Homogeneous Binary Zirconocenium Catalyst Systems for Propylene Polymerization. 1. Isotactic/Atactic Interfacial Compatibilized Polymers Having Thermoplastic Elastomeric Properties

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Homogeneous Binary Zirconocenium Catalyst Systems for Propylene Polymerization. 1. Isotactic/Atactic Interfacial Compatibilized Polymers Having Thermoplastic Elastomeric Properties

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ABSTRACT: Polypropylene with thermoplastic elastomeric properties was synthesized by homopolymerization of propylene using two metallocene catalysts of different stereospecificities: rac-ethylenebis(1-η5-indenyl)zirconium dichloride or rac-dimethylsilylenebis(1-η5-indenyl)zirconium dichloride as iso-specific catalyst precursors and ethylenebis(9-η5-fluorenyl)zirconium dichloride as an aspecific precursor. The catalysts formed by activation of the precursors with triphenylcarbenium tetrakis(pentafluorophenyl)borate and trisobutylaluminum exhibit a very high activity of 5 × 10^9 g of PP/[Zr]C₆H₄Cl₂ h). Products ranging from tough plastomers to weak elastomers were obtained by varying the ratio of the two types of precursors. The polymers containing less than half of the isotactic fraction display excellent thermoplastic elastomeric properties, which is attributable to an interconnected crystal line superstructure in an amorphous continuum compatibilized and bound together by a stereoblock copolymer at the interface against macrophase separation. Materials exhibiting elastic recoveries of 97–98%, which are relatively independent of elongation up to 500%, were obtained.

Introduction

The first Ziegler–Natta coordination catalysts comprise active centers with different stereospecificities which produced polypropylenes of different stereoisomeric structures.1,2 Most of the subsequent developments in homogeneous Ziegler–Natta catalysts, especially those in the industrial laboratories, were directed mainly toward maximizing the high stereoselective sites, which produce the valuable isotactic polypropylene (i-PP), and diminishing the low stereoselective centers, which form the stereoregular polypropylenes, by selective poisoning.3

The synthesis of polypropylenes with lower levels of stereoregularity have received some belated attention. The objective is to produce polypropylenes with useful elastomeric properties. Early efforts,4 including those of Natta et al.,1,2 did not result in a practical process. Not only were catalyst productivities low but also only a portion of the product had the desired properties, requiring removal of the isotactic fractions in order to isolate the elastomeric polymer.

Collett et al.5a of the Du Pont Co. made heterogeneous catalysts by reacting transition-metal alkyls R₄M (R is PhCH₂, (CH₃)₂C, or PhC(CH₃)₂C; M is Zr, Ti, or Hf) with partially dehydroxylated Al₂O₃, which polymerize propylene to afford elastomeric PP (herein given as e-PPA). The inventors demonstrated that the key component responsible for the elasticity is a high molecular weight ether-soluble fraction that can co-crystallize with more stereoregular components to form a cross-linked network. It seems likely that these catalysts comprise centers possessing both high and low stereoselectivities.

Wilson and Job6a disclosed a high productivity catalyst formed by reacting magnesium ethoxide with TiCl₄ in the presence of veratrole (1,2-dimethoxybenzene). It produces polypropylene (herein given as e-PPB) which is predominantly isotactic (greater than 60%), but also contains about 20% syndiotactic sequences and 15–25% atactic units.7

Advance in metallocene chemistry8 had led to the discoveries of many "single-site" catalysts. Metallocene precursors belonging to C₂, C₅, or C₇ space groups were shown to produce i-PP,9,10 syndiotactic polypropylene (s-PP),11,12 and atactic polypropylene (a-PP).13,14 The C₇ systems are employed for the production of linear low density polyethylene and ethylene–cycloolefin copolymers having narrow molecular weight and comonomer composition distributions. Chien et al.15 invented an asymmetric titanocene catalyst (C) to catalyze both stereospecific and stereorandom propylene insertion by the two interconverting sites i and a, respectively, as depicted in Scheme 1.15,16 The elastic stereoblock polypropylene product (herein given as e-sb-PPC), has a well-defined alternating crystalline (isotactic) amorphous (atactic) block microstructure which possesses low hysteresis and high recovery elastic properties.16

Essentially the same type of material (herein given as e-sb-PPD) was obtained with nonbridged zirconocenes having an indenyl ligand with a bulky substituent7 (D), which can interconvert between a rac-like site to a meso-like site as proposed in Scheme 2. Catalysts C and D both have low to modest productivities and produce e-PP with desired properties only within a narrow window of polymerization conditions, i.e. temperature (T_p) and propylene pressure. Significant changes in polymer microstructure usually require a different metallocene.17,18
The central purpose of this research effort is to find novel ways to produce d-PP. We report here a new process using a C2 and C4, symmetric homogeneous binary catalyst (HBC) to produce polypropylenes wherein the percentages of i-PP and a-PP, their molecular weights, isoelectricities, and melting transition temperatures \( T_m \) can all be independently controlled and varied. Fractionation and NMR studies showed that the HBC process produces sb-PP in addition to the expected i-PP and a-PP. The physical, mechanical, and rheological properties of the present d-PPP are described and its elastic properties are compared with those of d-PPA to D. A possible mechanism explaining the formation of sb-PP by the HBC process is proposed.

