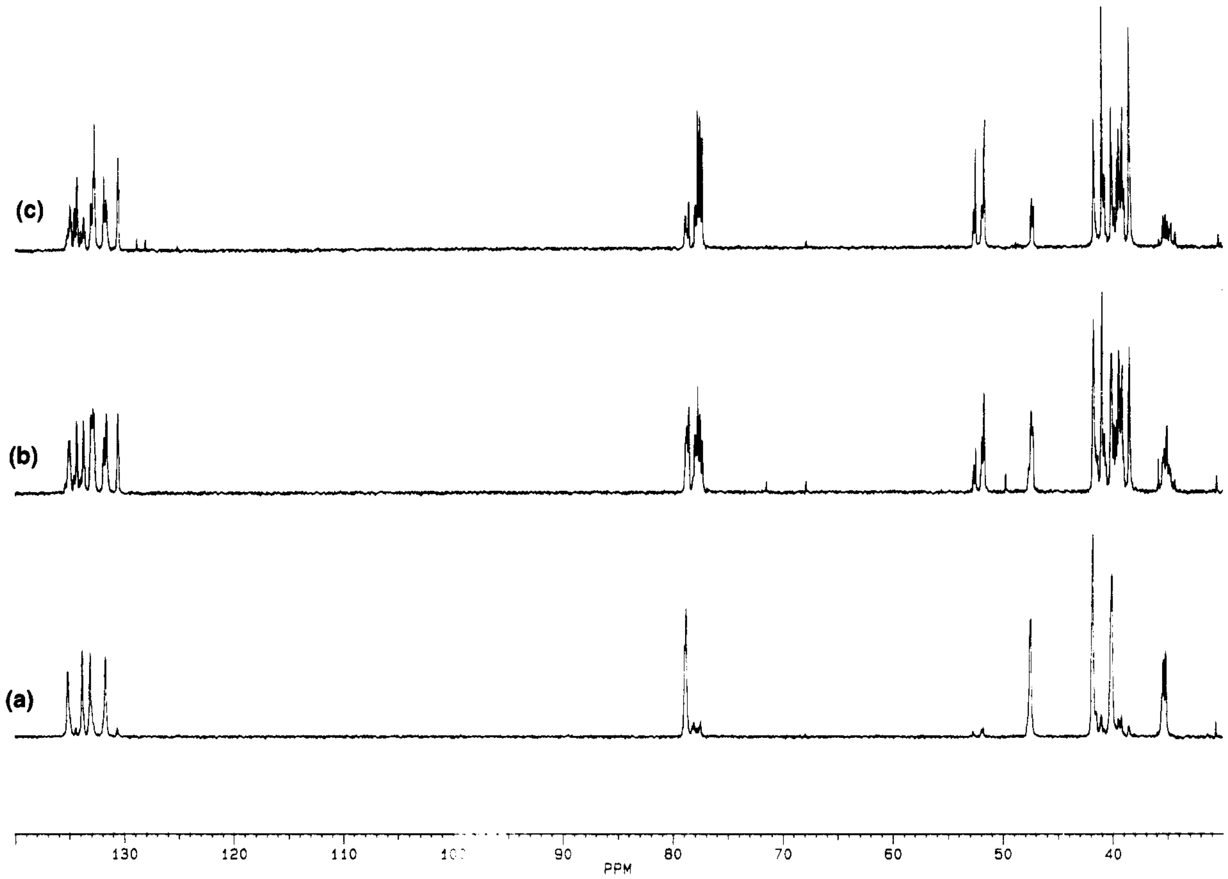


Figure 4. ^{13}C NMR spectra of PNBEOH. (a) 93% cis, (b) 48% cis, and (c) 24% cis.

