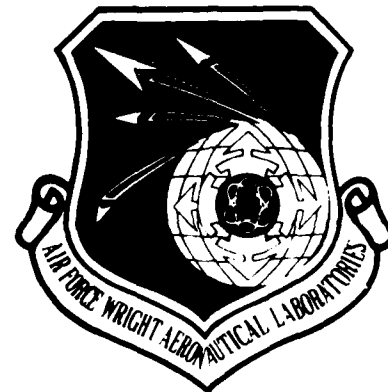


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INCORPORATION OF HIGH ENERGY MATERIALS INTO HIGH DENSITY POLYMERS

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September 1987

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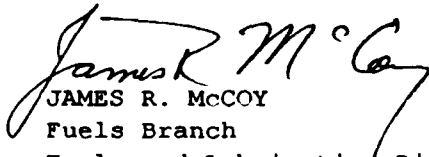
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This report has been reviewed by the Office of Public Affairs (ASD/PA) and is releasable to the National Technical Information Service (NTIS). At NTIS, it will be available to the general public, including foreign nations.

This technical report has been reviewed and is approved for publication.


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19. ABSTRACT (Continue on reverse if necessary and identify by block number) New graft terpolymers were synthesized and characterized, such as EPDM-g-PST and EPDM-g-PMST. Two methods of synthesis were successful: a macromonomer (a polymer containing a polymerizable head group) was copolymerized with ethylene and propylene to lead to the final product, and chlorination of a commercial EPDM allowed the chlorinated sites to serve as cationic initiation points so that grafts could be grown from these sites. The catalyst system $\text{Re}(\text{CO})_5\text{Cl}/\text{C}_2\text{H}_5\text{AlCl}_2$ promoted the polymerization of strained monomers, such as norbornene and the dimers of norbornadiene. The unusual feature of the polymerization is that the rings of the monomers are retained in the polymer. New methods for producing hafnacyclopentadienes have been developed. All compounds were obtained in high yields. A few potentially polymerizable carborane molecules were prepared, but these could not be incorporated into polymers in sufficiently high amounts. <i>Keywords: Ethylene</i> <i>polymerization, hafnacyclopentadiene (HCP)</i>					
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I. INTRODUCTION

The object of the research, carried out under contract number F83615-84-K-2458 was to synthesize high energy, high density compounds, primarily polymers, that could have an end use as solid fuels or energetic binders in cruise missiles. To this end, it was proposed to study a variety of new systems such as synthesis of new EPDM graft polymers, polymers containing carboranes, polymerization of monomers containing strained bonds, and chemistry of the Group IV B metals with the intention of incorporating stable titanium, zirconium, and hafnium compounds into polymeric materials.

This report describes our research activity in the areas mentioned above. In one case, approximately one pound of a sample (ring-retained polynorbornene) was sent to the Naval Weapons Center, China Lake, CA, for testing.

II. EXPERIMENTAL PROCEDURES

1. SYNTHESIS OF NEW EPDM GRAFT POLYMERS

Two approaches were used to synthesize graft terpolymers on an ethylene-propylene polymeric backbone. The first was to synthesize a polymer such as polyisobutylene, polystyrene, or polymethylstyrene containing a specific head group, e.g., dicyclopentadiene. The details of the synthesis may be found in four publications, three of which were generated from this project.^{1,2,3} Following here is a detailed description of the preparation of polyisobutenyl-dicyclopentadiene and its terpolymerization with ethylene-propylene to an EPDM-isobutylene graft.

a. Preparation of 1-chlorodicyclopentadiene, DCp-Cl. This compound was synthesized by the chlorination of dicyclopentadiene-1-ol according to Dilling et al.⁴ The carbinol was prepared by allylic oxidation of dicyclopentadiene using selenium dioxide according to Woodward and Katz.⁵

b. Preparation of PIB-DCp. The polymerization was carried out at -50°C in a dry box. A methyl chloride solution (1 L) containing 0.2 g (1.2×10^{-3} mol) DCp-Cl and 164 mL (2 mol) isobutylene was treated with 1×10^{-2} mol $(C_2H_5)_2AlCl$. The resulting polymer was purified by adding the charge to methanol, recovering the precipitated polymer, and reprecipitating from *n*-heptane-methanol. The last traces of solvent were removed in vacuum at ambient temperature, yielding 85 g of polymer. The PIB-DCp was cracked at 160°C under vacuum, which removed cyclopentadiene, leaving polyisobutenylcyclopentadiene PIB-Cp. The amount of DCp head group was determined by comparing

ultraviolet spectra of the PIB-Cp against a calibration curve of *n*-propylcyclopentadiene. The $\overline{M}_n$ of the polymer by GPC, was 27,000.

c. Preparation of ethylene-propylene-polyisobutylenyldicyclopentadiene terpolymer EPDM-g-PIB. The polymerization was carried out in a 500-mL, four-necked flask which was dried in an oven and then flamed out under nitrogen with a Bunsen burner. Into the flask was placed 200 mL dry *n*-heptane and a magnetic stirrer. Rubber septums were placed on three necks, and to the fourth was attached a pressure-equalized separatory funnel containing 50 mL of an *n*-heptane solution of PIB-DCp at a concentration of 0.09 g/mL. The flask was immersed in a water bath at ambient temperature. Ethylene and propylene were introduced into the *n*-heptane through individual septums from their respective trains. Both gases were passed through CuO catalyst at 150°C to remove any hydrogen, and then through Drierite to remove moisture. The flow rate of each gas was adjusted through flow meters at 1 liter/minute. The *n*-heptane solvent was saturated with the two gases (15 minutes), whereupon the PIB-DCp solution was added dropwise to the reaction mixture over a period of 7 minutes. Simultaneous with addition of the polymer solution, the catalyst components were added by means of a syringe pump (Sage Instruments Model 351) at a rate of 1 mL per minute. In this manner, the Al:V ratio is constant at 4:1. At the end of delivery of the macromer, the addition of catalyst components, ethylene and propylene was terminated. The solution was allowed to stir for 5 minutes, then poured into 500 mL of

methanol containing 5 g of N-phenyl- β -naphthylamine, resulting in the precipitation of the graft terpolymer. The polymer was then collected by filtration and redissolved in n-heptane. The n-heptane was removed by rotary evaporation; the last traces of solvent were removed in vacuum at 50°C. The yield was 7.5 g. The yield depends on the time of addition of the reactants. When the macromer was added over a period of 12 minutes, the yield was 14 g.

The preparation of EPDM-g-polystyrene and EPDM-g-poly- α methylstyrene are given in detail in references 2 and 3.

A second method of preparing graft terpolymers is grafting from the EPDM. In this case, a commercial EPDM polymer containing 7.7% ENB as the diene was used as the starting material.

d. Chlorination of the EPDM polymer. In a dry, 1L, single-necked flask was placed 10 g of purified EPDM polymer (7.7% ENB by weight and $\overline{M}_n = 50,000$) and a magnetic stirring bar. The polymer was dissolved in 500 mL of dry heptane, then 20.35 g of t-butyl hypochlorite was added and the reaction mixture was stirred for 2 hours while it was irradiated in a Rayonet Photochemical Reactor at 350 nm. The chlorinated polymer was precipitated in acetone, collected by filtration, and purified by redissolving and reprecipitating several times. The final polymer was dried under vacuum at 50°C.

e. Synthesis of graft copolymers by cationic grafting reactions. EPDM-g-PS and EPDM-g-P α MSt graft copolymers were prepared by the following method, starting from chlorinated, commercial EPDM polymer.

Into a 1L, three-necked flask with a magnetic stir bar, 1.0 g of the chlorinated EPDM and 160 mL of dry heptane were placed. After the polymer was completely dissolved, 50 mL of the dry monomer (styrene or α -methylstyrene) and the desired amount of cosolvent (methyl chloride for styrene and methylene chloride for α -methylstyrene) were added. When methyl chloride was used as the cosolvent, the flask was cooled to -40°C inside a dry box and the methyl chloride was condensed into the flask. Serum caps were placed on three necks, and the flask was quickly taken out of the dry box and placed in a dry ice/acetone bath maintained at -30°C. The reaction mixture was stirred to insure homogeneity, and 10 mL of a precooled 0.35M solution of diethylaluminum chloride in heptane/cosolvent mixture was injected into the flask. Grafting was initiated immediately as evidenced by the turbidity of the solution. Time periods up to 1 minute were used for the reactions to achieve the desired conversion of the monomer. The reaction was terminated by introducing 10 mL of precooled methanol into the flask, and the product was immediately precipitated by adding the reaction solvent to a 10-fold excess of acetone. The crude polymer was collected by filtration and the pure graft copolymer was isolated by selective solvent extraction.

f. Isolation of pure graft copolymers. The isolation of pure EPDM-g-PS was accomplished by dissolving the crude polymer in toluene and precipitating from a 10-fold excess of acetone. Usually, two or three acetone precipitations were required to dissolve all the homopolystyrene. The resulting solid material was extracted with heptane to dissolve ungrafted chlorinated EPDM. Two overnight extractions were sufficient for this purpose. The insoluble polystyrene graft copolymer was dissolved in toluene, the solution was filtered, and the material precipitated from methanol. The final graft copolymer was dried under vacuum at 50°C for further characterization.

For the purification of EPDM-g-PMSt, the above procedure was employed, except 2-pentanone was used instead of acetone.

2. SYNTHESIS AND ATTEMPTED POLYMERIZATION OF CARBORANE MONOMERS

Several approaches to the preparation of carboranes containing a polymerizable functional group were carried out. Following here are some representative examples.

a. Preparation of 1-vinyl-2-ethylcarborane. Into a 50 mL, four-necked, round-bottom flask equipped with a gas inlet, a thermometer, rubber septum and a water condenser connected with a gas adapter to an oil bubbler, 4.0 g (19.8 mmol) of $B_{10}H_{12}(CH_3CN)_2$ was placed. Then dry benzene (100 mL) was added through the septum with a syringe. The system was purged with argon and 1-hexene-3-yne (2.5 mL, 19.8 mmol) was added. The mixture was heated to the reflux temperature and stirred under argon for 2.5 hours. During the heating period the color of the solution changed from clear to red-orange. After this time, stirring

was stopped and the mixture was allowed to stand overnight under argon. The mixture was filtered and 2.5 g of unreacted $B_{10}H_{12}(CH_3CN)_2$ was isolated. The filtrate was poured into a one-necked round-bottom flask and the solvent was removed until there was about 2 to 3 mL of a viscous yellow-orange solution. Petroleum ether was added and a precipitate formed. The solid was isolated by filtration and was found to be a mixture of unreacted starting materials. The solvent was removed from the filtrate and a yellowish solid was obtained. The product was purified by dissolving it in a minimum amount of methanol then distilled water was added with gentle warming ($40^{\circ}C$) until a solution could be maintained. The solution was filtered and the filtrate was placed in an ice bath for several hours. A white solid was obtained, which was isolated by filtration and dried under vacuum. A second crop was obtained by adding some distilled water to the filtrate and cooling again. Finally, the white solid obtained was sublimed under vacuum at 80 to $98^{\circ}C$, giving a yield of 0.50 g (8.96%). The product, 1-vinyl-2-ethylcarborane is a white shiny solid which melts at 88 to $90^{\circ}C$. It is soluble in benzene, methanol, $CHCl_3$, petroleum ether, acetone and CCl_4 . This product was characterized by 1H nmr and ir spectroscopy as well as mass spectrometry (Found: m/e 198; calcd 198). Anal. Calcd. for $C_6H_{18}B_{10}$: C, 36.35; H, 9.09; B, 54.57%. Found: C, 36.17; H, 8.89; B, 54.58%. The preparation was repeated while allowing the reaction to go for 24 hours in an unsuccessful attempt to improve the yield of product.

TABLE 1. Carboranes Synthesized and Characterized

Carborane	Main IR Bands, cm^{-1}	^1H nmr Signals ppm
$\text{CH}_2\text{-CH-C}\begin{array}{c} \diagup \text{O} \diagdown \\ \text{B}_{10}\text{H}_{10} \end{array}\text{-C-CH}_2\text{CH}_3$	$\nu\text{C=C-H}$, 3100; $\nu\text{C=C}$, 1620 $\nu\text{C-H}$, 2900; $\nu\text{B-H}$, 2600	$\text{CH}_2\text{-CH=}$, 5.1-6.1 $\text{-CH}_2\text{-}$, 1.8-2.4 -CH_3 , 0.8-1.5
$\text{CH}_2\text{-CH-C}\begin{array}{c} \diagup \text{O} \diagdown \\ \text{B}_{10}\text{H}_{10} \end{array}\text{-C-(CH}_3)_3\text{-CH}_3$	$\nu\text{CH}_2\text{-CH}$, 3100; $\nu\text{C=C}$, 1600 $\nu\text{B-H}$, 2600; $\nu\text{C-H}$, 2900	$\text{CH}_2\text{-CH}$, 5.3-6.2 $(\text{CH}_2)_3\text{-CH}_3$, 0.6-2.3
$\text{CH}_2\text{-CH-CH}_2\text{-C}\begin{array}{c} \diagup \text{O} \diagdown \\ \text{B}_{10}\text{H}_{10} \end{array}\text{-C-(CH}_2)_2\text{-CH}_3$	$\nu\text{B-H}$, 2600; $\nu\text{C-H}$, 2900 $\nu\text{C=C}$, 1600; $\nu\text{CH}_2\text{-CH}$, 3100	$\text{CH}_2\text{-CH}$, 5-6 $(\text{CH}_2)_2\text{-CH}_3$, 0.3-3.2
$\text{Ph-C}\begin{array}{c} \diagup \text{O} \diagdown \\ \text{B}_{10}\text{H}_{10} \end{array}\text{-C-CH}_2\text{-CH}_2\text{-CH}_2\text{Cl}$	$\nu\text{C=C-H}$, 3100; $\nu\text{C-H}$, 2900 $\nu\text{B-H}$, 2600; C-Cl , 1590	$\text{C}_6\text{H}_5\text{-}$, 7.2-7.8 CH_2Cl , 3.0-3.4 $(\text{CH}_2)_2\text{-}$, 1.6-2.1
$\text{Ph-C}\begin{array}{c} \diagup \text{O} \diagdown \\ \text{B}_{10}\text{H}_{10} \end{array}\text{-C-CH}_2\text{-CH=CH}_2$	$\nu\text{C=C-H}$, 3100; $\nu\text{C-H}$, 2900 $\nu\text{B-H}$, 2550	$\text{C}_6\text{H}_5\text{-}$, 7.1-7.6 $\text{CH}_2\text{-CH=}$, 4.3-5.6 $\text{-CH}_2\text{-}$, 2.3-2.5
$\text{Ph-C}\begin{array}{c} \diagup \text{O} \diagdown \\ \text{B}_{10}\text{H}_{10} \end{array}\text{-C-CH}_2\text{-C}\begin{array}{c} \text{H} \\ \\ \text{C-Si(CH}_3)_3 \end{array}$	$\nu\text{B-H}$, 2600; $\nu\text{C=C-H}$, 3100 $\nu\text{C-H}$, 2900; $\nu\text{C-Cl}$, 1590 $\nu\text{C=C-C}$, 1920	$\text{C}_6\text{H}_5\text{-}$, 6.9-7.5 $\text{-Si(CH}_3)_3$, 0.0 -C=C-CH_2 , 2.2
$\text{Ph-C}\begin{array}{c} \diagup \text{O} \diagdown \\ \text{B}_{10}\text{H}_{10} \end{array}\text{-C}\begin{array}{c} \text{H} \\ \\ \text{C=C-C-Si(CH}_3)_3 \\ \\ \text{H} \end{array}$	$\nu\text{C=C}$, 2200	H-C=C-C , 4.6 $ $ H

Table 1 shows the carboranes synthesized in this work, along with the structurally significant IR bands and ^1H nmr signals.

A variety of approaches to prepare 1-dicyclopentadienyl-2-phenylcarborane were attempted, as follows.

b. Attempted synthesis of 1-dicyclopentadienyl-2-phenylcarborane. Into a four-necked 250-mL round-bottom flask equipped with a thermometer, two rubber septums, a magnetic stir bar and a gas adapter connected to the Firestone valve 1-phenylcarborane (3.0 g, 13 mmol) was placed. Dry ether (150 mL) was added and the solution cooled to -10°C by means of an ice-salt bath. At this temperature, 6.81 mL (13 mmol) of nBuLi/hexane was added dropwise. After addition was completed the solution was allowed to reach 0°C and was stirred at this temperature under argon for 45 minutes.

After this time, the solution was then cooled to -10°C and 2.34 g (14 mmol) of endo,anti-5-chlorotricyclo[5.2.1.0^{2,6}]deca-3,8-diene was added dropwise while keeping the temperature at -10°C . After the addition, no apparent reaction was observed; therefore, the mixture was stirred at -10 to 0°C for 20 minutes and then placed in the refrigerator (4°C) overnight.

By the next day, there was no formation of LiCl, so the solution was allowed to reach room temperature and poured into a 500 mL separatory funnel. The ether solution was extracted with 20% HCl/H₂O, (50 mL portions three times) and then with distilled water twice. Finally, the ether layer was separated, dried over sodium sulfate, filtered, and the solvent removed in the rotary evaporator. A light yellow oil was obtained which distilled as a

colorless oil under vacuum at 60 to 64°C and 1 torr. The yield of unreacted chloride was 2.09 g (89.23%). This material was characterized by ^1H nmr and ir spectra as the unreacted allylic chloride of dicyclopentadiene. The residue from the distillation was checked by ^1H nmr and shown to be unreacted phenylcarborane. The recovery of this material was quantitative.

Table 2 shows some other attempted reactions to prepare this compound.

It was suspected that steric problems were responsible for the attempted reactions described above. Therefore, the configuration of exo-DCp was converted to endo-DCp, by standard literature methods. Unfortunately, the preparation of the target molecule using the endo-DCp starting material was also not successful.

