Supported Constrained-Geometry Catalysts on Cross-Linked (Aminomethyl)polystyrene: Studies of Ethylene and 1-Octene Polymerizations

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The reaction of TiCl₄ with (chlorodimethylsilyl)(trimethylsilyl)cyclopentadiene results in the chemoselective elimination of Me₃SiCl and cleanly affords ((chlorodimethylsilyl)cyclopentadienyl)titanium trichloride (2). Likewise, the reaction of TiCl₄ with (chlorodimethylsilyl)(trimethylsilyl)tetramethylcyclopentadiene (6) also results in the chemoselective elimination of Me₃SiCl and cleanly affords ((chlorodimethylsilyl)tetramethylcyclopentadienyl)titanium trichloride (7). This observation is in sharp contrast to the reaction of 6 with ZrCl₄, which results in the chemoselective elimination of Me₃SiCl but affords a mixture of half-sandwich and zirconocene complexes. Support of complex 2 or 7 on (aminomethyl)polystyrene (AMPS, 1% cross-linking, 1.3 wt % N, 0.928 mmol of N/g of support), where the molar ratio of amine content of the support to precursor catalysts was selected to be 3:1, leads to the assembly of the constrained-geometry catalyst (CGCs) 8 or 9, respectively. From the ²⁹Si NMR, the presence of a single silicon species was observed in complex 9, which has been attributed to the CGC form. However, for 8 two silicon resonances were observed, one of which has been attributed to the CGC form and the other to a titanium amide moiety. The Ti:Si:Cl ratio for both 8 and 9 was found to be 1:1:4 through elemental analyses. Complexes 8 and 9, in conjunction with MAO as the cocatalyst, were tested for ethylene homopolymerization and ethylene/1-octene copolymerization. The thermal properties and the molecular weights of the resulting polymers were determined. The observation of ethylene-co-1-octene copolymer provides independent evidence for the formation of supported CGC from the synthetic protocol.

Introduction

Numerous efforts are being directed toward the synthesis of single-site catalyst (SSC) architectures for the polymerization of olefins to produce high-density polyethylene and branched polyethylene as well as isotactic and syndiotactic polypropylenes.¹⁻⁴ One subclass of SSCs comprises the constrained-geometry catalysts (CGCs), containing a cyclopentadienyl ring and an amido ligand, linked together with a dimethylsilyl unit.⁵⁻¹⁰ These catalysts are alternatives to the well-known Brintzinger and Kaminsky ansa-metallocenes.

Due to their open nature, CGCs are able to very efficiently polymerize α-olefins. Polyolefins made using these catalyst systems in homogeneous media have been studied extensively.¹¹

There are several different strategies by which the CGCs have been synthesized. One route is to synthesize [C₅R₄HSiMe₂NR′]¹¹¹ (R = CH₃, H) from (C₅R₄H)SiMe₂Cl and R‘NH Li with subsequent removal of lithium chloride. The basic ligand framework of constrained-geometry catalysts can then be obtained by metathetical reaction of the dilithium salt of 1 with MCl₄ (M = Ti, Zr) (Scheme 1, method A).⁵,⁸,¹² This route leads to a low yield of 3A, which has subsequently been improved by the use of TiCl₃(THF)₃/PbCl₂,¹³ while 3B is obtained in good yield. Other preparations include amine elimination from the reaction of homoleptic metal amides with 1 (Scheme 1, method B).¹⁴,¹⁵ In this preparative method, the eliminated amine is found to coordinate to the metal center. Reduced ethylene polymerization activity has been observed when these catalysts systems have been

used, and this could be attributed to inefficient activation of these metal amides by the cocatalyst and presence of coordinated amines.\textsuperscript{16,17}

An alternate synthesis involves the initial formation of the chlorodimethylsilylestimated monosilylcyclopentadienyl)trimethylsilyltitanium complex \( \text{eq 1} \). To date, this synthetic approach to CGC formation has been studied only in the case of the reaction of precursor catalyst \( \text{eq 2} \) with tert-butylamine. The scope of this synthetic approach to the formation of CGCs has been limited by the availability of suitable precursors.

