The Effect of Catalyst Isomerization on Polypropylene Properties

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Dedicated to Prof. Helgard G. Raubenheimer on the occasion of his 65th birthday

Two C_2-symmetric metallocene catalysts in solution were exposed to light, and the *rac-meso* conversion followed by NMR spectroscopy. Both exposed and unexposed catalyst solutions were used, in conjunction with a suitable cocatalyst, to polymerize propylene. The polymers were characterized with respect to their microstructure and fractionated according to crystallinity. The relationship between the catalyst isomerization and the polymer structure is illustrated. The effect of pre-activation of the catalyst before exposure to light was also studied and is reported on.

*Key words:* Metallocene, Isomerization, Polypropylene, Fractionation, Tacticity

Introduction

The C_2-symmetric *rac* isomers of bridged bis(indenyl) metallocenes, when activated with a suitable cocatalyst, are useful catalysts for the isospecific polymerization of propylene [1]. The *meso* isomers yield atactic polymers, usually with lower molecular weight [2 – 4].

One aspect that has received little attention lately is the photostability of the catalysts in solution. The photoinstability of the titanocenes was noted in a number of papers [5 – 10], before Kaminsky [1] reported the photoinduced *rac-meso* conversion of bridged bis(indenyl) zirconium dichlorides. According to Bosnich [11], the conversion can be illustrated as shown in Scheme 1.

It is clear that bond cleavage must occur for the transformation to take place. Kaminsky illustrated the *rac-meso* conversion for several substituted bridged zirconocenes [1]. For all these compounds, formation of the *meso* isomer was favoured. The *rac-meso* conversion did not go to completion, but reached a photostationary state, which differed depending on the zirconocene.

Recent papers [12] have indicated that the effect of solution isomerization of these catalysts is often ignored, and prompted a renewed study in our own laboratories to ascertain the effect of exposure to light of catalyst solutions. In particular, we wanted to show that the reaction product ob-
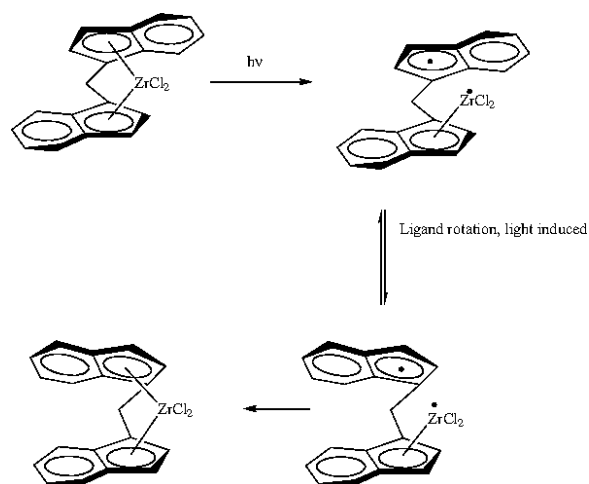
Scheme 1.

tained after using a catalyst solution exposed to sunlight was a mixture of the products of two different catalyst forms. To this end, two different C_2-symmetric catalysts, dimethylsilyl[bis(2-methyl-4,5-benzo-indenyl)]zirconium dichloride (*rac*-[Me$_2$Si(2-Me-4,5-benzoind)$_2$]ZrCl$_2$) (MBI), and ethylene[bis(1-indenyl)]zirconium dichloride (*rac*-Et(Ind)$_2$ZrCl$_2$) (EI) were exposed to UV radiation for set times and the *rac-meso* conversion followed by ^{1}H NMR spectroscopy. Both sunlight and a UV lamp were used as light sources. Similarly, catalyst solutions were exposed to light for the same periods of time used for
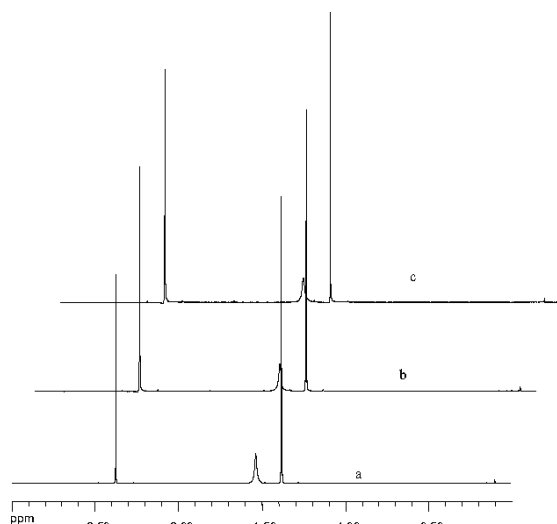
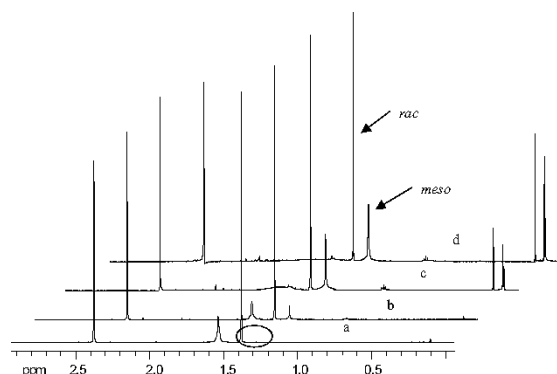Fig. 1. ¹H NMR spectra of MBI solutions (CD₂Cl₂) stored in darkness for (a) 0, (b) 14, and (c) 35 d.