The carboranes listed in Table 1 were subjected to homopolymerization and copolymerization reactions. These reactions were either not successful, or resulted in products obtained in extremely low yields.

3. RING-RETENTION POLYMERIZATION OF NORBORNENE

Details of catalyst preparation and solvent purification can be found in the literature.⁶ The preparation of polynorbornene is given below.

a. Polymerization (ring-retained) of norbornene. Into a 100-mL, three-necked, round-bottom flask, equipped with a thermometer, a magnetic stir bar, a rubber septum and a condenser connected with a gas adaptor to a Firestone valve, was placed 5 g (5.3 mmol) of norbornene, 0.19 g (0.54 mmol) of $\text{Re}(\text{CO})_5\text{Cl}$ and 35

TABLE 2. Attempted Synthesis of 1-Dicyclopentadienyl-2-Phenylcarborane

Starting Materials (mole ratio)	Solvent Temperature (°C)	Results
lithium phenylcarborane/endo, anti-5-chlorotricyclo[5.2.1.0 ^{2,6}] deca-3,8,diene (1:1)	Ether/4°C	No reaction
lithium phenylcarborane/endo, anti-5-methylenesulfonyltricyclo [5.2.1.0 ^{2,6}]-deca-4,8-diene (1:1)	Ether/4°C	No reaction
lithium phenylcarborane/endo, anti-5-chlorotricyclo[5.2.1.0 ^{2,6}] dec-3,8-diene/TMEDA (1:1:1)	Ether/-10°C	No reaction
lithium phenylcarborane/endo,syn- 5-bromotricyclo[5.2.1.0 ^{2,6}]deca- 4,8-diene (1:1)	THF/RT	Yield: 12.5%
lithium phenylcarborane/exo-anti- 5-chlorotricyclo[5.2.1.0 ^{2,6}]deca- 4,8-diene and exo,syn-5-chloro- tricyclo[5.2.1.0 ^{2,6}]deca-4,8-diene (1:1)	THF/RT	No reaction
lithium phenylcarborane/exo,anti- 5-chlorotricyclo[5.2.1.0 ^{2,6}]deca- 4,8-diene and exo,syn-5-chloro- tricyclo[5.2.1.0 ^{2,6}]deca-4,8-diene (1:1)	Ether/RT	No reaction

mL of chlorobenzene. The mixture was stirred under argon for 15 minutes, and 1.08 mL (1 mmol) of $C_2H_5AlCl_2$ in hexanes was added. The reaction mixture was stirred at 100°C for 24 hours.

After the mixture had cooled to room temperature, it was poured into 600 mL of rapidly stirred methanol. The polymer precipitated from solution, and the mixture was placed in a refrigerator for 48 hours. The polymer was then separated by filtration. The solid was dissolved in a minimum amount of benzene and passed down a 50 cm by 5.5 cm Florisil (60-100 mesh) column packed in benzene. Three fractions were collected: The first fraction was eluted with benzene, the second with $CHCl_3$, and the third with ether. The solvents were removed, and the fraction containing the highest yield was further purified by dissolving the polymer in chloroform and precipitating it from methanol. The polymer was filtered from solution and dried under high vacuum (yield: 1.34 g, 26.8%). The molecular weight of the polymer as determined by gel permeation chromatography in THF and by osmometry in toluene was: $\overline{M}_w$, 443,000; $\overline{M}_n$, 154,200; polydispersity, 2.14. The polymer softens at 220°C and melts completely at 260°C.

4. HOMO- AND COPOLYMERIZATION OF SOME NORBORNADIENE DIMER MONOMERS

A paper on this subject has been accepted, and describes the details of the preparation of starting materials.⁷ The experimental procedures in the preparation of the polymers are given below.

a. Polymerization of the exo-exo norbornadiene dimer.

Into a 100-mL three-necked, round-bottom flask equipped with a thermometer, a rubber septum, a magnetic stir bar, and a condenser connected with a gas adaptor to a Firestone valve, was placed 2.0 g (10 mmol) of the monomer, 0.04 g (0.11 mmol) of $\text{Re}(\text{CO})_5\text{Cl}$ and 15 mL of dry chlorobenzene. The mixture was stirred under argon and 0.22 mL (0.22 mmol) of EtAlCl_2 in hexane was added. The mixture was stirred at 110°C for 24 hours, during which time the color changed from yellow to orange to red-brown. The mixture was allowed to cool to room temperature and poured into 180 mL of methanol; a white polymer precipitated from solution. The polymer was filtered from solution, and purified by redissolving it in chloroform, filtering the insoluble material, and adding the chloroform solution dropwise to rapidly stirred methanol (180 mL). The final polymer was isolated by filtration and dried under high vacuum, yielding 0.60 g (47.6%). The molecular weight was determined by gpc in THF and by osmometry in toluene: $\overline{M}_w$, 462,300; $\overline{M}_n$, 180,000; polydispersity, 2.57. The polymer softens at 200° and melts above 300°C. Anal.: C, 83.18; H, 8.12; Re, 1.40; Cl, 5.86%.

b. Polymerization of the endo-endo norbornadiene dimer. A

procedure analogous to that described above was applied to the polymerization of this monomer. The amount of starting monomer was 2 g (10.8 mmol) and the yield of polymer was 1.28 g (60%). Molecular weight: $\overline{M}_w$, 55,600; $\overline{M}_n$, 37,300; polydispersity, 1.49. Anal.: C, 85.11; H, 8.28; Re, 0.93; Cl, 5.56; Al, 0.09%.

c. Copolymerization of the exo-exo norbornadiene dimer and norbornene. A procedure analogous to that described above was used to carry out the copolymerization of the two monomers. In this reaction 0.095 g (0.27 mmol) of $\text{Re}(\text{CO})_5\text{Cl}$, 2.45 g (13 mmol) of the exo-exo dimer, 1.25 g (13 mmol) of norbornene and 0.5 mL (0.5 mmol) of EtAlCl_2 were used in 35 mL of chlorobenzene solvent. After work-up, 2.0 g of the copolymer was obtained (54%), and the polymer melted at 130-160°C. Molecular weight: $\overline{M}_w$ 502,300; $\overline{M}_n$, 325,500; polydispersity, 1.54. Anal.: C, 87.35; H, 8.79; Re, 2.08; Cl, 2.98; Al, 0.1%.

d. Preparation of a diblock copolymer of norbornene and the exo-exo norbornadiene dimer. Into a reaction vessel equipped identically to that described above was placed 0.095 g (0.27 mmol) of $\text{Re}(\text{CO})_5\text{Cl}$, 1.25 g (13.5 mmol) of norbornene, and 20 mL of dry chlorobenzene. The system was purged with argon for 15 minutes, and 0.5 mL of EtAlCl_2 /hexanes was added. The mixture was heated at 100°C, and the disappearance of norbornene was monitored by ^1H nmr spectrometry. After 4 hours of reaction time, the norbornene had been consumed, and 2.45 g (13 mmol) of the exo-exo dimer was added, and the mixture was heated at 100°. The disappearance of the second monomer was also monitored by ^1H nmr spectrometry. When the exo-exo dimer had been consumed (3.5 hours), the reaction mixture was allowed to cool to room temperature, and the reaction was worked up as described above. The yield of soluble polymer was 0.58 g (15.5%) and showed a melting

point of 220-240°C. Molecular weight: $\overline{M}_w$, 262,000; $\overline{M}_n$, 95,300; polydispersity, 2.75. Anal.: C, 84.64; H, 8.45; Re, 4.06; Cl, 3.36; Al, 0.37%.

e. Fractionation of polymers and copolymers. The product was first extracted with heptane; the insoluble portion was then dissolved in a minimum amount of chloroform, heated with a heat gun, and methanol was added dropwise to the stirred solution until complete precipitation was achieved. The polymer was isolated by filtration, washed with methanol, and extracted with acetone for 24 hours at room temperature. The materials were dried under high vacuum at room temperature.

5. CHEMISTRY OF GROUP IV B TRANSITION METALS

In this area of research, much activity was directly toward making new compounds, including polymers, incorporating, Ti, Zr, and Hf metals. At the conclusion of this contract, most of the research on Ti and Zr is incomplete, and most compounds are poorly characterized. However, considerable success was achieved with new chemistry of hafnium, and experimental procedures are described below. Three papers on this subject have been accepted for publication, so details of solvent preparation, starting materials, etc., can be found in these references.^{8,9,10}

a. Synthesis of 1,1-di- η^5 -cyclopentadienyl-2,3,4,5-tetramethylhafnacyclopentadiene. A 250-ml, three-necked flask fitted with an argon inlet, a rubber septum and an outlet connected to an oil bubbler, was filled with argon by a series of evacuate/fill cycles. To the flask was added 1.896 g (5.0

mmol) of hafnocene dichloride, 0.607 g (25 mmol) of Mg powder, 1.354 g (5.0 mmol) of HgCl_2 and a magnetic stir bar. The flask was flushed with argon for 30 minutes, and 50 ml of freshly distilled THF was injected through the septum. The flask was cooled to -78°C and 2.16 g (40 mmol) of 2-butyne was added through the septum. The flow of argon was stopped, and after the contents of the flask warmed to ambient temperatures, the reaction mixture was stirred magnetically for 30 hours, during which time the color gradually changed to a greenish yellow. The solvent and unreacted 2-butyne were removed under vacuum and the flask was transferred to an argon-filled glove box. The residue was dissolved in a minimum amount of dry pentane and filtered over a pad of Celite packed on a fritted funnel. The Celite was washed several times with pentane, and the combined filtrate and washings were stripped to dryness by high vacuum, yielding 1.92 g (92.2%) of a yellowish-orange compound. This compound, which was obtained in reasonably analytically pure form without recrystallization, was characterized as 1,1-di- η^5 -cyclopentadienyl-2,3,4,5-tetramethylhafnacyclopentadiene on the basis of elemental analysis, mass, NMR, and infrared spectra, and the spectral properties of the organic ligand obtained after reaction with HCl. Found: C, 51.10; H, 5.39%. $\text{C}_{18}\text{H}_{22}\text{Hf}$. Calcd.: C, 51.86, H, 5.28%. MS: m/e 418 (M^+), 364 ($\text{M}-\text{CH}_3\text{C}\equiv\text{CCH}_3$), 349 ($364-\text{CH}_3^+$), 310 (Cp_2Hf^+). ^1H NMR (CDCl_3): δ 5.93 ppm (s, 10H, C_5H_5), 1.60 ppm (broad s, 12H, CH_3). IR (KBr) 2900s, 2835s, 1690w, 1594w, 1420m, 1357w, 1015s, 800vs, cm^{-1} .

b. Synthesis of the other hafnacyclopentadienes. The tetraethyl derivative, obtained as a yellow solid in 91.0% yield showed spectral properties identical to those reported by Sikora and Rausch¹¹, as well as acceptable C-H analyses. The tetraphenyl derivative was prepared in a flask wrapped with black tape to exclude any light, since the final compound is light sensitive. The golden yellow solid was obtained in 82.2% yield, and was characterized by comparing its spectral properties to those of the same compound prepared by Sikora and Rausch.¹¹

c. Reaction of the hafnacyclopentadienes with HCl. The metallacyclopentadienes were all treated with HCl to release the organic ligand. Since all three were carried out in the same manner, only the reaction with the tetramethyl derivative is described in detail.

The tetramethylhafnacyclopentadiene derivative (1.0 g, 2.4 mmol) was dissolved in 25 ml of methylene chloride and treated with 25 ml of 1.2 M HCl. The color of the solution instantly changed from red to pale yellow. The reaction mixture was magnetically stirred for 1 hour at room temperature, and the organic and aqueous layers were separated. The aqueous layer was extracted with three 15 ml portions of methylene chloride, which were combined with the CH₂Cl₂ fraction and dried over anhydrous MgSO₄. Distillation afforded 0.175 g (66.3% yield) of the pure 3,4-dimethyl-(2E,4E)-2,4-hexadiene (bp 132-134°C). The diene was identified as the single stereoisomer by comparison of its boiling point and spectral properties to those of an authentic compound.¹²

The tetraethyl derivative reacted with HCl to yield 0.25 g (72.3%) of pure 4,5-diethyl-(3E,5E)-3,5-octadiene (bp, 63°C, 750 torr). This pure stereoisomer exhibited spectral properties identical to those reported for the same characterized compound.¹³

The tetraphenyl derivative yielded 0.383 g (71.3%) of a white compound after reaction with HCl. The melting point was 183°C (lit., 182, 183°C).^{13,14}

d. Synthesis of 1,1-bis(n^5 -cyclopentadienyl)-2,5-bis(trimethylsilyl)-3,4-dimethylhafnacyclopentadiene. A 250-mL, two-necked flask fitted with an argon inlet and a rubber septum was filled with argon by a series of evacuate-fill cycles. To the flask was added 0.948 g (2.5 mmol) of hafnocene dichloride, 0.303 g (12.5 mmol) of Mg powder, 0.677 g (2.5 mmol) of HgCl₂ and a magnetic stir bar. The flask was flushed with argon for 30 minutes, and 50 ml of freshly distilled THF was injected through the septum, followed by 1.12 g (10 mmol) of 1-trimethylsilyl-1-propyne. The flow of argon was stopped and the reaction mixture was stirred for 27 hours at room temperature in a closed system, during which time the color gradually changed to brown. The volatiles were removed under vacuum and the flask was transferred to an argon-filled glove box. The residue was dissolved in a minimum amount of dry pentane and filtered over a pad of Celite packed on a fritted funnel. The Celite was washed several times with pentane and the combined filtrate and washings were stripped to dryness under high vacuum, yielding 1.21 g (90.9%) of a yellow compound. An analytically pure sample and crystals suitable for

structure determination were grown from dry pentane by cooling the solution to 0°C for one day. This product was characterized as a single stereoisomer, viz, 1,1-bis(η^5 -cyclopentadienyl)-2,5-bis(trimethylsilyl)-3,4-dimethylhafnacyclopentadiene on the basis of its spectral properties, spectral properties of the organic ligand obtained after reaction with HCl, and its crystal structure determination. Found: C, 50.08; H, 6.67. $C_{22}H_{34}Si_2Hf$ calcd.: C, 49.55; H, 6.38%.

An x-ray crystallographic study was carried out on Cp_2 -2,5-bis(trimethylsilyl)-3,4-dimethylhafnacyclopentadiene; the experimental details are described below and Table 3 summarize the experimental data on the compound.

e. Collection of the X-ray diffraction data. A yellow single crystal (dimensions 0.34 by 0.26 by 0.30 mm) suitable for examination by X-ray diffraction procedures was sealed in a thin-walled glass capillary in an argon filled drybox. The crystal was mounted for data collection on a Syntex P2₁ automated four-circle diffractometer. The compound was found to be triclinic and no systematic absences were observed suggesting the space group P1. Unit cell parameters and the orientation matrix were obtained and data collection was carried out using a 2θ - θ scan. Details relevant to the structure appear in Table 3. Data were corrected for Lorentz and polarization factors and were reduced to $|F_o|$ values.

f. Solution and refinement of the structure. The analytical form of the scattering factors for neutral hafnium, silicon and carbon were used throughout the analysis.^{15a} The contribu-

TABLE 3. Experimental Data for the X-Ray Diffraction
Study of $\text{Hf}(\text{C}_5\text{H}_5)_2\text{C}_4(\text{Si}(\text{CH}_3)_3)_2(\text{CH}_3)_2$.

formula	$\text{HfSi}_2\text{C}_{22}\text{H}_{34}$
formula weight	533.18 amu
space group	P1
a	9.067(3) Å
b	10.421(3) Å
c	12.296(4) Å
α	100.13(2)°
β	87.52(2)°
γ	105.07(2)°
volume	1170.1(6) Å ³
Z	2
$\rho(\text{calc})$	1.51 g/cc
crystal dimensions	0.34 x 0.30 x 0.26 mm
crystal faces	{1 0 0}, {-1 0 0}, {0 0 1}, {0 0 -1}, {0 -2 2}, {0 2 -2}
crystal volume	3.16 x 10 ⁻³ mm ³
diffractometer	Syntex P2 ₁
radiation	Mo K α (0.71073 Å)
monochromator	graphite crystal
linear absorption coefficient	45.214 cm ⁻¹
transmission factors	0.2876 - 0.4282
temperature	23°C
scan type	2 θ - θ
scan speed	3.91° min ⁻¹
scan range	1.0° below K α_1 to 1.0° above K α_2
2 θ scan limits	3.0° - 50.0°
standard reflections	3 per 100 reflections
indices	{1 2 -8}, {2 -7 1}, {6 -1 1}
crystal stability	No indication of standard reflection decay during data collection.
total reflections scanned	5344 (165 were standards)
unique data $F_o^2 \geq 0\sigma(F_o^2)$	4719
average absorption correction	0.6149
final number of variables	226
R(F) ($F_o^2 \geq 0\sigma F_o^2$)	0.047
R _w (F) ($F_o^2 \geq 0\sigma F_o^2$)	0.047
R(F) ($F_o^2 \geq 3\sigma F_o^2$)	0.038
R _w (F) ($F_o^2 \geq 3\sigma F_o^2$)	0.045

tions of all non-hydrogen atoms were corrected for both the real ($\Delta f'$) and imaginary ($\Delta f''$) components of anomalous dispersion.^{15b} The positions of the non-hydrogen atoms were found by direct methods.¹⁶ Interpretation of the MULTAN solution led to the location of the hafnium atom, both silicons and several of the cyclopentadienyl and butadiene carbon atoms. The remaining carbon atoms were located via a series of difference-Fourier syntheses, each being phased by an increasing number of atoms. All hydrogen atoms whose approximate positions could be obtained from the electron density map were placed in idealized positions, those remaining were included by calculation (all were based upon C-H = 0.95 Å, tetrahedral and trigonal angles and idealized thermal parameters with B = 1.0 Å² greater than the equivalent B of the atom to which it is attached).¹⁷ A numerical absorption correction was performed based on the indexed and measured faces of the crystal and the contents of the unit cell. Refinement was based on F and involved only those reflections having $F_o^2 \geq 0\sigma(F_o^2)$. Full-matrix least-squares refinement of positional and anisotropic thermal parameters for all non-hydrogen atoms led to final convergence with R(F) = 0.047, $R_w(F)$ = 0.047 and GOF = 1.52 for 226 variables and 4719 reflections.

