$ZrCl_4$ as Catalyst for Olefins and Styrene Polymerization: Effect of Ethereal Donors on the Activity and Stereospecificity

Antonio Proto,*,† Carmine Capacchione,† Oriana Motta,‡ and Francesco De Carlo§

Department of Chemistry, University of Salerno, via S. Allende, 84081 Baronissi (SA) Italy,
Department of Educational Science, University of Salerno, via Ponte don Melillo,
84084 Fisciano (SA), Italy, and Aristea spa Company, via Bosco Fili, 84091 Battipaglia (SA) Italy

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ABSTRACT: Complexes of $ZrCl_4$ incorporating neutral donors such as THF and Et_2O activated by methylaluminoxane have been found to be active homogeneous catalytic systems for the polymerization of ethylene. They also promote the propylene and styrene polymerization with high degree of iso- and syndiotacticity, respectively. The different behaviors in propylene and styrene polymerization using methylalumoxane containing different amounts of $Al(CH_3)_3$ with respect to isotactic propylene and syndiotactic styrene polymerization of these compounds suggest that the presence of neutral Lewis bases on the metal center plays a crucial role on the stereoselectivity of polymerization reaction.

Introduction

In the last few years, the development of nonmetallocene catalysts which promote the polymerization of α-olefins has widely increased.[1] Very high active catalytic systems for ethylene and high stereoselective for propylene and 1-hexene have been discovered inside the "classical" group 4 and, more recently, also among metals belonging to different groups such as groups 8 and 10.[2] Group 4 oxygen-based ligands, in particular those having combinations of bis(phenoxide) and additional donors such as S, N or O, arrange as "high" on the Gibson scale of ethylene activity.[3] The exploration of the coordinative chemistry of many alternative organic compounds has brought forth the development of new monoanionic or dianionic ligands with additional neutral donors. Experimental and theoretical works attribute the high activity of these complexes to the stabilization of the active cationic species due to the interaction between the neutral donor and the metal center.[4] The latest and most interesting examples of these non-metallocenic complexes are no doubt zirconium ones bearing FI ligands,[5] extremely active toward ethylene polymerization, and zirconium complexes bearing tetradentate [ONNO] ligands, which reproduce the symmetric properties of C_2 *ansa*-metallocenes, able to induce isospecific polymerization of 1-hexene[6] and propylene.[7] It is undoubtedly interesting to note that, despite the large interest and the great research endeavors surrounding and involving these new non-metallocenic complexes, there is an almost total lack in the literature of examples of group 4 metal tetrachloride derivatives bearing only neutral donors, and only in a few cases have they been tested in polymerization routes. Zirconium homogeneous Ziegler−Natta catalysts with neutral donors such as esters, were reported in 1989 by Young[8] to promote oligomerization and polymerization of ethylene. In 1996, Eberle[9] showed the structure of $ZrCl_4(THF)_2$ anticipating its potential interest as soluble catalyst in nonpolar solvents. Recently we observed that the presence of an organic Lewis base, such as THF, enhances the syndio-specificity of $ZrCl_4$ methylaluminoxane catalytic system toward the polymerization of styrene.[10] Here we present the results relative to the catalytic performance of $ZrCl_4$, when an additional Lewis base (LB) is present in the coordination sphere of zirconium in ethylene, propylene and styrene polymerizations.

Results and Discussion

(A) Ethylene. In Table 1, the results of ethylene polymerization in the presence of some zirconium compounds and MAO are reported.

As can be noted, $ZrCl_4(Et_2O)_2$ and $ZrCl_4(THF)_2$/MAO are only three times less active than Cp_2ZrCl_2 (Cp = cyclopentadienyl) (see runs 4, 9, and 11) and hundred times more than $ZrCl_4$ (see runs 4, 9 and 10); therefore, they could be considered of "high" rating using the Gibson scale.[1] ^{13}C NMR analysis shows that all these polymers are linear. Calorimetric measurements have been performed in order to analyze the thermal transitions occurring upon heating and cooling, and they show that these polymers have high melting temperatures, whose values are higher than those of the polyethylenes obtained with zirconocenes (see run 11 and 12).[11]

The lifetime of the $ZrCl_4(LB)$/MAO catalytic system toward ethylene polymerization has been investigated by performing the polymerization reaction for different times: 5, 15, 30, 60, 120, and 180 min. As reported in Table 1 the yield, the melting temperature and molecular weight increase with the increase of polymerization time. In Figure 1, the kinetic profile has been plotted, and it shows how the yield increases with time. This behavior demonstrates that the catalyst has rather long lifetime (at least 3 h). The GPC analyses show a broad molecular weight distribution, due to the formation of more than one catalytic species in the reaction between the precatalyst and methylaluminoxane; however, the molecular weight values increase with polymerization time.