Commercial polymerization processes using soluble SSCs have been utilized to synthesize elastomers and low-crystallinity polyolefins, which remain soluble throughout the polymerization process. In gas-phase, slurry, or bulk polymerization, the polyolefin produced is insoluble in the fluidizing gas or reactor diluent/liquid. Therefore, to operate in a continuous process, catalyst particles of uniform size and shape need to be fed continually into the reactor, thus making it necessary to support the catalyst on an insoluble solid matrix.\textsuperscript{20}

Metallocenes have been supported on organic, typically polymeric, and inorganic materials. Cyclopentadienyls containing silyl moieties have been used as anchoring points for metallocene complexes on silica supports.\textsuperscript{21,22}

In general the polymerization activity of these supported metallocenes has not been as high as that for the corresponding homogeneous systems. Interestingly, polyolefins of ultrahigh molecular weight and increased crystallinity have been observed when metallocene-supported systems have been utilized.\textsuperscript{23–25} In contrast to the large number of studies correlating the structure of the metallocene or CGC with the resulting catalyst performance and resulting polymer properties,\textsuperscript{10,26} the systematic investigation of heterogenized CGCs is not nearly as comprehensive.\textsuperscript{27–29}

Adaptation of the assembly protocol of Royo to the use of primary amine functionalized solid supports with precursor catalysts should provide a synthetic route to CGCs. Toward this goal, we have synthesized chlorodimethylsilyltrihexylsilyl derivatives of cyclopentadienes and investigated the silyl elimination chemistry with TiCl\(_4\) and ZrCl\(_4\) to provide precursor catalysts. Their reaction with (aminomethyl)poly styrene (AMPS) results in the formation of heterogenized CGCs. The immobilized CGCs have been investigated for ethylene homopolymerization and ethylene/1-octene copolymerization.

**Results and Discussion**

(Trimethylsilyl)tetrachlorotetranylenecyclodienec was deprotonated using MeLi in a mixture of ether and toluene at room temperature with constant stirring overnight. The addition of an equimolar amount of (CH\(_3\))\(_3\)SiCl\(_2\) affords (chlorodimethylsilyl)(trimethylsilyl)tetrachlorotetranylenecyclodienec, which was isolated by the removal of solvents in vacuo to yield a dark yellow viscous liquid in good yield and high purity. For the reactions of \( \text{eq 6} \) with MCl\(_4\) (\( M = \text{Ti, Zr} \)) there exists the question of chemoselectivity of the chloroalkylsilane eliminated. Literature precedence for the reaction of the mixed-silyl cyclopentadiene ((CH\(_3\))\(_3\)Si)((CH\(_3\))\(_2\)SiCl)\(_2\)C\(_6\)H\(_5\)) with TiCl\(_4\) demonstrated that there is chemoselective elimination of (CH\(_3\))\(_3\)SiCl and exclusive formation of \( \text{eq 2} \). Compound \( \text{eq 6} \) on treatment with TiCl\(_4\) in dichloromethane at room temperature for 3 days resulted in the exclusive formation of \( \text{eq 7} \) as a dark red solid in good yield (eq 2). In the \( \text{\textsuperscript{1}H} \) NMR spectrum of the reaction mixture of \( \text{eq 6} \) and TiCl\(_4\) with MeLi in toluene at room temperature, a peak at \( \delta 1.97 \) ppm due to the methyl group of the silane ligand is observed.

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The titanium precursor catalysts 2 and 7 have been treated with cross-linked (aminomethyl)polystyrene (AMPS, 1% cross-linking, 1.3 wt % N, 0.928 mmol of N/g of support). The mole ratio of amine content of the support to precursor catalysts was selected to be 3:1. The first amine equivalent of AMPS serves as the primary amine for the assembly of the CGC framework, and the other 2 equiv serves to scavenge the 2 equiv of HCl generated. The reaction of the precursor catalysts with swollen AMPS resin in hot toluene was allowed to proceed for 3 days, followed by numerous toluene washings to remove soluble byproducts and any residual precursor catalyst. The supports were then dried under vacuum at room temperature for a period of 12 h to afford CGC complexes 8 and 9, respectively (eq 3).\(^{33}\)

Moreover, the complete assembly of the CGC framework is indicated by the single \(^{29}\)Si resonance.

