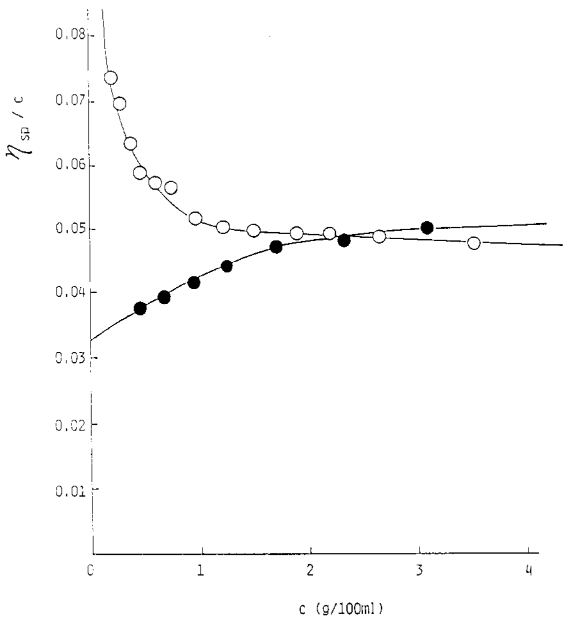

Figure 1. Reduced viscosity of II_A in aqueous solutions at 25 °C: (●) in pure water; (○) in 0.005 mol/L KCl.

°C in the presence and absence of potassium chloride. Figure 1 show plots of the reduced viscosity, η_{sp}/c, versus c for II_A in aqueous solutions, where c is expressed in grams per 100 mL. In pure water, η_{sp}/c was found to increase rapidly upon dilution, whereas the addition of potassium chloride eliminates the increase. Thus, polymer II_A shows polyelectrolyte behavior.

Acknowledgment. We thank the Research Center of Nitto Electric Co. Ltd., Osaka, Japan, for providing facilities for the measurement of GPC.

Registry No. I_A, 101707-61-3; I_A (homopolymer), 101707-62-4; I_B, 119296-72-9; I_B (homopolymer), 119296-76-3; I_C, 119296-73-0; I_C (homopolymer), 119296-77-4; II_A, 101647-92-1; II_B, 119296-74-1; II_C, 119296-75-2; potassium chloride, 7447-40-7.

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(10) Data: mp 129–131 °C; Yield 80%; IR (KBr) 1630 (m), 1655 (vs), 1598 (m) 1505 (vs) cm^{-1}; ^1H NMR (CD_3OD) δ 2.25 (s, 6, CH_3), 2.40–2.80 (m, 4, NCH_2CH_2CO), 4.96 (s, 2, CONH, OH). 6.70 (d, 2, aromatic ring protons), 7.30 (d, 2, aromatic ring protons). Anal. Calcd for $C_{11}H_{16}O_2N_2$: C, 63.44; H, 7.74; N, 13.45. Found: C, 63.29; H, 7.82; N, 13.17.

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(12) ^1H NMR ($CDCl_3$): (I_A) δ 2.55 (s, 6, CH_3), 2.65 (m, 2, NCH_2) 4.13 (m, 2, CH_2O), 4.36 (m, 4, methylene H of phospholane ring); (I_B) δ 1.43 (m, 18, CH_2), 2.56 (s, 6, CH_3), 2.67 (m, 2, NCH_2), 4.14 (m, 2, OCH_2), 4.37 (m, 4, methylene H of phospholane ring); (I_C) δ 2.50 (s, 6, CH_3), 2.40–2.80 (m, 4, NCH_2CH_2CO), 6.70 (d, 4, aromatic ring protons).

(13) II_A: ^1H NMR (CD_3OD) δ 3.30 (s, 6, CH_3), 3.50 (m, 4, N^+CH_2), 4.10–4.40 (m, 4, OCH_2); IR (neat) 1235 and 1080 cm^{-1} (POO^-). II_B: δ 1.32–1.50 (m, 18, CH_2), 3.32 (s, 6, N^+CH_3), 3.51 (m, 4, N^+CH_2), 4.12–4.43 (m, 4, OCH_2); IR (neat) 2840 (CH_2), 1235, 1080 cm^{-1} (POO^-). II_C: δ 3.33–3.40 (m, 6, N^+CH_3, 2, CH_2CO), 3.55 (m, 2, N^+CH_2), 4.15–4.46 (m, 4, OCH_2), 5.02 (s, 1, CONH), 6.70–6.75 (m, 4, aromatic ring protons); IR (KBr) 1660 (CON-H), 1600, 1500 (Ph), 1236, 1060 cm^{-1} (POO^-). Elementary analyses of polymers II_A–II_C were in good to excellent agreement with theory.