(B) Propylene. $ZrCl_4(LB)_2$ complexes, activated by MAO, lead to the production of isotactic polypropylene,

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* Corresponding author. E-mail: aproto@unisa.it. Fax: +39089−965296.

† Department of Chemistry, University of Salerno.

‡ Department of Educational Science, University of Salerno.

§ Aristea spa Company.

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Table 1. Polymerization of Ethylene in the Presence of $ZrCl_4(LB)_2$ Compounds and MAO

run	Al/Zr/(mol/mol)	catalyst/μmol	time/min	pressure/bar	yield/g	activity^e	T_m/°C	10^5M_w/(g/mol)	M_w/M_n
1^a	500	10	5	1	0.28	350	139.6	8.47	10.8
2^a	500	10	15	1	0.65	260	139.7	9.82	5.7
3^a	500	10	30	1	1.10	220	140.6	12.3	5.9
4^a	500	10	60	1	1.94	194	142.3	13.7	5.7
5^a	500	10	120	1	2.40	120	142.8	13.8	5.9
6^a	500	10	180	1	2.90	97	140.0	1.94	3.6
7^b	500	10	5	1	0.21	250	137.4	n.d.	
8^b	500	10	30	1	1.20	240	138.2	n.d.	
9^b	500	10	60	1	2.00	200	139.5	n.d.	
10^c	500	10	60	5	0.95	3.70	n.d.	n.d.	
11^d	500	10	60	1	4.5	458	137.5	n.d.	
12^d	5000	1	60	1	8.0	8000	138.4	n.d.	

[a] All the runs were performed at 50 °C by introducing sequentially in 220 mL of toluene the following reactants: MAO dissolved in 25.0 mL of toluene, $ZrCl_4(THF)_2$ in 5.0 mL of toluene, and ethylene. [b] All the runs were performed at 50 °C by introducing sequentially in 220 mL of toluene the following reactants: MAO dissolved in 25.0 mL of toluene, $ZrCl_4(OEt_2)_2$ in 5.0 mL of toluene, and ethylene. [c] The catalyst is $ZrCl_4$. 10 μmol suspended in 30.0 mL of toluene. The polymerization temperature was 50 °C. [d] The catalyst is Cp_2ZrCl_2. These runs were performed at 50 °C. [e] Activity = g(polymer)/mmol[Zr] × h × bar[monomer].

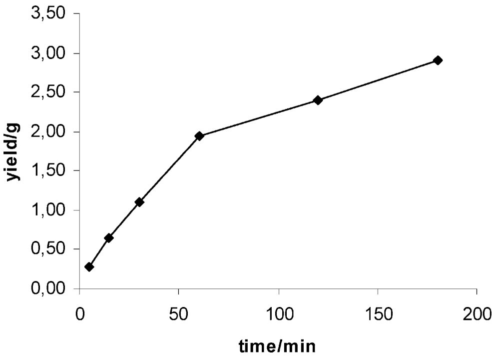

Figure 1. Dependence on the time of the yield.