**Experimental Section**

**Materials.** Solvents were dried over a Na/K alloy or CaH2 and distilled under argon prior to use. Methylaluminoxane (MAO) was obtained from Akzo Chemicals. Polymerization grade propylene was purchased from Marimor Graves and purified by passing through two Matheson Gas Purifiers (Model 6404). Davison 952 silica was a gift from Grace. Unless otherwise indicated, all other chemicals were obtained from Aldrich.

**Synthesis.** All reactions were carried out using Schlenk or glovebox techniques under an argon atmosphere. Previously detailed procedures were used to synthesize rac-ethyl

\[ \text{Scheme 1} \]

\[
\begin{align*}
\text{PCCl}_4 & \rightarrow \text{Si} \rightarrow \text{ZrCl}_2 + \text{MAO} \\
\text{PP} & \rightarrow \text{Si} \rightarrow \text{ZrCl}_2 + \text{MAO}
\end{align*}
\]

The polymerization was carried out in a 250-mL crown-capped glass pressure reactor with a magnetic stirring bar. The system was first evacuated and flushed with argon, and then 50 mL of toluene was injected. The reactor was evacuated again and saturated with propylene for ca. 20 min to 15 psig. Triisobutylaluminum (TIBA) and then the catalyst was injected to initiate the polymerization. The order of addition of the reactants given above must be adhered to in order to achieve maximum catalytic activity. The polymerization mixture was quenched with acidic methanol (containing 2% HCl) and filtered off, and the resulting solid was washed with anhydrous methanol, and dried at about 70 °C under vacuum to constant weight.

**Propylene Blends.** The catalyst system 2/MAO/SiO2 was used to give i-PP; a-PP was obtained with the catalyst system 3/MAO/SiO2. These polypropylene samples were combined to prepare blend specimens.

The solution-cast blend was prepared by codissolving i-PP and a-PP in the desired ratio under nitrogen atmosphere in one of three solvents: toluene (bp 110.6 °C), xylene (bp 137.8 °C), or mesitylene (bp 164.7 °C). The PP solution was poured into a Teflon dish, the solvent removed with a Dean Stark trap, and the solid dried under vacuum at 70 °C. About 1 wt % of BHT (2,6-di-t-butyl-4-methylphenol) was added as an antioxidant.

Quenched PP blend specimens were prepared by codissolving i-PP and a-PP in hot toluene under nitrogen atmosphere. This polymer solution was poured into an excess of methanol. The precipitated polymer was filtered and dried at 70 °C in vacuo.

**Physical Characterization of Polymers.** The polymer samples were fractionated with a Soxhlet apparatus to extract different stereoisomers of PP by refluxing acetone, diethyl ether, pentane, hexane, and heptane in a method devised by Pasquin.22 The Tg and heat of fusion \( \Delta H_f \) were measured by differential scanning calorimetry (DSC; Perkin-Elmer DSC4). The sample was annealed at 180 °C for 10 min and crystallized by cooling at a rate of 10 °C/min to 50 °C in the instrument prior to recording of the DSC curve.

The crystalline structure of the prepared PP was determined by X-ray diffractometry (XRD; Siemens D-500) using a Ni-filtered Cu Kα X-ray beam excited at 40 kV for 2θ = 2–40° in 0.1° steps. The sample was either recorded as polymerized or as annealed at approximately 120 °C in vacuo for 1 h.

The microstructure of PP was determined with a 13C NMR spectrometer (Bruker AMX-500; 125.77 MHz for 13C) in CD2-
Polymerization by a Single Zirconocenium Catalyst. Stereospecific polymerization of propylene to i-PP was catalyzed with either precursor 1 or 2, while 3 was used in aspecific polymerization to obtain a-PP. Polymerization was performed at 0 °C using 4/TIBA as the cocatalyst. The activity of polymerization for 1/4/TIBA is 1.9 × 10^7 g of PP/(mol of Zr [C3H6]h), the i-PP product, designated as D147 has Tm = 149.5 °C and ΔHf = 17.2 cal/g. Under the same conditions 2/4/TIBA exhibited Ap = 1.1 × 10^7 g of PP/(mol of Zr [C3H6]h). The i-PP obtained (D63) has Tm = 153.4 °C and ΔHf = 20.4 cal/g (Table 1); the higher Tm and ΔHf of D63 than D147 is consistent with the well-known superior stereoselectivity of precursor 2 than 1. The non-selective 3/4/TIBA polymerizes propylene with Ap = 4 × 10^7 g of PP/(mol of Zr [C3H6]h) to give a-PP (D55).

