Reduction and Hydroboration with Borane and Haloborane Complexes of Poly(propylene Sulfide) Grafted on Crosslinked Polystyrene

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Synopsis

Preparation of borane and haloborane complexes of poly(propylene sulfide) grafted on crosslinked polystyrene was investigated. Graft polymer–borane was prepared by reaction of graft polymer with B_2H_6 and BH_3–THF. Graft polymer–haloborane was prepared by reaction with haloborane–tetrahydrofuran and by reaction of borane-bound graft polymer with halogen. Graft polymers with high borane (2.44 mmol/g) and haloborane (163 mmol/g) content were reached. The use of these graft polymers as polymeric reagents for reduction of carbonyl compounds and hydroboration was investigated. Aldehydes, ketones, carboxylic acids, and esters were reduced in high yields to the corresponding alcohols by borane-bound graft polymer. The graft polymer showed good chemoselectivity in competative reduction of cyclohexanone and other ketones and aldehydes, as well as in competative reduction of acetophenone and benzaldehyde. Reactivity of graft and homopolymer–borane was similar to that of borane–methyl sulfide. Hydroboration of alkenes with these graft polymers, followed by alkaline oxidation, led to the formation of the corresponding alcohols in high yields. Hydroboration was highly regioselective. Stability of the graft polymer–borane and recycling of that graft polymer were investigated. Cleavage of the poly(propylene sulfide) by the borane bound polymer took place to some extent. At 0°C no borane loss was found over a 5-week period. When recycled, 85% of the original borane content could be regenerated at the end of the fourth cycle.

INTRODUCTION

Borane methyl sulphide (BMS) is a very useful reagent both for hydroboration and for the reduction of organic functional groups.[1] Quantitative hydroboration with BMS is possible under mild conditions in a variety of aprotic solvents.[2] A wide range of functional groups reached by BH_3–THF such as aldehydes, ketones, carboxylic acids, oximes, nitriles and amides can be reduced with this reagent.[3] Reactivity of BMS is parallel to that of borane–tetrahydrofuran,[3] which is a most commonly used hydroboration reagent[4] and is a reduction reagent too.[3] BH_3–THF has some disadvantages as a commercial source of borane. It can be kept only as a dilute solution in THF. The THF is slowly cleaved by BH_3 at room temperature. Sodium borohydride has to be added to the BH_3–THF solution in order to inhibit this cleavage reaction. BMS has been found to overcome these disadvantages.[3]

Insoluble polymers containing sulfide groups capable of complexing borane may be of interest as polymeric reagents of versatile use provided that they will maintain chemical reactivity similar to that of BMS and will not be cleaved by the borane-bound polymer. The use of borane-bound polymers

CCC 0021-8995/85/093589-16$04.00

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containing sulfide groups for reduction and hydroboration was suggested by Crosby[5]. Chloromethylated crosslinked polystyrene was converted into crosslinked polyvinyl benzyl methyl sulfide by reaction with potassium methyl sulfide. The corresponding borane complex of this polymer was prepared by reaction with diborane and was successfully used for the reduction of acetophenone and hydroboration of 1-decene. In a previous work[6] we reported the synthesis of graft polymers of poly(propylene sulfide) on crosslinked polystyrene beads. These graft polymers of high sulfide content (10 mmol S/g) were prepared by graft polymerization of propylene sulfide on lithiated crosslinked polystyrene beads. In the graft polymers the donor properties of the sulfide bonds in the poly(propylene sulfide) chains are combined with chemical and physical properties of the crosslinked polystyrene. In the present work the conversion of these graft polymers into the corresponding borane complex by exchange reaction with BH_3–THF or by direct reaction with B_2H_6 was investigated. Reduction of carbonyl compounds with the borane-bound graft polymer was studied and compared with that of homopoly(propylene sulfide)–borane and their low molecular weight analogue BMS. Alkenes are readily converted into organoboranes via hydroboration using reagents such as diborane, borane–tetrahydrofuran, and BMS to yield in a cis regioselective and stereoselective addition reaction alkyl boranes. The reaction was systematically studied by Brown and co-workers.[4,7,8] Hydroboration of alkenes followed by alkaline peroxide oxidation gives alcohols, which are difficult to obtain from alkenes in any other way.

The possible use of these borane-bound graft polymers for converting alkenes into alcohols via hydroboration was investigated. Monohaloborane and dihaloborane complexes of methyl sulfide were also used for hydroboration of alkenes.[9–11] These methyl sulfide complexes are prepared by reaction of methyl sulfide with haloborane–THF or by reaction of BMS with halogen.[12–14] Preparation of mono and dihaloborane–polymer complexes and their use as reduction and hydroboration reagents was studied.

High stability of the borane-bound graft polymer and possible recycling of the graft polymer is essential for its use as a polymeric reagent. BMS can be stored for months at room temperature without loss of hydride activity and is apparently stable indefinitely when refrigerated.[3] The commonly used BH_3–THF reagent is much less stable and is slowly cleaved by borane at room temperature. At 60°C the tetrahydrofuran is converted to tri-n-butylborate in 61% yield.[15] If the graft polymer-borane complex is to be used as polymeric reagent, borane loss, and cleavage reaction should be minimal. Borane-bound polymer stability and the extent of cleavage reaction of the grafted poly(propylene sulfide) were studied.