6. CATALYTIC PROPERTIES OF Cp_2HfCl_2

The $Cp_2HfCl_2/C_2H_5AlCl_2$ system was found to catalyze the oligomerization of alkynes and olefins.¹⁰ Experimental procedures for these reactions are given below.

a. Oligomerization procedure. The experimental procedures for the oligomerization of all alkynes are analogous; therefore, only one of these is described in detail.

b. Oligomerization of phenylacetylene. Into a 250-ml, two-necked flask fitted with an argon inlet and a rubber septum was added 0.759 g (2 mmol) of hafnocene dichloride. The flask was flushed with argon for 30 minutes, and 25 ml of CH_2Cl_2 was injected through the septum followed by 2 ml (2 mmol) of ethylaluminum dichloride in hexane. The solution became homogeneous instantly and acquired a pale yellow color. After 45 minutes the flask was cooled to -78°C and 4.0 g (40 mmol) of phenylacetylene was injected dropwise over a period of 10 minutes. The reaction was allowed to proceed for 1 h, and 10 ml of chilled methanol was added to deactivate the catalyst. The reddish-brown compound that precipitated from solution was collected by filtration, dissolved in a minimum amount of CCl_4 , and subjected to column chromatography on neutral alumina. Elution with 1:3(V/V) CCl_4 /hexane brought down the first band which upon evaporation of the solvent yielded a yellow solid. A second band was eluted with 1:1 (V/V) CCl_4 /ether and gave a yellow-red solid (combined yield = 3.1 g, 77.5%). The products were purified further by repeated recrystallization from CCl_4 / CH_3OH . Both products exhibited identical spectroscopic properties and were identified as polyphenylacetylene by their IR and NMR spectra and their molecular weights.

c. Oligomerization of the alkynes. The monomers 1-hexyne and 1-phenyl-1-propyne were also induced to oligomerize by methods analogous to those described above for phenylacetylene. Details are presented in Table 4.

TABLE 4. Monomers Oligomerized by $\text{Cp}_2\text{HfCl}_2/\text{C}_2\text{H}_5\text{AlCl}_2$

<u>Monomer</u>	<u>Conditions</u>	<u>Conversion Percent</u>	<u>M_n</u>	<u>M_w/M_n</u>
$\text{C}_6\text{H}_5\text{C}\equiv\text{CH}$	CH_2Cl_2 , -78°C	77.5	700	-
$\text{C}_6\text{H}_5\text{C}\equiv\text{CH}$	Toluene, -78°C	69.0	500	-
$\text{C}_4\text{H}_9\text{C}\equiv\text{CH}$	Toluene, RT	91.6	600	-
$\text{C}_6\text{H}_5\text{C}\equiv\text{CCH}_3$	Toluene, 70°C , 6 hr	21.5	700	-
Isobutylene	CH_2Cl_2 , -78°C	100	245,000	1.77
Styrene	CH_2Cl_2 , -60°C	100	37,000	3.15
Styrene	Toluene, -60°C	100	4,000	4.86

d. Polymerization of styrene. Styrene was induced to polymerize by methods analogous to those described above. In this case, 3.12 g of styrene was used and the reaction temperature was -60°C . The resulting white polymer was collected by filtration, dissolved in THF, and passed through a silicon gel column several times. The THF solution containing polystyrene was washed with sodium potassium tartrate solution and then with distilled water to remove any remaining aluminum residues. The polymer was then subjected to the cycle of dissolution in THF and precipitation with methanol. The dried polymer indicated a 100% conversion of the monomer.

The polymerization of isobutylene was also carried out in a manner analogous to that described for styrene.

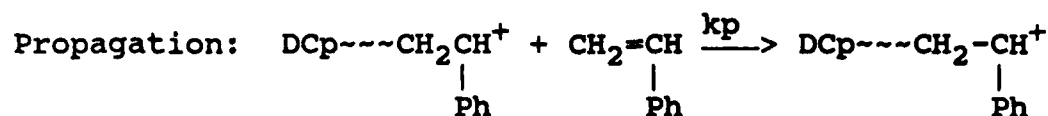
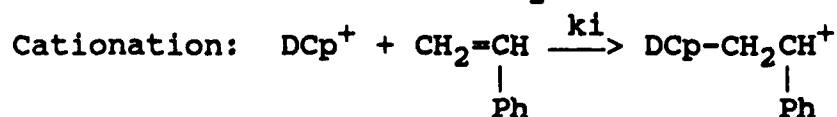
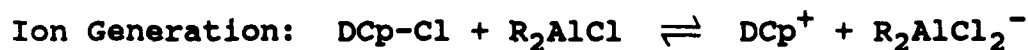
e. Reaction of 1-trimethylsilyl-1-propyne with $\text{Cp}_2\text{HfCl}_2/\text{C}_2\text{H}_5\text{AlCl}_2$. To a 250-ml, two-necked flask fitted with an argon inlet and rubber septum and containing 3.02 g (8 mmol) of hafnocene dichloride under argon, was added 25 ml of methylene chloride and 1.01 g (8 mmol) of neat ethylaluminum dichloride. After the catalyst aged for 45 minutes, 0.848 g (8 mmol) of 1-trimethylsilyl-1-propyne was added and the reaction mixture was stirred for 96 hours at room temperature. The reaction mixture was then cooled to 0°C and 3.23 g (32 mmol) of triethylamine was added followed by 0.8 mL of water. The reaction mixture was diluted with 50 mL of methylene chloride; the resulting red-brown solution was washed with water, 5% HCl, and a saturated solution of sodium bicarbonate, and dried over anhydrous sodium sulfate. The solvent was removed and the residue was taken up in methylene chloride and passed through a short silica gel column. The resulting product (0.42 g, 37.5% yield) was analyzed by GC-MS; that study indicated that two products were present, one of m/e 204.5 and one at m/e 176.5. A parallel control reaction duplicating the conditions employed above was carried out, except that hafnocene dichloride was absent.

III. RESULTS AND DISCUSSION

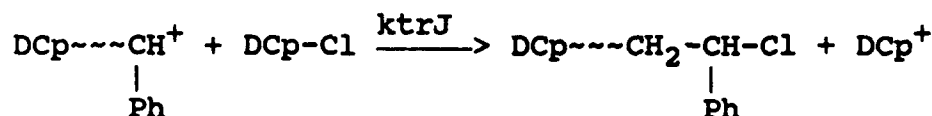
1. SYNTHESIS OF NEW EPDM GRAFT POLYMERS

One of the objectives of this research was to synthesize a glassy polymer with a desirable head group in order to incorporate it into an EPDM polymer. To this end, we prepared polystyrene attached to a DCp head group and used this macromer as the diene in the terpolymerization with ethylene and propylene.

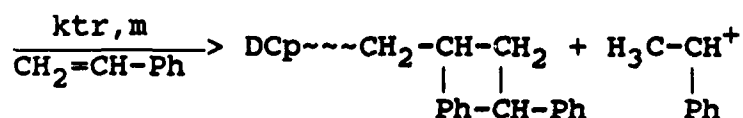
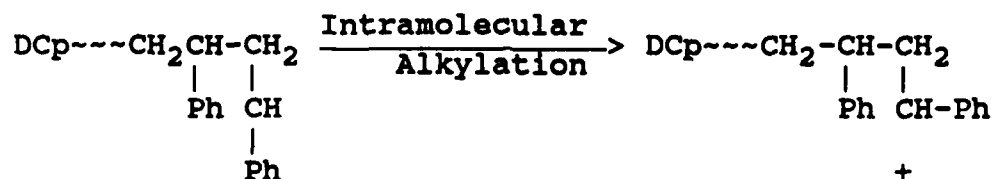
Following is the anticipated reaction scheme for styrene polymerization by the DCp-Cl/(C₂H₅)₂AlCl initiator.



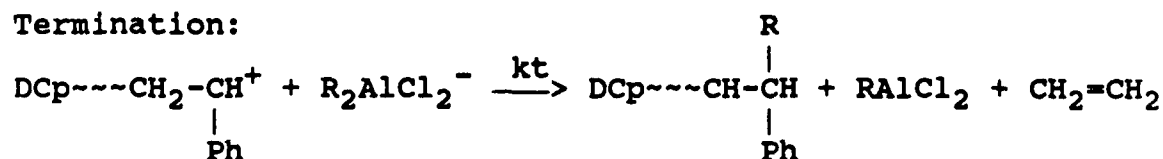
Transfer to the Initiator:



Transfer to the Monomer:



Termination:



The nature of the polymer head group is determined by the relative rates of cationation and chain transfer to monomer. The DCp head group is formed only during initiation. Chain transfer to monomer results in a sterile methyl group rather than the desired DCp head group. The growing polystyrene chain is believed to undergo chain transfer to monomer by intramolecular penultimate alkylation.^{18,19} Kennedy and co-workers observed chain transfer to monomer during their attempt to synthesize poly(isobutylene-b-styrene) by cationic polymerization.²⁰

For a DCp-headed polymer to form quantitatively, $k_{tr,m}$ must be zero. We believe that, under the conditions employed for the polymerization of styrene, i.e., high DCp-Cl concentration and low temperature, chain transfer to monomer will be negligible.

A series of polymerization studies were carried out to determine $k_{tr,m}$. The data are shown in Table 5.

TABLE 5. Experimental Data to Determine the Value of $k_{tr,m}$ *

Expt	[M]	[DCp-Cl]	[ET_2AlCl]	Conversion %	$\overline{M}_n$ by VPO
1	0.821M	-----	$1.23 \times 10^{-1}M$	2.5	-----
2	0.821M	$2.26 \times 10^{-2}M$	$1.23 \times 10^{-1}M$	100	6,700
3	0.671M	$2.26 \times 10^{-2}M$	$1.23 \times 10^{-1}M$	100	5,300
4	0.572M	$2.26 \times 10^{-2}M$	$1.23 \times 10^{-1}M$	100	5,000
5	0.372M	$2.26 \times 10^{-2}M$	$1.23 \times 10^{-1}M$	100	3,000

*Solvent = CH_2Cl_2 ; Time = 5 minutes; Temperature = 70°C; Total Volume-23.4 mL. Exp. 1 is the control (no DCpCl). **Determined by weight of polymer. Values are approximate.

A plot of $1/Dp_n$ vs. $1/[M]$ gives a straight line which passes through the origin, indicating that there is no chain transfer to

the monomer to a measurable extent (Fig. 1).

Since $k_{tr,m}$ appears to be zero, every polymer molecule must be headed by a DCp group. This can be verified by epoxidation titration of the number of double bonds in a polymer.²¹ DCp itself was used as the model olefin to show a quantitative reaction with *m*-chloroperbenzoic acid in a short reaction time. This was accomplished by carrying out the reaction in NMR tubes and recording the spectrum immediately. Olefinic signals were absent immediately after mixing the reactants (Tables 6 and 7).

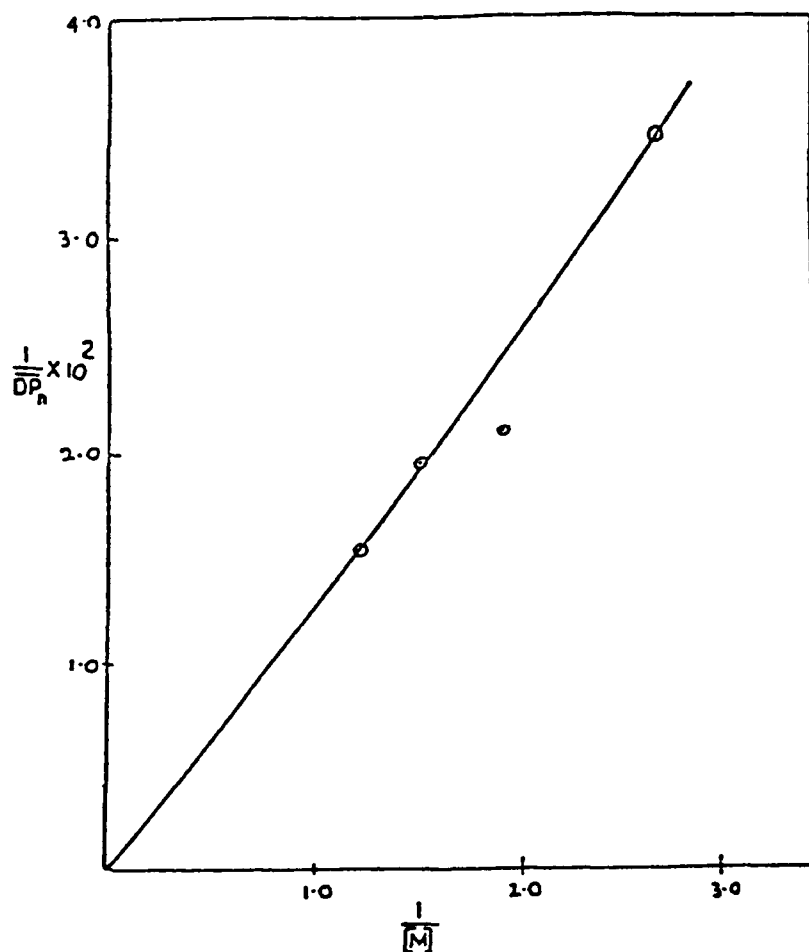


Fig. 1. Plot of $1/Dp_n$ vs. $1/[m]$

TABLE 6. Titration of DCp by m-Chloroperbenzoic Acid

g DCp	mol DCp	moles of db from titration	moles db/ mole DCp	Theoretical Value
0.0495	3.744×10^{-4}	7.6×10^{-4}	2.0299	2.0
0.0283	2.141×10^{-4}	4.3×10^{-4}	2.008	2.0

For the above titrations, 10 mL of CHCl_3 was used as the solvent and 5 mL of 0.3188M solution of m-CPBA in CHCl_3 was added to the titration mixture.

TABLE 7. Titration of DCp-PSt by m-Chloroperbenzoic Acid

$\overline{\text{Mn}}$	% of polymer	mole of $\text{polymer} \times 10^5$	mole of $\text{db} \times 10^5$	mole db/ mole polymer	Theoretical Value
10,240	0.251 ^a	2.45	5.0	2.04	2.0
	0.4991 ^b	4.88	10	2.049	2.0
	0.3491 ^b	3.41	8.0	2.3	2.0
13,650	0.20 ^c	1.47	3.0	2.041	2.0

10 mL of CHCl_3 was used for each titration.

- 5 mL of 0.1298M solution of m-CPBA was used.
- 5 mL of 0.1241M solution of m-CPBA was used.
- 5 mL of 0.0475M solution of m-CPBA was used.

From the data in Tables 6 and 7, it is evident that there is exactly one DCp group attached to every polymer chain.

Attempts were made to prepare two DCp-PSt macromers: one of $\overline{\text{Mn}} = 10,000$ and one of $\overline{\text{Mn}} = 20,000$. According to the $1/\text{Dp}_n$ vs. $1/[\text{M}]$ plot, it was necessary to use $[\text{styrene}] = 1.25\text{M}$ for the lower and 2.5M for the higher molecular weights at $[\text{DCp-Cl}] = 2.26 \times 10^{-2}\text{M}$. The samples prepared shown $\overline{\text{Mn}}$'s of 10,240 and 16,900 by GPC.

Fig. 2 shows a typical GPC curve of the graft terpolymer. The branches/backbone (b/B) ratio was calculated from molecular

weight studies and NMR spectrometry.

The graft terpolymer synthesized using the DCp-PSt macromer of $\overline{M}_n = 10,240$ showed a single, narrow, and symmetrical peak by GPC with $\overline{M}_n = 80,000$ (membrane osmometry). With respect to the $\overline{M}_n$ of the graft polymer and integration of the proton signals in the NMR spectrum, there are five polystyrene branches along the EPDM backbone. Molecular weight studies indicate a PSt/EP ratio of 63/37, while the proton signal integration studies show PSt/EP of 65/35.

