Isospecific Polymerization of Vinylcyclohexane by Zirconium Complexes of Salan Ligands

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Received November 7, 2007; Revised Manuscript Received December 30, 2007

ABSTRACT: The polymerization of vinylcyclohexane by C_2-symmetric dibenzylzirconium complexes of nonchiral and chiral Salan ligands that feature electron-withdrawing halo or alkyl substituents is reported. The catalysts containing the electron-withdrawing groups exhibited ultrahigh activities. In contrast to polymerization of less hindered α-olefins, highly isotactic poly(vinylcyclohexane) were obtained from all Salan complexes studied. This indicates that the isospecificity is not derived from the bulkiness of the phenolate substituents. Characterization of the polymers by differential scanning calorimetry and by X-ray powder diffraction reveals the formation of similarly crystalline polymers regardless of the nature of Salan catalysts. DSC measurements indicates that these polymers act as effective nucleation agents for polypropylene.

Introduction

Poly(vinylcyclohexane), PVCH, is a unique thermoplastic polymer having several potential applications derived from its uncommon physical properties.[1−4] Amorphous PVCH is a possible candidate for optical disk material, whereas the high melting isotactic poly(vinylcyclohexane), iPVCH, may function as a nucleating agent for isotactic polypropylene inducing a higher crystallization temperature and transparent iPP films. However, despite its potential applicability, the polymerization of vinylcyclohexane has received much less attention in comparison to the lower α-olefins. PVCH has been prepared through heterogeneous Ziegler−Natta catalysts with low activity or via hydrogenation of polystyrene. While the heterogeneous catalysts can yield only isotactic polymers,[5] the hydrogenation of polystyrenes of various tacticities afforded atactic and syndiotactic PVCH as demonstrated by Elias and Soga.[6,7]

Heterogeneous polymerization of vinylcyclohexane is sluggish because of two reasons. The first is the bulky cyclohexyl substituent in the vicinity of the double bond.[8,9] As demonstrated by Endo and co-workers, increasing the steric bulkiness of the α-olefins reduced dramatically their tendency to undergo polymerization using the heterogeneous catalysts. For example, a 200-fold decrease in activity of $TiCl_3/Et_2AlCl$ was noted on shifting the side-chain substitution from the β- to α-position, i.e., from 4-methyl-1-pentene to vinylcyclohexane. The second difficulty is the monomer's tendency to isomerize to ethylidencyclohexane during the polymerization process.[10] This side reaction is the main source of the low activities of the catalysts and the low molecular weights of the obtained polymers. Few examples for the polymerization of vinylcyclohexane by homogeneous catalysts are found in the literature. Longo described the polymerization of vinylcyclohexane in the presence of zirconocene catalysts of various symmetries to obtain isotactic polymers (via different control mechanisms).[11] Recently, we have shown that this monomer may be polymerized by the amine bis(phenolate) titanium and zirconium complexes to give atactic polymers of relatively low molecular weights (7500−12 000 g mol^{-1}).[12] Sita reported the isotactic polymerization of vinylcyclohexane using the half-sandwich zirconium acetamidinate catalysts.[13] A living polymerization of 200 equiv led to isotactic polymers of M_w of ca. 20 000 g mol^{-1}, by a proposed chain-end control mechanism.

The Salan ligands were first introduced to group 4 chemistry (Scheme 1) in the year 2000.[14] These tetradentate dianionic [ONNO]-type ligands prefer to wrap around the octahedral metal center in a *fac*−*fac* mode, leading to C_2-symmetric complexes in which the two labile groups are in *cis* disposition, making them suitable for α-olefin polymerization. We found that for zirconium complexes the activity of the catalysts and the nature of the obtained polymers are strongly dependent on the steric and electronic nature of the substituents on the phenolate rings.[14,15] While bulky *ortho* substituents led to isospecific polymerization, electron-withdrawing substituents led to very high activities accompanied, however, by loss of tacticity induction and reduction of the polymers molecular weights.[16] A similar dependence of isospecificity on phenolate substituents' bulkiness was found for zirconium Salan complexes when employed in propylene polymerization.[17]