Communications to the Editor

Poly(*exo*-5-hydroxynorbornene): A Functional Polymer Using Metathesis Polymerization of an Organoborane Derivative

Polymers that have a variety of functional groups are finding applications in areas such as solid-phase synthesis, polymer-bound catalysts, polymer-bound drugs, etc. The sensitivity of most organometallic catalysts toward functional monomers with heteroatoms, such as O, S, and N, has often hampered their utilization in the synthesis of functional polymers.

Ring-opening metathesis polymerization of functional monomers has met with only limited success.[1] Some very recent investigations using $RuCl_3$ catalysts, however, appear to hold more promise in terms of their application for the synthesis of functional polymers.[2] Considerable progress in the synthesis of transition metal (W and Mo) alkylidene complexes[3] during the past few years has led to a greater understanding of the steric and electronic environment around the metal center necassary for these complexes to effect living polymerization and also to be functional group compatible. At present, living ring-opening metathesis polymerization has been possible only with cyclic olefins that possess considerable ring strain, such as norbornene. In general, the living and functional group tolerant catalysts are thus relatively less active and therefore are most effective for the polymerization of strained ring olefins.[4] Our approach to functional polymers has been directed toward the development of monomers that are stable to transition-metal catalysts and are quantitatively convertible to functional polymers after polymerization. This approach would allow us to access a much wider range of monomers by using more reactive catalysts that are usually very susceptible to functional groups. The transformation of organoboranes to a variety of functional groups has been well established in small organic molecules.[5] We have recently demonstrated that alkenylboranes can be polymerized by a Ziegler–Natta process and that the poly(borane)s thus produced can be quantitatively converted to poly(alcohol)s.[6] Such monomers can further be copolymerized with 1-alkenes to give hydrocarbon polymers with varying degrees of functionalization.[7] We have now extended this approach to the synthesis of functional polymers by ring-opening metath-

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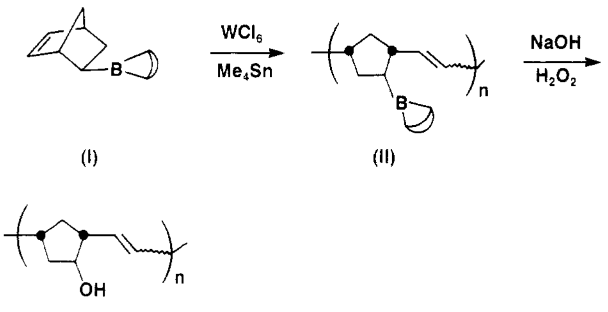
esis polymerization of appropriate cycloalkenylborane monomers.



(I) (II)

(III)

The monomer, *exo*-*B*-5-norborn-2-enyl-9-BBN (I) was synthesized by selective hydroboration of 2,5-norbornadiene with 9-BBN, using a 4-fold excess of the diene to minimize formation of the bishydroboration product. The monomer was isolated in pure form by fractional vacuum distillation [bp = 90–97 °C (10–15 μm)]. A yield of 62% was obtained. The ^{1}H and ^{13}C NMR spectra of the monomer confirmed the presence of only one isomer, the exo form.[8] Exo-substituted norbornenes have been found to polymerize more easily than the endo-substituted form.[9] This would be especially true in the case of very bulky groups, such as the 9-BBN group that is present in monomer I. The exclusive formation of the exo form, therefore, was well suited for the polymerization study.

The polymerization of I was carried out at room temperature in the presence of WCl$_6$/Me$_4$Sn with a 2 M monomer concentration. A catalyst to monomer ratio of WCl$_6$/2Me$_4$Sn/100 monomer was used. Typically, WCl$_6$ was dissolved in toluene and Me$_4$Sn was added to this solution. The catalyst solution was allowed to age for 5 min and the required quantity of monomer was then added. The polymerization was very rapid and caused an immediately observable increase in the viscosity of the reaction mixture. The reaction was terminated after 2 h by the addition of 2-propanol and the precipitated polymer was washed thoroughly with 2-propanol and redissolved in THF. The THF solution was then removed from the drybox and oxidized with alkaline H$_2$O$_2$ to cause the complete transformation of poly(borane) II to poly(*exo*-5-hydroxynorbornene) (III).[10] The oxidation was carried out at 50 °C for a period of 12–15 h. The oxidized polymer was then precipitated in water and dried. The overall yield of the polymer was 65%.[11] Poly(*exo*-5-hydroxynorbornene) 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.