Fig. 2. ¹H NMR spectra of MBI solutions (CD₂Cl₂) exposed to sunlight for (a) 0, (b) 180, (c) 330, and (d) 1500 min.

the NMR experiments and then activated with MAO and used in propylene polymerization. As a last experiment, catalysts were pre-activated with MAO prior to exposure to light and used for polymerization of propylene. Selected polymers were fractionated according to crystallinity.

Results and Discussion

Catalyst isomerization studies

With the MBI catalyst, the *rac-meso* interconversion could quite easily be followed by ¹H NMR spectroscopy, in particular by observing the downfield shift of the peak assigned to the protons of the methyl groups of the dimethylsilyl bridge. In Fig. 1, the ¹H NMR spectra are given for a solution of the
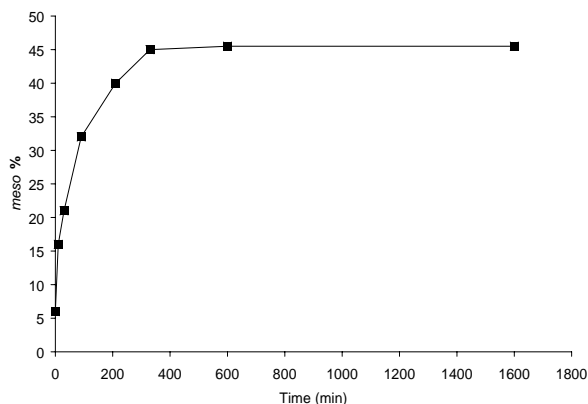

Fig. 3. *meso* Isomer detected as a function of exposure time: MBI catalyst in CD₂Cl₂ solution.

MBI catalyst stored for periods of 0 to 35 d in the dark. In Fig. 2, ¹H NMR spectra of catalyst solutions (MBI), exposed to light for periods of 0 to 1500 min, are shown. The *rac-meso* conversion stopped after about 330 min, but catalyst decomposition increased thereafter. The relationship between the *rac-meso* conversion and the exposure time is shown in Fig. 3. Interestingly, we found no conversion when exposing the catalyst solution to irradiation from the UV lamp.

There is a peak at 1.53 ppm which is due to the presence of a little moisture in the catalyst, while the peak appearing at 0.5 ppm appears to be due to decomposition products.

A photostationary state is reached after about 330 min, and the final *meso:rac* ratio is 1 : 1.17. It appears from the literature that the rate of conversion as well as the level of the photostationary state are dependent on the catalyst as well as on the solvents used [1, 13, 14]. The catalyst solution that was used as a control (stored in the dark) showed no signs of *rac-meso* interconversion or decomposition, even after 35 d. What we found interesting, however, was that the catalyst solutions exposed to the UV light source (257 nm, 15 W) showed no sign of interconversion. Kaminsky [1] reported that exposing the catalyst solution to a 75 W UV lamp of wavelength 336 nm caused more rapid interconversion than daylight. We can only assume that the conversion is wavelength dependent.

In the case of the EI catalyst, no *rac-meso* interconversion was observed. The catalyst did, however, decompose significantly after 210 min of exposure to sunlight. What is significant to us, is that the MBI catalyst showed significant *rac-meso* interconversion after very short periods of exposure to sunlight.

Table 1. Polymerization data.

Run	Al/Zr	Activity[a]	mmmm %	$\overline{Mw}$	MWD	T_m °C
1	6000/1	5500	98	365 764	2.4	152.7
2[b]	6000/1	7430	94	258 450	2.2	152
3	6000/1	7400	92	232 141	3.3	151
4	6000/1	3600	77	140 231	4.2	150
5	6000/1	860	27.5	35 149	4.7	146
6	6000/1	2540	99	804 885	3.6	153
7	6000/1	865	28	38 640	4.7	144

[a] Activity in g PP/g Zr/atm/h; [b] run 2 used double the catalyst concentration of run 1.

Table 2. ^{13}C NMR shifts for methyl sequences in polypropylene.