EXPERIMENTAL

Materials

Toluene, chloroform, methylene chloride, petroleum ether (Frutarom), cyclohexanone, cyclopentanone, cycloheptanone, tert-butylcyclohexanone, octanoic acid, benzaldehyde, heptaldehyde, 2-octanone, 2-methylcyclohex-

anone, acetophenone, cyclohexene, 1-methyl-1-cyclohexene, amylene (BDH), ethyl benzoate, diglyme, styrene, boron trifluoride etherate (Fluka), 1-octene, 2-cyclohexene-1-one (Aldrich) were dried and redistilled before use. THF (Frutarom) was dried by distillation from sodium benzophenone solution. Benzoic acid (Mallinckrodt), camphor (BDH), iodine, bromine, methanol, 30% hydrogen peroxide, glycerol (Frutarom), sodium borohydride (Bayer) were used. Borane–tetrahydrofuran complex, $1M$ solution in THF, borane–methyl sulfide complex, $1M$ solution in methylene chloride (Aldrich) were used. Graft polymers of poly(propylene sulfide) on copolymer of 98% styrene + 2% divinylbenzene 200–400 mesh (Fluka) were prepared as previously described.[6] Poly(propylene sulfide) was prepared by BF_3OEt_2 initiation. Mono- and dihaloborane–THF were prepared by reaction of $1M$ halogen solution in THF with $1M$ BH_3–THF solution according to a known procedure.[12-14]

NMR and IR Measurements

Nuclear magnetic resonance spectra were measured at room temp using Bruker WH-300 MHz. Infrared spectra were measured using Perkin-Elmer 177.

Determination of Borane Content

Borane content was determined according to known procedure[16] by volumetric determination of hydrogen released on hydrolysis of borane-bound polymer, in 1:1:1, glycerol:water:methanol solution.

Determination of Halogn in Haloborane-Bound Graft Polymer

Halogen in haloborane bound polymer was determined after hydrolysis by titration according to a known procedure.[14]

Determination of Reaction Products

Reaction products were determined by GLC using Packard gas chromatograph Model 7300/7400. Nitrogen was used as carrier gas. Glass column of 1.80 m and 0.25 in. tubing with solid support chromosorb W and 5% butane-diolsuccinate as liquid phase was used. Benzyl alcohol, α-phenyl ethyl alcohol were determined in 130°C column temp using biphenyl and dibenzyl as internal standards. Aliphatic alcohols were determined at 70°C column temp using naphthalene as internal standard.

Reaction of Graft and Homopoly(propylene Sulfide) with Diborane

Required amount of diborane was prepared by reaction of sodium borohydride with $BF_3 \cdot OEt_2$[17] Molar excess (twofold) was used. Diborane was passed through a flask containing graft polymer of 28.0% S (5.0 g) at 0°C for 1 h. Borane content was determined, 2.20 mmol BH_3/g corresponding to B/S = 0.25 molar ratio in the polymer was found. When liquid diborane was used, the diborane was liquefied in the reaction flask by immersing the flask containing the graft polymer (5.0 g) in liquid air. After 1 h the

flask was allowed to reach room temp and excess of diborane was flashed with dry nitrogen. The graft polymer contained 2.70 mmol BH_3/g, corresponding to B/S = 0.31. When borane-bound homopolymer was prepared poly(propylene sulfide), MW = 43.200 (15.0 g) was dissolved in toluene, chloroform, and methylene chloride (30 mL) and diluted to 50 mL. Reaction was carried out under constant stirring at 0°C. Molar excess (twofold) of gaseous diborane was used. Borane content of the polymer was determined by removing aliquots of the reaction solution. Borane content of 6.67, 6.50, and 7.05 mmol/g polymer in toluene, chloroform, and methylene chloride was found.

The IR spectra of the borane-bound homo- and graft polymer showed B—H stretching absorptions at 2400 (s), 2350 (w), 2260 (vw) cm^{-1}.

Borane Exchange between BH_3–THF and Graft Polymer

In a typical procedure graft polymer 27.0% S (1.0 g) in petroleum ether (14.0 mL) was allowed to react with $1.0M$ BH_3–THF solution (9.0 mL) at 0°C under constant stirring. After 1 h the graft polymer was isolated by filtration in dry atmosphere, washed with hexane (2 × 5 mL) and dried in vacuum at room temperature for 3 h. Borane content of 2.44 mmol/g was found. When complexation time dependence was followed, aliquots (0.5 mL) were removed from reaction mixture, and the borane content of the polymer was calculated from decrease in borane solution concentration.

