Formation of Elastomeric Polypropylene Promoted by Racemic Acetylacetonate Group 4 Complexes

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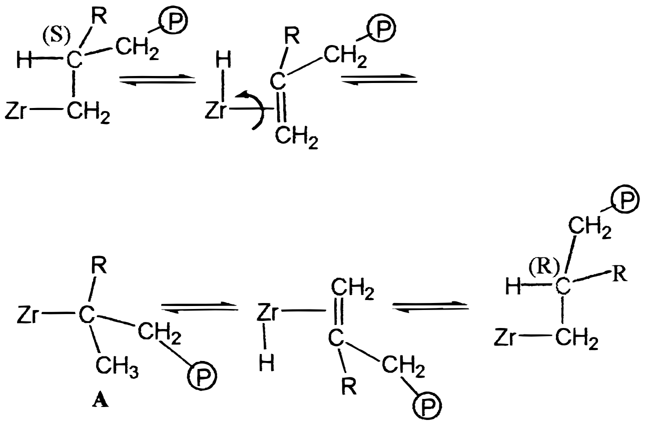
Received November 10, 1999

Summary: Treatment of racemic bis(acetylacetonato) group 4 complexes with MAO yields cationic complexes acting as active catalysts for the polymerization of propylene under high monomeric concentrations. By the appropriate choice of metal and solvent the properties of the polymer products can be tailored, allowing the formation of either elastomer to highly isotactic polypropylene.

During the last two decades, metallocene complexes have been utilized for the efficient polymerization of α-olefins.[1,2] Among the metallocenes, emphasis has been devoted to racemic mixtures, although lately, a large amount of work has been directed toward the constrained-geometry complexes.[3,4]

Recently, attention has been focused on complexes using alternative ligation to the cyclopentadienyl moiety. A few examples are chelating dialkoxides[5] and chelating diamido[6] or chelating benzamidinate[7] ancillary ligands. The catalytic polymerization of α-olefins using chelating bis(benzamidinate) complexes has been investigated by several groups, including ours. These complexes are obtained as a mixture of racemic C_2-symmetry *cis*-octahedral structures. When reacted with methylalumoxane (MAO) or $B(C_6F_5)_3$, these complexes produced an active cationic catalyst for the polymerization of ethylene, propylene, 1-hexene, and 2,5-hexadiene.[7,8]

Scheme 1



For propylene: R= CH_3; Ⓟ = polymer
For 1-octene: R=H ; Ⓟ = $(CH_2)_4CH_3$

In a recent communication from our laboratory,[9] we reported on racemic mixtures of bis(benzamidinate) group 4 complexes as new catalytic systems for the highly stereoregular polymerization of propylene (*mmmm* >95%). We have shown that the stereoregularity can be modulated by the concentration of the monomer in the solution. This result was found to be a consequence of the epimerization reaction of the growing polypropylene chain, at the last inserted monomer, acting as a competing reaction for the monomer insertion (Scheme 1).[10] Raising the monomeric concentration by increasing the propylene pressure has favored the insertion process, as compared to the epimerization pathway, leading to highly isotactic polypropylene, as expected for a C_2 symmetry octahedral complex.

An additional corroboration that the mechanism presented in Scheme 1 is responsible for the stereode-

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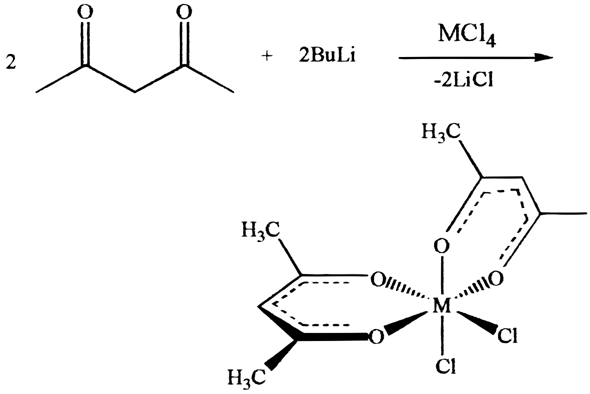
10.1021/om9908985 CCC: $19.00

fects in the polymerization of propylene was achieved by the reaction of benzamidinate complexes with MAO and 1-octene. Under these conditions the polymerization rate is extremely low; therefore, a β-hydrogen elimination is expected to occur either from the methyl group at the β-position in the intermediate complex **A** (R = H, without causing any change in the alkene), or from the β-position at the growing chain, inducing the isomerization of the double bond. We have shown that octahedral benzamidinate complexes are extremely active catalysts for the catalytic isomerization of internal and terminal olefins.[11]

These results have raised the conceptual question regarding any heteroallylic octahedral C_2 group 4 complexes acting as potential precursors for the stereoregular polymerization of propylene. To address this question, we have chosen to generate the catalytic polymerization of propylene using as precursors very simple and inexpensive bis(acetylacetonate) dichloride group 4 complexes.[12]

In this paper we report the activity of new catalytic systems based on acetylacetonate group IV complexes for the polymerization of propylene, producing elastomeric polymers with no parallel formation of atactic fractions. By the appropriate choice of metal and solvent, the stereoregularity of the polymer obtained can be tailored. To our knowledge, this is the first example of the formation of elastomeric polypropylene catalyzed by racemic mixtures of simple acetylacetonate group 4 complexes.[13]

The reaction of $MCl_4(THF)_2$ (M = Ti, Zr) with 2 equiv of lithium acetylacetonate afforded quantitatively disubstituted dichloro group 4 complexes (eq 1).