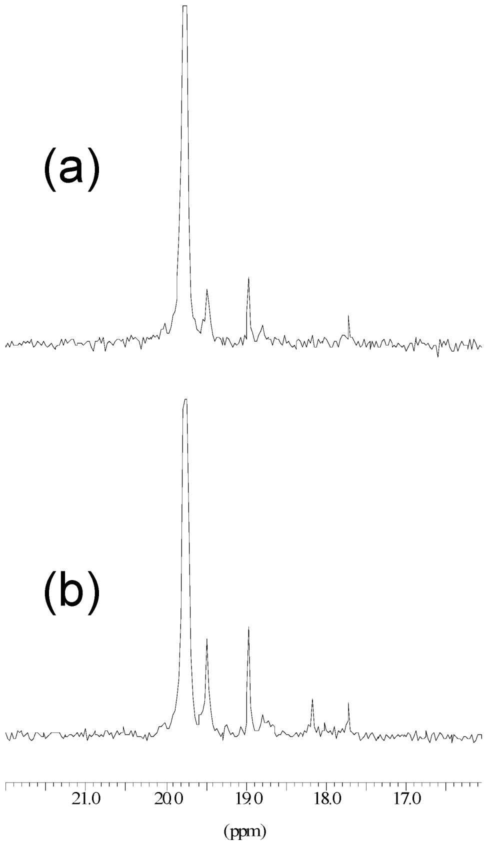

Figure 2. ^{13}C NMR spectra (methylene region is shown) of (a) heptane-insoluble and (b) heptane-soluble fractions of sample 13.

Table 2. Polymerization of Propylene in the Presence of $ZrCl_4(LB)_2$ Compounds and MAO

run	Al/Zr/(mol/mol)	time/min.	yield/g	activity^c	T_m/°C
13^a	1000	120	0.150	0.33	145.8
14^b	1000	120	0.460	0.92	146.1

[a] This run was performed at 30 °C by introducing sequentially in 170 mL of toluene the following reactants: MAO dissolved in 25.0 mL of toluene, 5.0×10^{-5}mol of $ZrCl_4(THF)_2$ in 5.0 mL of toluene, and propylene 5.0 bar. [b] This run was performed under the same conditions as run 13 using $ZrCl_4(Et_2O)_2$ as catalyst. [c] Activity = g(polymer)/mmol[Zr] × h × bar[monomer].

as can be deduced by the analysis of ^{13}C NMR spectra (Figure 2) of polymers reported in Table 2.

The structure of the polymers was determined by NMR analysis comparing the chemical shifts of the resonances with data reported in the literature[12] (Figure 2). Both fractions are relative to regioregular isotactic polypropylene; however, the soluble fraction is less stereoregular than the insoluble one. The resonances at 19.4, 18.9, and 17.7 ppm of methyl carbons are relative to the stereochemical pentads *mmmr*, *mrrm*, and *mmrr*.[13] The relative intensities of the resonances of these pentads are about 2:2:1, as expected from the statistical model of the "*enantiomorphic sites*" of stereospecific propagation.[14] The NMR fingerprints of the heptane fractions of these polypropylenes show that the microstructure is similar to that of the isotactic polypropylene obtained in the presence of group 4 based heterogeneous catalytic systems.[15] During further investigations, it was noticed that the use of different types of MAO led to important variations in polymer properties. Such an effect could depend on the presence of free $Al(CH_3)_3$ present in a commercial solution of MAO.

We thus determined, using a spectroscopic technique reported in the literature,[16] TMA percentage in three different types of MAO prepared as follows:

- MAO1, indicating solid dry MAO obtained from a 30% MAO solution by distillation of toluene and $Al(CH_3)_3$ under reduced pressure at 60 °C.
- MAO2, indicating solid dry MAO obtained from a 10% MAO solution by distillation of toluene and $Al(CH_3)_3$ under reduced pressure at 60 °C.
- MAO3, indicating solid dry MAO obtained from a 10% MAO solution by distillation of toluene and $Al(CH_3)_3$ under reduced pressure, further washing with *n*-hexane, and then drying under vacuum at 60 °C.

This spectroscopic technique exploits the interaction that happens between TMA and tetrahydrofuran to

Table 3. Polymerization of Propylene in the Presence of $ZrCl_4(LB)_2$ Activated by Different Types of MAO

run	Al/Zr/ (mol/mol)	yield/g	activity[c]	heptane-insoluble fraction/%	T_m/ °C	10^5 M_w	M_w/ M_n
15[a]	500 (MAO1)	0.200	0.40	8	137.5	4.61	7.8
16[a]	500 (MAO2)	0.150	0.30	32	145.8	7.34	3.3
17[a]	500 (MAO3)	0.095	0.19	70	162.0	7.04	2.4
18[b]	500 (MAO1)	0.600	1.2	8	138.2	n.d.	n.d.
19[b]	500 (MAO2)	0.460	0.92	35	146.1	n.d.	n.d.
20[b]	500 (MAO3)	0.280	0.56	70	163.2	n.d.	n.d.