More recently, we investigated chiral Salan ligands assembled around *trans*-1,2-diaminocyclohexane.[18,19] These ligands may wrap around group 4 metals to form two complexes of C_2-symmetry and *fac*−*fac* geometry having a diastereomeric relationship.[20] We found that while coordination to titanium leads to mixtures of diastereomers unless a certain set of substituents is chosen (i.e., *N*−H groups and small phenolate substituents),[18] the coordination around zirconium is very selective and leads to single C_2-symmetric diastereomers for a broad variety of chiral Salan ligands (Scheme 2).[19] Thus, a predetermination of chirality around the metal may be gained by choosing the specific ligand enantiomer (an (*R*,*R*)-Salan ligand enantiomer tends to coil around the metal in a Δ-wrapping). The activities and tacticity induction of the zirconium complexes of the chiral Salan ligands were found to follow those of the analogous catalysts derived from the nonchiral ligands,

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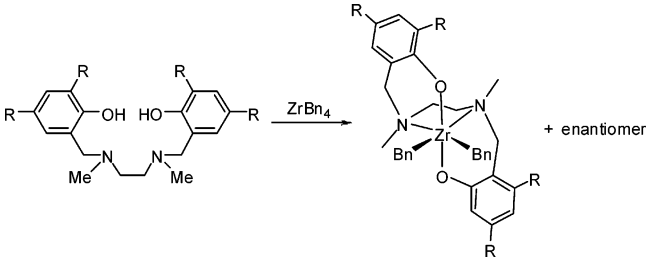
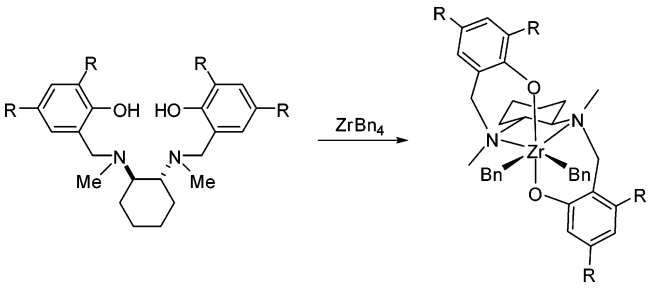
10.1021/ma7024682 CCC: $40.75 © 2008 American Chemical Society
Published on Web 02/06/2008

Scheme 1. Wrapping of Achiral Salan Ligands around an Octahedral Zirconium Center

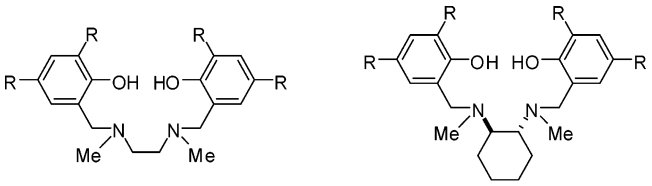


Scheme 2. Wrapping of Chiral Salan Ligands around an Octahedral Zirconium Center[a]



[a] An (*R,R*)-ligand yields a Δ-chiral complex.

Scheme 3. Achiral (Left) and Chiral (Right) Salan Ligands Whose Zirconium Complexes Are Employed in This Work



Lig^1H_2: $R^1=R^2=tBu$
Lig^2H_2: $R^1=R^2=Cl$
Lig^3H_2: $R^1=R^2=Br$

Lig^4H_2: $R^1=R^2=tBu$
Lig^5H_2: $R^1=Me$, $R^2=H$
Lig^6H_2: $R^1=R^2=Cl$
Lig^7H_2: $R^1=R^2=Br$

but higher molecular weight polymers rather than oligomers were obtained, a possible consequence of their higher rigidity.[21]

The broad range of activities exhibited by these catalysts toward linear α-olefins has prompted us to attempt the polymerization of the challenging monomer vinylcyclohexane by zirconium complexes of the two families of Salan ligands. Herein we describe for the first time the exceptionally high activities in vinylcyclohexane polymerization by Salan complexes, the characterization of the attained isotactic high molecular weight polymers, and the evaluation of these polymers' potential as nucleating agents for polypropylene.