Polymorphism by Homogeneous Binary Zirconocenium Catalysts (HBC Systems). Propylene polymerizations were carried out with either the HBC (2,3) or the HBC (1,3) catalyst in solution, where the numbers in the parentheses specify the precursors used. The reproducibility of polymerization was tested by running quadruplicates using the following conditions: 2 = 4 μM, 3 = 6 μM, 4 = 11 μM, [TIBA] = 6 mM, Tp = 0 °C, and P1/4 = 15 psig, in 20 mL of toluene. The polymer yields after 10 min of polymerization were 1.96, 2.22, 1.79, and 1.63 g for an average of 1.90 ± 0.32 g. The Ap values were 4.4 × 10^7, 4.9 × 10^7, 4.0 × 10^7, and 3.6 × 10^7 g of PP/(mol of Zr [C3H6]h) for an average of (4.23 ± 0.55) × 10^7 g of PP/(mol of Zr [C3H6]h). The ±13% deviation in Ap is considered to be good reproducibility for Ziegler–Natta polymerizations under these conditions. The propylene polymer produced has Tm values of 150.3, 150.9, 150.9, and 150.9 °C for an average of 150.7 ± 0.3 °C; the ΔHf values were 2.4, 2.6, 2.9, and 2.5 cal/g for an average of 2.6 ± 0.2 cal/g.

Both HBC systems were used to polymerize propylene at ratios of 1 to 2 or 3 from 8:2 to 1:9 with several experimental conditions. The results are shown in Tables 2 and 3. The catalytic activities of these binary systems (Ap,c) listed in column 10 of both tables, lie in the range of (1–10) × 10^7 g of PP/(mol of Zr [C3H6]h). These may be compared with expected Ap,c calculated from single metallocene polymerization activities. In the case of 1/3/4/TIBA, it is

\[ A_{p,c} = m_1 A_{p,1} + m_2 A_{p,2} + m_3 A_{p,3} \]  

where m1 and m3 are the mole fractions of 1 and 3, and A_{p,1} and A_{p,3} are their respective individual propylene polymerization activities. The Ap,c values are in good agreement with the Ap,c values. This is also the case for a similar comparison of the 2/3/4/TIBA catalyst system.

The single metallocene 2 produces i-PP with ΔHf = 20.4 cal/g. If this component forms the same i-PP in the presence of 3 in an HBC polymerization, then the expected ΔHf,c of the product would be

\[ \Delta H_{f,c}(2/3) = \frac{m_2 A_{p,2}}{m_2 A_{p,2} + m_3 A_{p,3}} \times 20.4 \text{ cal/g} \]

The expected ΔHf,c of the product obtained with HBC (1,3) would be
The physical state of the HBC-PP undergoes systematic change as its ΔH_{f,0} deviates from the enthalpy of fusion expected by eq 2 or eq 3: ΔH_{f,i} = ΔH_{f,c} − ΔH_{f,0}. When ΔH_{f,i} ≤ 0, the material resembles i-PP. As ΔH_{f,i} increases, the material assumes a leathery state and then becomes an elastomeric material. Finally, for HBC comprising an excess of C_{2v} metallocene 3, a gummy product was formed, which is predominantly amorphous PP.

The molecular weight distribution of PP formed by HBC is always broader than that of the homogeneous catalysis, but the cause is as yet uncertain. For instance, some zirconocene (precursor or cation) may reside in pores of silica which are too small or are overloaded with catalyst for the monomer to have easy access to the active center. There may also be side reactions between zirconocene species and the Brønsted acidic hydroxyls or the Lewis basic oxides to diminish the activity or even to alter the direction of stereoselection. For instance C_{2} symmetric anza-zirconocene supported on SiO_{2} can have greatly enhanced stereospecificity. In the case of C_{3} symmetric anza-zirconocene, its normally syndiospecific catalysis was changed to isotopic upon immobilization on silica.

Table 2. Propylene Polymerizations\(^a\) Catalyzed by the HBC(2,3) System\(^b\)

<table>
<thead>
<tr>
<th>run no.</th>
<th>1(^{[2]})</th>
<th>2(^{[2]}) (µm)</th>
<th>3(^{[2]}) (µm)</th>
<th>4(^{[2]}) (µm)</th>
<th>[TIBA] (mM)</th>
<th>T(_p) (°C)</th>
<th>time (min)</th>
<th>yield (g)</th>
<th>(A_p \times 10^{-7}) (g of PP/mol of Zr [C_{2v}H_{4}]), obsd</th>
<th>(A_p \times 10^{-7}) (g of PP/mol of Zr [C_{2v}H_{4}]), calcld</th>
<th>(\Delta H_f (\text{cal/g})), obsd</th>
<th>(\Delta H_f (\text{cal/g})), calcld</th>
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\(\Delta H_{f,c}(1,3) = \frac{m_1A_{p,1}}{m_1A_{p,1} + m_3A_{p,3}} \times 17.2 \text{ cal/g} \) (3)

However, the observed ΔH_{f,0} values are usually in discord with ΔH_{f,c} the variance appears to be influenced by the amount of TIBA present in the polymerization. For instance the PP’s in Table I produced with small amounts of TIBA (4 mM) are slightly more crystalline than that expected for [2] \(\ll\) [3] runs, where the deviation became negligible at [2] \(\ll\) [3]. In the presence of high [TIBA] (6 mM), the rate of polymerization is enhanced and the polypropylene formed is highly elastic (vide infra). The products have much lower crystallinities than expected for [2] \(\gg\) [3]; the crystallinity became greater at [2] \(\ll\) [3]. Similar behaviors were manifested for catalysis by HBC(1,3) (Table 3).