(1)

1 M= Ti

2 M= Zr

The stereochemistry of dihalo bis(acetylacetonato) complexes of group 4 metals has been the subject of a number of papers.[12] In the absence of any X-ray structural data, stereoisomeric studies have been conducted using NMR spectroscopy, vibrational spectroscopy, and dipole moment measurements, showing in all cases octahedral complexes with the *cis* configuration.[14]

The polymerization of propylene was carried out using precursors **1** and **2**, which were activated by MAO in either dichloromethane or toluene. To this mixture was added propylene under pressure that maintained liquid propylene at all times. After a measured time interval, the reaction was quenched by the addition of HCl/MeOH. Subsequently, the polymer was washed with H_2O and acetone followed by multiple extractions with hot hexane before drying the polymer under vacuum. No atactic polypropylene was observed.

A summary of the polymerization results is shown in Table 1.

The ^{13}C NMR spectrum (Figure 1) of the elastomeric polymer obtained in entry 12 (Table 1) exhibits in the methyl region a high signal (28%) corresponding to the *mmmm* pentad, ruling out the possibility of obtaining high-molecular-weight atactic polypropylene.[15] It is important to point out that in the ^{1}H NMR no vinylidene or internal vinylidene or isobutenyl end groups were observed.[16]

For complex **1** a noticeable increase in activity is observed for the polymerization performed in dichloromethane as compared to toluene (entries 2 and 10). This increase is even more significant when taking into account the fact that the reactions in toluene were carried out under higher concentrations of the catalyst, to obtain enough polymer. This increase in activity may result due to the polarity of CH_2Cl_2 causing a greater charge separation between the putative cationic complex and the MAO anion encouraging the insertion of the monomer.[17,18]

An increase in activity and in molecular weight is observed by using larger amounts of MAO (compare entries 4 and 6). This result suggests that higher MAO concentrations encourage monomer insertions (due to the formation of a more active cationic complex), yield-

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Table 1. Activity and Molecular Weight Data for the Polymerization of Propylene by Bis(acetylacetonato) Group 4 Complexes

entry	T, °C	cat.	solvent	Al:M ratio	pressure, atm	activity[a]	M_w	M_n	M_w/M_n	% *mmmm*	type[e]
1	0	**1**[b]	CH_2Cl_2	400:1	6.1	2.1×10^4	171 475	124 295	1.38	19	elastomer
2	20	**1**[b]	CH_2Cl_2	400:1	10.5	7.3×10^4	116 713	35 178	3.32	22	elastomer
3	50	**1**[b]	CH_2Cl_2	400:1	20.5	2.4×10^5				6	oil
4	20	**1**[b]	CH_2Cl_2	600:1	10.5	6.4×10^4	78 781	49 493	1.59	15	elastomer
5	20	**1**[b]	CH_2Cl_2	800:1	10.5	9.8×10^4	68 902	41 214	1.67	19	elastomer
6	20	**1**[b]	CH_2Cl_2	1000:1	10.5	1.2×10^5	108 451	72 446	1.50	15	elastomer
7	0	**1**[b]	CH_2Cl_2	800:1	6.1	7.5×10^4	112 184	64 778	1.73	14	elastomer
8	0	**1**[b]	CH_2Cl_2	1000:1	6.1	1.3×10^5	109 125	67 780	1.61	11	elastomer
9	50	**1**[b]	CH_2Cl_2	1000:1	20.5	6.2×10^4				5	oil
10	20	**1**[c]	toluene	430:1	10.5	1.9×10^4	167 206	129 346	1.29	15	elastomer
11	50	**1**[c]	toluene	430:1	20.5	1.2×10^4	108 487	65 575	1.65	12	elastomer
12	0	**2**[d]	CH_2Cl_2	480:1	6.1	900	129 139	71 008	1.82	28	elastomer
13	20	**2**[d]	CH_2Cl_2	480:1	10.5	2.3×10^3	106 542	57 324	1.86	19	elastomer
14	20	**2**[d]	toluene	480:1	10.5	9.5×10^3	65 903	53 125	1.24	99	isotactic

[a] In units of g of polymer (mol of cat.)$^{-1}$ h^{-1}. [b] [cat.] = 8×10^{-4} M. [c] [cat.] = 6.4×10^{-3}M. [d] [cat.] = 5.5×10^{-3}M. [e] The type was determined by mechanical studies of the polymers.