Haloborane-Bound Graft Polymers

Preparation by Exchange Reaction

In a typical procedure graft polymer 27.0% S (2.0 g) was allowed to react with $0.66M$ monoiodoborane solution in THF (28 mL) for 5 h at 0°C under constant stirring. The graft polymer was isolated as previously described. Hydride content of 2.80 mmol/g and halogen content of 1.42 mmol/g were found. IR spectra of the graft polymer showed B—H stretching absorptions at 2495 (m), 2410 (m), 2280 (w) cm^{-1}. Other haloborane-bound polymers were prepared similarly. Diiodo derivative absorbed at 2500 (s) cm^{-1} monobromo derivative at 2490 (m), 2415 (m), and 2280 (w) cm^{-1} and dibromo derivative at 2505 (s) cm^{-1}.

Preparation by Halogenation

In a typical procedure graft polymer–borane 27.0% S, 2.20 mmol BH_3/g (2.0 g), was suspended in benzene (10 mL), and $0.50M$ iodine solution in THF (4.5 mL) was added gradually over 30 min. Reaction mixture was cooled during addition of iodine solution and was kept at room temperature for an additional 5h under constant stirring. By that time all iodine had reacted. The polymer was isolated as previously described. Hydride content of 3.32 mmol/g and iodine content of 1.61 mmol/g were found.

Reduction and Hydroboration

Reduction and hydroboration were carried out under dry nitrogen in a closed flask equipped with a self-sealing cap for the introduction of reagents by syringes under constant magnetic stirring. The graft polymer–borane complex was transferred to the reaction flask in a dry glove box.

Reduction of Carbonyl Compounds

In a typical procedure graft polymer (0.42 g, 1.0 mmol BH_3) was allowed to react with cyclohexanone (0.30 mL, 3.0 mmol) in toluene (5.0 mL) containing naphthalene (0.1 g) as internal standard. Reaction was carried out at room temp. After 1 h 2% methanolic hydrochloric acid (1.0 mL) was added. The polymer was removed by filtration and reaction products were determined by gas chromatography. Competitive reduction was carried out similarly. When time dependence was determined, aliquots (0.25 mL) were removed and 2.0% methanolic hydrochloric acid (0.2 mL) was added prior to gas chromatography analysis.

Reduction with BMS was carried out similarly using $1M$ BMS solution in methylene chloride.

Hydroboration

In a typical procedure graft polymer–borane 27.0% S (0.42 g, 1.0 mmol BH_3) was allowed to react with 1-octene (0.47 mL, 3.0 mmol) in toluene (5.0 mL) for 1 h at room temp. Water (0.5 mL) was added, and the polymer was removed by filtration, $3N$ NaOH (1.0 ml) and 30% H_2O_2 (0.5 mL) were added and allowed to react for 1 h at 50°C. The organic phase was separated washed with water, and dried over $MgSO_4$. Reaction products were determined by gas chromatography. Hydroboration of 1-octene with haloborane bound graft polymers was carried out similarly using 1:1 hydride:alkene ratio.

Decrease in Molecular Weight of Poly(propylene Sulfide)–Borane

Poly(propylene sulfide)–borane 6.67 mmol BH_3/g (15 g) in toluene (50 mL) was kept at 0 and 25°C. Aliquots (5.0 mL) were removed and analyzed for borane content. The polymer was isolated by precipitation in methanol (30 mL). Molecular weight was determined from its limiting viscosity number in benzene at 20°C.[18]

Recycling of the Graft Polymer

Graft polymer 27.0% S (5.0 g) was allowed to react with $1M$ BH_3–THF solution for 1 h. The graft polymer was isolated. The polymer was hydrolyzed by water, glycerol, methanol hydrolysis solution (20 mL), washed with water, methanol, and chloroform, dried in vacuum overnight and recycled.

RESULTS AND DISCUSSION

Graft Polymer–Borane and Haloboranes Complexes

Crosslinked polystyrene beads grafted with poly(propylene sulfide) were used for the preparation of the graft polymer borane and haloborane complexes. The synthesis of these graft polymers of high poly(propylene sulfide) content has already been reported.[6] The graft polymer–borane complex was prepared by reaction of the graft polymer beads with diborane and by exchange reaction with BH_3–THF. Reaction with diborane was carried out without a solvent. Reaction with BH_3–THF was carried out in THF in which the graft polymer is highly swollen and in THF–petroleum ether solution in which the graft polymer is partially swollen. Borane content was determined volumetrically after hydrolysis. Reaction of graft polymer beads with molar excess of gaseous diborane led to maximum content of 2.20 mmol/ g, corresponding to 0.25 B/S molar ratio in polymer of 28.0% S. When excess of liquid diborane was used, borane content of 2.70 mmol/g, B/S = 0.31 was reached. Reaction between the graft polymer and diborane is carried out under heterogeneous conditions, which may affect extent of sulfide participation in complexation of borane. Complexation under homogeneous reaction conditions of homopoly(propylene sulfide) was repeated in toluene, chloroform, and methylene chloride solution. The B/S molar ratios found, 0.49, 0.50, and 0.53, respectively, are higher than those found for the insoluble graft polymer. Insolubilization of the poly(propylene sulfide) by graft polymerization on a crosslinked polymer affected its borane complexation.