**Supported Metallocene Catalyst.** Propylene was polymerized in the presence of a supported metallocene catalyst. SD3 is a catalyst of 2 supported alone on silica. At 0 °C using SD3 containing 60 µmol of Zr, activated with equal amount of 4 and 5 mM TIBA in 20 mL of toluene, propylene polymerized at an \(A_p\) of 5 \times 10^6 g of PP/mol of Zr [C_{2v}H_{4}]. The product has \(T_m\) = 153.9 °C and \(\Delta H_f = 17.3 \text{ cal/g}\). The activity of silica-supported metallocene is generally an order of magnitude lower than that of the homogeneous catalysis, but the cause is as yet uncertain. For instance, some zirconocene (precursor or cation) may reside in pores of silica which are too small or are overloaded with catalyst for the monomer to have easy access to the active center. There may also be side reactions between zirconocene species and the Brønsted acidic hydroxyls or the Lewis basic oxides to diminish the activity or even to alter the direction of stereoselection. For instance C_{2} symmetric anza-zirconocene supported on SiO_{2} can have greatly enhanced stereospecificity. In the case of C_{3} symmetric anza-zirconocene, its normally syndiospecific catalysis was changed to isotopic upon immobilization on silica.
Table 4. Thermal Properties of i-PP/a-PP Blends

<table>
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<th>blend component</th>
<th>sample preparation</th>
<th>T_m1 (°C)</th>
<th>T_m2 (°C)</th>
<th>ΔH_f (cal/g)</th>
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Δ -PP, D-41. a -PP Blends are reported in Table 4. The DSC thermograms are shown in Figure 1. The blend samples have ΔH_f values close to the values calculated by

\[ \text{wt fraction of i-PP} \times \Delta H_{f, \text{i-PP}} \]  

using 20.4 cal/g for \( \Delta H_f \) of the i-PP of this system. The agreement is indicative of macrophase separation into large crystalline domains. However, the \( T_m \) values of the blends are generally lower than that of the i-PP D41, and some of the thermograms even display two \( T_m \) peaks, which suggests the presence of smaller phase domains. The methanol-quenched blend exhibits the highest \( T_m \) among the blend specimens, which is interpreted to mean the absence of appreciable phase boundary mixing. The solution-cast blends have a lower \( T_m \) value which decreases as boiling point of the solvent increases. This suggests more mixing at phase boundaries and small crystallite sizes for specimens cast at high temperature.

Mesitylene solution-cast blend specimens were prepared with i-PP:a-PP ratios of 5:5, 3:7, and 1:9 designated as mix 9, mix 10, and mix 11, respectively. The first two materials exhibit two melting peaks; the lower \( T_m \) is found in the vicinity of 139 °C. This transition is too weak in mix 11 to be discerned. The upper transition increases in temperature as the a-PP content increases. However, the magnitude of \( \Delta H_f \) changes in the opposite direction. On the basis of the values of \( T_m \) and \( \Delta H_f \), mesitylene solution-cast blends are judged to be better mixed than the other blends in Table 4.

X-ray Diffraction Analysis. The XRD patterns of various PP samples were compared in Figure 2. Pure i-PP is characterized by sharp \( \alpha \)-type crystal reflections (Figure 2a), whereas only a diffuse amorphous halo is seen with a-PP (Figure 2e). The blend in Figure 2b has an XRD pattern which is a superposition of the two patterns indicating the presence of i-PP domains. The i-PP reflections are considerably weaker and broader in the PP synthesized by a supported binary catalyst, which suggests smaller i-PP domains than in the former.
The XRD of HBC-PP D-66 (Figure 2d) did not exhibit sharp reflections but only inflections at the appropriate 2θ positions superimposed on the background halo. Deconvolution analysis (Figure 3) showed the presence of α-type crystallites of the appropriate crystallinity. The expected heat of fusion was found by DSC determination. The broadness of these XRD reflections indicates the crystallites to be of minute dimensions.

**Dynamic Viscoelastic Properties.** Polymeric network formation can be treated rheologically as a gelation process. The formation of a gel is characterized by the emergence of a critical gel which presents an incipient transition state between a viscoelastic liquid (pregel) and a viscoelastic solid (postgel). The time dependence of its relaxation modulus \( G(t) \) features mathematical simplicity and is consistent with experimental observations.

