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Supported BF_3 catalyst on crystalline polyolefins; carbocationic polymerization of isobutylene

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Summary

This paper describes a new supported Lewis acid catalyst which involves BF_3 species chemically bonded to the crystalline polyolefins, such as polypropylene and poly(1-butene). The supported catalysts are active in the carbocationic polymerization of isobutylene and are recovered and reused for many reaction cycles without significantly losing their activity. Several advantages, such as chemical and physical stabilities of the substrate, convenient implantation to load high concentration of catalyst to the substrate and high catalyst reactivity, have been observed. In addition, polyisobutylene obtained in this process has high terminal unsaturation.

Introduction

Catalyst recycling presents several important advantages in chemical production processes. These include waste reduction, lower cost and simpler product purification. All of them also save energy and environment. These considerations become even more important when the reaction requires a large quantity of catalyst, such as in the oligomerization of olefins. Substantial results have been reported in the supported catalysts for the oligomerization of olefins. Most of them are prepared by dispersing metal salts on inorganic substrates[1,2], such as magnesium oxide, alumina, silica, zeolite, followed by calcination/reduction. These highly dispersed particles allow effective metal utilization. However, the supported catalysts are usually hydrolyzed and become part of the waste stream after a reaction cycle.

There are some examples of using polymers as the solid substrates. The most common one is crosslinked polystyrene[3,4]. Unfortunately, the activity of polymer-bonded Lewis acid catalyst is always relatively low and the activity of catalyst decreases after a few reaction cycles. The reasons for the deactivation may be related to the insufficient stability of the polymer substrate and the slow diffusion of the catalyst into the polymer matrix. It is clear that a scientific challenge exists to develop a new type of polymer substrate which not only offers catalysts recoverability but also maintains long term stability and activity.

In our previous publication[5], the use of crystalline polyolefin as the substrate was introduced. $EtAlCl_2$ was chemically bonded to polypropylene. The active species PP-O-$AlCl_2$ was used as the catalyst for the carbocationic polymerization of isobutylene. This catalyst can be recovered and reused for many reaction cycles without significant loss of reactivity. The resulting polyisobutylenes are similar to those prepared by conventional aluminum catalysts[6], such as $AlCl_3$, $EtAlCl_2$ and Et_2AlCl, under similar reaction conditions. One important feature of polyisobutylenes prepared by aluminum catalysts is an internal double bond in each polymer.

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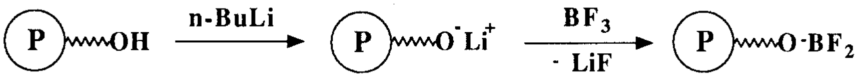
However, it is very desirable to have terminal unsaturation for functionalization reactions. It is known that BF_3 catalyst provides high concentration of terminal unsaturation[7,8] in PIB. BF_3, however, has been causing great environmental concerns in industrial practice.

Results and Discussion

In this paper two hydroxylated polymers, isotactic polypropylene with 5 mole % of hydroxyl groups and isotactic poly(1-butene) with 12 mole % of hydroxy groups, were used as substrates. They were prepared by Ziegler-Natta polymerization with the use of borane comonomers[9,10]. Both functionalized polyolefins have "brush-like" microstructures[11]. Polypropylene segments crystallize and highly branched segments form amorphous phases on the surface of the crystalline phase. DSC shows that the PP-OH has approximately the same melting point (~ 164 ^{0}C) as that of isotactic polypropylene, and that the actual depression in melting point caused by the functional groups is less than 5 ^{0}C. The similarity in the crystalline phase implies that the branched segments with functional groups are mostly located in the amorphous phase. Preservation of crystallinity of the propylene copolymer is apparently due to its brush-like microstructure. This morphology is formed during the polymerization. The polymer is precipitated from solution during the polymerization and is insoluble in common solvents up to 120 ^{0}C. In the amorphous region the functional groups are connected to the polymer backbone by methylene units, which offer good mobility of the anchor sites for catalysts.

Attachment of BF_3 to Partially Crystalline Polyolefins

Both hydroxylated polyolefins, polypropylene and poly(1-butene), were used as substrates for the immobilization of BF_3. The chemical reactions are illustrated by Equation 1.