Results and Discussion

The polymerization of vinylcyclohexane was studied employing dibenzylzirconium complexes of the two families of ligands outlined in Scheme 3. These were chosen to address several structure−activity relationships, including tacticity induction and catalyst activity as a function of phenolate substituents, and the effect of the increased rigidity of the diamine backbone (i.e., diaminocyclohexane vs diaminoethane) on catalyst activity and polymer properties. In addition, we wanted to investigate the possibility of forming single helices of PVCH by employing enantiomerically pure catalysts. Such polymers, which might retain their chiral conformational identity because of high barrier for interconversion, may be useful in various applications.[22] Therefore, all the chiral Salan ligands were employed in their (*R,R*)-enantiomerically pure form.

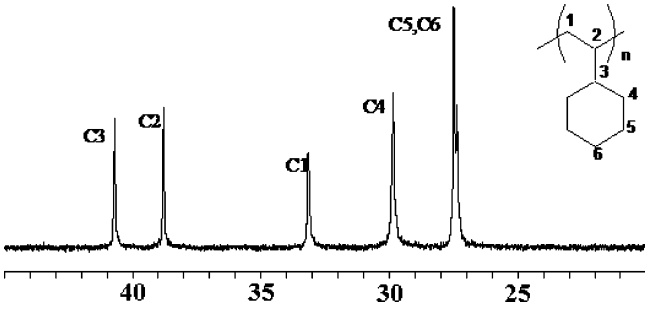
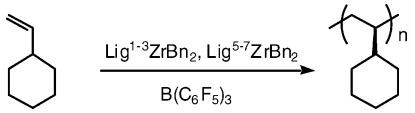


Figure 1. Representative ^{13}C NMR spectrum of the obtained polyvinylcyclohexanes.

Scheme 4. Polymerization of Vinylcyclohexane by the Salan Zirconium Complexes



The vinylcyclohexane polymerization experiments were done by activating of the dibenzylzirconium complexes $Lig^{1-7}ZrBn_2$ of all Salan ligands by tris(pentafluorophenyl)borane in the neat monomer at room temperature (Scheme 4). These conditions are comparable to those employed in 1-hexene polymerization, so that relative activity assessments could be made. On activation, $Lig^{1-3}ZrBn_2$, the three complexes of the nonchiral ligands, all polymerized vinylcyclohexane. Lig^1ZrBn_2 featuring the bulky *tert*-butyl phenolate substituents led to an activity of ca. 4.5 g $mmol^{-1}$ h^{-1}. While this activity is mild, it is only 4 times lower than the polymerization activity toward 1-hexene by the same catalyst. In other words, no significant reduction in activity is observed on increasing of the monomer steric bulkiness. The same trend was observed for the zirconium complexes of the electron-poor Salans, Lig^2ZrBn_2 and Lig^3ZrBn_2, which led to activities of 1800 and 3600 g $mmol^{-1}$ h^{-1}, respectively. These activities are unexpectedly high considering the resistance of this monomer to be polymerized and are only ca. 2-fold lower than the activities of toward 1-hexene polymerization by the same catalysts. To our knowledge, these figures represent the highest activities ever reported for vinylcyclohexane polymerization with either homogeneous or heterogeneous catalysts under any conditions.[23,24] These results indicate that, in contrast to homogeneous catalysts such as the metallocenes and, even more so, in contrast to heterogeneous catalysts, the activity of the C_2-symmetric Salan−zirconium catalysts is not hampered substantially by increasing the bulkiness of the monomer.[9] It is also noteworthy that a substantially lower activity of vinylcyclohexane polymerization than 1-hexene polymerization (>100-fold) was observed for the isomeric C_s-symmetric amine bis(phenolate) zirconium complexes.[12]

The polymeric products were analyzed by NMR. ^{13}C NMR indicated that all three catalysts induced highly isospecific polymerization of vinylcyclohexane (Figure 1). Only six narrow peaks corresponding to six different carbons of the isotactic PVCH were detected. The absence of peaks corresponding to stereoerrors excludes the elucidation of stereochemistry control mechanism (enantiomorphic site control vs chain-end control) in these reactions. In addition, no chain-end groups were detected in the spectra, signifying the formation of long-chain polymers by all the above catalysts. It is notable that in polymerization of 1-hexene the highly active electron-poor catalysts Lig^2ZrBn_2 and Lig^3ZrBn_2 acted as aspecific catalysts and yielded short polymeric chains. The current polymerizations represent the first example in which Salan complexes act as