The \(^{29}\)Si NMR of 8 showed the presence of two silicon resonances. The resonance at \(\delta = -19.67\) is attributed to the assembled CGC,\(^{30}\) and the resonance at \(\delta = -10\) can be attributed to a species bearing the chlorodimethylsilyl moiety, presumably not the precursor catalyst 2 given the number of toluene washings but rather a titanium amide complex. The elemental analyses showed the Ti:Si:Cl ratio to be 1:1:4, and the N:Ti ratio was found to be 3:1. The loading efficiency of the precursor is quantitative on the basis of both the results from elemental analysis and the infrared spectrum of 8 (KBr pellet), which shows the absence of NH and NH\(_2\) stretches in the region of 3100–3500 cm\(^{-1}\). However, the assembly of the CGC is incomplete, as seen from the \(^{29}\)Si NMR results.

The supported catalyst systems 8 and 9 were tested for ethylene and ethylene/1-octene polymerizations. The cocatalyst used in these polymerization studies was MAO (30 wt % in toluene). An excess of cocatalyst was used to both activate the CGC and to scavenge the ammonium salts formed during the support protocol. Olefin polymerizations were conducted by charging a mixture of 10.0 mL of toluene and 1.0 mL of 30% MAO with a quantity of supported catalyst in a thick-walled glass reactor vessel. The system was pressurized with 60 psig of ethylene for a suitable time period with constant stirring. For 1-octene copolymerization studies the comonomer was added by means of an additional cylinder simultaneously with the ethylene. The ethylene overpressure was delivered into the reactor without the removal of the nitrogen atmosphere. At the end of the polymerization, the ethylene supply was stopped and the reactor was vented. The reaction mixture was quenched by the addition of 10% hydrochloric acid solution in methanol; the polymer was isolated by filtration and dried in a vacuum oven overnight. Experimental conditions, the yield of polymer, polymerization activity, molecular weights, and melting points of the polymers are shown in Table 1.

Using complex 9 in conjunction with MAO in a toluene slurry under 4 atm of ethylene pressure afforded polyethylene (Table 1, entry 1). Thermal analysis of the resulting polymer showed the presence of a unimodal melting peak for HDPE in both the first and second melt scans (DSC) with a final \(\Delta H_f\) value of 56.9 J/g. The degree of crystallinity of this sample is substantially lower than that of corresponding HDPE samples prepared using soluble GC. Presumably, the support is suppressing the crystallinity of the polymers as they are being synthesized. The extent to which a support may influence the degree of crystallinity for polyolefins prepared via heterogeneous SSC at this moment is not known. Molecular weight analysis using GPC of the polymer gives an \(M_n\) value of 529 000 and a PDI of 1.58. The response signals for both light scattering and refractive index detectors were unimodal. The physical characteristics of the polyethylene are fully consistent with the formation of HDPE from an SSC, presumably the heterogenized CGC complex 9. However, it is possible that during polymerization processes using this supported catalyst in slurry mode, fragmentation of cyclopentadienyltitanium moieties may occur.\(^{20,25}\) The
CGCs and leached fragments. Ethylene/1-octene co-
vides a method for discerning between heterogenized
R
with a heterogeneous SSC.
conclusively the form of the active catalyst, or catalysts,
ethylene to HDPE. It is thus difficult to ascertain
resulting solubilized fragments would also polymerize
for ethylene polymerization have been reported for the
attempted detection of leached species from support
metallocene catalysts. Another possible origin of the
HDPE observed in the copolymerization experiments
could be a result of diffusion limitation of 1-octene to a
certain CGC site within the cross-linked polystyrene
bead. However, diffusion limitations of the comonomer
to catalyst sites dispersed throughout the AMPS was
eliminated using a surplus of 1-octene in a well-stirred
solvent—comonomer swollen bead.
The homopolymerization of ethylene using the mixed
catalyst system 8 affords HDPE (Table 1, entry 3).
Soxhlet extraction with refluxing toluene afforded two
fractions, a lower molecular weight sample of lower
crystallinity (PE 3a) and a higher molecular weight
sample with higher crystallinity (PE 3b). This mixture
of PE 3 fractions correlates with the 29Si NMR data, which
showed the presence of two silicon moieties.
The copolymerization of ethylene and 1-octene using
for ethylene polymerization was reported for the
mixed catalyst 8 was performed. Analysis of the
resulting polymer by DSC reveals the presence of two
melting endotherms during the first melt (Table 1, entry
5). These correspond to a mixture of LLDPE and HDPE
fractions. Slow cooling of the melt to ambient temper-
ature followed by a second melting revealed a single
endotherm due to the cocrystallization of LLDPE and
HDPE. The depression in melting point has been
attributed to incorporation of 2.0 mol % of 1-octene. The
polymer was extracted from the support using hot
trichlorobenzene. Molecular weight analysis by GPC
reveals a trace with an overall