In this study, the solidification of the thermoplastic elastomeric polypropylenes (TPE-PP) sample was investigated using rheology to determine transition temperatures and rates for a wide range of blends with different composition in atactic and isotactic components. The variation of \( G^* \) vs temperature is given in Figure 4. A steplike function of large magnitude characterizes the melting and crystallization of the isotactic component. At the initially high temperatures the materials are viscoelastic liquids characterized by loss moduli mostly greater than storage moduli \( G'' > G' \). This information can be gained from additional plots of \( G' \), \( G'' \) vs frequency (same data in a different representation). The material is thermorheologically simple at these high temperatures: master curve construction and time–temperature superposition apply in the accessible frequency range without indication of morphological change. This analysis will be described elsewhere. At temperatures below \( T_m \), the materials acquire properties of viscoelastic solids; the storage moduli are mostly greater than the flow moduli. Since crystallization progresses with a finite rate which is slower than the cooling rate, materials are not always in equilibrium during the cooling procedure. This can be seen from the differences between cooling and heating scans (compare parts a and b of Figure 4).

D61 PP obtained with HBC has initially the consistency of an heavily cross-linked rubber material with a high elastic modulus. The sample undergoes a phase transition, after which it shows the typical features of a fast relaxing, flowing, and viscoelastic liquid. It behaves in the liquid phase like a compatible blend with a zero shear viscosity close to that of the pure α-PP. Blend mix 10 has almost the same composition and consists of components with the same molar weight as the HBC produced D61 and has a complex modulus below those of the pure constituents. The zero-shear viscosity at the same reference temperature is lower (by 2–3 orders of magnitude) than those of the pure components. This substantially contributes to the observed larger height of the step, and is a behavior which is characteristic for incompatible blends (depression of steady-shear viscosity by 0.5–1 order of magnitude) in the liquid phase. The very large change of \( G^* \) at the transition is then attributed to incompatibility of the broad components resulting in macrophase separation. In contrast D61, during crystallization, forms a co-continuous crystalline phase (to be envisioned e.g. as branched dendrites), penetrating the whole sample volume. This superstructure adds to the elasticity. The macrophase-separating blend, on the other hand, shows probably only spherulitic growth in the atactic matrix. The less branched superstructure yields less strength and lower moduli under same conditions of observation.

The PP obtained with a HBC such as 2/3 should produce, at 0 °C, i-PP and a-PP by the corresponding zirconocene species of 2 \( \times \) 10^8 and 5 \( \times \) 10^6 molecular weight, respectively, in amounts proportional to a 2:3 ratio. Figure 5 contains the \( G^* \) vs \( T \) data for five such polymers; their \( \Delta H_f \) values are given in brackets. The

**Figure 3.** Deconvoluted XRD for D66 of Figure 2d.

**Figure 4.** Complex modulus vs temperature comparison of (a) blend mixture 10, 35 wt % i-PP shown in O; (b) PP D61 made by binary catalyst 2/3 in 2:8 ratio containing ca 41 wt % of i-PP shown in ∆. Key: (A) heating scans at a constant frequency of 10 rad s⁻¹; (B) cooling scans.
results indicate a constancy of the phase transition
temperatures but a strong dependence of the modulus
changes on the composition. There is a direct correla-
tion between phase transition enthalpy and the height
\( \Delta G^* \) step. The results suggest that an increasing
amount of isotactic component leads to the formation
of bigger, better developed, and interconnected crystal-
line domains, which increases the elasticity in the
viscoelastic solid.

The versatility of the present synthesis of TPE–PP
is the free choice of \( C_2 \) and \( C_2 \) symmetric precursors
and the ratio of their concentrations (vide supra), \( T_p \), and
monomer pressure. Figure 6 gives the data for PP
formed by the HBC(1,3) and HBC(2,3) catalyst systems
at three \( T_p \) values. The phase transition temperature and
\( \Delta G^* \) are strongly dependent on both \( T_p \) and on the
\( C_2 \) symmetric precursor. To understand the contribu-
tion from the two factors, polymerizations were per-
formed with the two catalyst systems at the same
\( T_p \) (Figure 7). It is clear that catalyst 2/3 gave a lower
phase transition temperature and \( G^* \) than 1/3. Com-
parison of the behaviors of D154 and D156 in Figure 8,
which were prepared at 25 °C with the D159 in Figure
7, showed the importance of \( T_p \). A lower \( T_p \) gave an
HBC PP with a higher transition temperature.