Table 1. Melting Temperature, T_m, and Crystallization Temperature, T_c, of the iPVCH Samples

precatalyst	T_m (°C)	T_c (°C)
Lig^{1}ZrBn$_2$	381.4	273.9
Lig^{2}ZrBn$_2$	333.4, 343.1	233.3
Lig^{3}ZrBn$_2$	368.7	281.3
Lig^{5}ZrBn$_2$	376.1	287.9
Lig^{6}ZrBn$_2$	351.4	249.3
Lig^{7}ZrBn$_2$	371.4	279.3

isospecific catalysts irrespective of the bulkiness of the phenolate substituents. Yet, it would seem that the C_2 symmetry of the Salan complexes does play a role in the isotacticity induction, since in comparison, the isomeric zirconium complexes of the amine bis(phenolate) ligands carrying a side-arm donor and featuring a C_s symmetry led to aspecific polymerization of vinylcyclohexane.[12]

We found that the solubility of the iPVCH samples in organic solvents such as THF or toluene decreased as their molecular weights increased. The iPVCH produced by the precatalyst Lig^{2}ZrBn$_2$ was relatively soluble, and its molecular weight was determined by GPC in THF at room temperature to be M_w = 40 000 g mol^{-1}. The polymer produced by the precatalyst Lig^{3}ZrBn$_2$ was insoluble even in boiling THF, and its molecular weight, determined by high-temperature GPC in 1,2,4-trichlorobenzene at 150 °C, was found to be exceptionally high—M_w = ca. 3 000 000 g mol^{-1}.[25] The iPVCH produced by Lig^{1}ZrBn$_2$ was highly insoluble, and therefore its molecular weight could not be determined. We presume that its molecular weight could be even higher. These ultrahigh molecular weights may signify a partial activation of the precatalysts.

The polymers obtained were analyzed by differential scanning calorimetry (DSC) to determine their melting temperature, T_m, and crystallization temperature, T_c. The results are summarized in Table 1 (also refer to the Supporting Information). The high melting points of around 360 °C deduced from the thermograms are in good agreement with their high degrees of isotacticity. No thermal effects associated with glass transitions in the range of 70−200 °C were observed.

In contrast to Lig^{1}ZrBn$_2$, the analogous zirconium complex of the chiral ligand that features the same *tert*-butyl phenolate substituents, (*R*,*R*)-Lig^{4}ZrBn$_2$, did not catalyze the polymerization of the vinylcyclohexane under the same conditions.[26] However, (*R*,*R*)-Lig^{5}ZrBn$_2$, featuring the smaller methyl phenolate substituents, yielded iPVCH with a substantial activity (similar to that observed in 1-hexene polymerization)[19] of 410 g mmol^{-1} h^{-1}. The crystalline polymer obtained was too insoluble for molecular weight determination by high-temperature GPC. The two catalysts featuring the chiral Salan ligands carrying electron-withdrawing phenolate substituents ((*R*,*R*)-Lig^{6}ZrBn$_2$ and (*R*,*R*)-Lig^{7}ZrBn$_2$) led to ultrahigh activities of 2900 and 3600 g mmol^{-1} h^{-1}, respectively. The close similarity between these activities and the activities toward 1-hexene exhibited by these catalysts[19] implies that, for this series as well, increasing the monomer bulkiness does not reduce its polymerization rate substantially. GPC measurements at room temperature for these relatively high THF-soluble polymers indicated high molecular weights of ca. 65 000 g mol^{-1} by (*R*,*R*)-Lig^{6}ZrBn$_2$ and 106 000 g mol^{-1} by (*R*,*R*)-Lig^{7}ZrBn$_2$. (Similar values for these two polymers were obtained by high-temperature GPC measurements.) NMR spectra supported the formation of highly isotactic polymers, with no observable chain-end groups. The high melting points of these polymers obtained from DSC measurements (see the Supporting Information) were consistent with formation of highly isotactic high molecular weight polymers.