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<th>Activity (kg/ (mol of Ti) h (atm of C2H6))</th>
<th>Tm°C (°C)</th>
<th>ΔH (J/g)</th>
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a Ethylene pressure of 60 psig for 120 min. b Ethylene pressure of 60 psig for 45 min. c Second melt of DSC scan. d Monomer incorporation calculated according to ref 31.

resulting solubilized fragments would also polymerize
ethylene to HDPE. It is thus difficult to ascertain
conclusively the form of the active catalyst, or catalysts,
when conducting ethylene polymerization beginning
with a heterogeneous SSC.
The demonstrated ability of CGCs to incorporate
α-olefins during copolymerization with ethylene pro-
vides a method for discerning between heterogenized
CGCs and leached fragments. Ethylene/1-octene copo-
olymerization was used to verify the presence of the
assembled CGC complex 9 on the AMPS support (Table
1, entry 2) and to probe for the presence of leached Ti
species. Thermal analysis of the resulting polymer
reveals two melting endotherms. The lower melting
peak occurs at 119.45 °C and has been attributed to the
incorporation of 1-octene units. It is well-documented
that a depression in melting point occurs with incorpo-
ration of α-olefins in a random fashion. The melting
point has been correlated to the amount of comonomer
incorporated into the HDPE, and this was determined
to be 2.2 mol % of 1-octene, as determined by the
depression in melting point of the copolymer through
dSC and 13C NMR of the copolymer. A higher melting
peak at 135.2 °C has been attributed to the formation
of HDPE. This could be a consequence of an ethylene-
only polymerization catalyst being formed by the ab-
straction of a titanium fragment by the action of MAO.
The observed multimodality of the DSC endotherms
and broadening of GPC peaks that result from the
copolymerization of ethylene and 1-octene is indicative
of multiple catalysts being present during the reaction.
To ascertain that the phenomena of leaching is the
primary reason for the production of HDPE during
copolymerization, the reactions were quenched with
methanol at reaction times ranging from 20 min to 2 h
(Supporting Information, Table 2 and Figures S3 and
S4). The initial formation of LLDPE continues through-
out the course of the reactions, and the formation of
HDPE is observed only at longer reaction times. The
action of MAO on the supported catalysts presumably
leads to a leached Ti species that is selective for ethylene
homopolymerization. On the other hand, precontacting
9 with MAO followed by filtration and use of the filtrate
for ethylene homopolymerization and ethylene/octene
copolymerization indicated a low activity of 10% relative
to the activity for the supported catalysts in ethylene
polymerization. Furthermore, the absence of 1-octene
incorporation in the ethylene/octene copolymerization
experiment using the filtrate is noted. Similar results
silyl elimination reaction of 6 with ZrCl4. The rate of double insertion is comparable to that of half-sandwich formation, leading to the observed mixture of products. The reactivity differences between TiCl4 and ZrCl4 may be attributed to the differences in their size and in the Lewis acidities of the metal centers. Protocols for supporting titanium complexes 2 and 7 on an AMPS matrix, affording catalysts 8 and 9, respectively, have been established. The reaction chemistry of 2 with AMPS results in the formation of a mixture of CGC and a titanium amide. However, the reaction of 7 with AMPS exclusively affords the formation of CGC 9, as confirmed by NMR and FT-IR analyses. Verification of the presence of the support CGC framework is evident by the formation of LLDPE from the copolymerization studies of ethylene and 1-octene. Characterizations of the molecular weight, molecular weight distributions, melting points, and enthalpies of fusion have been determined for these copolymers. The degrees of crystallinity of the polyolefins synthesized from these supported catalysts are substantially reduced relative to polymers produced using soluble CGCs. Copolymerization studies of ethylene and α-olefins provide an easy means for determining the efficiency of support of CGCs. The observation of LLDPE formation during ethylene/1-octene copolymerization using 9 is independent confirmation of the supported CGC form. However, an ethylene-only polymerization catalyst is apparently being formed by leaching of a titanium fragment from 9 at long reaction times. This is the first example of a supported catalyst system wherein the copolymerization ability of the supported and leached species differ such that by means of the leached species from the starting supporting catalyst.