It is well-established that the molecular weight of PP
catalyzed by 1 or 2 diminishes with the increase of \( T_p \),
whereas a similar dependency is absent for 3/4 for \( T_p < 
70^\circ C \). To show the influence of an increasing concen-
tration of the low MW isotactic component on the
relaxation time spectrum in the liquid phase, the \( G^* \) and
\( G'' \) data are plotted vs \( \omega \) in Figure 9. Compared with
the atactic components at the terminal zones, there is
a steady shift of the curves toward higher frequencies
with an increased content of i-PP for a similar molecular
polydispersity at the same reference temperature. It
indicates a steady shortening of the maximum relax-
tion time, caused by a decrease of average molecular
weight. Figure 9a reveals further the difference be-
tween the HBC-PP D61 synthesized by the binary 2/3
in a 2:8 ratio and a solution-cast blend (“mix-
ture 10”) of the same composition with components
synthesized at the same temperature as D61. The cast
blend mixture has a much lower maximum relaxation
time, resulting in a significantly lower viscosity. It
behaves like a phase-separated or filled material prob-
ably because of the lower degree of interpretation of
atactic and isotactic components than that seen in the
HBC PP.

**Mechanical Testing.** Typical stress–strain curves
obtained from expansion testing on selected materials
(synthesized at 0 °C and molded at 175 °C) are given in
Figure 10a. The HBC-PP (curve a) increases in strength
with strain up to 1100% elongation which is character-
istic of a cross-linked elastomer. The a-PP (curve d)
does not show any yield point, but a nearly perfect stress
plateau until break is considered to be due to the high
degree of entanglement in the high molecular weight
atactic polymer. The application of the high extension

![Figure 5](image5.png) G* vs T in five samples synthesized with HBC(2,3) at 0 °C and by 2 alone (D41) and 3 alone (D55) measured at 10 rad s⁻¹. Numbers in brackets give \( \Delta H_f \) in cal g⁻¹.

![Figure 6](image6.png) G* vs T in sample synthesized by the catalyst and temperature as indicated at 10 rad s⁻¹.

![Figure 7](image7.png) G* vs T in samples synthesized by HBC(2,3) (D159) and by HBC(1,3) (D61) and (D62) at 0 °C.

![Figure 8](image8.png) Same as Figure 7 except for polymerization at 25 °C.
rate of 1000%/min does not allow the material to disentangle in experimental time and to flow. The PP produced by supported binary catalyst SD-4 has decreasing stress with strain after reaching the yield point (curve b). This is consistent with macrophase-separated domains. In the case of the PP blend, (mix 11, curve c) the decrease of strength is greater than in the former. This difference suggests fairly complete phase separation in the blend but some phase boundary mixing for the PP made with supported catalyst.

The mechanical property is of course sensitive to the sample preparation condition. To show the influence of the molding conditions, dog-bone specimens were also press molded at 80 °C; the data from the measurements are given in Figure 10b. Comparison with the results in Figure 10a showed virtually no difference in mechanical behavior for the a-PP molded at different temperatures. On the other hand the PP blend becomes a brittle substance without strength, indicating complete macrophase separation in this specimen. The HBC-PP is slightly weaker but has greater elongation to break in Figure 10b than in Figure 10a. This is consistent with growth of crystals to form stronger cross-links due to annealing effect in the latter. The opposite effect was observed for the PP obtained with supported binary catalyst, suggesting some phase mixing when molded at low temperature. Annealing at higher temperature promoted phase separation for this material.

The mechanical strength is dependent on the crystallinity of the HBC-PP. Figure 11 shows that an increasing content of i-PP increases Young's modulus. Simultaneously, the elongation to break drops from nearly 2000% to about 400%. With the exception of D52, which is too tough and slips at the grip, none of the other materials shows a yield point. If the different materials are compared, the observed stress plateau kept increasing with the content of isotactic component at high concentrations of i-PP, with a steady increase of stress until material failure was detected. The high moduli and plateau stresses of the three HBC polymers are regarded as due to the cross-linking effect of the interpenetrating crystalline structure of the i-PP. The observed increasing tendency in stress becomes stronger.
The failure occurs at a lower strain than for the Young's modulus but low stress plateau at large strains. (mix 11) further points to the influence that the degree of crystallization with the isotactic content, indicating stress-induced elasticity. The specimen were increased at higher strain, the recovery rate of the polymer was consistent at 97–98% between 100% to 500% elongation. In comparison, a-PP alone or a blend of i-PP with a-PP is virtually without elasticity according to these measurements.

Fractionation and $^{13}$C-NMR Spectra. If the two zirconocene species act completely independently of each other, then HBC-PP should be the same as i-PP/a-PP blend. Yet all the properties compared are very different, which may be explained by the formation of a material capable of compatibilizing i-PP and a-PP in HBC-PP.

Solvent extraction is the established method to separate a heterogeneous polymer specimen into components differing in microstructures.22 Table 5 contains the hexane fractionation results. The i-PP (D147) obtained with the 2/4/TIBA single zirconocene system comprises 5.9% hexane-soluble and 94.1% hexane-insoluble materials. The methyl region of the $^{13}$C NMR spectrum for the hexane-insoluble fraction exhibits only the mmmm pentad resonance. The a-PP sample (D55) is completely soluble in hexane and shows the $^{13}$C NMR spectrum expected for it. The D104 PP sample produced by the supported binary catalyst system is comprised of only hexane-insoluble i-PP and hexane-soluble a-PP, their relative amounts depending on the ratio of the two zirconocenes and on the polymerization condition.