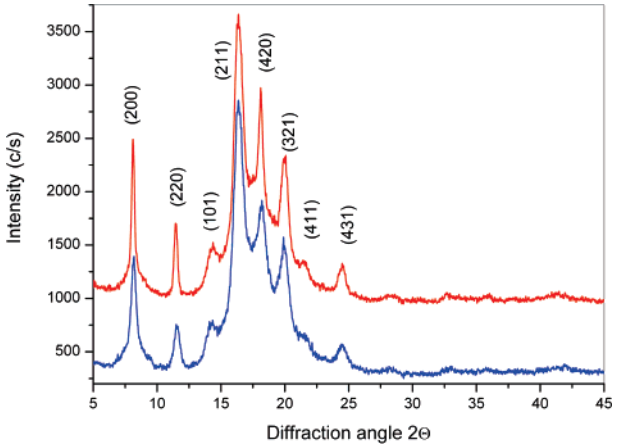


Figure 2. XRD patterns of the PVCH produced from (*R*,*R*)-Lig^{6}ZrBn$_2$ (lower curve) and Lig^{2}ZrBn$_2$ (upper curve).

As described above, the helical conformation of isotactic polymers may be frozen if the side chains are bulky enough to prevent unwrapping.[27] If such polymers are prepared from enantiomerically pure catalysts, and the stereocontrol is brought about by the catalyst's chirality (enantiomorphic site control), and the polymer does not racemize before precipitating from solution, then optically active polymers may be obtained. Such polymers may be useful in applications such as chiral stationary phase for chromatographic separations.[28] The soluble polymeric products were tested and found to be optically inactive. The lack of optical activity may result either from its absence in the first place or from post-racemization of the originally formed optically active polymers in solution. Thus, we turned to examine the insoluble polymers, which precipitated from the monomer solution immediately after their formation, without dissolving them in organic solvents. We presumed that if single helices were formed, they would pack in a different arrangement from that known for the regular racemic iPVCH. This difference should be expressed in their unit cell dimensions. We therefore examined them by X-ray powder diffraction measurements.

X-ray diffraction (XRD) patterns of crystalline polymeric samples prepared by employing the enantiomerically pure (*R*,*R*)-Lig^{6}ZrBn$_2$ precatalyst and by the racemic Lig^{2}ZrBn$_2$ precatalyst are shown in Figure 2 as bottom and top curves, respectively. The best indexing was clearly attained in the tetragonal space group $I4_1/a$, in full agreement with those reported by Natta, De Rosa, and co-workers.[29,30] The samples prepared from (*R*,*R*)-Lig^{6}ZrBn$_2$ and Lig^{2}ZrBn$_2$ have practically the same unit cells with in-plane lattice parameter a = 21.813 (0.054) and 21.915 (0.041) Å and out-of-plane lattice parameter c = 6.511 (0.018) and 6.490 (0.015) Å, respectively. The Bragg peaks of the sample prepared from the enantiomerically pure (*R*,*R*)-Lig^{6}ZrBn$_2$ catalyst are a bit wider than those prepared from Lig^{2}ZrBn$_2$, probably due to somewhat different preparation procedures. The similar patterns obtained from both samples give a strong indication that the enantiomerically pure catalyst led to a racemic mixture of helices of iPVCH. We are currently investigating the possible source for formation of racemic mixture of helices.

As noted above, one of the potential industrial applications for the isotactic polyvinylcyclohexane is as nucleating agent in the crystallization of polypropylene.[31] Following the establishment of Kakugo[1] that effective nucleating agents for PP should be crystalline during PP crystallization and the high melting points of the iPVCH produced from the above Salan complexes, we were encouraged to test it in this application. Samples of iPVCH prepared by Lig^{1}ZrBn$_2$ and Lig^{2}ZrBn$_2$ were tested as