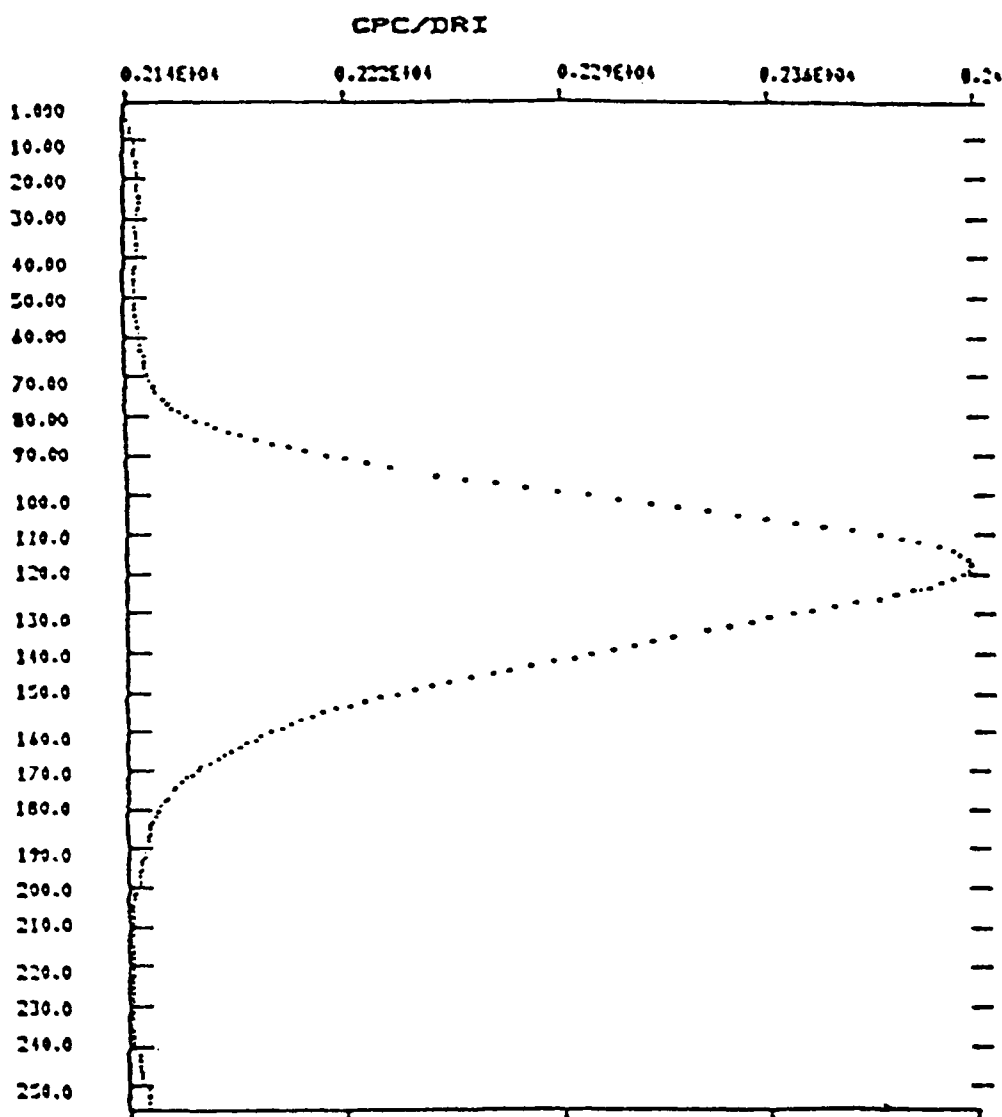


Fig. 2. GPC Curve of EPDM-g-PST

The original synthetic method for terpolymerization was modified slightly in an attempt to improve the yield. Thus, a DCp-PSt macromer of $\overline{M}_n = 16,900$ was dissolved in CH_2Cl_2 and placed in the reaction flask, rather than added dropwise. The resulting graft polymer showed a $\overline{M}_n = 58,500$ and two polystyrene branches per EPDM backbone. It showed PSt/EP ratios of 58/42 and 55/45 by integration of the proton NMR signals. Evidently the yield has not significantly increased.

In conclusion, the data presented clearly show that a new polystyrene macromer, DCp-PSt, can be conveniently prepared by cationic polymerization using DCp-Cl/ Et_2AlCl at -70°C . The yields are very high and the DCp head group can be incorporated quantitatively--chain transfer to the monomer is absent under the conditions employed.

A graft copolymer consisting of a rubbery ethylene-propylene random copolymer backbone and glassy polystyrene branches can be successfully prepared by terpolymerizing ethylene propylene along with the DCp-PSt macromer, using conventional Ziegler-Natta catalysts. The number of polystyrene branches per backbone can be controlled by changing the concentration of the macromer. The graft terpolymer (EPDM-g-PSt) is expected to behave as a thermoplastic elastomer.

In the report on the synthesis of EPDM-g-PSt, an anticipated reaction scheme was proposed for the styrene polymerization by DCp-Cl/ $(\text{C}_2\text{H}_5)_2\text{AlCl}$ initiator. An analogous scheme exists for the polymerization of methylstyrene by the same initiator. One of the steps is a possible chain transfer to the monomer by

intramolecular alkylation. In order to determine whether each P- α MSt chain bears a DCp head group, a series of polymerization studies was carried out to determine $k_{tr,m}$. The value of $k_{tr,m}$ must be zero for a DCp-headed polymer to form quantitatively. Table 8 displays the data of the polymerization studies, and Fig. 3 shows a plot of $1/DP_n$ vs. $1/[M]$.

TABLE 8. Experimental Data to Determine the Value of $k_{tr,m}^*$

Exp.	$[M]$	$\overline{M}_n$ by VPO	DP_n	$1/DP_n \times 10^2$	$1/[M]$
1	0.821M	6550	55.42	1.80	1.22
2	0.671M	5400	45.74	2.19	1.49
3	0.522M	4050	34.31	2.92	1.92
4	0.372M	2940	24.84	4.03	2.69

*Solvent = CH_2Cl_2 ; time = 2 min.; temp. = $-66^\circ C$;

$[DCp-Cl] = 2.99 \times 10^{-2} M$; $[Et_2AlCl] = 1.44 \times 10^{-1} M$;

$[Et_2AlCl]/[DCp-Cl] = 4.8$

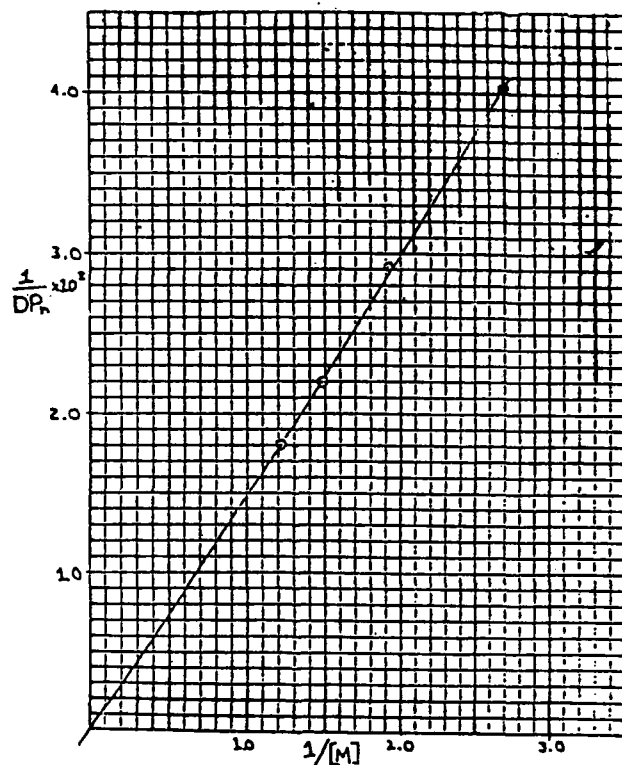


Fig. 3. Plot of $1/DP_n$ vs. $1/[M]$

It is seen from Fig. 1 that the plot of $1/DP_n$ vs. $1/[M]$ gives a straight line that passes through the origin, indicating that there is no chain transfer to the monomer under the conditions employed. Furthermore, the epoxidation titrations clearly show two double bonds per polymer chain, indicating that every chain is headed by one DCp group.

Fig. 4 shows a typical GPC trace of the graft terpolymer. The number of branches per backbone ratio was calculated from molecular weight studies and nmr spectrometry.

The macromer used in these studies demonstrated a $\overline{M}_n$ of 7,500 (64 monomer units) by membrane osmometry, while EPDM-g-P- α MSt showed a $\overline{M}_n$ of 29,200. The GPC curve of the terpolymer (Fig. 4) showed a single, rather narrow, symmetrical peak with a polydispersity of 2.8.

The 1H nmr spectrum exhibits an integrated intensity ratio of aromatic to EP protons of 5:13 or 1:2.6. Consequently, the average molecular weight of the EP backbone is 14,200, and using the data of $\overline{M}_n$ and nmr integrated intensities of EPDM-g-PMSt, it is calculated that the terpolymer contains an average of 2.2 branches per chain. The composition of the terpolymer is 51% P- α MSt and 49% EP.

TGA studies on the terpolymer show a weight loss (degradation) starting at 340°C, and a second weight loss starting around 450°C (Fig. 5). A TGA study of the macromer, PMSt-DCp, showed a single weight loss starting at 340°C. Therefore, the terpolymer, EPDM-g-P- α MSt, degrades first at the PMSt branches.

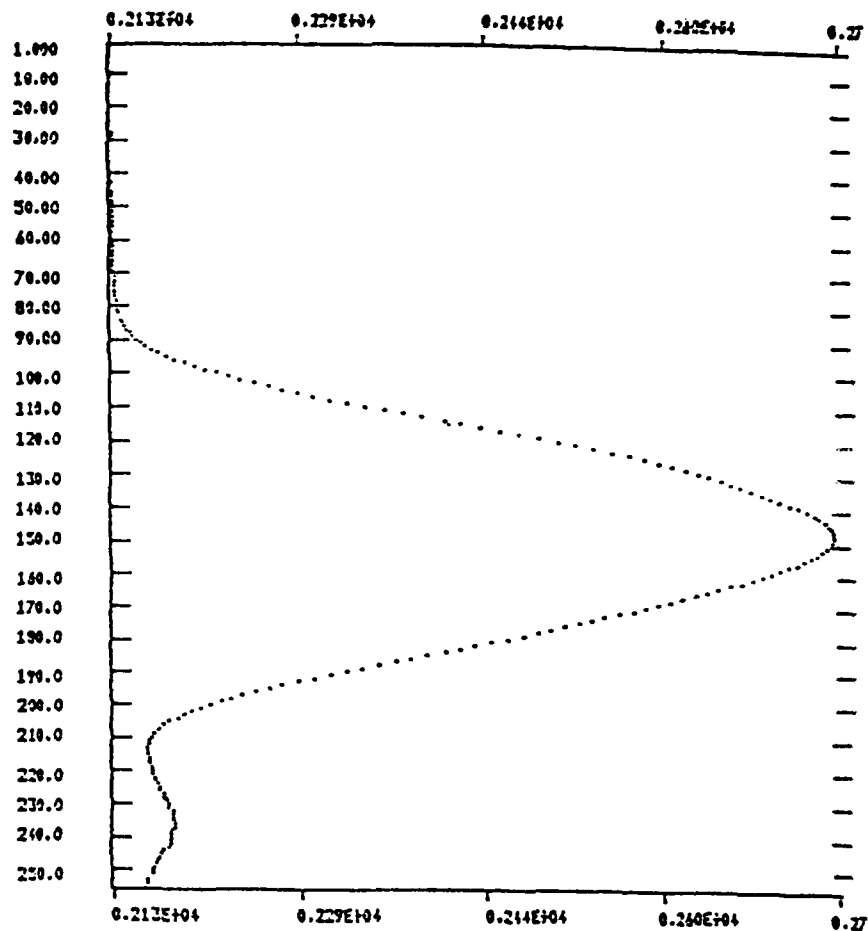


Fig. 4. GPC Curve of EPDM-g-P- α MST

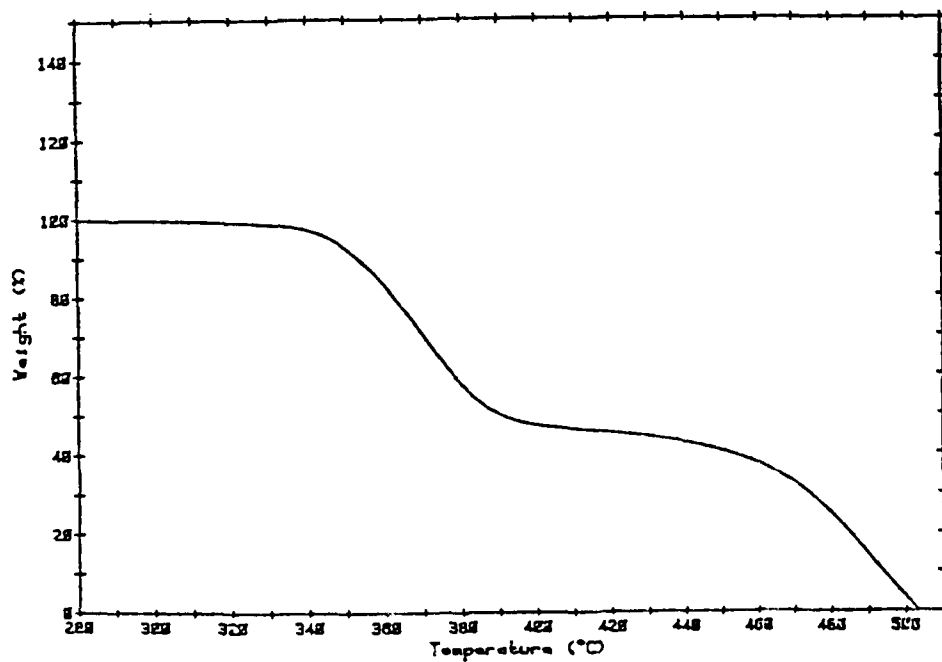


Fig. 5. TGA Curve of EPDM-g-P- α MSt

The data show that a new macromer, PMSt-DCp, can be prepared conveniently at low temperatures by cationic polymerization. The yields are high and chain transfer to the monomer is essentially non-existent.

A graft EPDM terpolymer consisting of the elastomeric ethylene-propylene backbone and glassy poly- α -methylstyrene branches can be prepared, using the macromer as the diene, with conventional Ziegler-Natta catalysts. Like EPDM-g-Pst, the graft terpolymer prepared in this work is expected to behave as a thermoplastic elastomer.

For the chlorination of the commercial EPDM polymer, irradiation in the presence of t -BuOCl was deemed preferable to the use of N -chlorosuccinimide because of its high selectivity for halogen substitution at the allylic position. The polymer chosen for chlorination contains 7.7% ENB by weight, and has a molecular weight ($\overline{M}_n$) of 50,000. Therefore, there is an average of 32 ENB units along the polymer chain. When one allylic position per ENB molecule is achieved, the chlorine content will be 2.75%. This was achieved with 2.1 g of t -BuOCl (30.2:1, t -BuOCl:ENB) per gram of EPDM polymer in the chlorination reaction. It is possible to achieve greater amounts of chlorine in the polymer, but this is accompanied by large amounts of gel formation.

Investigation of the chlorinated polymer revealed a molecular weight ($\overline{M}_n$) of 50,000, and molecular weight broadening was not observed in the gpc curve. These results indicate that degradation of the polymer does not occur during the chlorination process.

The "grafting from" technique was employed for the preparation of the graft copolymers. Cationic polymerization of styrenic monomers was initiated from the chlorinated positions using Et_2AlCl .

The solubility characteristic of the EPDM polymer imposed a severe temperature limitation on the experimental conditions. Efficient grafting could only be obtained in the presence of 10 to 20 percent of a polar solvent, e.g., methyl chloride or methylene chloride. Since the EPDM polymer is insoluble in polar solvents, a heptane/polar solvent mixture was used as the grafting medium; however, the EPDM polymer did not dissolve in this solvent medium below -30°C . Hence, all grafting reactions had to be carried out at -30°C or above. These relatively high grafting temperatures led to a considerable amount of homopolymer formation, mainly because of chain transfer to the monomer, which decreases the grafting efficiency (GE).

Various amounts of polar solvent (methyl chloride) were used and the effect on the grafting efficiency was studied. When methylene chloride was used as a cosolvent, the grafting reaction rates were high, and high (>80 percent) monomer conversions were obtained in a very short time period leading to gel formation. After carrying out a number of preliminary experiments, it was observed that gel formation could be avoided by maintaining the monomer conversion below 25 percent. When α -methylstyrene was used as the monomer, the grafting reactions were much faster than

styrene as the monomer and the α -MeSt conversion was almost uncontrollable. To monitor the α -methylstyrene conversion in these reactions, the coinitiator solution was added dropwise over a very short period of time (0.5 minutes).

The main objective of this research was to synthesize graft copolymers with higher branch/backbone (b/B) ratios. It was thought that by increasing the chlorine content of the EPDM backbone, a higher number of branches could be incorporated into the graft polymers. The effect of changing the chlorine content from 2.0 to 4.0 percent in the Cl-EPDM backbone on the b/B ratio has been studied and the results are shown in Table 9.

TABLE 9. Effect of Chlorine Content of Cl-EPDM on the b/B Ratio of the Graft Copolymer

Exp	% Cl in Cl-EPDM	Monomer Conv. %	$\overline{Mn}(h)^*$	$\overline{Mn}$ (graft)		Glassy Polymer Content % by wt	b/B
				Obs.	Cal.		
1	2.0	10.8	9,500	57,500/59,500		13	0.8
2	2.75	14.0	10,000	68,600/70,000		27	1.86
3	4.0	22.1	15,500	125,000/127,500		60	4.84
4	4.0	20.2	17,000**	99,400/101,000		50	2.91

Conditions: Solvent = heptane/methyl chloride (80/20);
monomer conc. = 1.5M; temp. = -30°C ; weight
of Cl-EPDM = 1.0 g; total volume = 260 mL;
[Et₂AlCl] = $1.35 \times 10^{-2}\text{M}$. When α -MeSt was
used as a monomer total volume = 265 mL; [M]
= 1.45M.

*h = homopolymer

**Homopoly- α -methystyrene

Only a limited number of experiments were possible since our efforts to prepare Cl-EPDM samples containing more than 4.0

percent chlorine were unsuccessful. In all these experiments, the reaction conditions were essentially the same; only the amount of chlorine in the backbone was varied. All the experiments were terminated at an appropriate time interval to give monomer conversions in 10 to 25 percent range.

The main conclusion is that in the limited range of chlorine content studied, the number of chlorine atoms per backbone does have some influence on the branch/backbone ratio. The monomer conversion is higher and a greater number of branches were incorporated into the graft copolymers indicating that a greater number of chlorine sites were activated at higher chlorine content.

The influence of the polarity of the medium on the GE was examined at -30°C by adding various amounts of methyl chloride to the heptane solution of Cl-EPDM. The amount of methyl chloride was varied in the range of 0 to 20 percent by volume. The styrene concentration and the total volume of the system were kept constant by decreasing the heptane concentration to compensate for the increased amounts of methyl chloride. A significant increase in GE was observed with increasing methyl chloride concentration.