Equation 1

P is the partially crystalline polyolefin with 5 to 12 mole % of hydroxyl groups. The direct reaction between BF_3 and hydroxyl group is very slow, and possibly forms BF_3/OH complexes. More effective condensations were carried out by using alkoxides. The metalation of hydroxyl groups was done by simply mixing polymer particles with n-butyllithium solution. After washing out the excess n-butyllithium, the polymer particles were mixed with a BF_3/CH_2Cl_2 solution for few hours before vacuum-removal of excess reagents. Both metalation and attachment were carried out at room temperature. A control experiment was carried out in parallel by using 1-pentanol under similar conditions. Figure 1 compares the ^{11}B NMR spectra of the supported catalyst in poly(1-butene) (PB-OBF_2)and the C_5-OBF_2. Both spectra are almost identical with a peak at 0 ppm, corresponding to the -OBF_2 group[12]. This result was also confirmed by elemental analysis yielding a mole ratio of 1: 2 between B and F. Similar reaction mixtures were obtained under homogeneous and heterogeneous conditions. The results indicate that the hydroxyl groups in solid poly(1-butene) are readily available during the reaction. The crystallinity of poly(1-butene) may offer high surface area of hydroxyl group for the reaction.

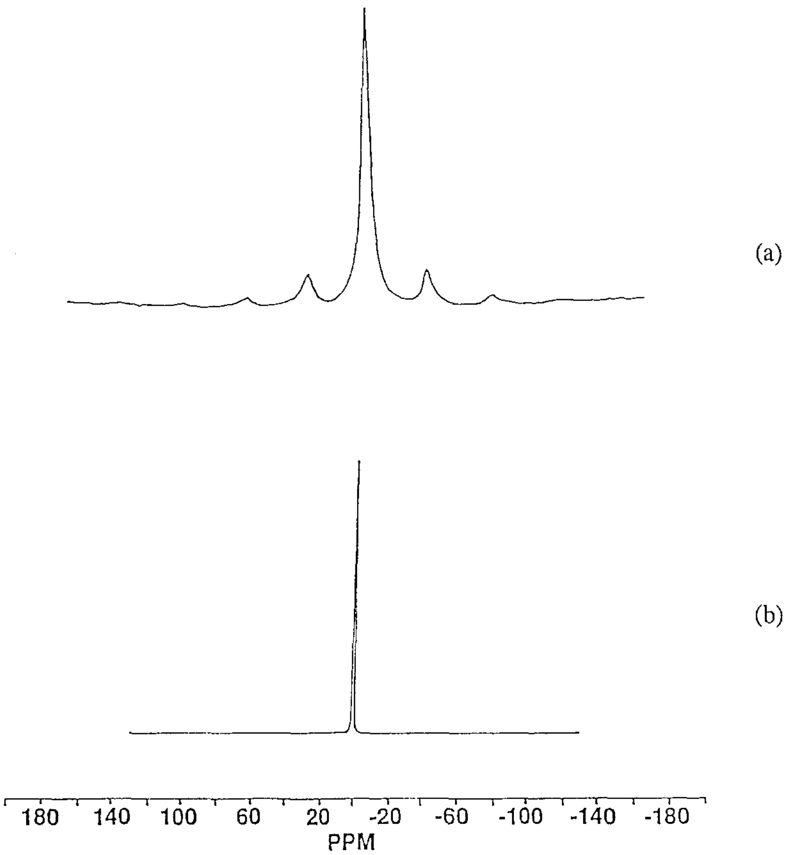
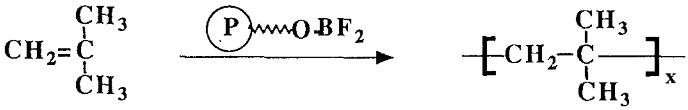


Figure 1: ^{11}B NMR spectra of PB-OBF_2 (a) and C_5-OBF_2 (b).