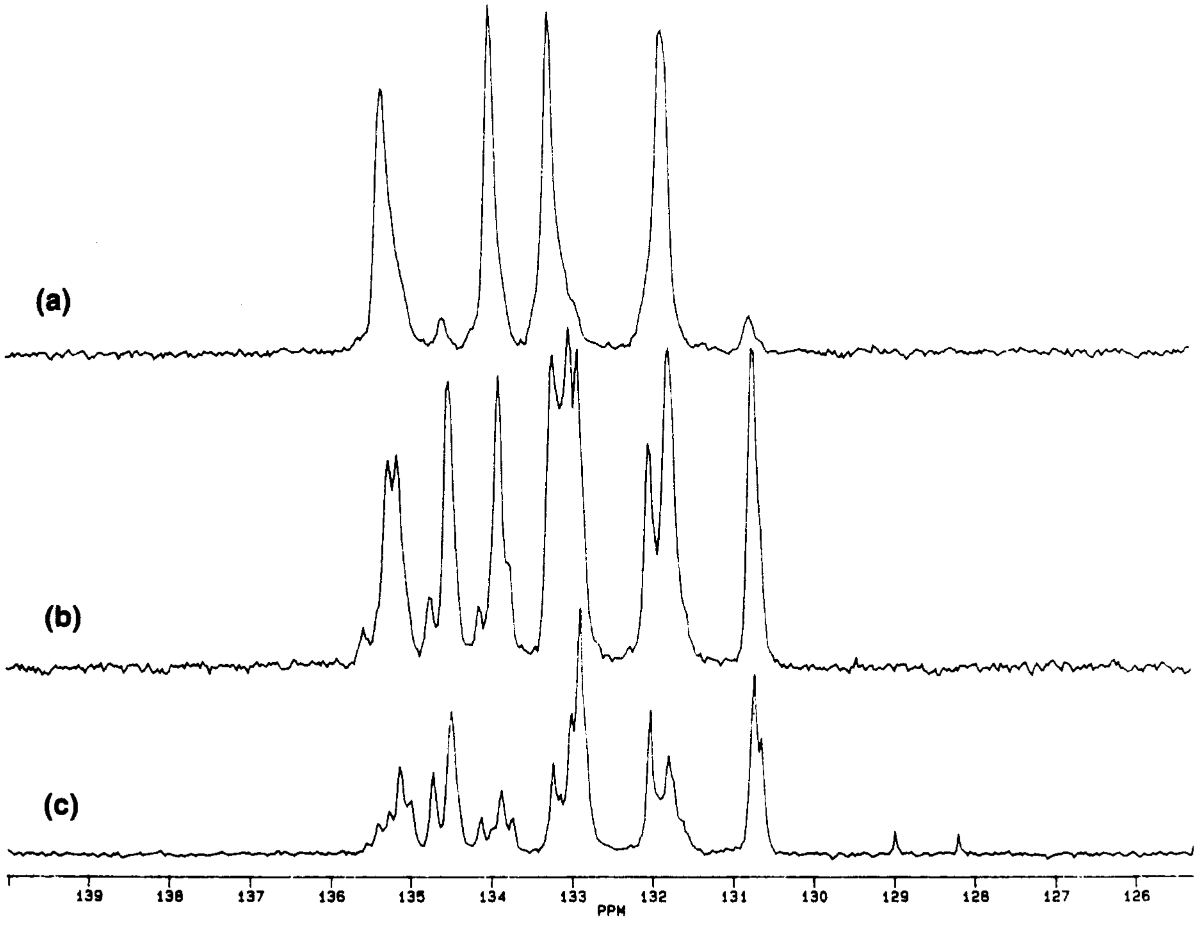


Figure 5. Expanded vinylic region of the ^{13}C NMR spectra of PNBEOH. (a) 93% cis, (b) 48% cis, and (c) 24% cis.