[a] All the runs were performed at 30 °C over 120 min by introducing sequentially in 170 mL of toluene thefollowing reactants: MAO dissolved in 25.0 mL of toluene, 5.0×10^{-5} of $ZrCl_4(THF)_2$ in 5.0 mL of toluene, and 5.0 bar of propylene. [b] These runs were performed under the same condition as run 15 by using $ZrCl_4(Et_2O)_2$. [c] Activity = g(polymer)/mmol[Zr] × h × bar[monomer].

solve and integrate the signal of TMA protons, which is normally superimposed to that of MAO protons. TMA percentages determined in these types of MAO are

$$\mathrm{MAO1} = 6.5\%\ \mathrm{of\ TMA}$$

$$\mathrm{MAO2} = 5.3\%\ \mathrm{of\ TMA}$$

$$\mathrm{MAO3} = 3.0\%\ \mathrm{of\ TMA}$$

We then used $ZrCl_4(LB)_2$ with MAO1, MAO2, and MAO3 as catalytic systems in polymerization routes, whose results are reported in Table 3.

As can be noticed from the analysis of data reported in Table 3, an increasing TMA content results in an improvement of the catalytic activity, a lowering of the polymer fractions insoluble in heptane, and a broadening of the molecular weight distribution. These results suggest that TMA content plays an important role in forming the catalytic active species and thus the polymer microstructure, as can be deduced by ^{13}C NMR analysis (Figure 3).

Figure 3 shows how the decrease of meso stereosequences of the polymers is strictly related to the increasing TMA content.

The lowering of polymer melting points could be related both to the decrease of polypropylenes stereoregularity and to a reduction of polymer molecular weights being chain-termination reactions favored by an increasing content of TMA.

(C) Styrene. MAO1, MAO2, and MAO3 have been used as cocatalysts of $ZrCl_4(LB)_2$ complexes also in styrene polymerization, and the results of the experiments are reported in Table 4.

As one can note, the activity and the amount of acetone-insoluble fraction are strongly affected by the amount of $Al(CH_3)_3$ present in the methylalumoxane used, following a trend that is quite similar to that observed in propylene polymerization.

The most surprising experimental evidence is however the "dramatic" effect that the increasing TMA content has on polystyrenes stereoregularities, as can be clearly evicted by the analysis of both quaternary and methylenic carbons regions in ^{13}C NMR spectra of polystyrenes.

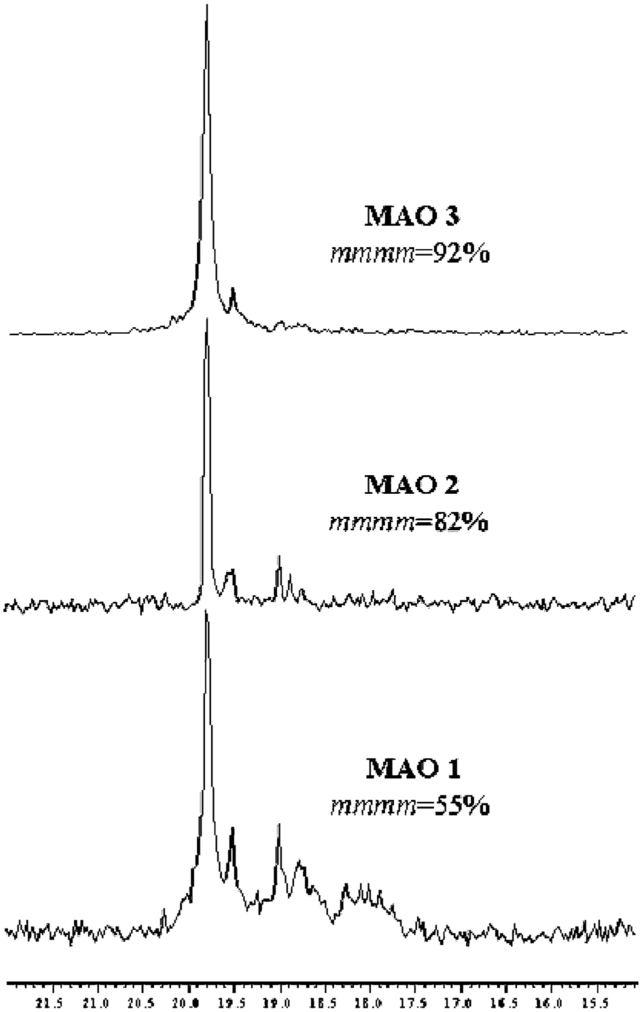

Figure 3. ^{13}C NMR spectra of samples of runs 18, 19, and 20.