In pure heptane medium, a negligible amount of homopolystyrene was formed and no graft copolymer could be isolated. This increase in GE with increasing polar solvent concentration is likely related to the increase in the degree of polymerization with increased dielectric constant of the medium in cationic polymerization.

The efficiency of the grafting process is proportional to

the amount of graft polymer (PS or P- α -MeSt), relative to the total amount of polymer formed during grafting and is defined as:

$$\text{Grafting \% Efficiency} = \frac{\text{Grafted Polymer}}{\text{Grafted Polymer} + \text{Homopolymer}} \times 100$$

The amount of grafted polymer can be calculated from the weight of the graft copolymer formed and its composition. The exact weight of the homopolymer formed in the reaction can be found by extracting the homopolymer in a suitable solvent and then evaporating the solvent on a rotary evaporator.

The branch/backbone ratio was calculated by the following equation:

$$b/B = \frac{\overline{Mn} (g) - \overline{Mn} (B)}{\overline{Mn} (h)}$$

where $\overline{Mn} (g)$, $\overline{Mn} (B)$ and $\overline{Mn} (h)$ are the number average molecular weights of the graft, the backbone, and the homopolymer isolated from the crude product, respectively. The validity of the above relation is based on the assumption that the $\overline{Mn}$ of the homopolymer formed is the same as that of the grafted branches. Although there is no conclusive evidence for this assumption, excellent agreement between the predicted (on the basis of $\overline{Mn}$ of the homopolymer) and the observed molecular weights of the graft copolymers supports the assumption. Fig. 6 shows the relation between the glassy polymer content of the graft copolymer versus the number average molecular weight of the graft polymer. The solid line demonstrates the relationship based on the calculated $\overline{Mn}$ of the graft copolymer.

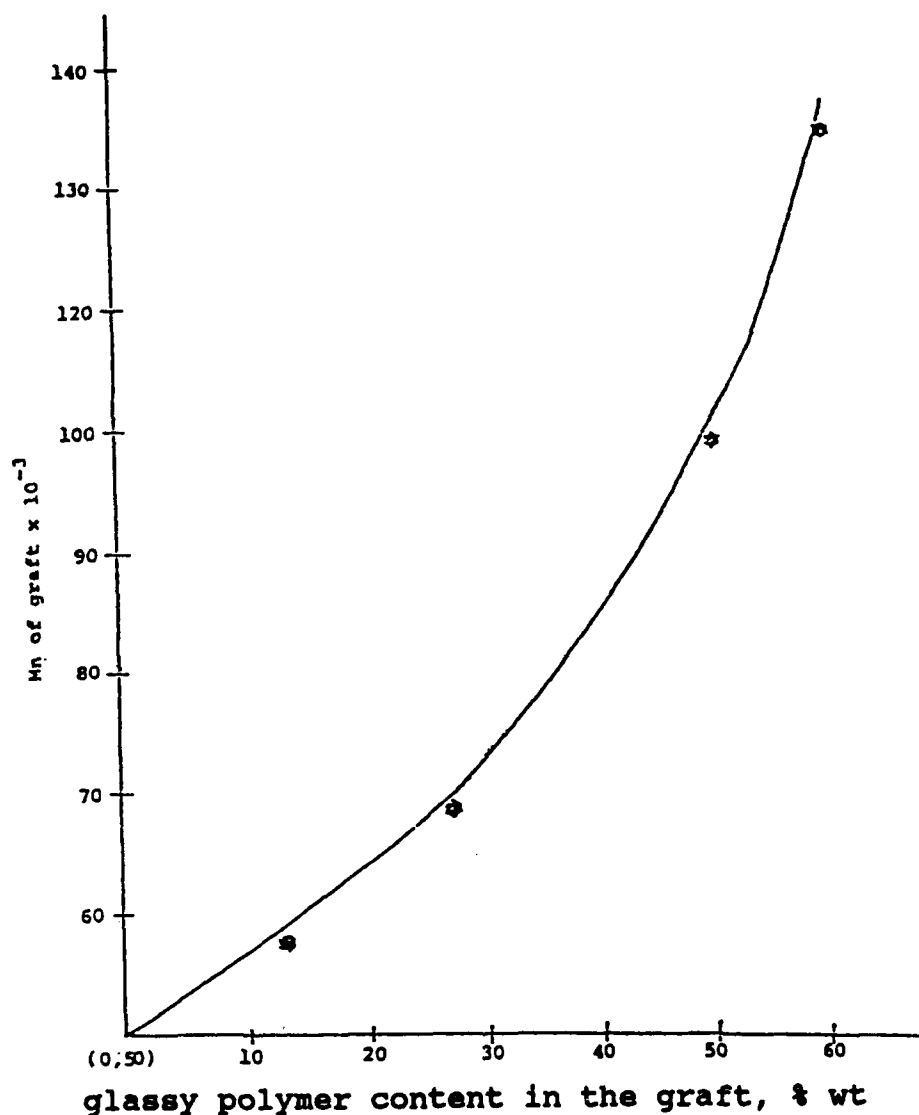


Fig. 6. Glassy Polymer Content in the Graft Polymer
versus Mn of the Graft Polymer

The graft polymers consist of a rubbery EPDM backbone carrying glassy polystyrene or poly(α -methylstyrene) branches, and can be categorized as thermoplastic elastomers. Films of some graft copolymers were cast from solution, as well as by compression molding. Tensile properties of these films are shown in Table 10.

TABLE 10. Tensile Properties of the Graft Copolymers

Type of Glassy Polymer	Glassy Polymer Content % by wt	Modulus 300% kg/cm^2	Elongation at Break %	Tensile Strength kg/cm^2
PS	13	26.0	310	27.0
	27	56.0	315	57.0
	60	--	210	137.0
P- α -MeSt	50	158	325	164.0

Representative stress-strain curves are given in Fig. 7. The graft polymers examined contained from 13 to 60 weight % glass (PS or P- α -MeSt) polymer.

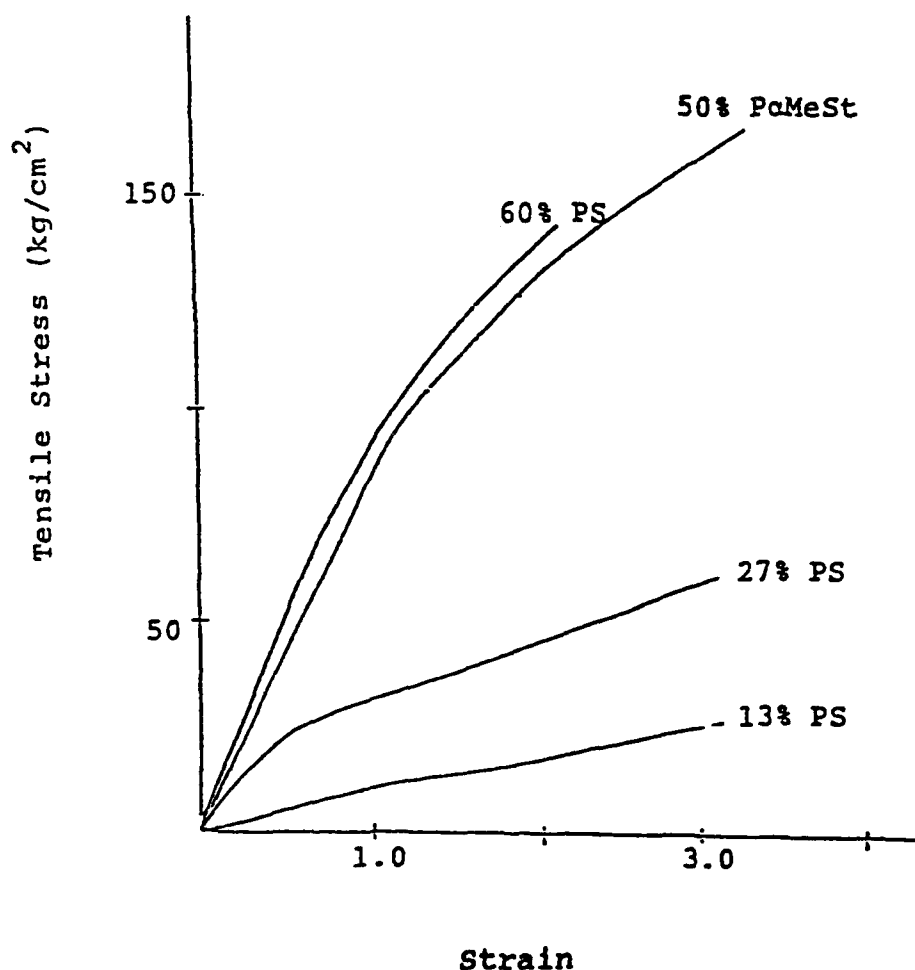


Fig. 7. Stress-Strain Curves of the Graft Copolymers

As shown in Table 10, the tensile strengths and the moduli increase with increasing glassy polymer content of the graft copolymers. Although the tensile strengths and the 300 percent modulus are high for all the samples which were tested, most of the specimens broke at rather low elongations. This might be due to some flaw in the films. It was interesting to note that the tensile properties of two graft copolymers, one containing 60 percent PS and the other 50 percent P- α -MeSt, are almost identical. The stress-strain curves indicate that the graft polymers with higher glassy polymer content are tough plastics.

2. SYNTHESIS AND ATTEMPTED POLYMERIZATION OF CARBORANE MONOMERS

The preparation of new carborane derivatives is of basic importance because they serve as the monomers for polymerization and copolymerization reactions. It was hoped that incorporation of carbon-boron-hydride clusters (carboranes) into a polymer backbone or having them pendant to it would be an enhancement for a solid fuel, due to the high heat of combustion of boron. The new carboranes which have been in this work synthesized are shown in Table 1, along with the structurally significant IR bands and ^1H nmr signals.

The formation of the carboranes was monitored by observing the disappearance of the $\text{C}\equiv\text{C}$ stretching band in the infrared spectrum, since carboranes are prepared from the reaction of the corresponding acetylene with the diadduct, $\text{B}_{10}\text{H}_{12}(\text{CH}_3\text{CN})_2$. In addition, the appearance of a new band at 2600 cm^{-1} is attributable to the B-H stretching band of the borohydride cage, $\text{B}_{10}\text{H}_{10}$.

The ^1H nmr spectra of all carboranes show slight downfield shifts in the proton signals of the hydrogen attached to carbon, as compared to the spectra of the free organic compounds. This is due to the electron withdrawing properties of the boron cage. In addition, there is a broadening of the peaks due to the quadrupole moment of the boron.

When the carborane derivatives were prepared from the reaction of lithium phenylcarborane and halogenated hydrocarbons, the reactions were monitored by observing the disappearance of the carbon-halogen stretching band, as well as the appearance of the B-H-stretching band, in the infrared spectrum. Proton nmr spectra were also valuable in monitoring the reaction. It was found that the yields of these new carboranes varied from 4 to 58 percent. On the basis of these results, several attempts were made to improve the yields of the carboranes. These results are shown in Table 11. It is not well understood why the yields of the carboranes are so low. In some cases, such as the reaction between $\text{B}_{10}\text{H}_{12}(\text{CH}_3\text{CN})_2$ and 1-octen-3-yne or 1-octen-4-yne, it was found that heating the reaction mixture caused the acetylene to polymerize before it reacted with the borohydride substrate. It was also found that higher yields of carboranes were obtained from the reaction of the carborane anion with halogenated alkyls, such as 1,3-dichloropropane or allyl bromide.

The model compound used in various approaches to improve the yield of the carboranes was phenylacetylene. The general reaction of phenylacetylene with $\text{B}_{10}\text{H}_{12}(\text{CH}_3\text{CN})_2$ proceeds as follows:

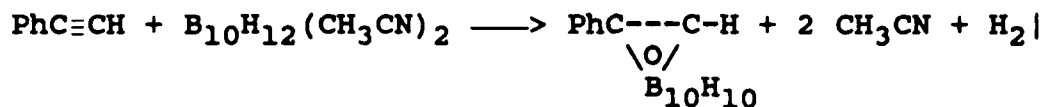
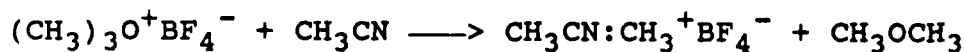


TABLE 11. Attempts to Improve the Yield of Phenylcarborane
(model compound)

Reaction Materials/Ratio	Yield %
$(\text{CH}_3)_3\text{O}^+\text{BF}_4^-/\text{B}_{10}\text{H}_{12}(\text{CH}_3\text{CN})_2/$ Phenylacetylene (2:1:1)	15.33
$(\text{CH}_3)_3\text{O}^+\text{BF}_4^-/\text{B}_{10}\text{H}_{12}(\text{CH}_3\text{CN})_2/$ Phenylacetylene - Reflux (2:1:1)	13.36
Palladium on Charcoal/ $\text{B}_{10}\text{H}_{12}(\text{CH}_3\text{CN})_2/\text{Phenylacetylene}$ (1:1)	0.0
Literature Procedure	27

The first approach was to try to trap the acetonitrile released in the reaction to prevent any equilibrium from occurring that might lower the yield. To this end, $(\text{CH}_3)_3\text{O}^+\text{BF}_4^-$ was placed in the reaction mixture to trap CH_3CN .



In this case, the yield decreased from 27 percent, without the methylating agent, to 15.3 percent. The next attempt was to run the reaction in the presence of Pd on charcoal in order to absorb H_2 and shift the possible equilibrium toward the desired product.

No product was obtained in this reaction; apparently, Pd on charcoal inhibits the forward process.

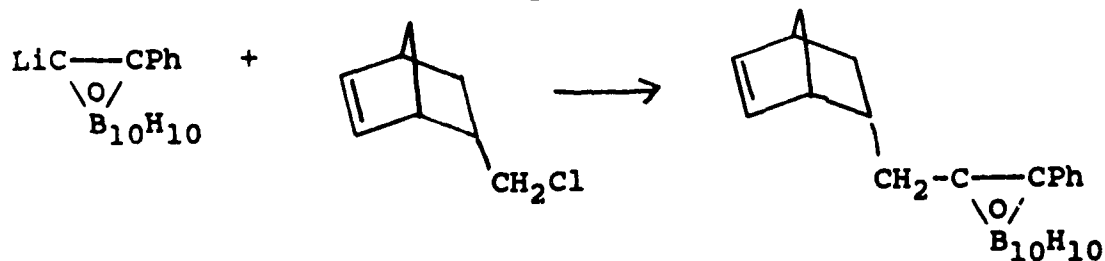
The carboranes, 1-phenyl-2-allylcarborane and 1-vinyl-2-ethylcarborane were used for homopolymerization and copolymerization initiated by the Ziegler-Natta catalyst $\text{VOCl}_3/\text{Et}_3\text{Al}_2\text{Cl}_3$. This polymerization was unsuccessful, probably due to the bulkiness of the carborane nucleus, which would interfere with coordination of the olefinic part of the molecule to the metal.

The 1-phenyl-2-allylcarborane and 1-vinyl-2-ethylcarborane were also inert to copolymerization with ethylene and propylene. The reason why these attempted copolymerizations were unsuccessful may be due to the difference in the reactivity ratios of these monomers with respect to ethylene and propylene. The ethylene and propylene have very high reactivity ratios (reactivity ratio for ethylene using $\text{VOCl}_3\text{Al}_2\text{Cl}_3$ is 10.1) while allyl and vinylcarborane are much less reactive with respect to these gases. The low reactivity of the carboranes can be understood if one considers that the carborane nucleus behaves as an electron withdrawing group, and therefore, will decrease the electron density of the olefin attached to it. Steric problems are also present in the coordination of these monomers to the catalyst center. In addition, the reactivity ratios in copolymerization are a function of the mode of catalyst addition and determination of these ratios by the normal copolymerization equation do not correctly predict the sequence distribution of the polymer, since this equation does not take into consideration steric hindrance. In the copolymerization reaction of 1-phenyl-2-allylcarborane with ethylene and propylene, a copolymer containing less than 1 percent boron was obtained.

In another attempt to incorporate a boron-hydride cluster to a polymer backbone, we tried to synthesize 1-dicyclopentadienyl-2-phenylcarborane, which has a polymerizable double bond far away from the nucleus, and hence might possibly be homopolymerized and copolymerized with other monomers. In addition, since higher yields of carboranes were obtained in the reaction between phenylcarborane lithium and an allyl halide, we believed that this approach could be used for the synthesis of 1-dicyclopentadienyl-1-phenylcarborane. All attempts to prepare this target compound resulted in very low or zero yield of product. The only reaction which gave the product employed the endo-syn-5-bromotri-cyclo[5.2.1.0^{2,6}]deca-4,8-diene, but the product was obtained in very low yields. This led to the thought that changing the configuration of the cyclopentadienyl ring would enhance the extent of the reaction, since steric hindrance might be less with the endo form of the molecule.

Several attempts to prepare the target compound (1-dicyclopentadienyl-2-phenylcarborane) were unsuccessful under a variety of reaction conditions.

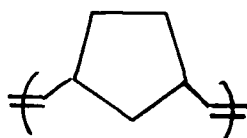
In view of the results obtained with the dicyclopentadienyl system, attempts to synthesize norbornene derivatives of carboranes were carried out. It was anticipated that steric problems would be minimal in a reaction between the phenylcarborane anion and chloromethylnorbornene, as shown below:



Therefore, several attempts were made to synthesize the endo- and exo-5-phenylcarboranylmethyl-2-norbornene. All these attempts were unsuccessful. It was found that the nBuLi used to deprotonate the phenylcarborane tends to add across the double bond.