Formation of graft polymer–borane complexes by exchange reaction between BH_3–THF and the graft polymer is a fast reaction (Fig. 1) and can be accomplished, when high BH_3–THF concentration is used, within 5 min. At room temperature reaction is even faster. Maximum borane content of 2.44 mmol/g corresponding to B/S = 0.29 was reached both in petroleum ether and in THF. The same borane content was reached when exchange reaction was carried out at different ratio of BH_3–THF to sulfide groups in the graft polymer at constant BH_3–THF concentration (Fig. 2). This method was applied for the preparation of borane-bound graft polymers.
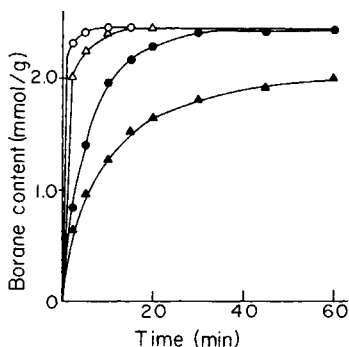
Fig. 1. Borane exchange between BH_3–THF and graft polymer–concentration dependence. Graft polymer 27.0% S, 8.4 mmol S/g (1.0 g), was allowed to react with BH_3–THF solution in petroleum ether (9.0 mmol BH_3) at 0°C: (○) 1.0M; (△) 0.4M; (●) 0.2M; (▲) 0.1M.
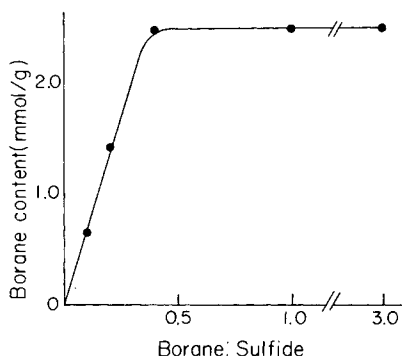
Fig. 2.   Borane complexation by graft polymer at different BH_3–THF/sulfide molar ratio. Graft polymer 27.0% S, 8.4 mmol S/g (1.0 g), was allowed to react with 0.2 M THF–BH_3 solution in petroleum ether for 30 min at 0°C.

Low molecular weight monosulfides such as methyl sulfide and ethyl sulfide[19,20] are fully converted into their borane complex by reaction with equivalent or molar excess of diborane. Similarly, low molecular weight disulfide, dimethyl-1,2-ethane disulfide[21] ($CH_3SCH_2CH_2SCH_3$) is converted in 85% yield to the corresponding borane complex [H_3BCH_3-$S(CH_2)_2SCH_3BH_3$]. Sulfide groups in homo and graft poly(propylene sulfide) could not be fully converted into their borane complex. Even when complexation was carried out under homogeneous reaction conditions, no more than 53% of sulfide groups of the polysulfide participated in complexation. It is obvious that the polymeric substituents of each sulfide group are responsible for the lack of participation of all sulfide groups in borane complexation. The maximal B/S = 0.53 reached may indicate participation of two sulfide groups in complexation of one borane molecule, though the low molecular weight analog dimethyl 1,2-ethane disulfide does not form such chelate. An attempt to clarify this point by the use of ^{1}H NMR spectra of poly(propylene sulfide)– borane was made. It was reported in literature[22] that chemical shift of methyl protons of methyl sulfide and BMS vary by 0.13 ppm. It is expected that ^{1}H NMR spectra of a polymer in which 50% of the sulfide groups are complexed by borane will have different resonance lines for hydrogen atoms attached to carbon α to complexed and uncomplexed sulfide groups. If complexation is by chelate formation, such differentiation will not be found. It is also expected that smaller chemical shifts will be found if two sulfide groups will participate in borane complexation. Comparison of ^{1}H NMR (300 MHz) spectra of poly(propylene sulfide)–borane B/S = 0.50 in $CDCl_3$, H^1 δ 1.34 (3H), δ 2.58 (1H), and δ 2.86 (2H), with that of poly(propylene sulfide), ^{1}H δ 1.35 (3H), δ 2.65 (1H), and δ 2.90 (2H), may support the assumption that two sulfide groups are associated with one borane molecule.

Mono-, dibromo and iodoborane bound graft polymers were prepared by exchange reaction of the corresponding haloborane–THF complex with the graft polymers. Mono- and diiodoborane bound graft polymers were also prepared by reaction of iodine with borane bound graft polymer. Results are reported in Table I. The haloborane content of the graft polymers is generally lower than that reached with borane. Monohaloborane content

TABLE I
Haloborane Bound Poly(propylene Sulfide) Graft Polymers[a]

| Haloborane | Hydride in polymer (mmol/g) | Halogen in polymer (mmol/g) | Hydride/halogen[b] | | Haloborane-bound polymer | |
			Calcd	Found	(mmol/g)	B/S
BH₂I	2.80	1.42	2.00	1.97	1.40	0.206
BHI₂	1.11	2.10	0.50	0.53	1.12	0.186
BH₂Br	2.68	1.29	2.00	2.08	1.33	0.176
BHBr₂	1.22	2.50	0.50	0.49	1.22	0.184
BH₂I[c]	3.32	1.61	2.00	2.06	1.63	0.251
BHI₂[c]	1.21	2.50	0.50	0.48	1.24	0.220

[a] Graft polymer 27.0%, 8.4 mmol S/g (1.0 g), was allowed to react with equimolar amount of 1M haloborane solution in THF for 5 h at 0°C.