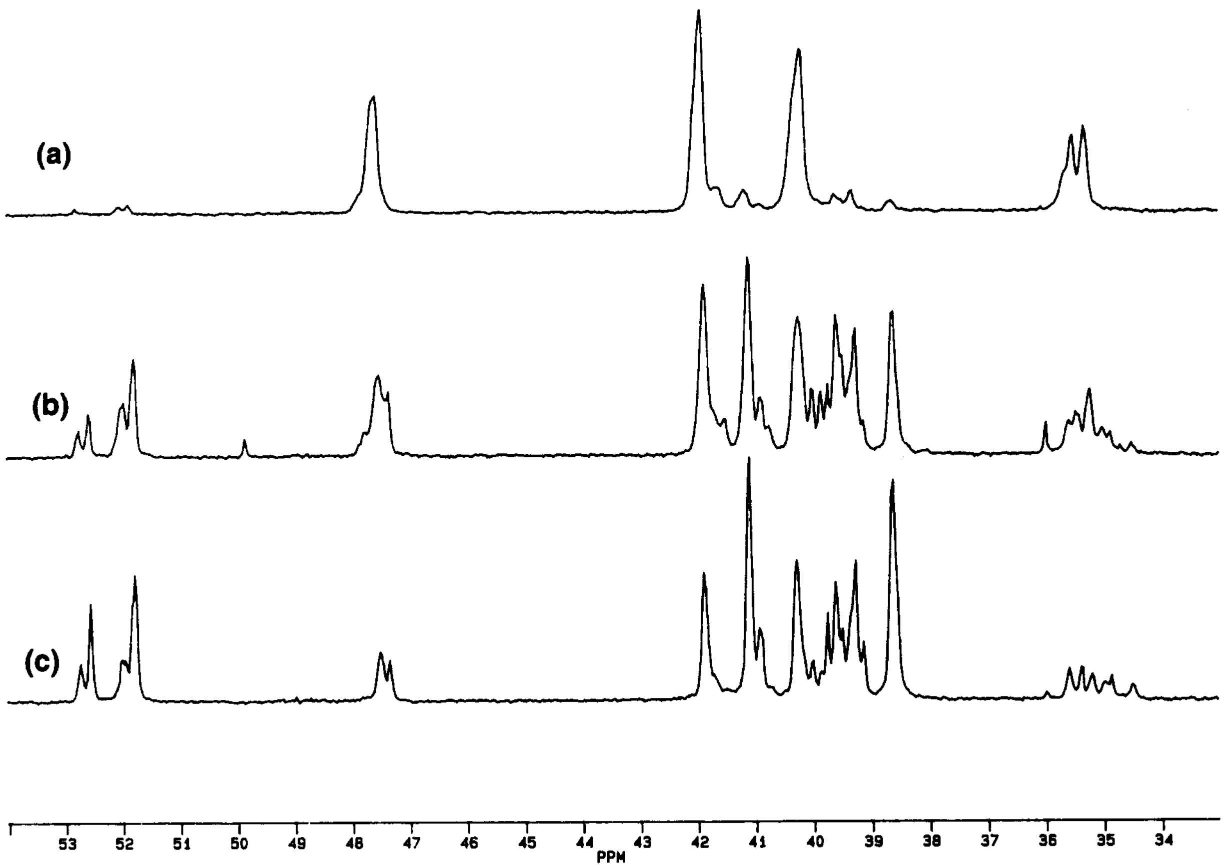
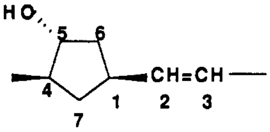


Figure 6. Expanded aliphatic region of the ^{13}C NMR spectra of PNBEOH. (a) 93% cis, (b) 48% cis, and (c) 24% cis.

unlike the case of norbornene, where the catalyst reacts with the double bond in the monomer to give a cis-specific reaction, but it reacts with one on the polymer chains to give a reversed specificity, yielding trans bonds. On the other hand, the use of "living" catalyst[14] of W(CH-*t*-Bu)(NAr)(O-*t*-Bu)$_2$ results in a high trans polymer with a polydispersity ($M_w/M_n = 1.6$) that is slightly higher than the expected value. The broadening in molecular weight distribution may be caused by side reactions.[6] For example, a boric acid and alcohol coupling reaction can cause partial cross-linked polymer, during the oxidation reaction.