Table 4. Polymerization of Styrene in the Presence of $ZrCl_4(LB)_2$

run	Al/Zr (mol/mol)	yield/g	activity[c]	acetone-insoluble fraction/%	$10^4 M_w$	M_w/M_n
21[a]	500 (MAO1)	0.300	3.40	<3	7.9	11
22[a]	500 (MAO2)	0.170	1.93	4	1.3	1.7
23[a]	500 (MAO3)	0.150	1.70	35	1.2	2.2
24[b]	500 (MAO1)	0.120	1.35	3	n.d.	n.d.
25[b]	500 (MAO2)	0.110	1.25	5	n.d.	n.d.
26[b]	500 (MAO3)	0.090	1	40	n.d.	n.d.

[a] All the runs were performed at 50 °C, over 2 h by introducing sequentially the following reactants: 5.0×10^{-3} mol of MAO dissolved in 3.0 mL of toluene, 1.0×10^{-5} mol of $ZrCl_4(THF)_2$ dissolved in 2.0 mL of toluene, and 5.0 mL of styrene. [b] These runs were performed under the same condition as run 21 by using $ZrCl_4(Et_2O)_2$. [c] The activity is expressed in g(polymer)/mmol[Zr]× h × [styrene].

The increasing TMA content leads to a total loss of stereoregularity in the produced polystyrenes. A possible explanation of this catalytic behavior, could be made by considering the different "acid strength " possessed by Al centers in MAO and in TMA, as was also seen via spectroscopic TMA determination.

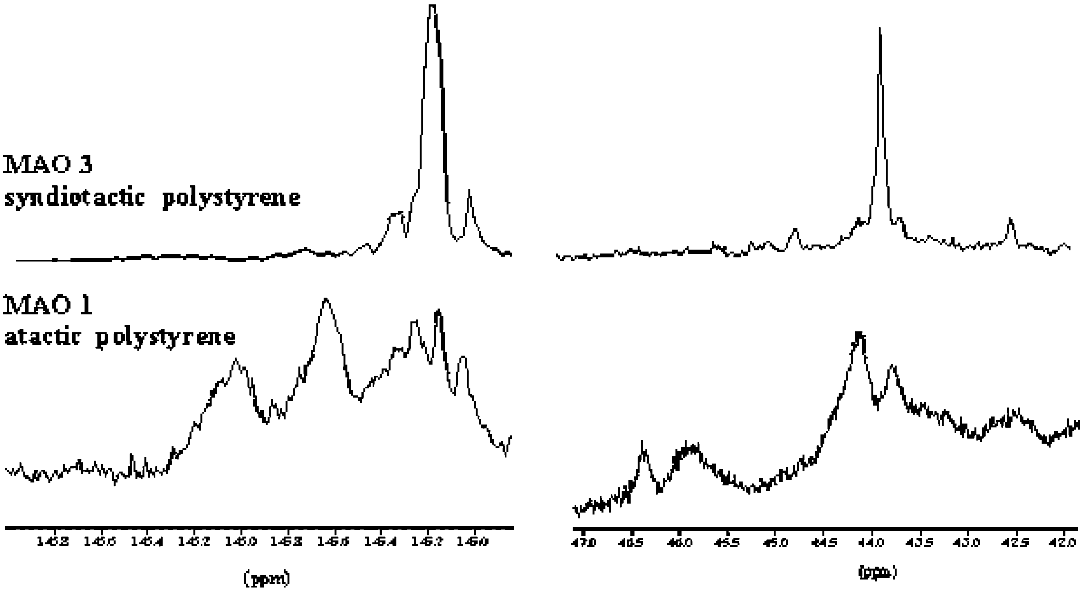

Figure 4. Quaternary and methylenic carbons regions in ^{13}C NMR spectra of samples of runs 21 and 23.

We could thus suppose that TMA, if it is free in the polymerization system, could remove Lewis bases coordinated at the Zr center, leading to the formation of an active species not able to induce stereocontrol in styrene and propylene polymerization. The experimental evidence that the simple ZrCl$_4$, activated by MAO, is an aspecific catalyst of styrene could confirm this hypothesis.