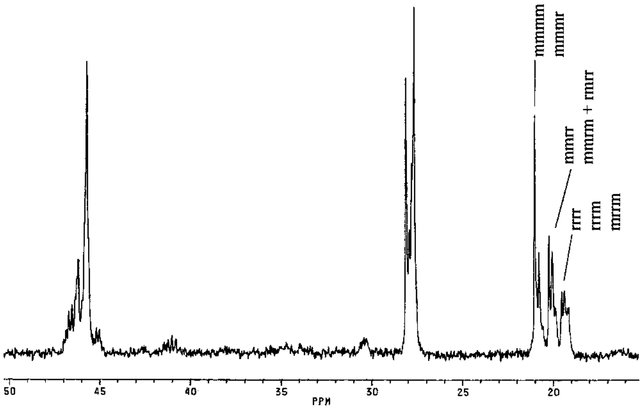

Figure 1. ^{13}C NMR of the elastomeric polypropylene obtained in entry 12 of Table 1: [*mmmm*] = 28.3%, [*mmmr*] = 12.2%, [*mmrr*] = 11.7, [*mmrm*] + [*rmrr*] = 15.0%, [*mrmr*] = 7.8%, [*rrrr*] = 6.0%, [*rrrm*] = 10.5%, [*mrrm*] = 8.5%.

ing polymers with higher molecular weights. In addition, for complex **1**, a higher amount of MAO induces larger amounts of 2,1- and 3,1-insertions as indicated by ^{13}C NMR.[1d]

The temperature effect on the activity is remarkable only for the polymerization in CH_2Cl_2; thus, for complex **1** (entries 1−3) an increase in temperature induces an increase in activity. The polymerization at high temperature (50 °C) in CH_2Cl_2 produces an oily atactic polypropylene (entries 3 and 9). It seems that at this temperature the epimerization reaction is favored over the monomer insertion. To rule out that the complex partially decomposes under these conditions, blank reactions were carried out by heating the catalytic mixture, in either solvent, at 50 °C for a few hours followed by performing the polymerization at room temperature. In all cases the catalytic activity and polymer properties were preserved.

Interestingly, an elastomeric polymer can be obtained at 50 °C simply by changing the solvent from CH_2Cl_2 to toluene, though the increase in stereoregularity is at the expense of the activity (entries 3 and 11). This result is presumably due to the coordinative saturation of the solvent impeding the epimerization process.[4b]

The elastomeric polypropylene obtained by complex **2** at 0 °C (entry 12) has a T_g temperature of −6.7 °C and exhibits a very broad melting region from 137 to 156 °C. Mechanical properties of the polymer indicate a tension strength of $\sigma = 157$ kg/cm^2 when extended by 160%. The polymer shows a remarkable memory effect, returning to its initial position.

To corroborate that the epimerization reaction is responsible for the formation of elastomeric polypropylene, we decided to react complex **1** activated by MAO and 1-octene. This reaction resulted in the rapid isomerization of 1-octene to a mixture of (*E*)-2-octene (64%), (*Z*)-2-octene (4%), (*E*)-3-octene (25%), and (*E*)-4-octene (7%), as well as a myriad of saturated and unsaturated dimers and trimers. This result indicates that during the polymerization the metal is able to migrate through the growing polymeric chain to adjacent carbons, inducing the formation of the *mmrr* and other *xxrr* ($x = m$, r) containing pentads.[13i] The formation of a large number of unsaturated and saturated dimers or trimers gives further evidence for the epimerization mechanism.

Carrying out the polymerization of propylene in CH_2Cl_2 using complex **2** has a temperature effect on the activity similar to that found for complex **1** (entries 12 and 13). It is important to point out that in toluene two polymeric fractions were obtained: a highly isotactic polypropylene (entry 14, mp 156 °C) and an elastomeric polymer, in 76% and 24% yields, respectively. This result argues that in toluene complex **2** may be in two different isomeric forms, allowing for two different polymerization pathways.

In summary, a new approach for the formation of *elastomeric* polypropylene is introduced. Controlling the polymeric product by changing the solvent and metal is presented. The titanium complex was found to be active for the polymerization of propylene to elastomers, whereas for the less active Zr complex highly stereoregular polypropylene is obtained. It seems that one of the most important roles in the stereoregular polymerization of α-olefins is the symmetry of the catalyst, regardless of the nature of the ancillary ligand. This study therefore promotes the development of new octahedral catalysts for new types of polymeric materials.

Acknowledgment. The research was supported by the Israeli Ministry of Science by the Fund for the Promotion of Research at the Technion and by the Technion VPR Fund E. and J. Bishop Research Fund.

Supporting Information Available: Text giving synthetic procedures for the synthesis of complexes **1** and **2** and detailed experimental procedures for the polymerization of propylene. This material is available free of charge via the Internet at http://pubs.acs.org.

OM9908985