Fractionation of D76, which is produced in the presence of 2/3 in 2:8 ratio activated with 4/TIBA, afforded ca. 90% hexane-soluble and 10% hexane-insoluble polymers. The $^{13}$C NMR spectra of the former (Figure 14b) is the same as that of a-PP (Figure 14a). However, the latter fraction’s spectrum is a superposition of isotactic and atactic spectra (Figure 14c) in a 1:1.3 ratio. Therefore, D76 contains up to 10% of stereoblock copolymer.

To get a closer estimate of the content of stereoblock copolymer in a typical HBC-PP preparation (D52), it was fractionated using several solvents. Table 6 showed that about half of the D52 was soluble in diethyl ether, which has a $^{13}$C NMR spectrum (Figure 15c) for a-PP. There is no material extractable by either pentane or hexane. The heptane-insoluble fraction showed a sharp mmmm resonance with some peaks for the other pentads (Figure 15a). The integrated intensity of the latter is about 11% of the total intensity. If one-fourth of the intensity in the m region is attributed to the atactic sequences and is subtracted from the total spectrum, then a content of approximately 6.5% stereoblock PP (sb-PP) can be estimated in this heptane-insoluble fraction. Finally, the $^{13}$C NMR spectra of the heptane-soluble but hexane-insoluble fraction (Figure 15b) exhibits both a sharp mmmm peak and atactic peaks, which corresponds to mm, mr, and rr triads for elongation, after relaxation, and at maximum elongation, respectively. Although the residual expansion of the specimen were increased at higher strain, the recovery rate of the polymer was consistent at 97–98% between 100% to 500% elongation. In comparison, a-PP alone or a blend of i-PP with a-PP is virtually without elasticity according to these measurements.

**Table 5. Hexane-Fractionation Results of Isotactic/Atactic Polymer**

<table>
<thead>
<tr>
<th>polymer (run no.)</th>
<th>$\Delta H$ (cal/g)</th>
<th>$C_2$-soluble fraction</th>
<th>$C_2$-insoluble fraction</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>wt %</td>
<td>% [mmmm]</td>
<td>wt % [mmmmm]</td>
</tr>
<tr>
<td>i-PP (D147)</td>
<td>20.4</td>
<td>5.9</td>
<td>&lt;2</td>
</tr>
<tr>
<td>HBC-PP (D76)</td>
<td>2.3</td>
<td>89.8</td>
<td>2.4</td>
</tr>
<tr>
<td>SBC-i-PP (D104)</td>
<td>4.5</td>
<td>74.7</td>
<td>3.0</td>
</tr>
<tr>
<td>a-PP (D55)</td>
<td>0</td>
<td>100</td>
<td>&lt;2</td>
</tr>
</tbody>
</table>

*Supported binary zirconocene catalyst SD4.
0.5% stereoblock materials. Therefore, there is a total of about 7% stereoblock polymers in D52.

The finding of sb-PP among the products of single-site catalysis is unexpected even for HBC systems (vide infra). The stereorigid ligand framework of the ansa-zirconocene would preclude oscillation between rac-like and meso-like sites as proposed by Waymouth et al.\textsuperscript{17} for nonbridged, sterically encumbered zirconocenes.

Possible Mechanisms of Formation of Stereo-block Polypropylene. It is interesting and useful for the stimulation of further research to speculate on possible mechanisms by which sb-PP is formed in the present investigation. One possibility is that a growing chain undergoes $\beta$-hydrogen transfer to eliminate an $R$-olefin molecule of a certain molecular weight from one type of catalytic site which then reinserts into a catalytic site of another type. This is said to take place in the case of Dow's INSITE technology.\textsuperscript{29} Dow's "constrained geometry catalyst" has a sterically open active center which is particularly favorable for the insertion of oligo-$\alpha$-olefin to form polyolefins with long chain branching. The precursors of this work are not known to incorporate oligo-$\alpha$-olefins. In fact, precursor 4 specifically has little or no facility to polymerize olefins having four or more carbon atoms.\textsuperscript{14}

We recall that the dominant mechanism of chain termination in the heterogeneous TiCl$_3$ type Ziegler-Natta catalyst is transfer to aluminum alkyls.\textsuperscript{2,30} In contrast, with a metallocene catalyst, when used with a MAO cocatalyst, with metal alkyl chain transfer is superseded by the $\beta$-hydrogen elimination process of chain termination. In the present case, the metallocene species are formed\textsuperscript{10d} by alkylation of the zirconocene dichloride with trialkyl aluminum ($R_3$Al) followed by alkyl anion extraction by 4. When $R_3$Al is present in excess, it can promote the exchange of polypropylene chains between the two kinds of active centers and $R_3$Al to result in the formation of sb-PP. Siedle et al.\textsuperscript{31} had employed $^{13}$C NMR to demonstrate the occurrence of exchange of methyl groups between (CH$_3$)$_3$Al and Cp$_2$Zr(CH$_3$)$_2$, [C$_5$(CH$_3$)$_5$]$_2$Zr(CH$_3$)$_2$, Ind$_2$Zr- (CH$_3$)$_2$, or Me$_2$Si(C$_5$H$_4$)$_2$Zr. The authors proposed the participation of zirconocene species in this type of exchanges, especially when MAO is the alkylaluminum compound.