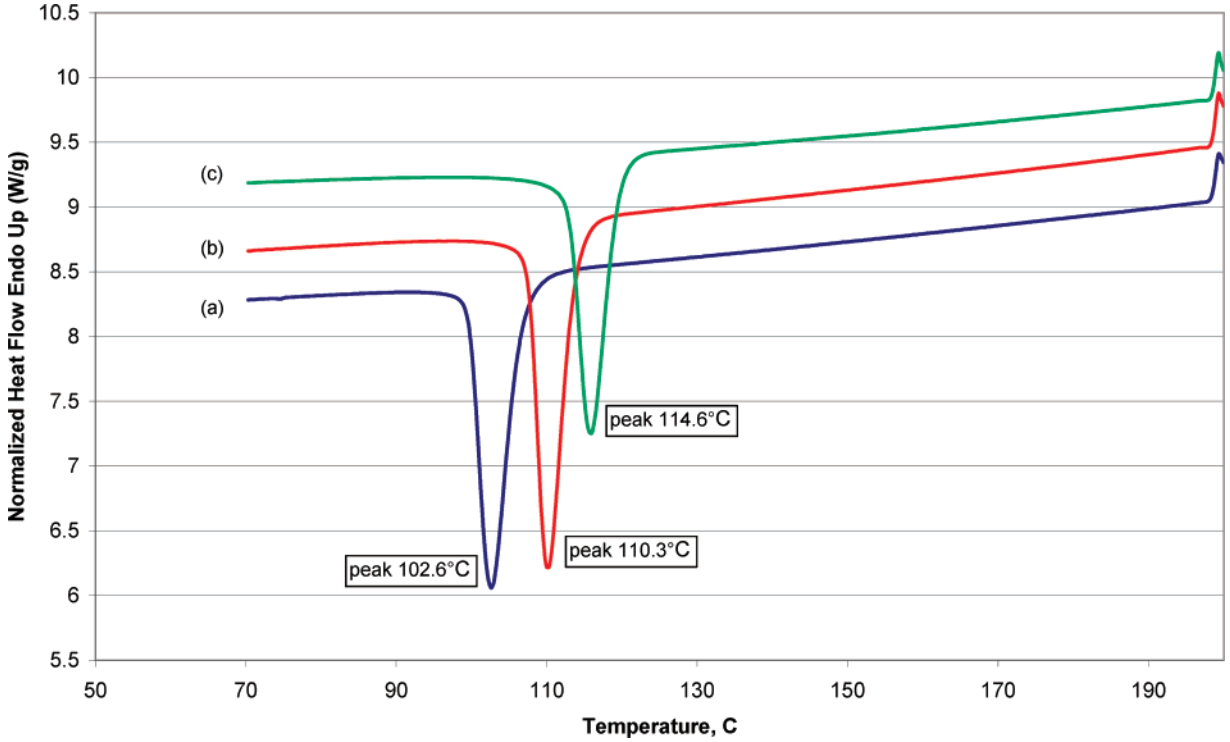


Figure 3. Crystallization temperatures of random PP copolymer containing ca. 3% ethylene (a) without a nucleating agent, (b) in the presence of 0.15% iPVCH produced using Lig^2ZrBn_2, and (c) in the presence of 0.30% iPVCH produced using Lig^1ZrBn_2.