The IR spectra of the polymers were recorded by using a photoacoustic IR spectrophotometer. Figure 2 shows the regions of the spectra that are of interest. The two peaks that are indicators of the isomer composition of the polymers are the peaks at 965 and 740 cm^{-1}. These are due to the trans and cis C–H out-of-plane bending vibrations, respectively. As seen from the spectra, the ratio of these peaks varies in the three polymers. PNBEOH-A has a high cis content, while PNBEOH-C has a high trans content. The quantitative determination of the isomer contents using these peaks is difficult due to the shape and baseline correction involved in this process. Since the quantitative isomer composition is easily retrievable from the NMR spectra, the IR spectrum was used only to give qualitative information to confirm the assignment of the NMR peaks.

The ^1H NMR spectra of the three polymers are shown in Figure 3. The vinylic region (5.0–5.5 ppm) shows distinct changes with the isomer composition. While the high cis polymer (3a) has a rather simple vinylic region, the cis–trans mixtures have several peaks resulting from various cis–cis, cis–trans, and trans–trans diads. The peaks at 3.0 and 2.3 ppm appear to be largely due to cis and trans allylic hydrogens on the C4 carbon, β to the OH group. The overall intensity of these peaks exceeded the value expected for a single hydrogen, suggesting contributions from other hydrogens. For this reason, the cis contents obtained with these peaks are less accurate than those obtained from the ^{13}C NMR spectra. The carbon atoms in the polymer repeating unit are numbered as shown below according to the scheme followed by Ivin and co-workers.[15]



The C5 hydrogen appears at 3.8 ppm and corresponds to a single proton in all cases. As the spectra were recorded in mixed CDCl$_3$/CD$_3$OD solvent, the OH protons undergo rapid exchange and appear along with the protic impurity usually present in CD$_3$OD.

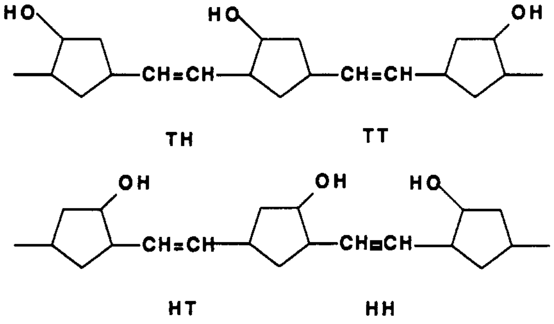
Analysis of the ^{13}C NMR Spectra. The ^{13}C NMR spectra of the polymers are shown in Figure 4. One notices that the high cis form (4a) has a rather simple spectrum. As the trans content in the polymers increases, the spectra begin to get complex due to the presence of various cis–cis (cc), cis–trans (ct), trans–trans (tt), and trans–cis (tc) diad sequences. The assignment of the various peaks was made knowing the expected shifts caused by hydroxyl group substitution on the chemical shifts of high *cis*-polynorbornene. The chemical shift parameters, $\alpha = 47.7$, $\beta = 9.4$, $\gamma = -2.2$, for a cyclic five-membered ring secondary alcohol were used for the calculations.[16] The chemical shift values thus calculated for the pure *cis*- and *trans*-poly(5-hydroxynorbornene)[17] along with the observed values are given in Table II. Overall, this table indicates quite good agreement between the calculated and observed values in the ring carbons.

Table II
Summary of Chemical Shifts in ^{13}C NMR Spectra of High *cis*- and High *trans*-PNBEOH

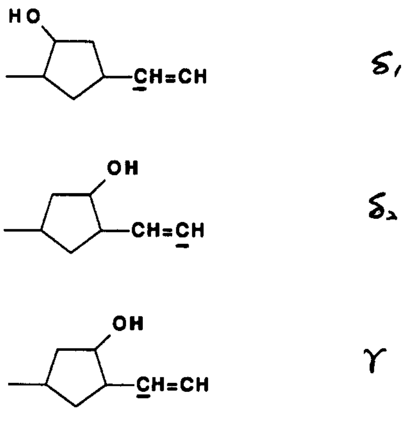
samples	chemical shifts, ppm						
	C1	C2	C3	C4	C5	C6	C7
cis-polynorbornene	38.60	133.88	133.88	38.60	33.21	33.21	42.70
cis-PNBEOH							
obsd[a]	35.30 35.65	135.36 134.00	133.24 131.88	47.55	79.15	42.24	40.35
calcd[b]	36.40			48.00	80.91	42.61	40.50
trans-polynorbornene	43.15	133.10	133.10	43.15	32.30	32.30	41.40
trans-PNBEOH							
obsd[a]	38.72	134.42 132.90	132.05 131.78	51.78 52.55	78.10	41.11	39.31 39.65
calcd[b]	40.95			52.55	80.00	41.70	39.20