Polymerization of Isobutylene by Polyolefin Supported Catalysts

The polymer supported catalyst was used in the carbocationic polymerization of isobutylene, as shown in Equation 2.



$$CH_2{=}\underset{CH_3}{\overset{CH_3}{C}} \xrightarrow{\textcircled{P}\sim\sim O{-}BF_2} -\!\!\left[CH_2-\underset{CH_3}{\overset{CH_3}{C}}\right]_x\!\!-$$

Equation 2

After the reaction, polyisobutylene (PIB) was obtained by filtering the supported catalyst, then removing the solvent and unreacted monomers under vacuum. The recovered catalyst was mixed with fresh isobutylene/hexane solution, followed by the same separation and recovery processes. This reaction cycle was repeated for more than ten times. Table 1 summarizes the results of PIB's obtained by using the PB-OBF_2 catalyst in the fine powder form (particle size < 1 mm).

Table 1 : A Summary of PIB Prepared by PB-O-BF_2 (Powder)

Run #	Temp (^{0}C)	Time (Min.)	Mn (g/mole)	PDI	yield (%)
1	25	15	400	1.1	100
2	25	15	450	1.2	100
3	25	15	450	1.2	100
4	25	15	420	1.4	100
5	0	15	580	1.2	100
8	0	15	640	1.5	100
*	25	5	500	1.9	100
*	0	5	1080	2.0	100

(* C_5-O-BF_2 Soluble Catalyst)

Typically, the monomer (isobutylene) to catalyst (-OBF_2) ratio was about 500 to 1. The PB-OBF_2 catalyst is very active. In most reaction cycles, the conversion from monomer to polymer was complete within 15 minutes. The same high catalyst activity was observed during the reaction cycles. This unusually high and stable catalyst activity must be due to a high and stable surface area. The advantages in the use of semicrystalline polyolefin as the substrate are mainly (1) the chemical stability of polyolefin which allows the application of the supported catalyst under acidic reaction conditions, (2) the crystallinity of polyolefin offers not only good mechanical strength to maintain catalyst integrity under agitation, but also results in high and stable catalyst surface areas. The crystallinity of polyolefin may restrict heteroatom groups (active species) on the surfaces of crystalline phases, (3) The flexibility of the side chain between the catalyst and polymer backbone may offer some advantage in the polymerization.

Molecular Structure Studies

The molecular weight of PIB prepared by polyolefin-supported boron catalysts was about 450 g/mole in hexane solution at 25 ^{0}C. The molecular weight of PIB increased to 600 g/mol when the reaction temperature decreased to 0° C. The molecular weight-temperature relationship is usually reciprocal in carbocationic polymerization[6]. The rate of chain transfer, mainly β-proton elimination, decreases with a decrease of temperature.

The detailed structure was examined by ^{1}H NMR studies. Figure 2 (a) shows the ^{1}H NMR spectrum of PIB prepared by PB-O-BF_2 at room temperature. The major peaks, at 0.95 and 1.09 ppm, respectively are due to $C\underline{H}_3$ and $C\underline{H}_2$ protons in the PIB. There are some small peaks located in the olefinic region, between 4.5 and 6.0 ppm. Two singlets at 4.88 and 4.66 ppm are indicative of two types of nonequivalent vinylidene hydrogens which are located at the end of polymer chain. The small peak at 5.18 ppm corresponds to an internal double bond which has the olefinic hydrogens coupled to the methyl group, as shown in Table 2. Comparing the integrated intensities between olefinic peaks, the PIB prepared at 0 ^{0}C contains more than 85 % of terminal double bonds, which is higher than that (~ 65%) of the soluble BF_3 case. This result is obviously very different from PIB's prepared by $AlCl_3$, $EtAlCl_2$, Et_2AlCl, C_5-O-$AlCl_2$ and PP-O-$AlCl_2$, which usually give more than 70 mole% of internal double bonds[5,13].