Conclusions

We have performed the polymerization of ethylene, propylene, and styrene in the presence of ZrCl$_4$(LB)$_2$/MAO catalytic systems. The simple introduction of additional neutral donors on the metal center strongly increases the catalytic performance in the ethylene polymerization of ZrCl$_4$. Furthermore, these catalysts are able to produce isotactic polypropylene and syndiotactic polystyrene. The amount of TMA present in MAO does influence the activity toward propylene and styrene polymerization, but, above all, it greatly affects the polymer streospecificity, leading to a reduction of the isotactic index of poypropylenes and to a total loss of stereoregularity in polystyrenes produced. A tentative explanation of this behavior could be attributed to the partial removal from the zirconium coordinative sphere of the LB ligands by the TMA, which possess a stronger Lewis acidity with respect to MAO.

The experimental evidence that the simple ZrCl$_4$, activated by MAO, is an aspecific catalyst of styrene could strengthen this hypothesis, confirming that the presence of the neutral donor on the metal center plays a crucial role in increasing both the activity and stereoselectivity in olefins and styrene polymerization.

Experimental Section

Materials. Toluene (Carlo Erba) was refluxed for 48 h under nitrogen atmosphere over sodium and benzophenone before using. Styrene was treated with CaH$_2$ for 5 h and distilled under reduced pressure before using. Other reagents were purchased from Aldrich and used without purification. Toluene and Al(CH$_3$)$_3$ present in MAO 10% or 30% (Witco) solution were distilled under reduced pressure. The residual white powder was washed with *n*-hexane, dried in a vacuum, and stored in glovebox. The MAO was characterized by the ^{1}H NMR determination reported in the literature.[16]

Polymerization. Polymerizations of ethylene and propylene were carried out in a Buchi 500 mL glass autoclave thermostated with external water flow. Styrene polymerizations were performed in a glass neck flask equipped with magnetic stirrer. The amounts of reagents and the polymerization conditions are reported in Tables 1−3. All of the runs were stopped by injecting ethanol. The polymers, coagulated with acidified ethanol, were washed several times with ethanol and then recovered by filtration and dried in a vacuum at 70 °C. The polymers were fractionated by using a continuous Kumagawa extractor.

Nuclear Magnetic Resonance. The ^{13}C NMR spectra were recorded on an AM 250 Bruker spectrometer operating at 62.89 MHz in a Fourier transform mode at 375 K. The samples of polyethylene and polypropylene were prepared by dissolving in a NMR tube 40 mg of the polymers with 0.5 mL of 1,2-tetrachloroethane-d_2 and 1.0 mL of 1,2,4-trichlorobenzene. Hexamethyldisiloxane (HMDS) was used as an internal standard reference.

The polystyrene samples were dissolved in CDCl$_3$ and the spectra recorded at 290 K.

Gel Permeation Chromatography Analyses. GPC measurements were carried out at 140 °C using 1,2,4-trichlorobenzene as solvent and narrow MWD polystyrene standard sample as reference. The instrumentation used is a PL-GPC 210 with four PL-gel mixed A columns. The analyses were performed by using refractive detector at 800 nm (Viscotek) and H502 viscometer (Viscotek).

Thermal Analysis. The calorimetric measurements were carried out on a Mettler TC 11 differential scanning calorimeter operating under nitrogen flow and calibrated by the measurement of the melting point of indium. The samples were first heated at a rate of 10 °C min to 200 °C and held at this temperature for 10 min to allow the complete melting of the crystallites, then cooled to room temperature. The samples were then heated from 30 to 200 °C at 10 °C min, and the value of melting temperature related to the second heating is reported.

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(13) The polymer of run 13 was fractionated with boiling heptane. Methyl pentads of soluble fraction (65%) are as follows: *mmmm*, 83.1%; *mmmr*, 5.0%; *mmrr*, 4.9%; *mmrm* + *rmrr*, 2.6%; *rrrr*, 2.0%; *mrrm*, 2.4%. Insoluble fractions (35%) are as follows: *mmmm*, 88.0%; *mmmr*, 3.6%; *mmrr*, 3.5%; *mmrm* + *rmrr*, 1.5%; *mrrm*, 1.6%; *rrrr*, not detected.

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