**Experimental Section**

**Reagents and General Techniques.** All reactions were performed under nitrogen in Schlenk glassware or in an inert-atmosphere drybox. All solvents used were obtained from a solvent manifold.32 The chlorosilanes such as (CH3)3SiCl and (CH3)2SiCl2 were distilled from calcium hydride. Tetramethycyclopentadiene, CH3Li (1.4 M in ether), TiCl4, and presublimed ZrCl4 were obtained from Aldrich and used as received. (CH3)2SiCl2 were distilled from calcium hydride. Tetramethylylcyclopentadiene, CH3Li (1.4 M in ether), TiCl4, and presublimed ZrCl4 were obtained from Aldrich and used as received. (CH3)2SiCl2 (3.87 mL, 30 mmol), and the mixture was stirred overnight to ensure complete deprotonation. To this solution was added dropwise (CH3)3SiCl (4.8 mL, 44 mmol), and the solution was stirred for 24 h at room temperature to ensure complete silylation. Lithium chloride was removed by filtering through Celite, and the volatiles were subsequently removed in vacuo; compound 5 was isolated as a pale yellow liquid (6.9 mL, 95% yield).

**Synthesis of 1-(Trimethylsilyl)-2,3,4,5-tetramethylcyclopentadiene (5).** To a solution of 2,3,4,5-tetramethylcyclopentadiene (5.0 mL, 44 mmol) in a mixture of ether and toluene (1:4 v:v, 20 mL total) was added dropwise CH3Li (44 mmol, 3.5 mL), and the resulting mixture was stirred overnight to ensure complete deprotonation. To this solution was added dropwise (CH3)3SiCl (4.8 mL, 44 mmol), and the solution was stirred at 75 MHz using Bruker DPX 300 in the continuously proton rotor at a spinning rate of 4500 Hz. Mass spectral data were obtained on an AMPS matrix, affording catalysts 8 and 9, respectively, and second melt with a heating and cooling scan of 10 °C/min. Infrared analyses were performed using a Perkin-Elmer 2000 FTIR on samples prepared as KBr pellets.

**Synthesis of 1-(Dimethylchlorosilyl)-1-(trimethylsilyl)-2,3,4,5-tetramethylcyclopentadiene (6).** To a solution of 5 (5.79 mL, 30 mmol) in a mixture of ether and toluene (1:4 v:v, 20 mL total) was added CH3Li (30 mmol, 2.15 mL), and the resulting solution was stirred overnight to ensure complete deprotonation. To this resulting solution was added dropwise (CH3)2SiCl2 (3.87 mL, 30 mmol), and the mixture was stirred at room temperature for 3 days. Lithium chloride was removed by filtering through Celite, and the solvents were subsequently removed in vacuo. Compound 6 was isolated as a viscous yellow liquid (7.7 mL, 90% yield).

**Synthesis of 1-(Chlorodimethylsilyl)-1-(trimethylsilyl)-2,3,4,5-tetramethylcyclopentadienyltitanium Trichloride (7).** Compound 6 (3.0 mL, 9.45 mmol) was added dropwise to a solution of TiCl4 (1.8 mL, 9.45 mmol) in 20 mL of dichloromethane, and the reaction mixture was stirred at room temperature for 3 days. Volatiles were then removed in vacuo; the residue was redissolved in 2 mL of dichloromethane to which 4 mL of hexane was added. Recrystallization at –30 °C over a period of 5 days afforded a dark red microcrystalline solid (2.03 g, 89% yield).