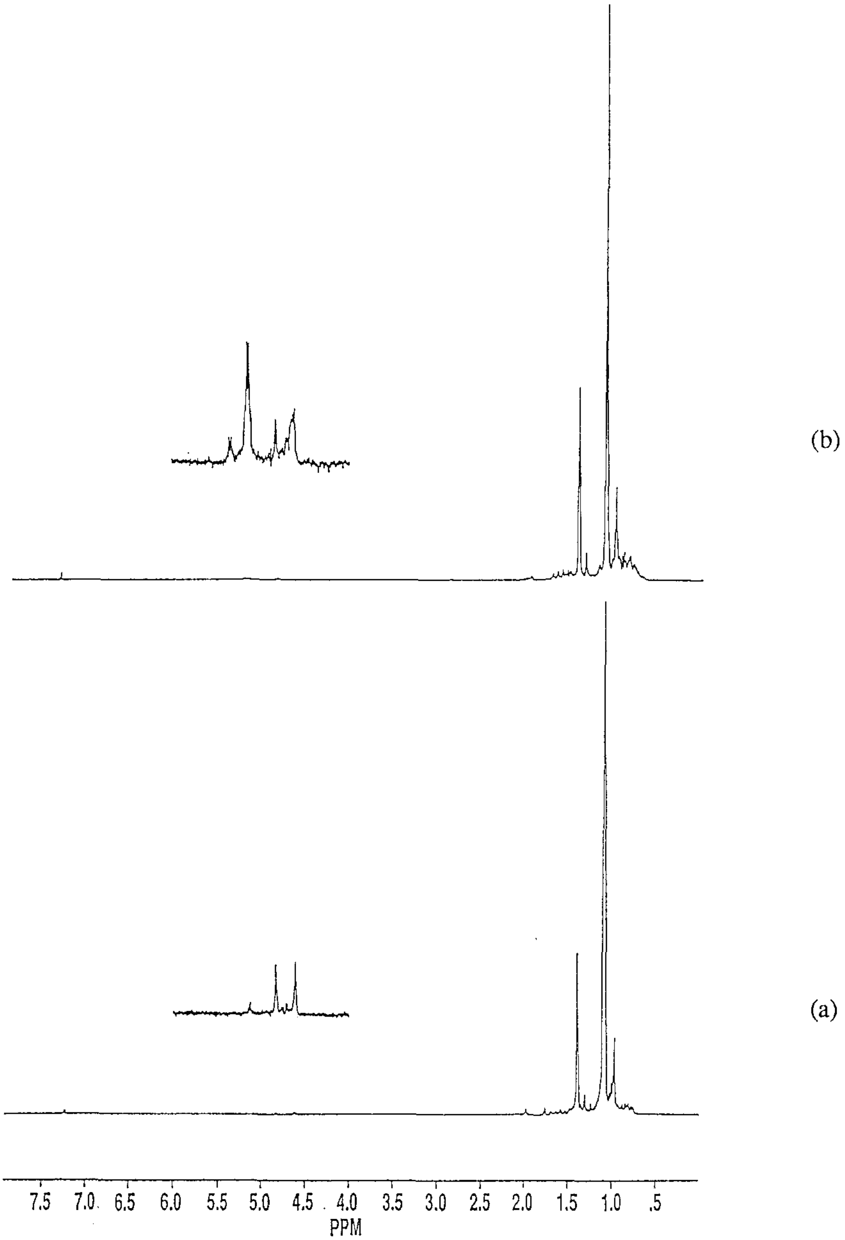
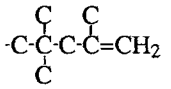
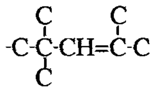
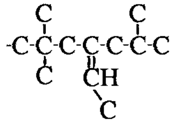
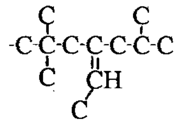


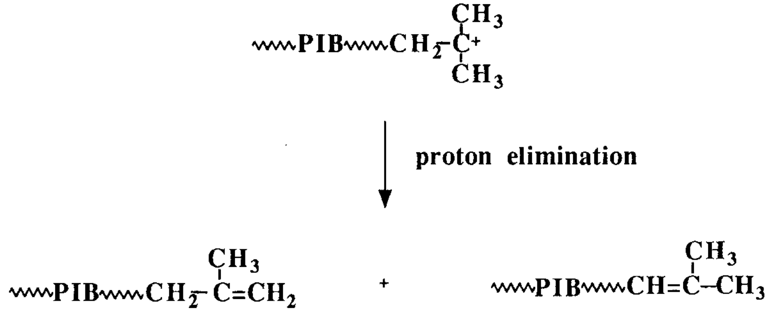
Figure 2: ^{1}H NMR spectra of PIB prepared by PB-O-BF$_2$ (a) and PP-O-AlCl$_2$ (b) catalysts at 0 ^{0}C.