3. RING-RETENTION POLYMERIZATION OF NORBORNENE

Polynorbornene, prepared in this work by the $\text{Re}(\text{CO})_5\text{Cl}/\text{C}_2\text{H}_5\text{AlCl}_2$ catalyst system, is essentially of the ring-retained type (double bond opening) rather than ring opening. The ^1H NMR spectrum shows a broad aliphatic hydrogen signal in the 0.5 to 3 ppm range and a minor, broad signal at $\delta 5.2$ (olefinic hydrogens). The relative intensities of these signals are about 65 to 1, aliphatic to olefinic hydrogens. Polynorbornene of the ring-opened type would show an integration of 4 to 1, aliphatic to olefinic hydrogens. With relative intensities of 65 to 1, the polymer contains 10 monomers with ring retention for every monomer with a double bond. The structures of the ring-opened and ring-retained polymers are shown below.



Ring-opened Polynorbornene



Ring-retained Polynorbornene

In order to show that the polymer grows on the Re atom, the reaction of norbornene was carried out under the same conditions but without the use of $\text{Re}(\text{CO})_5\text{Cl}$. The polymer obtained where

only $\text{C}_2\text{H}_5\text{AlCl}_2$ was the catalyst is also of the ring-retained type, but the molecular weight is very low (7,200). No evidence was found for any double bonds in the oligomer.

It appears that the polymer obtained from the $\text{Re}(\text{CO})_5\text{Cl}/\text{C}_2\text{H}_5\text{AlCl}_2$ catalyst system is a single species which contains mainly a saturated chain with an occasional double bond. This conclusion is based on the gel permeation chromatogram which shows a single, rather narrow peak. It is unlikely that two separate polymers, one totally saturated (major product) and one of the ring-opened type (minor product) are present in the final sample, in light of the purification procedures and the gpc results.

The question arises whether ring-opening polymerization would occur if a metal carbene species could be made prior to reaction with norbornene. Such an approach is possible with the $\text{Re}(\text{CO})_5\text{Cl}/\text{C}_2\text{H}_5\text{AlCl}_2$ catalyst system; the metathesis of 1,7-octadiene gives essentially quantitative conversion to cyclohexene, which is inert at 90°C , and ethylene, which is driven off. Therefore, at the end of the metathesis of 1,7-octadiene, two metal alkylidene species will be present: $(\text{CO})_y\text{Re}=\text{CH}_2$ and $(\text{CO})_y\text{Re}=\text{CH}(\text{CH}_2)_4\text{CH}=\text{CH}_2$.

Accordingly, the metathesis of 1,7-octadiene was carried out to completion, and then norbornene was added at 90°C . The polymerization was monitored by NMR, and after 2 hours, the olefinic signals at $\delta 6.0$ ppm of the norbornene monomer disappeared, and a new olefinic signal at $\delta 5.0$ to 5.5 ppm appeared. However, the relative intensities of the aliphatic to olefinic

hydrogen atoms in the purified polymer were 9.5 to 1. Therefore, this polymer is also not of the completely ring-opened type, but indicates a polymeric structure composed of about 50 percent ring-retained, and 50 percent ring-opened monomeric units. Once again, the gpc curve of this material shows the existence of a single type of polymer, rather than a mixture of ring-retained and ring-opened species.

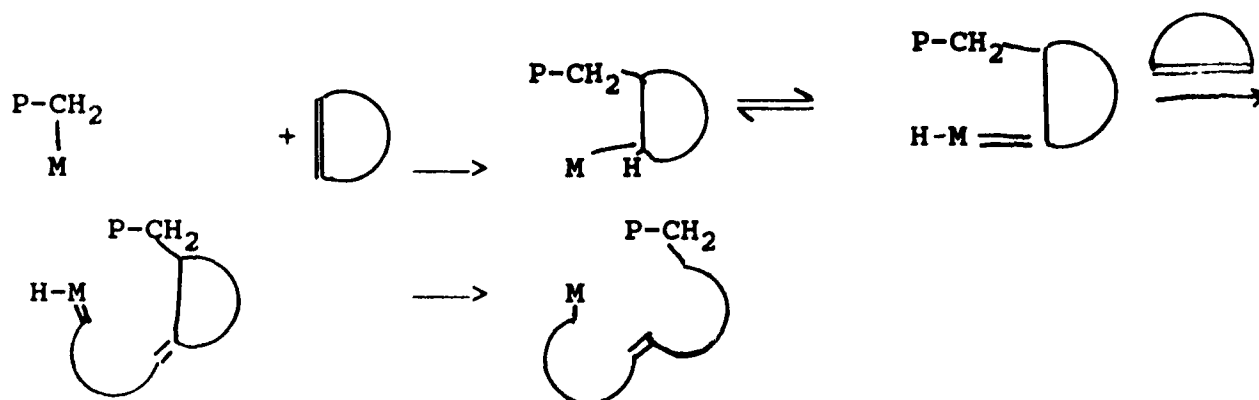
The much lower molecular weight of this polymer, and probably some additional double bonds can probably be attributed to metathesis of the double bonds of the polymer with residual amounts of 1,7-octadiene.

The IR spectra of the purified polymers always show the presence of metal carbonyl bands, and elemental analysis indicates that Re is present in the polymers to the extent of 1 to 2 percent. A test was carried out to determine whether the Re atom attached to the final polymer was through a metal-carbene bond, which might constitute a living end. Addition of 1,7-octadiene at 90°C did not remove the Re catalyst, and the polymer was recovered unchanged.

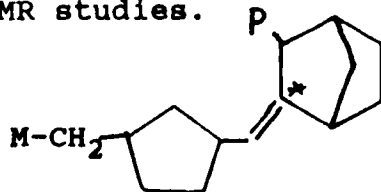
Several cases of polymerizations of cyclic olefins have been reported in which the final polymer contained both double bond-opened (ring-retained) and ring-opened monomer units. For example, a variety of cyclobutenes and cyclobutene derivatives were reported to give polymers containing both ring-opened and ring-retained units.^{22,23} These results prompted the speculation of the possibility of Ziegler-Natta and ring-opening mechanisms occurring on the same catalyst. The only evidence for this

speculation comes from two patents where IR spectra showed that ethylene and cyclopentene could be copolymerized to give an unsaturated polymer containing both ring-retained and ring-opened units.²⁴

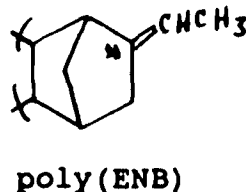
Ivin has proposed a mechanism to account for the possibility of double bond opening and ring opening in the same polymer.²⁵



If we apply Ivin's proposal to the polymerization of norbornene, then β -hydrogen abstraction followed by an olefin metathesis step to give a ring-opened unit, and migration of hydrogen to give a metal alkyl bond, generates a unique olefinic carbon atom which contains no attached hydrogen. This should be detectable by ¹³C NMR studies.



As a model compound, oligomeric poly(ENB) was prepared, and the ¹³C NMR spectrum taken to locate the signal of the unique carbon.



A number of signals appear in the δ 120 to 140 ppm (olefinic) region of the ^{13}C NMR spectrum of poly(ENB), but a signal at 138 ppm disappears in the DEPT spectrum, showing conclusively that the signal at 138 ppm arises from a carbon without a hydrogen bonded to it. The highly magnified ^{13}C NMR spectrum of polynorbornene also shows an olefinic carbon signal at 138 ppm, which also is absent in the DEPT spectrum of the same compound.

It appears, therefore, that Ivin's proposal is correct. A carbon atom in a norbornene unit without a hydrogen atom attached to it most likely arises from α -hydrogen abstraction to create a metal-carbene complex, which then would undergo olefin metathesis to give a ring-opened monomer unit. Any subsequent ring-opening steps that occur before migration of hydrogen would give ring-opened units with a hydrogen on every carbon.

It is interesting that the polynorbornene generated from a metal-carbene initiator is not completely ring-opened. The mechanism to account for ring-retention in a polymer initiated by a metal-carbene species presented by Tsonis and Farona,²⁶ coupled with Ivin's proposal, can account for the structure of this polymer.

4. HOMO- AND COPOLYMERIZATION OF SOME NORBORNADIENE DIMER MONOMERS

The next area of investigation was the homo- and copolymerization of the exo-exo and endo-endo norbornadiene dimers, also by the $\text{Re}(\text{CO})_5\text{Cl}/\text{C}_2\text{H}_5\text{AlCl}_2$ catalyst system.

It is known that transition metals interact with strained carbon-carbon bonds to cause rearrangements in organic molecules. Therefore, it was necessary to establish whether the caged structure of these dimers remained intact during the polymerization process; this was accomplished by ^{13}C spectrometry. The ^{13}C signals for the exo-exo and endo-endo norbornadiene dimers, along with their assignments and carbon numbers are shown below in Table 12.²⁷

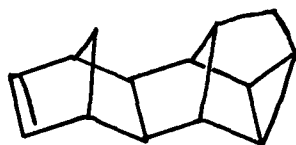
The ^{13}C signals of concern are C(4,5, and 6), i.e., the cyclopropane part of the molecules. After polymerization of the dimers, the ^{13}C nmr spectra are essentially identical to those of the monomers except for the virtual disappearance of the C(12,13) (olefinic C) signals. The high field signals are observed, showing the cage is still intact. The ^1H nmr spectra of the homopolymers of the norbornadiene dimers also show the high field signals (0.7 to 0.9 ppm region) associated with the hydrogen atoms attached to carbons 4, 5, and 6. Similarly, the copolymers of the exo-exo and endo-endo norbornadiene dimers with norbornene also exhibit ^{13}C and ^1H signals in their respective nmr spectra indicative of complete retention of the cage.

Although the homopolymers are both of the ring-retained type (double bond opening rather than ring opening) a minor olefinic signal appears in the ^1H nmr spectrum of each. The nmr integration is 1 to 32, olefinic to aliphatic hydrogens, in the homopolymer of the exo-exo dimer. A completely ring-opened

structure would show an integration of 1 to 7 for the same hydrogens. This is analogous to the structure of polynorbornene, the model compound, and the ^{13}C signal at 138 ppm in polynorbornene, which was shown not to contain an attached

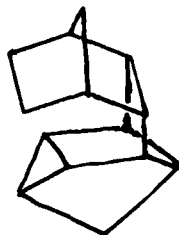
TABLE 12. ^{13}C Chemical Shifts of
Hexacyclo[9.2.1.0^{2,10}.0^{3,8}.0^{4,6}.0^{5,9}]tetradec-12-enes.

$\delta\text{ppm (TMS, CDCl}_3\text{)}$								
<u>C(1,11)</u>	<u>C(2,10)</u>	<u>C(3,9)</u>	<u>C(4,5)</u>	<u>C(6)</u>	<u>C(7)</u>	<u>C(8)</u>	<u>C(12,13)</u>	<u>C(14)</u>
49.30	45.12	44.77	18.16	14.30	33.77	39.07	138.50	43.39



exo-exo

47.25	45.38	45.38	14.13	20.11	27.31	48.68	133.16	57.48
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endo-endo

hydrogen atom, also occurs in the ^{13}C nmr spectrum of the homopolymer of the exo-exo dimer. Consequently, the mechanism of polymerization is essentially that of Ziegler-Natta insertion,

with an occasional olefin metathesis step occurring from time to time. The fact that a ring-opening mechanism does not occur lends support to the mechanism proposed for the formation of the initiator for olefin metathesis with the $\text{Re}(\text{CO})_5\text{Cl}/\text{EtAlCl}_2$ catalyst: an abstractable, allylic hydrogen is required for the formation of a metal-carbene species.²⁸

The ^1H nmr spectrum of the random copolymer of norbornene and the exo-exo norbornadiene dimer reveals the disappearance of the olefinic signals at 6.0 ppm corresponding to the monomers. The somewhat broad signal at 0.7 to 0.9 ppm arises from the protons of the cyclopropane ring, which means that the exo-exo cage has not opened during polymerization. The rest of the aliphatic signals can be attributed to the two monomers in the chain, by comparison with the nmr spectra of the two homopolymers. Clearly, both monomers are incorporated in the polymer with ring-retention.

A block copolymer of the ring-retention type, composed of norbornene and the exo-exo norbornadiene dimer monomers, was also synthesized. The diblock was prepared by sequential addition of the monomers, and monitored by observing the disappearance of the olefinic protons by ^1H nmr spectrometry. The gpc evidence for a diblock is predictable. At the time of addition of the second monomer, some of the catalytic centers are inactive. Therefore, the diblock will show a higher molecular weight than the dead polymers and also show a narrower polydispersity than the homopolymer. These predictions were confirmed by the gpc data of

the diblock copolymer. In addition, the nmr spectra of the random and diblock copolymers are significantly different in the aliphatic region.

5. CHEMISTRY OF THE GROUP IV B METALLOCENES

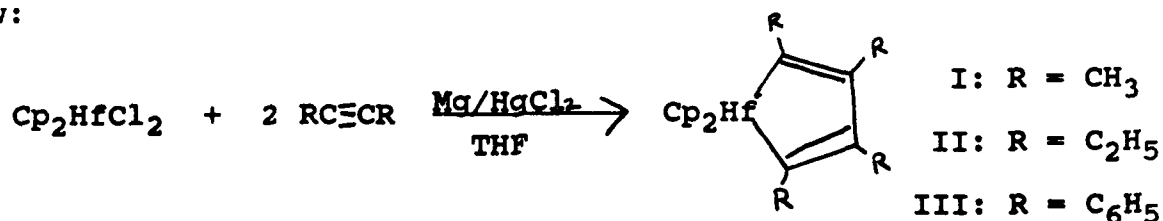
In this area of research, the completed and characterized compounds were with the hafnium systems, and the discussion will be limited to the synthesis and characterization of hafnacyclopentadiene compounds, and the catalytic properties of $\text{Cp}_2\text{HfCl}_2/\text{C}_2\text{H}_5\text{AlCl}_2$.

The one-step synthesis reported in this work for the substituted bis(cyclopentadienyl)hafnacyclopentadienes appears to give the highest yields of these compounds reported to date. Other than the synthesis using $\text{Cp}_2\text{Hf}(\text{CO})_2$ as the starting material,¹¹ other existing preparations of metallacyclopentadienes are lengthy, or result in low net yields.²⁹⁻³⁷

Two of the compounds prepared in this work, the tetraethyl and tetraphenyl derivatives, have been synthesized and characterized previously. The tetraphenylhafnacyclopentadiene was prepared by the photolysis of $\text{Cp}_2\text{Hf}(\text{CH}_3)_2$, with diphenylacetylene.^{33,38} As previously mentioned, both the tetraphenyl and tetraethyl derivatives can be obtained from $\text{Cp}_2\text{Hf}(\text{CO})_2$ with the appropriate alkynes.^{11,39} Attempts to prepare bis(cyclopentadienyl)-2,3,4,5-tetramethylzirconacyclopentadiene from $\text{Cp}_2\text{Zr}(\text{CO})_2$ failed; no attempt to prepare the analogous hafnium derivative was reported. However, our method produces both the zirconium and hafnium derivatives in high yields.

The use of mercuric chloride is necessary in the reduction of Cp_2HfCl_2 as with the analogous Cp_2ZrCl_2 ; ⁴⁰ without it, reductions are slow and reactions are incomplete. Apparently, magnesium reduces HgCl_2 to metallic mercury, which forms an amalgam with the excess magnesium powder. The amalgamated magnesium is, therefore, the principal reducing agent. This contention is supported by the fact that the use of an equivalent amount of metallic Hg in place of HgCl_2 gives the same results as described above.

The general reaction carried out in this work is shown below:

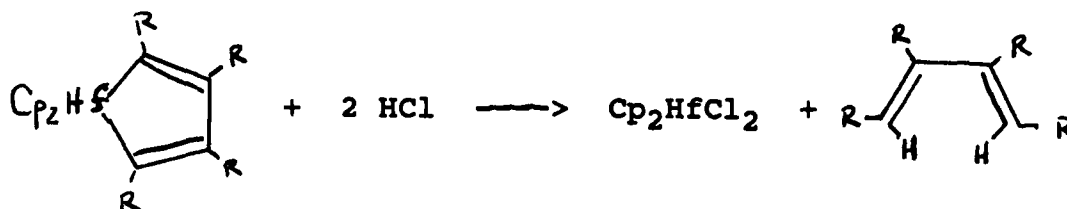


The new tetramethylhafnacyclopentadiene (compound I) was characterized by elemental analysis, mass, infrared, ^1H nmr and ^{13}C nmr spectral studies, and also by its degradation product after reaction with HCl. The yellow-orange crystalline product exhibits a sharp singlet at $\delta 5.93$, assignable to the 10 equivalent cyclopentadienyl protons. The inequivalent methyl protons are observed as overlapping singlets at $\delta 1.60$ ppm. The mass spectrum shows a parent ion peak at m/e 418 together with fragments at m/e 349 and 310 from successive loss of 2-butyne. The structurally significant bands in the infrared spectrum appear at 3100 (CH stretching, Cp), 2900, 2835 (CH stretching), 1594 ($\text{C}=\text{C}$

stretching), 1440 (CC stretching), 1015 (CH in-plane deformation) and 798 cm^{-1} (CH out-of-plane deformation). These bands are characteristic of metallocene-type structures.⁴⁰

The spectral properties of the tetraphenyl and tetraethyl derivatives, compounds II and III, are in good agreement with those reported elsewhere for the characterized products.