**Synthesis of Complex 8.** To a slurry of AMPS copolymer (1 g of XL AMPS, 1.3 wt % of N, 0.928 mmol of N/g of support) in toluene was added 74 mg (0.247 mmol) of complex 2, and

EI (electron impact) mode. Elemental analysis was performed using three Exeter Analytical Inc. 240XA CHN analyzers, and a Leeman Labs Inc.-Dual View-DRE-Sequential-ICP was used to analyze the Ti and Si loadings in the samples. Gel permeation chromatography was performed with Polymer Laboratories PL-220 high-temperature GPC equipped with a Wyatt MiniDawn (620 nm diode laser) high-temperature light scattering detector and refractive index detector at 135 °C using 1,2,4-trichlorobenzene as solvent. The dn/dc value for polyethylene used was –0.11. Thermal analysis was performed using a TA DSC 2910 instrument equipped with a liquid nitrogen cooling accessory unit under a continuous nitrogen purge (50 mL/min). Data reported were gathered for the first and second melt with a heating and cooling scan of 10 °C/min. Infrared analyses were performed using a Perkin-Elmer 2000 FTIR on samples prepared as KBr pellets.
the solution was stirred at 80 °C for 3 days. The support was
then washed with a dichloromethane/toluene mixture (1:4 v:v)
umerous times, and the supported catalyst was recovered and
vacuum-dried overnight at 60 °C, affording 0.8 g of yellow
powder. Anal. Found: C, 80.10; H, 7.95; N, 1.79; Ti, 2.10; Cl,
6.29; Si, 1.4. 29Si NMR (CP-MAS): δ −10.0, −19.67. IR (v, cm−1;
KBr pellet): 3100 (s), 3028 (s), 2922 (s), 2849 (m), 1943 (m),
1872 (s), 1803 (m), 1601 (s), 1492 (s), 1452 (s), 1182 (m), 1155
(m, Si–N stretch), 1027 (m, Ti–N stretch), 907 (m), 840 (w),
697 (s), 467 (w, Ti–Cl stretch).

Synthesis of Complex 9. To a slurry of AMPS copolymer
(1 g, 1.3 wt % of N, 0.928 mmol of N/g of support) in toluene
was added 90.82 mg (0.23 mmol) of 7, and the solution was
stirred at 80 °C for 3 days. The supported catalyst was then
washed with a dichloromethane/toluene mixture (1:4 v:v)
umerous times, and the support was recovered and vacuum-
dried at 50 °C overnight, affording 0.9 g of yellow-orange
powder.

Anal. Found: C, 82.71; H, 7.38; N, 1.21; Ti, 1.5; Cl, 4.76; Si,
1.0. 29Si NMR (CP-MAS): δ −20.75. IR (v, cm−1; KBr pellet):
3010 (s), 2979 (s), 2947 (s), 2882 (w), 2739 (m), 2623 (s), 2605
(s), 2532 (w), 2498 (s), 2359, 1445 (s), 1398 (s), 1365 (m), 1261
(m), 1173 (m, Si–N stretch), 1037 (s, Ti–N stretch), 851 (m),
807 (s), 697 (w), 462 (w, Ti–Cl stretch).

Representative Polymerization of Ethylene using
Complex 8. To a mixture of 10 mL of toluene and 1.0 mL of
30% MAO placed in a polymerization reactor along with a stir
bar was added 25.3 mg of complex 8, and the reactor was
pressurized with 60 psig of ethylene for 2 h at room temper-
ature with constant stirring. After 2 h, the ethylene supply
was stopped and the reactor was vented to remove excess ethylene, the reaction mixture was quenched with a 10% hydrochloric acid–90% methanol mixture, and the polyethyl-
ene was filtered out and dried in a vacuum oven overnight to afford 900 mg of polyethylene (Table 1, entry 5).

Representative Copolymerization of Ethylene and
Octene using Complex 8. To a mixture of 10.0 mL of toluene
and 1.0 mL of MAO in a polymerization reactor was added
112.9 mg of 8. To this system was added 1-octene (5 mL), and
ethylene at a pressure of 60 psig was supplied for 2 h at room
temperature with constant stirring. The ethylene supply was
stopped and the reactor was vented to remove excess ethylene, the reaction mixture was quenched with a 10% hydrochloric acid–90% methanol mixture, and the polymer was filtered out and dried in a vacuum oven overnight to afford 315 mg of product (Table 1, entry 6).

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Supporting Information Available: A table and figures
giving additional data for the ethylene/1-octene copolymer-
ization. This material is available free of charge via the Internet
at http://pubs.acs.org.