[b] Molar ratio.

[c] Prepared by reaction of graft polymer-borane (1.0 g, 2.2 mmol BH₃), with the required equivalent amount of iodine in THF solution for 5 h at room temp.

is higher than that of the corresponding dihaloborane. Preparation of haloborane by reaction of halogen with borane-bound graft polymer yields higher haloborane content than the exchange reaction between haloborane–THF and the graft polymer.

Reduction with Borane-bound Graft Polymer

Reduction of aldehyde or ketone with borane-bound graft polymer is described below.

$$\text{(P)} - BH_3 + 3R - \overset{O}{\overset{\|}{C}} - R' \longrightarrow \text{(P)} + B(O - \overset{R}{\underset{H}{\overset{|}{\underset{|}{C}}}} - R')_3 \xrightarrow{H^+/CH_3OH} R - \overset{OH}{\underset{H}{\overset{|}{\underset{|}{C}}}} - R + H_3BO_3$$

R' = H, R
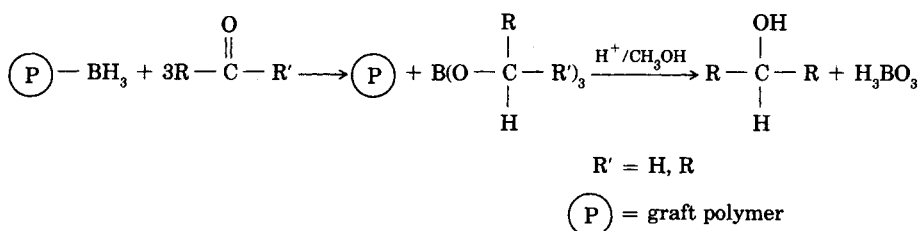
(P) = graft polymer

Reduction was carried out in toluene. The borate ester is not complexed by the graft polymer and is found in solution. The alcohol formed was identified by gas chromatography after hydrolysis of the borate ester with methanolic hydrochloric acid solution.

Reduction of cyclohexanone with borane bound graft and homopolymer and their low molecular weight analog BMS is reported in Fig. 3. Reaction was carried out using borane: ketone molar ratio of 1:3. The borane-bound polymer is as reactive as its low molecular weight analog. The somewhat higher reactivity of homopoly(propylene sulfide)–borane is most probably due to higher concentration of the borane in this polymer as compared with that of the graft polymer and BMS. When excess of borane-bound graft polymer is used, all borane molecules participate in the reduction though part of the borane hydrides remain intact. Thus in the reduction of cyclo-
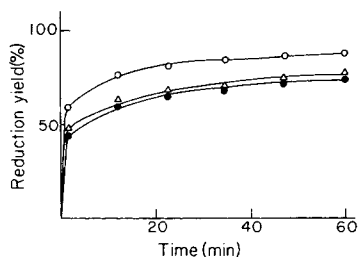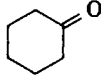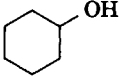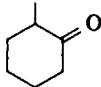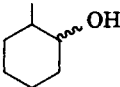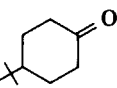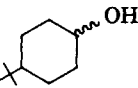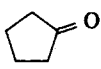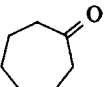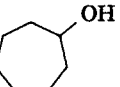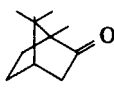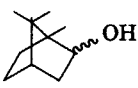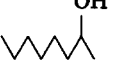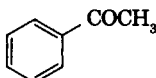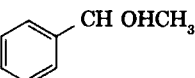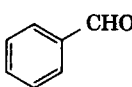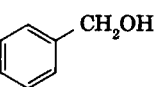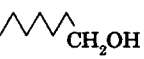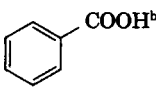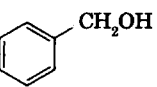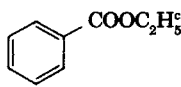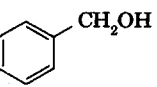
Fig. 3. Reduction of cyclohexanone with borane-bound graft, homopolymer and BMS. Graft polymer–borane 2.44 mmol BH_3/g (0.42 g), homopolymer–borane 6.67 mmol BH_3/g (0.15 g) in toluene (0.5 mL), and 1.0M BMS solution in methylene chloride (1.0 mL) were allowed to react with cyclohexanone (0.3 mL, 3.0 mmol) in toluene (5.0 mL): (●) Borane-bound graft polymer; (○) borane-bound homopolymer; (△) BMS.

hexanone with borane-bound graft polymer at 1:1 reactants molar ratio, no reactive hydrides were found in the polymer when reduction was completed. At full conversion the reaction solution contained all the unreacted hydrides. The ratio of cyclohexanol to reactive hydrides in solution was found to be 1:1.91, indicating that all borane molecules participate in the reduction reaction. Consumption of all borane-bound graft polymer can be explained by the difference in reactivity between its three hydrides. Reduction of different aldehydes, ketones, carboxylic acids, and esters with borane-bound graft, homopolymer, and BMS is reported in Table II. Reduction of aldehydes and ketones was carried out using 3:1 carbonyl compound: borane molar ratio. Full conversion of aldehydes and ketones into the corresponding alcohols was reached within 1 h. The graft polymer was as reactive as the homopolymer and BMS. Reduction of carboxylic acids and esters was carried out using 1:1 reactants molar ratio.