Pentad	δ (exp.) (ppm)	δ (calc.) (ppm)	Pentad	δ (exp.) (ppm)	δ (calc.) (ppm)
mmmm	21.52	21.52	mmmr	21.25	21.244
rmmr	21.07	20.97	mmrr	20.73	20.792
rmrr	20.5	20.511	rmrm	20.33	20.319
rrrr	19.99	20.021	rrrm	19.85	19.808
mrrm	19.64	19.58			

Polymerization results

A series of experiments with exposed EI catalyst solutions yielded polymers with a decreased activity but no real changes in the overall tactity. As we observed no *rac-meso* interconversion in the catalyst solutions this was expected.

The results of propylene polymerization with *rac* [Me$_2$Si(2-Me-4,5-benzoind)$_2$]ZrCl$_2$ (MBI) are summarized in Table 1. All polymerization conditions are shown in the Table. The catalyst solutions used in runs 1, 3, 4 and 5 were exposed to the UV source (sunlight) for 0, 30, 60 and 180 min, respectively. The catalyst concentration in run 2 was double the catalyst concentration in run 1. Initially we found that if the catalyst is used immediately after exposure to light, the activity was noticeably lower than if the solution was first stored in darkness after the irradiation experiment. We can only assume that the recombination of the photoreaction products only occurs after the light source is removed.

We see a decrease in activity of the catalyst as the exposure time increases. At the same time, the isotacticity (measured as *mmmm%*) decreases from 98 % in run 1 (no exposure) to 27.5 % in run 5 (180 min). In general this is accompanied by a decrease in molecular weight and an increase in polydispersity.

The ^{13}C NMR spectra of the polymer produced can be used to investigate the stereoerrors present in the polymer. According to theory, the C_2-symmetric catalysts function by enantiomorphic site control, and, as such, should only allow the pentads *mmmm*, *mrrm*, *mmrr* and *mmmr* (= *rmmm*). However, the *meso* form of the catalyst (achiral C_s-symmetry) will allow the whole range of 9 stereoerrors. The ^{13}C NMR chemical shifts for these errors can be calculated [15], and the experimental shifts found in our case and the calculated shifts are presented in Table 2.

In Fig. 4, the ^{13}C NMR spectra of polymers produced by freshly prepared as well as exposed catalyst
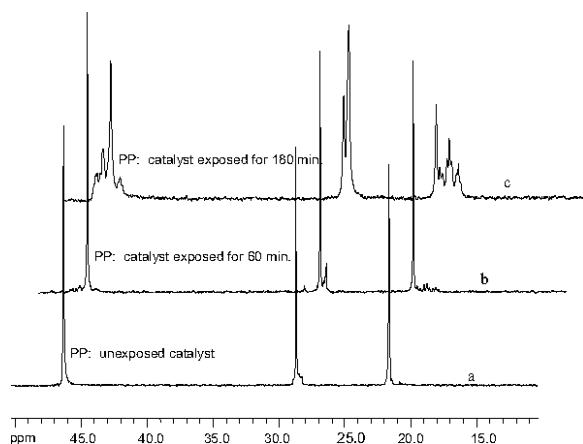

Fig. 4. ^{13}C NMR spectra of polypropylene made by catalyst solutions (a) unexposed, (b) exposed to light for 60 min, and (c) exposed to light for 180 min.

solutions are shown. We see a clear change in tacticty, as well as in the types of methyl pentads present, as evidenced by the NMR spectra. The ^{13}C NMR results do not conclusively prove that this decrease in the tacticity is due to two different active sites in the catalyst solution, although this is the most likely explanation. This decrease could conceivably arise from the presence of stereoirregular sequences in the polymer chains that are produced with one active site. If, however, two active species were present, the polymer will be a mixture of soluble, atactic materials, and insoluble, isotactic material.