[a] Major peaks in the spectra of high *cis*- and high *trans*-PNBEOH. [b] Calculation based on the chemical shift parameters for cyclic five-membered ring with secondary alcohol, $\alpha = 47.7$, $\beta = 9.4$, $\gamma = -2.2$.

The expanded vinylic regions is shown in Figure 5. The high *cis*-poly(*exo*-5-hydroxynorbornene) has four major peaks (135.36, 134.00, 133.24, and 131.88 ppm) with equal intensity, which is very similar to high *cis*-poly(*exo*-5-methylnorbornene).[15] It is clear that the peak splitting is strongly relative to the sequence distribution. Four possible diad arrangements, TH (tail–head), TT (tail–tail), HH (head–head), and HT (head–tail), are shown below.



The exact values of the substitution parameters for this system can be calculated by using the chemical shift for *cis*-polynorbornene (133.88 ppm) and three different substitution parameters, δ_1, δ_2, and γ, which are defined for the vinylic carbons as shown below.



The four equally intense peaks are expected to be displaced from that of *cis*-polynorbornene by $\delta_1 + \delta_2$ (two tail side carbons in TH and HT diads), δ_3 (two head side carbons in HT and TH diads), δ_1 (both carbons in TT diad), and $\delta_2 + \gamma$ (both carbons in the HH diad). Based on the observed chemical shifts for the various TH, TT, HH, and HT diads, the values obtained for the *cis*-poly(*exo*-5-hydroxynorbornene) are $\delta_1 = 0.12$, $\delta_2 = 1.36$, and $\gamma = -2.0$. Using the same argument and the assumption of similar substitution parameters, we also estimate the chemical shifts for the various TH, TT, HH, and HT diads in *trans*-PNBEOH, four calculated peaks, 134.48, 133.22, 132.46, and 131.10 ppm, which are quite close to four major observed peaks, 134.42, 132.90, 132.05, and 131.78 ppm, in Figure 5c for high *trans*-PNBEOH. The unassigned peaks in Figure 5b for the mixed composition may contribute to the splitting of cis and trans peaks, due to various cc, ct, tt, and tc diad sequences. The even intensity in all peaks implies that the mixed composition of PN-BEOH-N has a random distribution of cis and trans isomers and head and tall sequences.

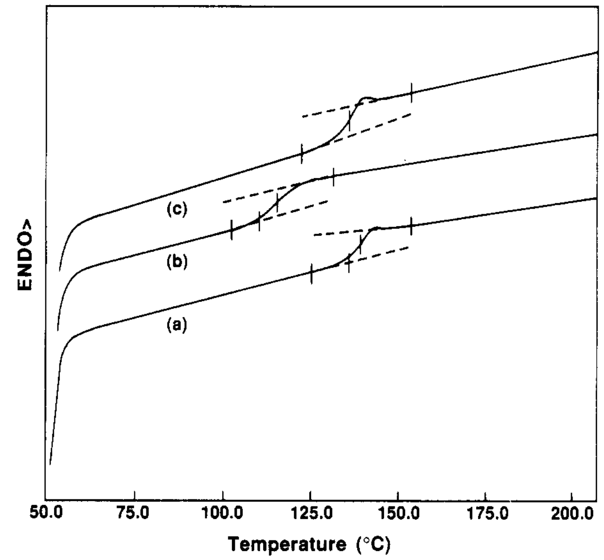


Figure 7. DSC results of PNBEOH. (a) 93% cis, (b) 48% cis, and (c) 24% cis.