Benzoic acid was reduced in the presence of the equivalent amount of trimethyl borate. Benzaldehyde is an intermediate in the reduction of benzoic acid. Its presence during reduction was determined by gas chromatography. Moderate yields were obtained in the reduction of benzoic acid and ethyl benzoate while better yield was found in the reduction of octanoic acid. Using molar excess of borane bound polymer (fivefold) led to a complete reduction of these carbonyl compounds. Though high reduction yields were generally obtained in the reduction of aldehydes and ketones with borane-bound graft polymer, variation in reduction yield between different ketones and aldehydes suggests its use as a chemoselective reduction reagent. Chemoselectivity of the borane-bound graft polymer was determined in competitive reduction of several ketones and aldehydes in the presence of cyclohexanol (Table III). Reaction was carried out at borane: cyclohexanone:carbonyl compound 1:3:3 molar ratio. The ratio of alcohol produced to cyclohexanone was determined after 1 h. It can be seen that the graft polymer can be used as a chemoselective reduction reagent. Time dependence of competitive reduction of benzaldehyde and acetophenone with borane bound polymer at 1:3:3 and 1:1:1 reactants molar ratio is reported in Table IV. At 1:3:3 reactants molar ratio, after all the borane-

TABLE II
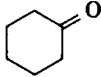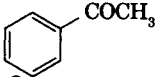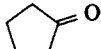Reduction of Carbonyl Compounds with Graft and Homopoly(propyelene Sulfide)–Borane[a]
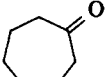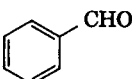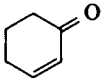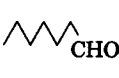
Carbonyl compound	Reduction product	Reduction yield (%)		
		Graft polymer	Homopolymer	BMS
⬡=O	⬡–OH	100	100	100
⬡=O (methyl)	⬡–OH	98 (27–cis)	96 (27–cis)	—
⬡=O (tert-butyl)	⬡–OH	93 (13-cis)	95 (13-cis)	—
⬠=O	⬠–OH	96	96	95
⬡(7)=O	⬡(7)–OH	100	100	98
camphor =O	camphor –OH	99 (47-endo)	98 (47-endo)	—
⋀⋀⋀C=O	⋀⋀⋀OH	98	97	—
Ph–COCH₃	Ph–CH OHCH₃	84	80	—
Ph–CHO	Ph–CH₂OH	98	98	100
⋀⋀⋀CHO	⋀⋀⋀CH₂OH	91	93	—
Ph–COOH[b]	Ph–CH₂OH	58	65	94
⋀⋀⋀COOH[c]	⋀⋀⋀CH₂OH	88	99	—
Ph–COOC₂H₅[c]	Ph–CH₂OH	56	61	—

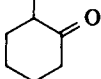[a] Graft polymer–borane 27.0% S, 2.44 mmol BH_3/g (0.42 g), homopolymer–borane 6.67 mmol BH_3/g (0.15 g) in toluene (0.5 mL) and 1.0M BMS solution in methylene chloride (1.0 mL) were allowed to react with carbonyl compound (3.0 mmol) in toluene (5.0 mL) for 1 h at 25°C.

[b] Reaction was carried out at 1:1:1 borane:benzoic acid:trimethyl borate molar ratio.

[c] Reaction was carried out at 1:1 borane:carbonyl compound molar ratio.

TABLE III
Relative Reactivity of Ketones and Aldehydes to Borane Bound Graft Polymer via
Competitive Reductions Versus Cyclohexanone[a]

Carbonyl Compound	R^b	Carbonyl Compound	R^b
cyclohexanone	1.00	acetophenone (COCH$_3$)	0.03
cyclopentanone	0.15	4-methylpentan-2-one	0.01
cycloheptanone	1.14		
2-methylcyclohexanone	0.03	benzaldehyde (CHO)	4.2
cyclohexenone	0.00	hexenal (CHO)	4.6

[a] Graft polymer 27.0% S, 2.44 mmol BH$_3$/g (0.42 g) was allowed to react with a mixture of carbonyl compound (3.0 mmol) and cyclohexanone (3.0 mmol) in toluene (5.0 mL) for 5 h at 0°C.
[b] Ratio of alcohol produced to cyclohexanol.