The metallacycles were treated with aqueous HCl in a manner similar to that reported by Freedman.⁴¹ The general reaction is shown as follows:



Because of the solubility of Cp₂HfCl₂ in water, the yield of recovery was low in the methylene chloride extract. However, its identity was determined by its melting point (230 to 233°C) and ¹H nmr spectrum. Also isolated from all these reactions was the stereospecific E,E isomer of the substituted 1,3-butadiene. The tetramethyl derivative led to specifically 3,4-dimethyl-(2E,4E)-2,4-hexadiene (bp 134°C), and compared identically to that of an authentic sample in terms of spectral properties (uv, ir, nmr).⁴²

Compound II, after reaction with HCl, gave 4,5-diethyl-(3E,5E)-3,5-octadiene (bp 63°C), and was identical in spectral properties to that reported for the same compound.⁴³ The HCl

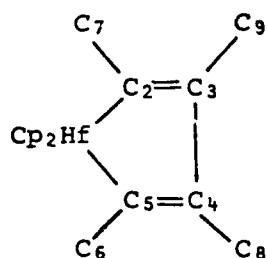
degradation product of III yielded 1,2,3,4-tetraphenyl-(1E,3E)-1,3-butadiene (mp 183°C), which is identical in various spectral properties reported earlier.^{41,43}

Whereas Rausch et al. have assigned ^{13}C nmr signals to some titanacyclopentadiene systems,⁴⁴ and Jones and Peterson have performed analogous assignments to zirconacyclopentadienes³⁶ as did Thanedar and Farona,⁴⁵ ^{13}C nmr assignments have not yet been made for the corresponding hafnium compounds. We have investigated the ^{13}C spectra of the three compounds prepared in this work; data are shown in Table 13.

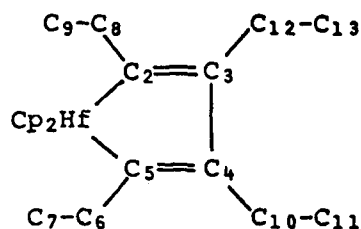
For Compound I, proton-decoupled and off-resonance decoupled (ORD) ^{13}C nmr spectra were obtained. The singlet at $\delta 109.19$ ppm is split into a doublet in the ORD spectrum; hence, this peak is assigned to the equivalent carbon atoms of the Cp rings. The signals in the aliphatic region at $\delta 20.31$ and 14.95 ppm are split into quartets in the ORD spectrum, and are attributable to $\text{C}_6\text{-C}_9$. The quaternary carbon atoms, C_2 and C_5 in the metallacyclic ring are bonded directly to hafnium and are substantially shifted downfield from the other two ring carbons (C_3 and C_4). This shift is diagnostic of a metallacyclopentadiene system and has been observed previously.⁴⁴ As expected, the signals at $\delta 184.97$ and 131.99 remain unchanged in the ORD spectrum.

In order to assign the signals in the ^{13}C spectrum of compound II, proton-decoupled and attached proton test (APT) ^{13}C spectra were obtained. The Cp carbons are assigned to the signal at $\delta 109.03$ ppm. The aliphatic region exhibits four peaks at 14.01 , 14.25 , 21.14 and 29.21 ppm. When subjected to APT, the

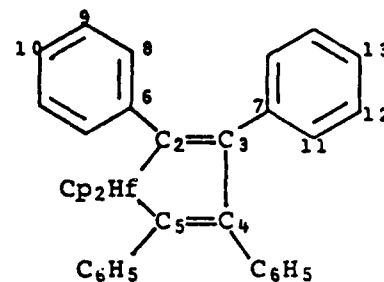
TABLE 13. ^{13}C NMR Data of Substituted Hafnacyclopentadienes.*



I



II



III

δ , ppm
Cp: 109.19
C(2,5): 184.97
C(3,4): 131.99
C(6,7): 20.31
C(8,9): 14.95

δ , ppm
Cp: 109.03
C(2,5): 192.77
C(3,4): 134.22
C(6,8): 29.21
C(7,9): 21.14
C(10,12): 14.25
C(11,13): 14.01

δ , ppm
Cp: 110.92
C(2,5): 196.82
C(3,4): 148.73
C(6): 141.65
C(7): 139.94
C(8-13): 130.84, 127.52
127.32, 126.34
124.28, 122.89

* CDCl₃ was the solvent. TMS was the internal standard.

signals at δ 21.14 and 29.21 ppm are inverted, whereas the other two are not. Consequently, those which are inverted correspond to the secondary methylene carbons (C_6 , C_8 , C_{10} , C_{12}) while the others are attributed to the methyl carbon signals. The carbon atoms of the CH_2 and CH_3 groups closest to the metal (C_6 , C_8 , C_7 , C_9) are more strongly deshielded than the groups away from hafnium. Hence, the signals at δ 29.21 and 21.14 ppm are assigned to the C_6 , C_8 and C_{10} , C_{12} atoms, respectively. The signals at 14.25 and 14.01 ppm, therefore, arise from C_7 , C_9 and C_{11} , C_{13} , respectively. Finally, the signals at δ 192.77 are assigned to C_2 , C_5 , whereas the δ 134.42 peak is due to C_3 , C_4 . This is further confirmed in the APT spectrum, where both signals are inverted.

The ^{13}C chemical shift values for compound (III) are in good agreement with those of the titanium analogue, reported by Rausch, et al.⁴⁴, and are assigned accordingly, as shown in the table.

Several unsymmetrically substituted hafnacyclopentadienes were also synthesized. To the best of our knowledge, none of the compounds shown below have been reported previously. The substituents on these compounds are:

- (IV): dimethylbis(trimethylsilyl)
- (V): dimethyldiphenyl
- (VI): diphenyl

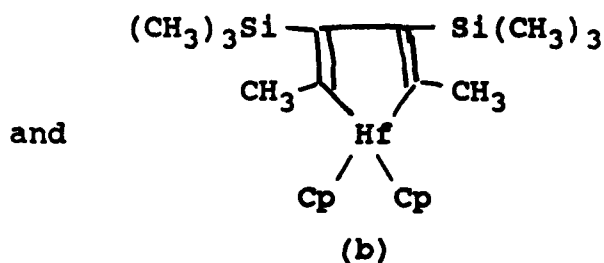
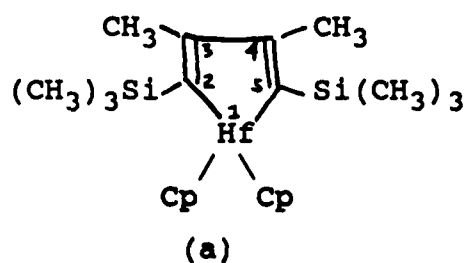
For compound (IV), which is a yellow, crystalline material, the structurally-significant bands in the infrared spectrum appear at 2950 (CH aliphatic stretching), 1590 ($C=C$ stretching),

1435 (CC stretching), 1020 (CH in-plane deformation) and 790 (CH out-of-plane deformation) cm^{-1} . These bands are characteristic of metallocene-type structures.

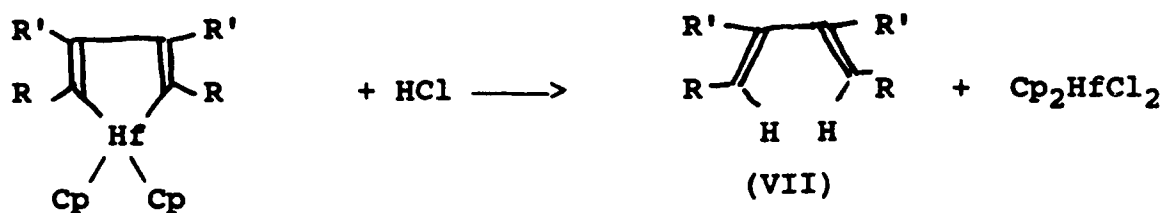
Compound (I) exhibits a sharp singlet at $\delta 6.1$ ppm, assignable to the 10 equivalent cyclopentadienyl protons. Eighteen equivalent methyl resonances of the trimethylsilyl group appear at $\delta 0.16$ ppm as a singlet. The singlet at $\delta 1.86$ ppm is attributable to the six equivalent protons of the two methyl groups on the ring.

The proton decoupled ^{13}C nmr spectrum of (IV) shows the Cp carbons as a singlet at $\delta 109.91$ ppm. The quaternary carbons at positions 2 and 5 in the metallacyclic ring which are bonded directly to hafnium are substantially shifted downfield ($\delta 200.32$ ppm) from carbon atoms 3 and 4 ($\delta 144.75$ ppm). This shift is diagnostic of a metallacyclopentadiene ring system and has been observed previously. The aliphatic region exhibits two signals at $\delta 25.47$ and 2.47 ppm, which are assigned to the carbon atoms of the methyl groups, and the carbon atoms of the trimethylsilyl group, respectively.

Compound (IV) is clearly a single geometric isomer, based on the data above. Two structures are possible which satisfy the spectral data, compounds (a) and (b) shown below.



Compound (IV) was treated with HCl, releasing the organic ligand:



Compound (VII), obtained after purification by column chromatography, exhibited a sharp singlet at $\delta 0.16$ ppm ($\text{Si}(\text{CH}_3)_3$, 18H) a sharp singlet at $\delta 1.80$ ppm (CH_3 , 6H), and a sharp singlet at $\delta 5.4$ ppm, (olefinic, 2H) in the ^1H nmr spectrum. These data clearly rule out structure (b) as a possibility; the structure of (a) was confirmed by a crystal structure determination, shown later in this report.

The ^1H nmr spectrum of (V) indicated that it was an isomeric mixture of the dimethyldiphenylhafnacyclopentadiene structure. Two signals are observed at $\delta 6.00$ and $\delta 6.09$ ppm (10H), which are attributable to two sets of equivalent cyclopentadienyl protons, whereas a broad multiplet at $\delta 6.8$ -7.2 ppm is assigned to the aromatic protons. Three singlets at $\delta 1.26$, 1.66, and 2.00 ppm are observed with an intensity ratio of 2:1:1, respectively. These signals are assigned to the three sets of nonequivalent methyl protons.

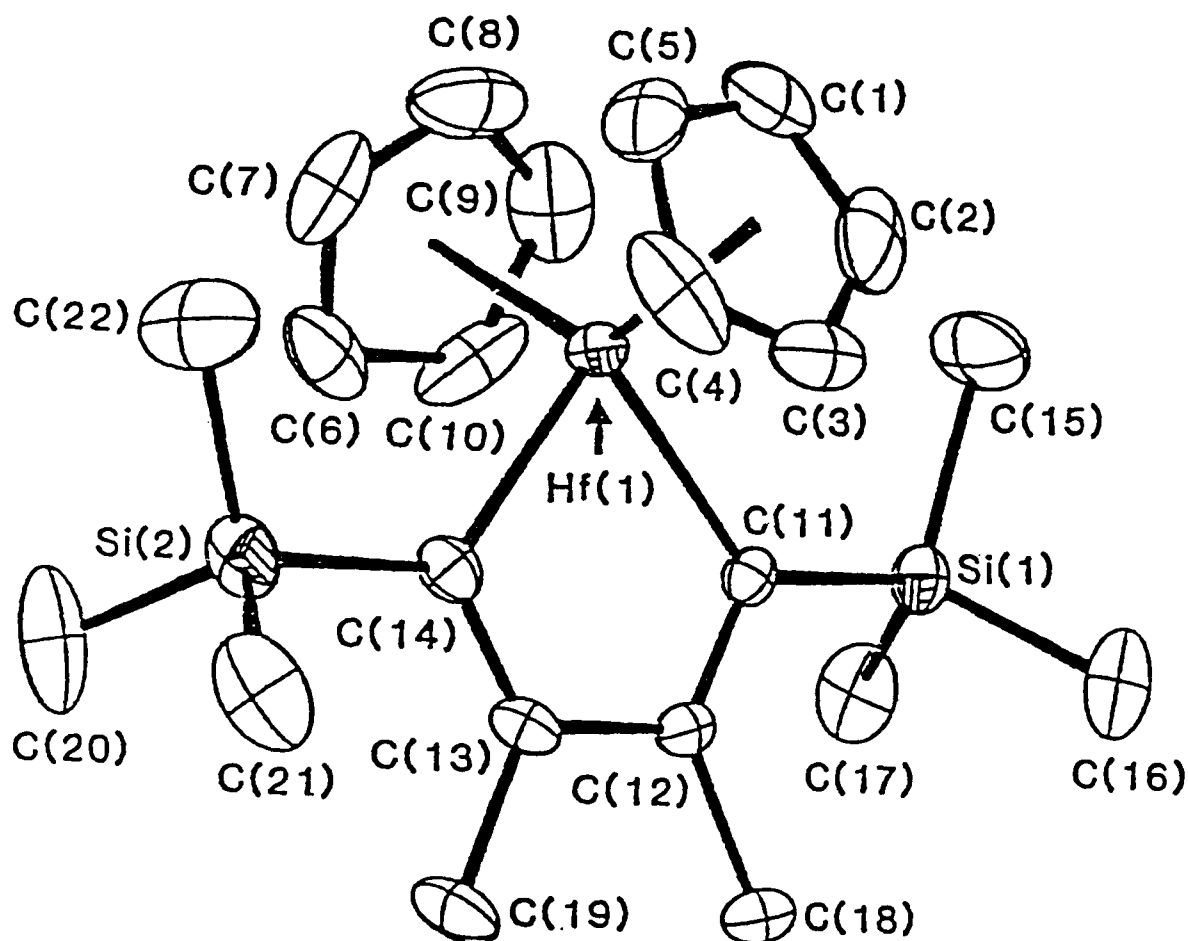
After reaction of (V) with HCl, the two organic ligands were separated, purified by column chromatography, and identified as 1,3-diphenyl-2-methyl-(1E,3E)-1,3-pentadiene and 1,4-diphenyl-2,3-dimethyl-(1E,3E)-butadiene by comparison of physical and spectral properties with those reported for the same compounds elsewhere.⁴⁶

The ^1H nmr spectrum of (VI) indicated that it was an isomeric mixture of a diphenylhafnacyclopentadiene compound. Two sharp signals at $\delta 6.00$ and $\delta 6.03$ ppm (Cp, 10H), a broad multiplet at $\delta 6.73$ - 7.03 ppm (aromatic, 10H) and a broad multiplet at $\delta 5.73$ - 5.86 (olefinic, 2H) are observed. The mass spectrum showed a parent ion peak at m/e 512.5 (M^+) together with fragments at m/e 435 ($M-\text{C}_6\text{H}_5^+$), and m/e 358 ($435-\text{C}_6\text{H}_5$). The fragment at 310 corresponds to Cp_2Hf^+ . Attempts to separate these hafnacycles by column chromatography on neutral alumina led to decomposition, and reaction with HCl yielded a sticky, polymeric compound. It is known that 1,3-diphenyl-1,3-butadiene dimerizes at room temperature.⁴⁷

Crystals of compound (IV) were grown and subjected to X-ray diffraction analysis. Following is a discussion of the X-ray data.

Description of the structure. Important interatomic distances and angles and their standard deviations (esd's) are shown in Tables 13 and 14. The molecular structure and atom numbering scheme of $\text{Hf}(\text{C}_5\text{H}_5)_2\text{C}_4(\text{Si}(\text{CH}_3)_3)_2(\text{CH}_3)_2$ are shown in Fig. 8. A stereoview of the molecule is presented in Fig. 9. The configuration of the complex is clearly that of a metallocycle with the four butadiene carbons being coplanar with the hafnium atom as opposed to a η^4 -metal-coordinated butadiene.⁴⁸

The hafnium-butadiene-bis-cyclopentadienyl portion of the molecule is nearly identical to the analogous portion of 1,1-bis(η^5 -cyclopentadienyl)-2,3,4,5-tetraphenylhafnole (V).⁴⁹ The cyclopentadienyl rings exhibit a staggered conformation with the



The thermal ellipsoids are drawn at the 20% probability level.
The hydrogens have been omitted for clarity.

Fig. 8. ORTEP Labeling Diagram for $\text{Hf}(\text{C}_5\text{H}_5)_2\text{C}_4(\text{Si}(\text{CH}_3)_3)_2$.

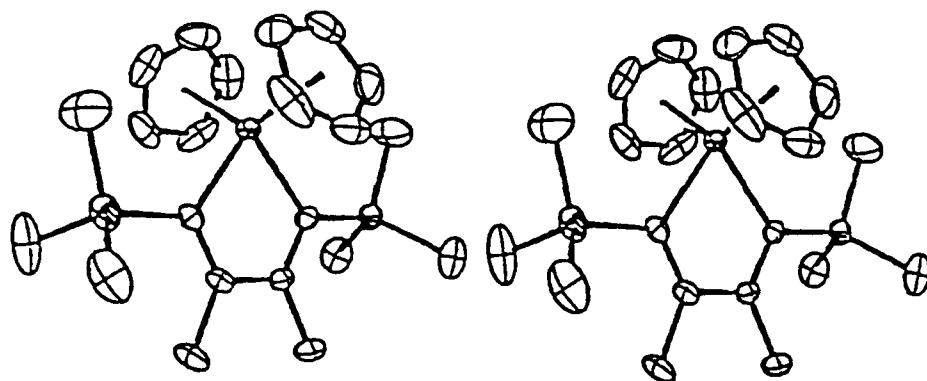


Fig. 9. Stereoscopic View of the $\text{Hf}(\text{C}_5\text{H}_5)_2\text{C}_4(\text{Si}(\text{CH}_3)_3)_2(\text{CH}_3)_2$ Molecule, showing the Coordination Geometry about the Hafnium Atom.

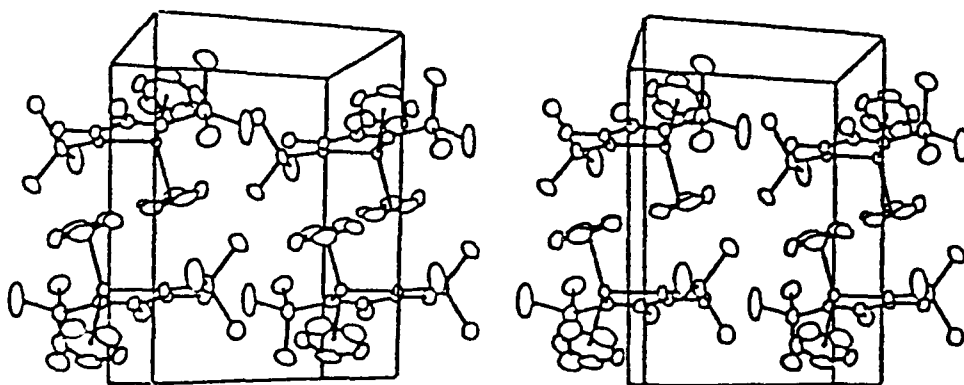


Fig. 10. Stereoscopic View of the Crystal Packing of Four Molecules of $\text{Hf}(\text{C}_5\text{H}_5)_2\text{C}_4(\text{Si}(\text{CH}_3)_3)_2(\text{CH}_3)_2$.