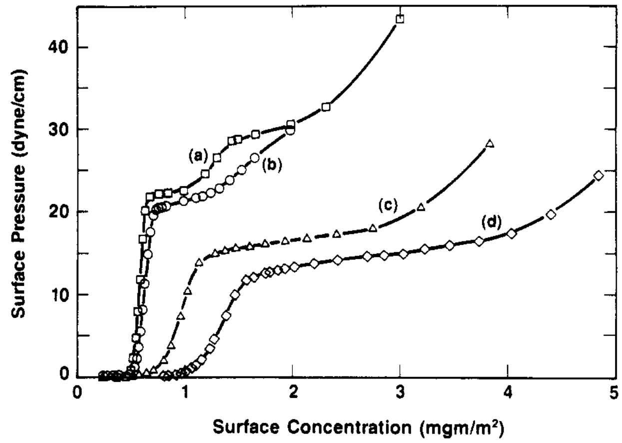


Figure 8. Surface pressure versus surface concentration of PN-BEOH. (a) 93% cis, (b) 90% cis, (c) 48% cis, and (d) 24% cis.

The expanded aliphatic region of the polymers is given in Figure 6. The peaks due to the various cis–cis, cis–trans, trans–cis, and trans–trans diad sequences have been similarly assigned. In some of the carbons, fine structure due to the presence of TH, TT, HH, and HT sequences can also be seen. The peaks that are most suited for the determination of the isomer composition are the peaks due to the allylic C4 carbon. This peak appears at around 52 ppm for the trans form and around 47 ppm for the cis form. Due to the unambiguous assignment and absence of any overlapping peaks, these peaks were used to calculate the isomer composition of the polymers. Although a DEPT pulse sequence was used to obtain the spectra, the comparison of the areas of the same carbon in different polymers is subjected to minimal errors. The compositions thus obtained are listed in Table I.

Thermal Properties. The thermal properties of the polymers were studied by DSC. As shown in Figure 7, all polymers exhibit a single glass transition temperature (T_g). Those for the high cis (140 °C) and mainly trans (138 °C) polymers are significantly higher than that of the cis–trans polymer (118 °C). A lower value for the cis–trans polymer is expected from its less regular microstructure compared with the other two. The presence of only one T_g in all isomers again shows the absence of microscopic phase separation; both head–tail and cis–trans sequences are randomly distributed along all polymer backbones.

Air–Water Interface Studies. One of the best methods to examine the molecular structure is to study the two-dimension monolayer. The hydrophilic groups (OH) in these otherwise hydrophobic polymers allow the formation of stable monolayers at the air–water interface. The Langmuir surface balance technique was used to measure the surface pressure–surface area.[18] As shown in Figure 8, preliminary data suggest that there is a significant difference in the area occupied per repeating unit of the various isomers. The high cis polymer (PNBEOH-A) occupies 38 Å^2/monomer unit, which is a much larger area than those occupied by the other isomeric polymers; only 9 Å^2/monomer unit was observed in high trans polymer (PNBEOH-C). This suggests that the cis polymer is rather rigid and lies stretched on the water surface with most of the OH groups at the interface. On the other hand, with increasing trans content, the polymer becomes more coiled and a smaller fraction of the OH groups lies at the interface, causing a reduction in its interfacial area.

Conclusion

Poly(*exo*-5-hydroxynorbornene) with varying cis–trans isomer composition was syntheized by ring-opening metathesis polymerization using different catalysts. The standard WCl_6/Me_4Sn catalyst gave a polymer having essentially equal amounts of cis and trans isomers. The more reactive tungsten carbene gave a highly enriched cis material, while the less reactive one gave a high trans polymer. These materials was structually characterized by using IR, ^1H NMR, and ^{13}C NMR spectroscopy. The peaks due to the various head–tail, head–head, tail–head, and tail–tail diads, along with the cis–cis, cis–trans, trans–cis, and trans–trans sequences were assigned. Preliminary results indicate a significant difference in the molecular orientation of the polymers having different cis–trans isomer compositions, suggesting that the cis polymer has extended structure, while the trans polymer is coiled. A detailed paper on the spreading behavior of the various isomers on the air–water interface using a Langmuir balance will be published elsewhere.

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