The IR spectrum of the polymer showed a strong absorption in the region between 3100 and 3500 cm^{-1} due to the presence of the OH group. The absorptions at 962 and 740 cm^{-1} due to the presence of both trans and cis double bonds in the polymer were also present. The ^{1}H NMR spectrum (Figure 1a) shows a complex pattern in the vinylic region due to the presence of both *cis* and *trans* double bonds in the polymer along with various head-to-head, head-to-tail, and tail-to-tail sequences. A similar complex cluster of peaks in the olefinic region is also seen in the ^{13}C NMR spectrum of the polymer. The relative integrated intensity of the peak at 3.8 ppm, due to the hydrogen α to the OH group, corresponds to a single proton. This suggests that the transformation of the borane to the alcohol is essentially complete. The synthesis of polymers with varying cis–trans isomer contents, to enable complete assignment of the various peaks in the ^{13}C NMR spectrum, is now under way.

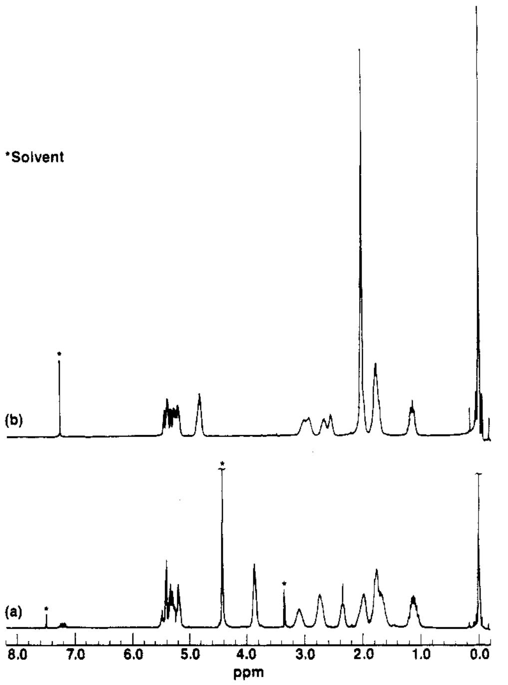


Figure 1. ^{1}H NMR spectra of (a) poly(*exo*-5-hydroxynorbornene) in CDCl$_3$/CD$_3$OD and (b) acetylated poly(*exo*-5-hydroxynorbornene) in CDCl$_3$.

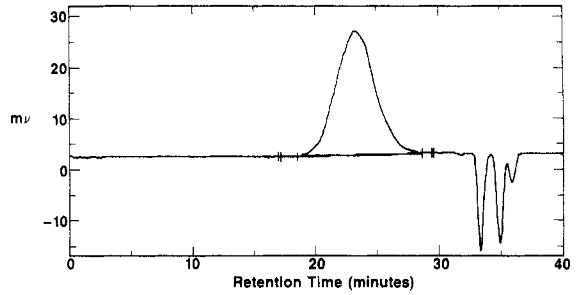


Figure 2. GPC elution of acetylated poly(*exo*-5-hydroxynorbornene).

The polymer was acetylated in order to determine its molecular weight. The acetylation reaction was carried out by using acetyl chloride/pyridine in a mixed CHCl$_3$/CH$_3$OH solvent. An excess of the reagent was used to compensate for the presence of methanol in the reaction mixture. The polymer was precipitated in excess methanol, washed thoroughly, and dried. The acetylation could also be done using DMF instead of methanol as cosolvent. The ^{1}H NMR spectrum (Figure 1b) shows the disappearance of the peak at 3.8 ppm, due to the methylene proton α to the OH group, and the appearance of a new peak at 4.8 ppm upon acetylation, indicating the complete transformation of OH to OCOCH$_3$. The GPC of the polymer, using THF as the solvent, gave the elution profile shown in Figure 2. The number-average molecular weight M_n was found to be 58000, using polystyrene as the GPC standard, and the polydispersity M_w/M_n was found to be 2.3. Under similar conditions, polynorbornene, having a M_n of 150000–200000, was obtained. The lower molecular weight in the former case may be due to the very bulky 9-BBN substituent. The different hydrodynamic volume and/or some kind of interaction with the GPC column may also result in this apparent lowering of the molecular weight in the former case.