Figure 2 (b) shows the ^{1}H NMR spectrum of PIB prepared by PB-O-AlCl$_2$ at 0 ^{0}C. There are two quartets at 5.38 and 5.18 ppm and two singlets at 4.88 and 4.66 ppm. The quartets at 5.38 and 5.18 ppm correspond to internal double bonds and have relatively high intensities. The ^{1}H NMR peak assignments are summarized in Table 2.

Table 2: Olefin Structures from ^1H NMR Shifts

Structure				
^1H Chemical Shifts (ppm)	4.88, 4.66 singlet	5.15 singlet	5.18 quartet	5.38 quartet

The reason for such a high percentage of terminal double bonds in the products obtained with PB-O-BF_2 is not clear. Chain tranfer by β-proton elimination as shown in Equation 3 can yield both terminal and internal double bonds.



Equation 3

The PIB obtained with a high concentration of terminal double bonds is a desirable material which can be further functionalized under mild conditions. In a commercial process, the terminal double bonds react directly with maleic anhydride, however the internal unsaturation requires chlorination before maleic anhydride addition[14]. The current commercial "reactive PIB"[7] is a low molecular weight (500 - 2000 g/mole) PIB with 60 - 70% terminal double bonds, usually prepared by BF_3 catalyst. Functionalized and derivatized PIB's are being used in many applications, such as additives in lubricating oil[15].

Experimental

Materials and Measurements

The hydroxylated polyolefins were prepared by the method described in the previous papers[8,9]. Isobutylene (Matheson) and BF_3 (Aldrich) were used as received. HPLC grade hexane was distilled from sodium anthracide. Dichloromethane was dried with CaH_2 and distilled under N_2. The molecular weight of polyisobutylene was determined using a Waters GPC apparatus. The columns used were Phenomenex Phenogel of 10^4, 10^3, 500 and 100 A. The flow rate was 0.7 ml/min and the mobile phase was THF. Narrow molecular weight polystyrene samples were used as standards. The solution NMR spectroscopies were done on a Bruker AM 300 instrument with deuterated chloroform as solvent. MAS ^{11}B NMR were done on a Chemagnetics CMX 300 NMR spectrometer (^{11}B resonance frequency of 95.4 MHz and 4 KHz MAS speed).

Implantation of Boron Trifluoride

In a typical reaction, the powder form of hydroxylated poly(1-butene) (150 mg) was reacted with 0.1 mL of n-BuLi (10 M) in 7 mL of toluene. After 1 hour, the polymer powder was filtered and washed with hexane to remove excess lithium compounds. The resulting polymer was then mixed with a saturated BF_3/CH_2Cl_2 solution (10 mL) at room temperature for 3 hours. The PB-O-BF_2 was obtained by vacuum removal of excess BF_3 and CH_2Cl_2. For the control reaction, a solution containing pentanol (0.5 mL) and ether (5 mL) was cooled to -78°C, then was mixed with 5.5 mL of n-BuLi/ether (1 M) solution. The mixture was warmed to room temperature and stirred for 10 additional minutes before removing the ether by vacuum. The resulting lithium pentoxide (200 mg) was then dissolved in 5 mL of CH_2Cl_2 and was reacted with 20 mL of saturated BF_3/CH_2Cl_2 solution at room temperature. After stirring for 15 minutes, CH_2Cl_2 and BF_3 were removed by vacuum to obtain C_5-O-BF_2.

Polymerization of Isobutylene

The polymerization was carried out in a high vacuum apparatus which consists of two 100 mL flasks (A and B) and one stopcock (a) to separate the flasks. Other stopcock (b) was used to control the vacuum conditions and nitrogen flow. In a dry box, 100 mg PB-O-BF_2 were charged to the flask A. After closing the valve (b), the whole apparatus was moved to a vacuum line and was pumped to high vacuum. Isobutylene (4 mL) and hexane (20 mL) were vacuum-distilled into flask B. Isobutylene solution was then warmed to the required temperature and transferred to the catalyst in flask A. After stirring the reaction mixture for the required time, PIB solution was separated from the supported catalyst by filtration in a dry box. PIB was obtained by evaporating the solvent. The recovered catalyst was recharged to flask A and the entire process was repeated.

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