TABLE IV
Competitive Reduction of Benzaldehyde and Acetophenone with Borane-Bound
Poly(propylene Sulfide) Graft Polymer[a]

Borane complex	Reactants molar ratio	Reaction time (min)	Reduction yield (%)	
			Benzaldehyde	Acetophenone
Graft polymer	1:3:3	10	87.3	4.8
		30	89.3	4.8
		60	89.4	5.1
		90	91.1	4.9
		150	93.5	4.9
		300	95.0	4.9
Graft polymer	1:1:1	5	15.4	0.0
		25	80.7	6.8
		40	89.1	12.6
		160	91.8	36.3
		260	98.3	76.2
BMS	1:1:1	5	37.5	0.0
		25	72.3	7.6
		90	96.9	16.8
		160	94.2	23.5
		260	97.6	72.2

[a] Graft polymer 27.0% S, 2.44 mmol BH$_3$/g (0.42 g, 1.0 mmol BH$_3$) (1.26 g, 3.0 mmol BH$_3$) and BMS in solution in methylene chloride (3.0 mL) were reacted with a mixture of benzaldehyde (0.30 mL, 3.0 mmol) and acetophenone (0.36 mL, 3.0 mmol) in chloroform at 0°C.

bound graft polymer had been consumed, 95% of the benzaldehyde was converted to benzyl alcohol while only 5% of the acetophenone was reduced. When excess of borane-bound polymer was used, most of the benzaldehyde was reduced prior to the reduction of the acetophenone. The borane-bound graft, homopolymer and BMS showed similar chemoselectivity.
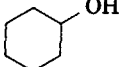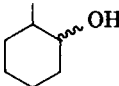
Reduction with Haloborane-Bound Graft Polymers

Reduction of 2-octanone to 2-octanol with mono- and dibromo and with mono- and diiodoborane bound graft polymers was carried out successfully. The reduction yields of 88, 92, 94, and 89% were found, respectively. The mono- and dihaloboric acid ester derivatives formed were not complexed by the graft polymer and were found in solution. The alcohol was identified after hydrolysis.

Hydroboration

Reaction of different alkenes with borane bound graft and homopolymer was carried out at alkene:borane, 3:1 molar ratio. The trialkylborane was not complexed by the graft polymer and was found in solution. The trialkyl boranes formed were not isolated and were oxidized by hydrogen peroxide in the presence of sodium hydroxide to the corresponding alcohol. Results of hydroboration followed by alkaline oxidation are reported in Table V.

TABLE V
Hydroboration with Graft and Homopoly(propylene Sulfide)–Borane[a]

| | | Reaction yield (%) | |
| | | Graft polymer | |
Reactant	Product		Homopolymer
	OH	96	95
	OH	91 (27-cis)	93 (27-cis)
$CH_3(CH_2)_5CH=CH_2$	a. $CH_3(CH_2)_6CH_2OH$ b. $CH_3(CH_2)_5CHOHCH_3$	88 (95-a)	91 (95-a)
$C_6H_5CH=CH_2$	a. $C_6H_5CH_2CH_2OH$ b. $C_6H_5CHOHCH_3$	40 (90-a)	50 (90-a)
$CH_3CH=C(CH_3)_2$	a. $CH_3CHOHCH(CH_3)_2$ b. $CH_3CH_2COH(CH_3)_2$	88 (98-a)	85 (95-a)

[a] Graft polymer-borane 27.0% S, 2.44 mmol BH_3/g (0.42 g), homopolymer–borane 6.67 mmol BH_3/g (0.15 g) in toluene (0.5 mL), were allowed to react with alkene (3.0 mmol) in toluene (5.0 mL) for 1 h at 25°C. Oxidation was carried out with 30% hydrogen peroxide solution (0.5 mL) in the presence of 3 M sodium hydroxide solution (1.0 mL) for 1 h at 50°C.

TABLE VI
Hydroboration of 1-Octene with Haloborane-Bound Graft Polymer[a]

Haloborane bound graft polymer	Reaction yield (%)	
	1-Octanol	2-Octanol
BH_2Br	5.0	83.6
$BHBr_2$	2.1	81.1
BH_2I	4.4	90.5
BHI_2	2.5	77.7

[a] Haloborane bound graft polymer (1.0 mmol active hydride) was allowed to react with 1-octene (1.0 mmol) at room temp for 25 h. Oxidation was carried out with 30% hydrogen peroxide solution (0.5 mL) in the presence of 3N sodium hydroxide solution (1 mL) for 1 h at 50°C.

There is no difference in reactivity between borane-bound graft polymer and borane-bound homopolymer. Conversion of alkenes to alcohols was achieved in high yields. Hydroboration was highly regioselective.