TABLE 14. Bond Lengths ($\text{\AA}$) for Hafnium, Silicon and Carbon
in $\text{Hf}(\text{C}_5\text{H}_5)_2\text{C}_4(\text{Si}(\text{CH}_3)_3)_2(\text{CH}_3)_2$.

FROM	TO	DISTANCE	FROM	TO	DISTANCE
Hf(1)	C(1)	2.486(9)	Si(2)	C(21)	1.889(11)
Hf(1)	C(2)	2.521(9)	Si(2)	C(22)	1.866(13)
Hf(1)	C(3)	2.505(9)	C(1)	C(2)	1.323(16)
Hf(1)	C(4)	2.494(9)	C(1)	C(5)	1.338(15)
Hf(1)	C(5)	2.480(9)	C(2)	C(3)	1.308(18)
Hf(1)	C(6)	2.501(8)	C(3)	C(4)	1.344(18)
Hf(1)	C(7)	2.480(9)	C(4)	C(5)	1.434(19)
Hf(1)	C(8)	2.463(10)	C(6)	C(7)	1.355(17)
Hf(1)	C(9)	2.474(9)	C(6)	C(10)	1.375(17)
Hf(1)	C(10)	2.477(8)	C(7)	C(8)	1.302(18)
Hf(1)	C(11)	2.230(5)	C(8)	C(9)	1.271(19)
Hf(1)	C(14)	2.215(6)	C(9)	C(10)	1.328(18)
Si(1)	C(11)	1.861(6)	C(11)	C(12)	1.370(8)
Si(1)	C(15)	1.861(11)	C(12)	C(13)	1.503(9)
Si(1)	C(16)	1.850(10)	C(12)	C(18)	1.539(8)
Si(1)	C(17)	1.866(10)	C(13)	C(14)	1.346(9)
Si(2)	C(14)	1.879(6)	C(13)	C(19)	1.531(8)
Si(2)	C(20)	1.847(12)			

TABLE 15. Interbond Angles ($^\circ$) for Hafnium, Silicon and Carbon
in $\text{Hf}(\text{C}_5\text{H}_5)_2\text{C}_4(\text{Si}(\text{CH}_3)_3)_2(\text{CH}_3)_2$.

FROM	THRU	TO	ANGLE	FROM	THRU	TO	ANGLE
C(11)	Hf(1)	C(14)	82.7(2)	Si(2)	C(14)	C(13)	122.7(5)
C(11)	Si(1)	C(15)	112.6(4)	C(2)	C(1)	C(5)	110.6(11)
C(11)	Si(1)	C(16)	114.7(4)	C(1)	C(2)	C(3)	108.3(13)
C(11)	Si(1)	C(17)	110.4(4)	C(2)	C(3)	C(4)	110.9(11)
C(15)	Si(1)	C(16)	104.1(6)	C(3)	C(4)	C(5)	105.0(9)
C(15)	Si(1)	C(17)	104.9(6)	C(1)	C(5)	C(4)	105.2(10)
C(16)	Si(1)	C(17)	109.6(5)	C(7)	C(6)	C(10)	105.4(10)
C(14)	Si(2)	C(20)	112.2(4)	C(6)	C(7)	C(8)	108.2(11)
C(14)	Si(2)	C(21)	112.9(4)	C(7)	C(8)	C(9)	110.2(12)
C(14)	Si(2)	C(22)	111.1(4)	C(8)	C(9)	C(10)	109.8(12)
C(20)	Si(2)	C(21)	107.0(6)	C(6)	C(10)	C(9)	106.5(10)
C(20)	Si(2)	C(22)	109.4(8)	C(11)	C(12)	C(13)	122.8(5)
C(22)	Si(2)	C(21)	103.9(7)	C(11)	C(12)	C(18)	121.0(6)
Hf(1)	C(11)	Si(1)	130.9(3)	C(13)	C(12)	C(18)	116.2(5)
Hf(1)	C(14)	Si(2)	129.2(3)	C(12)	C(13)	C(14)	120.9(5)
Hf(1)	C(11)	C(12)	105.6(4)	C(12)	C(13)	C(19)	115.6(6)
Hf(1)	C(14)	C(13)	107.9(4)	C(14)	C(13)	C(19)	123.5(6)
Si(1)	C(11)	C(12)	123.5(4)				

Hf-C(cyclopentadienyl) bond lengths ranging from 2.463(10) Å to 2.521(9) Å. The distances from the hafnium to the ring centers are 2.208 Å and 2.218 Å. The Cent-Hf-Cent' angle,⁵⁰ at 133.12° is greater than the expected tetrahedral angle of 109°, presumably due to steric interactions between cyclopentadienyl rings, but comparable to that of its analog.⁴⁹ The centroid-Hf-C(α -carbon of the butadiene) angles average 107.36°. The C(11)-Hf-C(14) bond angle is 82.7(2)°, but is considerably less than the expected tetrahedral angle. This compression is presumably a result of the interaction between the cyclopentadienyl rings and the substituents of the butadienes.

The geometry of the five membered heterocyclic ring system in $\text{Hf}(\text{C}_5\text{H}_5)_2\text{C}_4(\text{Si}(\text{CH}_3)_3)_2(\text{CH}_3)_2$ shows equivalent bond distances, within esd's, to those of $\text{Hf}(\text{C}_5\text{H}_5)_2\text{C}_4(\text{C}_6\text{H}_5)_4$ and are listed in Table 13. The bond angles, however, vary slightly with Hf-C(α -carbon)-C(α -carbon) bond angles being 105.6(4)° and 107.9(4)° and the C(α -carbon)-C(α -carbon)-C(α -carbon)' bond angles at 122.8(5)° and 120.9(5)°. The Hf-C(α -carbon)-Si angles at 130.9(3)° and 129.2(3)° are greater than the ideal value of 120° for an sp^2 carbon atom. The other silicon-carbon and carbon-carbon distances and angles are unremarkable.

A moderate to high amount of thermal motion is seen in the thermal ellipsoids of the cyclopentadienyl rings and terminal carbons of the $-\text{Si}(\text{CH}_3)_3$ ligands, shown in Fig. 8. Fig. 10 shows a stereoscopic packing diagram of four molecules entering a unit cell.

In our original attempts to synthesize unsymmetrically-substituted hafnacyclopentadienes, the approach was to add equimolar amounts of two symmetrically-substituted acetylenes, such as diphenylacetylene and 3-hexyne, or 2-butyne and 3-hexyne, and the like. However, this approach, somewhat surprisingly, led only to the isolation and/or spectral identification of symmetrically-substituted hafnacyclopentadienes. Little, if any, of the mixed compounds could be detected.

Another approach would be to assume a stepwise coordination of the alkyne to " Cp_2Hf ", analogous to that of the synthesis of titanacyclopentadienes⁵¹ and add the various acetylenes individually at certain times during the reaction. The problem with this approach is the rather lengthy reaction time to obtain high yields of the hafnacycles. It is difficult to estimate the time of addition of the second alkyne.

Furthermore, in our attempts to synthesize unsymmetrically-substituted titanacyclopentadienes by stepwise addition of two different alkynes, starting from both $\text{Cp}_2\text{Ti}(\text{CO})_2$ and $\text{Cp}_2\text{TiCl}_2/\text{Mg}$, only the symmetrically-substituted final compounds were observed as the major products.⁵² Shur, et al. have had success in synthesizing unsymmetrical titanacyclopentadienes by stepwise addition of two different symmetrical acetylenes.⁵³ However, this approach, in our hands, did not lead to the desired materials as major products of the reactions.

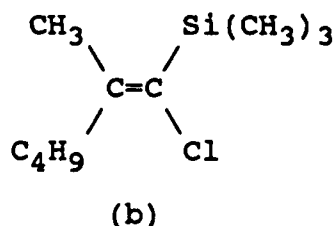
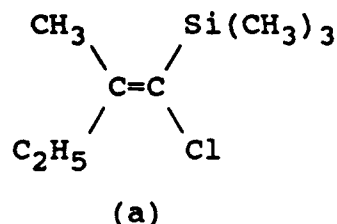
6. CATALYTIC PROPERTIES OF Cp_2HfCl_2

Like the $\text{Cp}_2\text{ZrCl}_2/\text{C}_2\text{H}_5\text{AlCl}_2$ catalyst system, the hafnium system produced linear, polyconjugated polymers, exclusively. The IR and NMR spectra of polyphenylacetylene indicate that the double bonds in the polyconjugated structure are mainly trans. This comes from an investigation of the 915 and 890 cm^{-1} band intensities in the IR spectrum of the polymer, in which the 915 cm^{-1} band is clearly the predominant one.⁵⁴ The spectral properties of the other polyalkynes compare favorably with those reported elsewhere for the same polymers.^{55,56} The polyolefins prepared in this work are similar in ^1H NMR spectral and T_g studies (110°C and -60°C) reported earlier by other workers.^{57,58}

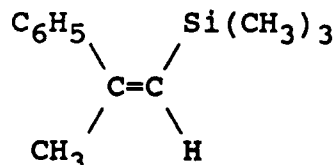
In the proton NMR spectrum of polyphenylacetylene, a broad olefinic proton signal appears to overlap the aromatic absorption. The deshielding of the olefinic proton is attributed to the conjugation of the polymer backbone with the aromatic rings pendant to the chain. Furthermore, the first fraction of the polymer obtained after chromatographic purification shows the presence of an ethyl group in the ^1H NMR spectrum ($\delta 2.35$, 2H, q; $\delta 0.8$, 3H, t). The ethyl group most likely arises from the initiation step, where the initiating species is believed to be $\text{Cp}_2\text{HfC}_2\text{H}_5^+\text{AlCl}_4^-$.

Mechanism. The reaction of the catalyst system with 1-trimethylsilyl-1-propyne, a sterically bulky, alkynyl substrate, which would limit alkyne insertion largely to the initial step, was carried out with the expectation that isolation of the

first formed product could provide insight into the mechanism of oligomerization. Two products were separated and identified by a gas chromatographic-mass spectrometric studies:



Recently, Eisch et al. studied the interaction of equimolar amounts of the titanocene dichloride/methylaluminum dichloride catalyst system with $\text{C}_6\text{H}_5\text{C}\equiv\text{CSi}(\text{CH}_3)_3$, and intercepted the initial insertion product.⁵⁹ The compound isolated, after hydrolysis, was

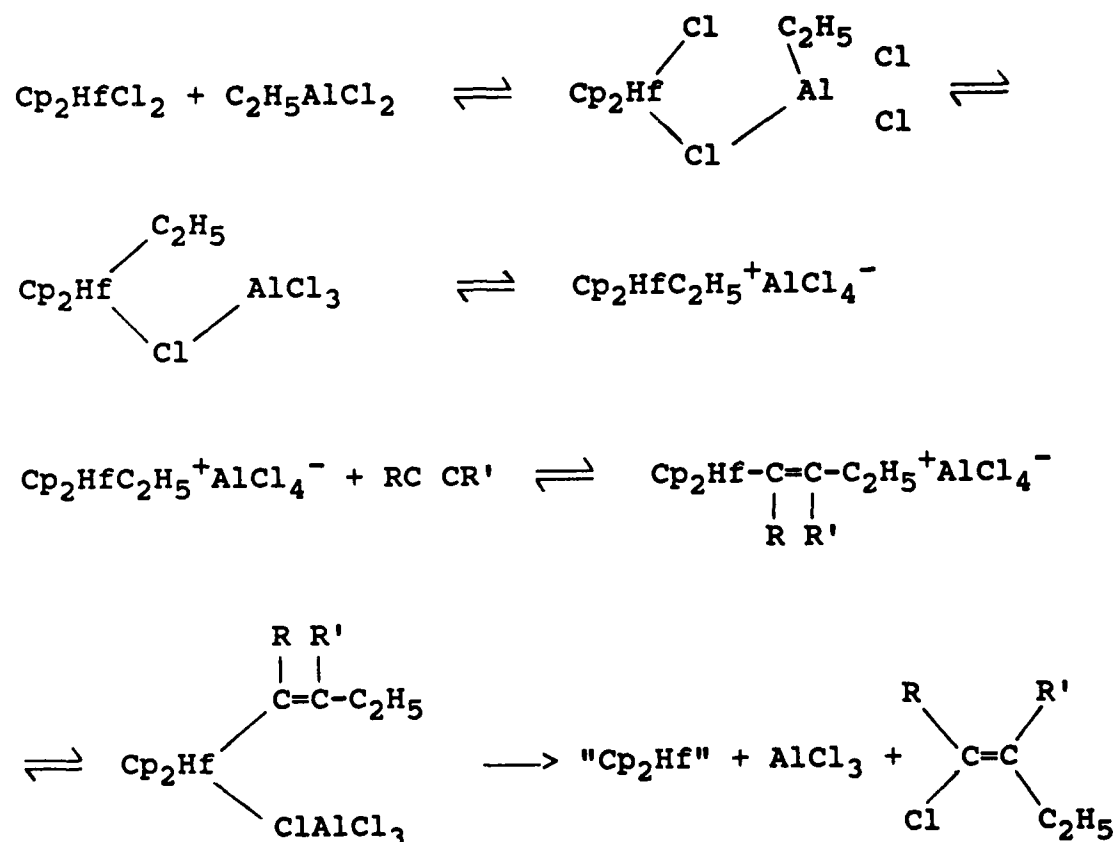


which led to the conclusion that the initiating species for polymerization of olefins is $\text{Cp}_2\text{TiCH}_3^+\text{AlCl}_4^-$, and propagation occurs by insertion of the olefin into the Ti-C bond. Jordon, et al., have studied the dimethylzirconocene catalyst and confirmed the initiating species for polymerization of olefins as $\text{Cp}_2\text{ZrCH}_3(\text{THF})^+\text{BPh}^-$.⁶⁰

Oligomerization of alkynes by the $\text{Cp}_2\text{HfCl}_2/\text{C}_2\text{H}_5\text{AlCl}_2$ system appears to be analogous to the titanocene and zirconocene systems above. In the reaction of the catalyst with $\text{CH}_3\text{C}\equiv\text{CSi}(\text{CH}_3)_3$, the products (a) and (b) can be explained as arising in the following manner.

In the case of product (b), where a butyl group has taken the place of the ethyl ligand in (a), the C_4 fragment can arise from prior insertion of ethylene into the $Hf-C_2H_5$ bond. Ethylene is generated in small amounts from $C_2H_5AlCl_2$.⁶⁰

Further evidence that propagation proceeds by an insertion of the alkyne into a Hf-C bond comes from polymerization studies



of styrene with the same catalyst system. There is a significantly higher molecular weight obtained when methylene chloride is used as the solvent ($\overline{M}_n = 37,000$) than when toluene is used ($\overline{M}_n = 4,000$), showing the polar nature of the initiator. Complete inhibition of polymerization of styrene and isobutylene was observed in the presence of such Lewis bases as ether and also where the monomer dimethylacetylene dicarboxylate was used, showing that coordination of such bases blocks the coordination site of the monomer and prevents insertion.

IV. CONCLUSIONS

Various areas of research were carried out under this contract. New graft terpolymers were synthesized and characterized, and these can find used as compatibilizers and models for new materials where chemical bonds exist between rubbers and plastics.

Ring-retained polynorbornene could serve as a solid fuel for cruise missiles; the density is about 1.1 g/cm^3 and contains a strained ring per monomer in the polymer. It is also a low cost material and easily synthesized with the proper catalyst system. Similarly, the polymers of the dimers of norbornadiene also show promise as solid fuels, provided they can be obtained in high yields.

The hafnacyclopentadienes prepared in this work were obtained in high yields with the new synthesis that we developed. These compounds are stable at room temperature under an inert atmosphere, but unfortunately, decompose slowly exposed to moisture and air. Therefore, these compounds are not practical for use as solid fuels, even though their heats of combustion should be relatively high.

What appeared at the beginning of this research to be the most promising area to synthesize products that could be used as energetic fillers or binders, turned out to be very disappointing. The synthesis of carborane monomers either failed or were obtained in low yields. Furthermore, monomers that are

polymerizable by transition metal catalysts must have the carborane portion of the molecule well-removed from the double bond, thus lowering the density of the polymer obtained.

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Abbreviations, Acronyms, and Symbols

DCp	=	Dicyclopentadiene
DCp-Cl	=	1-chlorodicyclopentadiene
DCp-OH	=	1-hydroxodicyclopentadiene
EPDM	=	Ethylene-propylene diene monomer
PIB	=	polyisobutylene
PSt	=	polystyrene
PMST	=	poly- α -methylstyrene
EPDM-g-PIB	=	ethylene propylenediene monomer- graft-polyisobutylene polymer
ENB	=	5-ethylidene-2-norbornene
IR	=	infrared
UV	=	ultraviolet
NMR	=	nuclear magnetic resonance
Ph	=	phenyl
Cp	=	η^5 -cyclopentadienyl
Macromer	=	polymer containing a polymerizable head group
DPn	=	degree of polymerization
VPO	=	vapor pressure osmometry
GPC	=	gel permeation chromatography
GE	=	grafting efficiency
DEPT	=	distortionless enhancement by polarization transfer
ORD	=	off resonance decoupled
APT	=	attached proton test