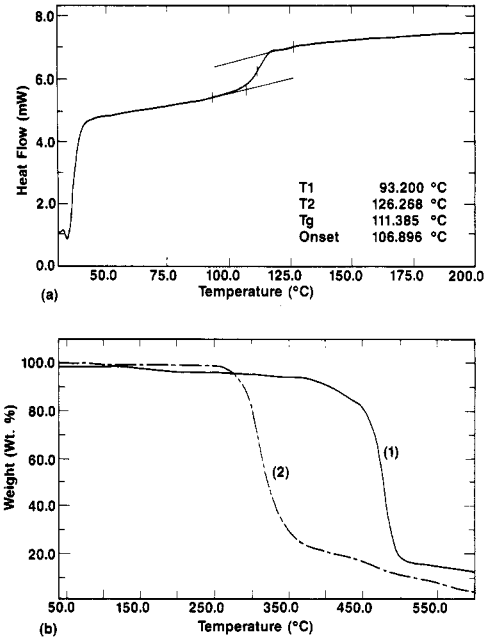


Figure 3. (a) DSC curve of poly(*exo*-5-hydroxynorbornene). (b) Curves 1 and 2 represent the TGA thermograms of poly(*exo*-5-hydroxynorbornene) and poly(vinyl alcohol), respectively.

The DSC curve of the polymer (Figure 3a) shows a glass transition temperature T_g at 111 °C. As expected, this is significantly higher than that of poly(norbornene). The TGA curve (Figure 3b) indicates that the polymer undergoes no significant weight loss up to a temperature of about 400 °C. This is in sharp contrast to poly(vinyl alcohol),[12] also a secondary alcohol, which begins to loose weight due to dehydration at a temperature as low as 260 °C (curve 2). The higher dehydration temperature of polymer III may be due to the presence of the OH group on the ring carbon that precludes the possibility of anti elimination. Another important reason could be the unfavorable introduction of ring strain upon dehydration. Furthermore the formation of a conjugated system in the case poly(vinyl alcohol) may cause its accelerated dehydration.

The growing interest in the area of metathesis polymerization and the development of new living metathesis catalyst systems makes the borane approach an attractive one for the synthesis of functional polymers with greater control over the final polymer structure. Further work toward the synthesis of polymers with other functional groups, such as NH_2, is currently under way.

Registry No. I, 121211-71-0; 9-BBN, 280-64-8; WCl_6, 13283-01-7; Me_4Sn, 594-27-4; 2,5-norbornadiene, 121-46-0.

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(9) Reference 1, page 260.
(10) For more experimental details check ref 5.
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Anionic Polymerization of Fluorine-Containing Vinyl Monomers. 9. Hexafluoro-1,3-butadiene

Although tetrafluoroethylene is readily polymerized under free-radical conditions, numerous fluorinated vinyl monomers have not been polymerized with radical initiators. Ito et al. have reported methyl 2-(trifluoromethyl)-acrylate (MTFMA) gives no polymer by the initiations with α,α'-azobis(isobutyronitrile) (AIBN), benzoyl peroxide, or γ-ray radiation.[1-3] Then 2-trifluoromethyl-acrylates have been readily polymerized by anionic polymerization technique because the e-value of MTFMA is very large.[4-6]

Fluorinated vinyl monomers possessing fluorine atoms at α-carbon of vinyl groups are more difficult to polymerize.[7] To obtain preliminary information on the general trend of the anionic polymerization of fluorinated butadienes, the present paper is concerned with the investigation of polymerization conditions of hexafluoro-1,3-butadiene (HFBD) by systematically surveying the typical anionic polymerization initiators and solvents. Radical polymerization of HFBD reported by Toy et al. has produced low molecular weight polymers,[8] and 1,4- and 1,2-addition reactions are found to take place with infrared spectrum of the polymer.

Anionic polymerization may thus be preferable to radical polymerization from the standpoint of production of poly(HFBD) possessing controlled microstructures.

Results of anionic polymerization of HFBD[9] (40 mmol) with cesium fluoride as initiator (0.8 mmol) in toluene or tetrahydrofuran (THF) (20 mL) are summarized in Table I. The polymerization system successfully produces high yields of poly(HFBD) both in toluene and THF. The polymers obtained are white solid material. This polymerization system is the first case that yields the appreciable amount of poly(HFBD) among the initiators examined in the series of this study. No polymer was obtained without cesium fluoride at 60 °C in toluene and THF.

The polymers obtained with cesium fluoride initiations are insoluble in any solvents such as hexane, cyclohexane, benzene, toluene, diethyl ether, THF, dioxane, methanol, ethyl acetate, acetone, chloroform, dichloromethane, pyridine, dimethyl sulfoxide, dimethylacetamide, hexamethylphosphoric triamide, *N,N,N′,N′*-tetramethylethylenediamine, 1,2- and 1,4-bis(trifluoromethyl)benzene,

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