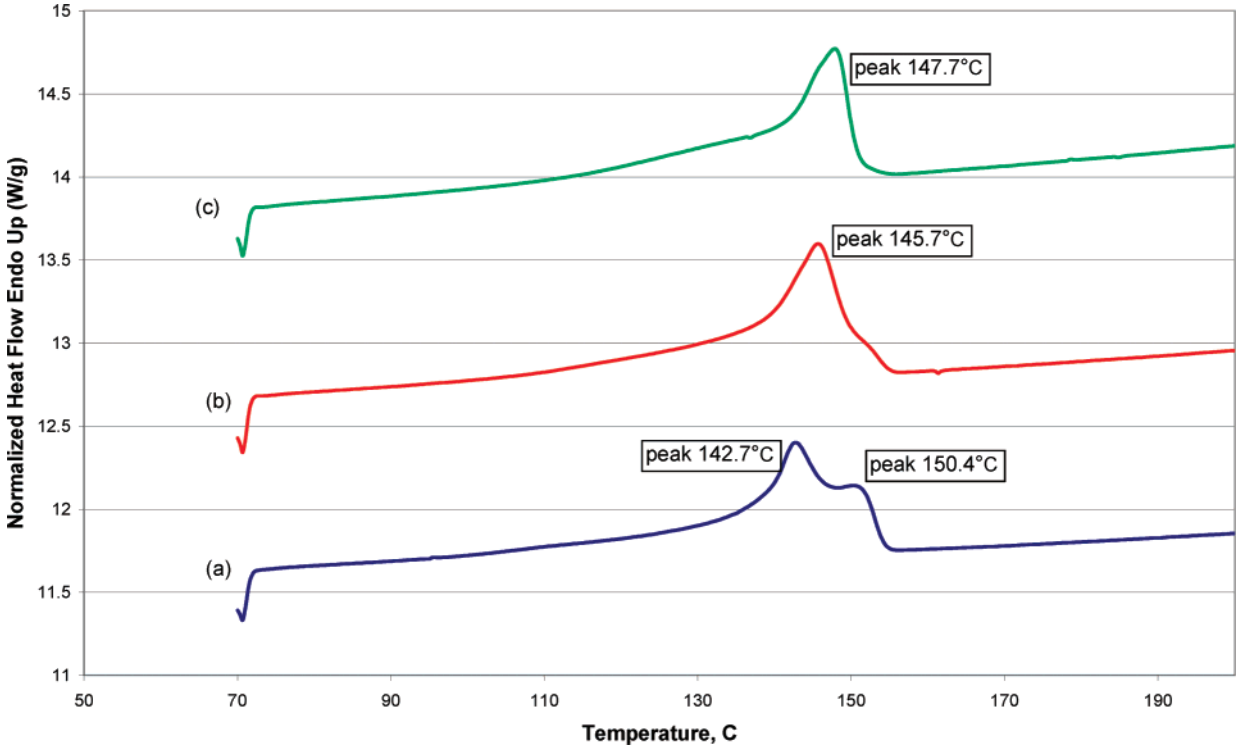


Figure 4. Melting temperatures of the random PP copolymer containing ca. 3% ethylene (a) without a nucleating agent, (b) in the presence of 0.15% iPVCH produced using Lig^2ZrBn_2, and (c) in the presence of 0.30% iPVCH produced using Lig^1ZrBn_2.

nucleating agents for random PP copolymer containing ca. 3% ethylene (prepared by a heterogeneous catalyst). We evaluated the crystallization−melting behavior of the PP copolymer containing different amounts of the two iPVCH samples in comparison to the raw polymer. Figure 3 clearly reveals that the blending of 0.15% of iPVCH led to significant (8 °C for polymer prepared from Lig^2ZrBn_2; 10 °C for Lig^1ZrBn_2, not shown) increase of the crystallization temperatures (T_c) of the copolymer, while 0.30% of iPVCH (Lig^1ZrBn_2) led to 12 °C increase in crystallization temperature. These significant changes in the T_c indicate a strong nucleation effect.

Figure 4 shows the melting behavior of the PP that crystallized with and without the crystalline iPVCH. The melting endotherms of PP random copolymers usually display a bimodal behavior due to the presence of both β-polymer (the lower temperature peak) and α-polymer crystallites. The addition of the iPVCH nucleating reagent led to increase of the higher temperature peak, possibly due to increased population of the

Table 2. Vinylcyclohexane Polymerization

precatalyst	monomer amount, g	polymerization time, min	yield, g	activity, g mmol^{-1} h^{-1}	mol wt, g mol^{-1}	PDI
Lig^1ZrBn_2	2.0	120	0.1	4.5		
Lig^2ZrBn_2	ca. 3	5	2.3	1800	40 000	2.5
Lig^3ZrBn_2	ca. 3	3.5	2.8	3600	2 800 000[a]	1.4
Lig^4ZrBn_2	ca. 3	overnight	0.0	0.0		
Lig^5ZrBn_2	2.6	9.5	1.2	410		
Lig^6ZrBn_2	3.5	2.5	1.4	2900	65 000	2.1
Lig^7ZrBn_2	3.5	3.5	2.0	3600	106 000	2.0

[a] This material was analyzed by two laboratories. The first yielded that number, and the second concluded that the material was too insoluble for high-temperature GPC.