Monohaloborane and dihaloborane methyl sulfide complexes[9-11] are used for the synthesis of dialkyl and monoalkyl haloboranes. Hydroboration of alkenes with dimethyl sulfide complexes of dihaloboranes[10] affords alky-dihaloborane–dimethylsulfide complexes in good yields. If sulfide groups in the graft polymer will behave similarly, hydroboration of alkene with dihaloborane bound graft polymer will yield the corresponding alkyl dihaloborane–graft polymer complex. The alkyl haloborane will remain bound to the graft polymer and will not be found in solution. Hydroboration of 1-octene with mono- and dibromo and iodoborane bound graft polymer is reported in Table VI. When reaction was completed all octanyl mono- and dihaloborane were found in solution. Complexation of octanyl dihaloborane by sulfide groups in the graft polymer did not take place. Hydroboration by the haloborane bound graft polymer is regioselective. 1-Octene was converted to 1-octanol in high yield.
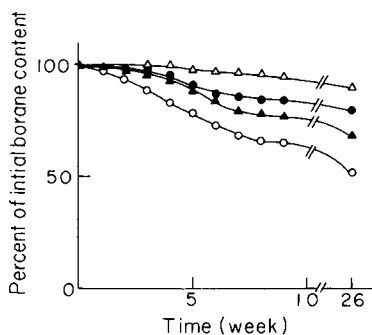

Fig. 4. Stability of borane-bound graft and homopoly(propylene sulfide). Graft polymer-borane 25.0% S, 2.00 mmol BH_3/g, and homopolymer-borane, 6.67 mmol BH_3/g 30% solution in toluene, were kept under nitrogen. Graft polymer–borane: (△) 0°C; (▲) 25°C. Homopolymer-borane: (●) 0°C; (○) 25°C.
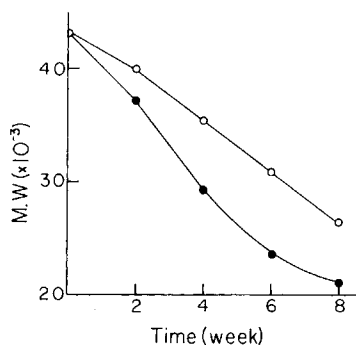
Fig. 5. Decrease in poly(propylene sulfide) molecular weight. Experimental conditions as in Figure 4: (○) 0°C; (●) 25°C.

Stability and Recycling of the Graft polymer–Borane Complex

If the borane bound graft polymer is as stable as BMS, it is expected that borane loss will be minimal as well as cleavage reaction of sulfide bonds in the polymer. Change in borane content of dry graft polymer–borane and homopolymer–borane in toluene at 0 and 25°C is reported in Figure 4. At 0°C no change in borane content over a 5-week period took place. After 26 weeks at that temperature a 10% decrease in borane content was found. Borane loss of the homopolymer–borane was somewhat higher. Decrease in borane content as a result of cleavage of the sulfide bonds will lead to a decrease in molecular weight of the poly(propylene sulfide). Grafted poly(propylene sulfide) chains will be shortened, and soluble fragments will be removed during borane hydrolysis. Sulfur analysis of the graft polymer after hydrolysis of the borane should decrease. Decrease in homopoly(propylene sulfide) molecular weight (Fig. 5) and poly(propylene sulfide) content of the graft polymer (Fig. 6) during the time these polymers were kept as their borane complex indicates that cleavage reaction takes place and is parallelled by borane loss. At 0°C over a 5-week period cleavage reaction is negligible.

Cleavage reaction of the grafted poly(propylene sulfide) will affect the borane content of the graft polymer. When recycled, the cleaved
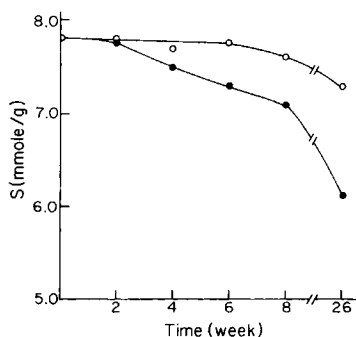

Fig. 6. Decrease in sulfur content of the graft polymer. Experimental conditions as in Figure 4: (○) 0°C; (●) 25°C.

TABLE VII
Recycling of Poly(propylene Sulfide) Graft Polymer[a]

Cycle no.	S (%)	Percent of initial sulfide content (%)	Borane content (mmol/g)	Percent of initial borane content (%)	B/S[b]
0	27.0	100	2.44	100	0.29
1	26.2	97	2.35	98	0.29
2	25.1	93	2.26	94	0.29
3	24.0	89	1.97	82	0.26
4	22.7	84	2.04	85	0.29
5	21.0	78	1.51	63	0.23
6	20.2	75	1.68	70	0.27
7	18.4	68	1.63	68	0.28
8	17.8	66	1.51	63	0.27
9	15.7	58	1.34	56	0.27
10	14.8	55	1.25	52	0.27

[a] Graft polymer 27.0% S (5.0 g) was allowed to react with $1M$ BH_3–THF solution (25 mL) for 1 h. The graft polymer–borane was isolated and hydrolyzed.
[b] Molar ratio.

poly(propylene sulfide) fragments will dissolve and lower borane content will be reached (Table VII). Decrease in poly(propylene sulfide), content of the graft polymer occurred during recycling. Up to the fourth cycle 85% of the original borane content could be regenerated, while after the tenth cycle only 52% could be reached. Extent of participation of sulfide groups in borane complexation did not change with decrease in the molecular weight of the grafted poly(propylene sulfide)side chains, as can be seen from the B/S ratio in the polymer.

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