Direct site-chain interchange between zirconocene species may also be important. An X-ray molecular structure had been determined for the catalytically active dimeric \{Cp'ZrMe$_3$(Me)MeZrCp'\}[MePB]{. This is a model structure of an intermediate for site-chain exchange between a zirconocene alkyl and a zirconocenium alkyl species.\textsuperscript{32} Radioactive isotopic labeling demonstrated that ansa-zirconocenes are nearly quantitatively converted to their active zirconocene species by cocatalyst 4/TiBA even at low temperature.\textsuperscript{10e} Similar transformations occurred with non-bridged\textsuperscript{33} and ansa-zirconocenes\textsuperscript{10c} by MAO at ambient or higher temperatures. In such cases direct site-chain interchange may involve two zircono-
### Table 7. Comparison of el-PP

<table>
<thead>
<tr>
<th>el-PP type</th>
<th>Elongation</th>
<th>Tensile set</th>
<th>% Recovery</th>
<th>% I-PP</th>
<th>ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>B</td>
<td>300</td>
<td>82–93</td>
<td>69–73</td>
<td>~60</td>
<td>6b</td>
</tr>
<tr>
<td>A</td>
<td>300</td>
<td>30–50</td>
<td>83–90</td>
<td>18</td>
<td>4</td>
</tr>
<tr>
<td></td>
<td>300</td>
<td>50–120</td>
<td>60–83</td>
<td>39</td>
<td></td>
</tr>
<tr>
<td></td>
<td>300</td>
<td>100–200</td>
<td>33–60</td>
<td>93</td>
<td></td>
</tr>
<tr>
<td>C</td>
<td>100</td>
<td>90</td>
<td>15,16</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>200</td>
<td>86</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>300</td>
<td>81</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>D</td>
<td>300</td>
<td>50</td>
<td>83</td>
<td>17</td>
<td></td>
</tr>
<tr>
<td>E</td>
<td>300</td>
<td></td>
<td>97</td>
<td></td>
<td>present work</td>
</tr>
</tbody>
</table>

The results are summarized in Table 7. The catalysts employed by Wilson and Job are heterogeneous mixtures. They produce el-PP-B, which comprises isotactic, atactic, and syndiotactic sequences with high tensile set and poor recovery. The el-PP-A described by Collette et al. and blends with i-PP are also poor in elasticity. Both el-PP-C and D are formed by site-switching catalysts. They have about 80% recovery at 300% elongation. The block lengths are rather short in these sb-PP moieties.

The TPE-PP of this work exhibits excellent elastic recovery which is insensitive to elongation up to 500%. The strength of the material probably derives from the high molecular weight of the a-PP (500 000) and of the i-PP (180 000), bound together by sb-PP into highly branched (dendritic) superstructures.

The present HBC synthesis of el-PP is very versatile. By selecting the appropriate C2 and C3 symmetric metallocenes, elastic materials of desired molecular weights and stereoregularity can be produced which have desired phase transition temperature, Young's modulus, elastic recovery, and other properties. For a given C2 symmetric stereorigid precursor, polymerization conditions such as Tm, [monomer], [H2], [catalyst], and solvent polarity can be utilized to fine tune the structure and properties of the crystalline component, as had been detailed for 10a and 2. Furthermore, similar influences on the structure of a-PP can be affected by experimental conditions as reported for 3,36 The combined effects of the conditions of polymerization can produce many types of naturally compatible blends of i-PP/a-PP as shown in Tables 1 and 2.

The principles described above have been extended to synthesize other naturally compatible blends such as s-PP/a-PP and s-PP/i-PP.37

Previously mixtures of titanocene and zirconocene and of zirconocene and hafnocene were employed with MAO cocatalyst to synthesize polyethylene having bimodal molecular weight distribution. GPC chromatograms of the product were faithful superpositions of similar polymerization using the two metallocenes separately. Neither the structure nor the properties of polyethylene would be noticeably affected by site-chain interchange except for a narrowing of molecular weight distribution as compared to the total absence of site-chain interchange for HBC polymerization.

### References and Notes

(2) Natta, G.; Mazzanti, G.; Crespi, G.; Moraglio, G. Chim. Ind. (Milan) 1957, 39, 27.
(7) Job employed a variety of reagents to modify the reaction of Mg(OCl)2 and TiCl4 to form catalysts which produce el-
PP having predominantly syndiotactic sequences and minor amounts of isotactic and atactic sequences.