α-crystallites.[31]

In conclusion, the zirconium Salan catalysts were found to promote highly isospecific polymerization of vinylcyclohexane regardless of the nature of the phenolate substituents, while those catalysts containing electron-withdrawing halo substituents led to ultrahigh activities. This desired combination of catalyst properties stands in sharp contrast to the activities of the Salan catalysts toward nonbulky α-olefins, for which either high iospecificity (requiring bulky phenolate substituents) or high activity (requiring electron-withdrawing substituents) could be attained, but not their combination. No significant difference between the activities of racemic Salan complexes based on the diaminoethane skeleton and the activities of the enantiomerically pure complexes based on the more rigid diaminocyclohexane was found. The high melting polymers obtained were found to act as efficient crystallization promoters for polypropylene. The similar activities of the Salan catalysts toward α-olefins of different steric bulkiness indicate that they may be useful for production of random copolymers of linear and branched α-olefins with any desired ratio. We are currently studying the polymerization of other bulky monomers by these catalysts.

Experimental Section

General Remarks. Manipulation of air- and moisture-sensitive materials was carried out under a dry nitrogen atmosphere in a nitrogen-filled glovebox. Pentane was washed with HNO_3/H_2SO_4 prior to distillation from Na/benzophenone/tetraglyme. Toluene was refluxed over Na and distilled. Tris(pentafluorophenyl)borane, obtained from Strem Chemicals, was used as received. Vinylcyclohexane was passed through alumina prior to use. The zirconium complexes were synthesized as previously reported.[14,15,18] NMR data for the PVCH samples in chloroform-d were recorded on a Bruker AC-400 spectrometer. The PVCH molecular weights were determined either on a Jasco instrument using TSKgel GMHHR-M column with THF as eluent at room temperature (for the soluble polymer samples) or on an Alliance GPC-200 high-temperature GPC using 3 Styragel HT and GARD columns at 150 °C with 1,2,4-trichlorobenzene as the eluent (for the insoluble and some of the soluble polymer samples). The molecular weights are relative to polystyrene standards.

X-ray data were collected in symmetrical Bragg geometry with Cu Kα radiation on Θ−Θ powder diffractometer "Scintag" equipped with liquid-nitrogen-cooled Ge solid-state detector. XRD patterns processing included profiles fitting of Bragg diffraction lines, their indexing, and cell refinement.

The thermal behavior of the iPVCH samples was studied using a Perkin-Elmer differential scanning calorimeter DSC-7 operating under a N_2 atmosphere. The melting−crystallization behavior of all samples was conducted in the temperature range 180−400 °C. The samples were heated, cooled, and repeatedly heated at a heating rate 10 °C/min. Attempts were made to detect glass transition of the polymer samples in the temperature range 70−200 °C, which were heated, cooled, and repeatedly heated at a rate of 20 °C/min. For polypropylene nucleation evaluation, random polypropylene copolymer with ca. 3 wt % ethylene content was used. Small amounts of iPVCH were melt-blended with the polymer in a HAAKE batch melt mixer at 180 °C, 150 rpm, under a nitrogen blanket. Samples after the blending were tested using the DSC technique. The testing procedure included heating−cooling−second heating runs in the temperature range 70−200 °C. Heating and cooling rates were 10 °C/min.

General Polymerization Procedure. $B(C_6F_5)_3$ (15 mmol) was dissolved in ca. 1 mL of vinylcyclohexane and added to a stirred solution of Lig^xZrBn_2 ($x = 1-7$, 12 mmol) in vinylcyclohexane. The remaining olefin was evaporated under vacuum to give polyvinylcyclohexane as a white powder. Traces of the monomer were removed either on a high-vacuum line or by a combination of pentane washings (that were analyzed by NMR to reveal the presence of monomer only) and high vacuum. The polymerization experiments are summarized in Table 2.

Nuclear Magnetic Resonance (NMR) of Polymers Samples. The ^{13}C NMR spectra of all the PVCH samples indicated that the polymers were isotactic ($CDCl_3$ 100.63 MHz): δ 40.81 (*C*H), 38.89 (*C*H), 33.25 (*C*H_2), 29.94 (*C*H_2), 27.57 (*C*H_2), 27.45 (*C*H_2).

Acknowledgment. We thank Dr. Michael Gishvoliner (Carmel Olefins Ltd.) for helpful discussions. We thank the U.S.−Israel Binational Science Foundation and the Ministry of Science for financial support.

Supporting Information Available: DSC thermograms of all the PVCH samples. This material is available free of charge via the Internet at http://pubs.acs.org.

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MA7024682