Preparative TREF experiments conducted on the polymer made in run 4 (60 min exposure) yielded 9 distinctly different fractions (separated by crystallization). Results are shown in Fig. 5. It can be seen that about 70 % of the polymer is eluted between 85 and 115 °C. The only other significant fraction is that represented by the fraction eluted at 25 °C, the so-called soluble fraction. This soluble fraction comprised about 15 % of the total material recovered, and was virtually atactic material. This is in contrast, for example, with the fractions recovered at elution tem-
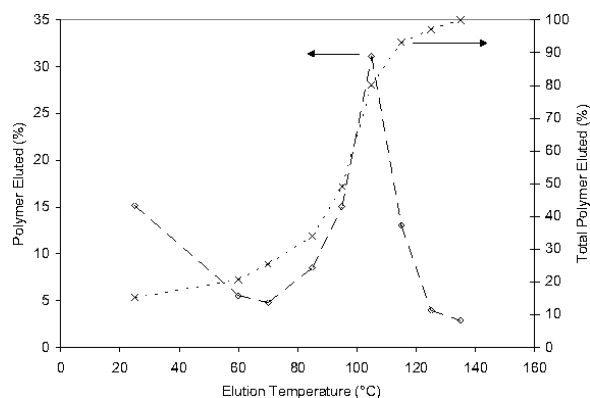
Fig. 5. Prep-TREF results for polypropylene made in run 4. Weight fractions eluted at given temperatures and total percentage polymer eluted.
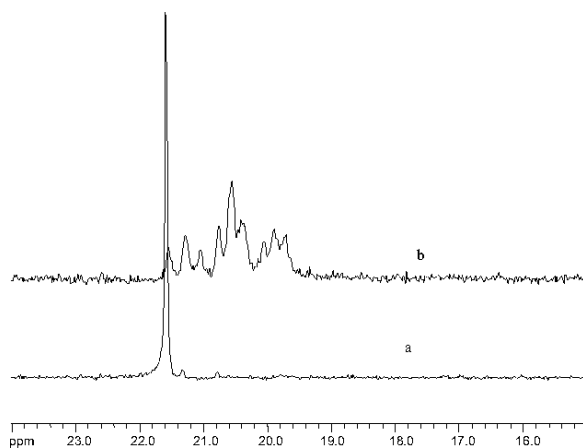

Fig. 6. ^{13}C NMR spectra (methyl region) of polymers made with (a) pre-activated catalyst (run 6, Table 1) and (b) pre-exposed (run 7, Table 1) catalyst solutions.

peratures of 95, 105 and 115 °C. A comparison of ^{13}C NMR spectra (methyl region) of the soluble fraction and that of the fraction eluted at 115 °C is shown in Fig. 6. This clearly indicates that the polymer contains at least 2 fractions, being completely atactic material and highly isotactic material. This is a clear indication that at least 2 different catalytic species were present during the polymerization reaction. Solution crystallization (Crystaf) analyses also have shown that the amount of soluble material increases as the exposure time of the catalyst solution increases.

In a separate experiment, a single catalyst solution was made up, and then split into 2 equal fractions. One solution was activated with MAO, and both solutions then exposed to sunlight for 180 min. The second solution was activated with MAO, and both solutions then

used to catalyze propylene polymerization under identical conditions. The results, shown as runs 6 and 7 in Table 1, clearly indicate that pre-activation of the catalyst solution prevents catalyst isomerization from occurring. While the activity of the catalyst is lower than in the case of the control experiment (run 1), the polymer made in run 6 has a high tacticity and high molecular weight, while the pre-exposed catalyst solution yields a polymer with low taticicy and low molecular weight (similar to run 5).

Conclusion

The results clearly indicate that significant *rac-meso* conversion of a solution of a C_2-symmetric catalyst can readily occur if the solution is exposed to light. Utilizing catalyst solutions previously exposed to light for the polymerization of a pro-chiral olefin like propylene leads to a mixture of stereoregular (crystalline) and irregular (non-crystalline) polymers. These materials can easily be fractionated by means of preparative TREF. Pre-activation of the catalyst solution prior to exposure to light results in no isomerization. As the isomerization occurs very rapidly, care should be taken in routine polymerization experiments to prevent exposure of catalyst solutions to light, or an early activation of the catalyst solution with the cocatalyst carried out.

Experimental Section

The catalysts, dimethylsilyl[bis(2-methyl-4,5-benzo-indenyl)]zirconium dichloride, (*rac*-[Me$_2$Si(2-Me-4,5-benz-oind)$_2$]ZrCl$_2$) (MBI), and ethylene[bis(1-indenyl)]zirconium dichloride, (*rac*-Et(Ind)$_2$ZrCl$_2$) (EI), were obtained from Boulder Scientific and Aldrich, respectively, and were used as received. All procedures were carried out in a nitrogen atmosphere. Typically a solution of the catalyst in CD$_2$Cl$_2$ was prepared in an NMR tube (3 mg catalyst was dissolved in 0.5 mL solvent) and the solution exposed to UV light (UV lamp, λ = 257 nm, or sunlight) for different times, varying from 0 to 1500 min. The change in the catalyst structure was investigated by ^{1}H NMR spectroscopy. At every exposure time spectra were recorded using a standard pulse sequence on a 600 Varian ^{Unity}Inova NMR spectrometer equipped with an Oxford magnet (14.09 T) operating at 600 MHz for ^{1}H, using a 5 mm inverse detection PFG probe. Simultaneously, a similar solution of the same catalyst was prepared (for both types of catalysts) and stored in the dark. ^{1}H NMR spectra of these control solutions were recorded after 24 h, 12 d, and 35 d. The spectra of the catalyst solution that was kept in the dark were used to investigate the effect of the storage time on the catalyst

structure in terms of the symmetry of the catalyst, and the catalyst decomposition.

For polymerization studies, catalyst solutions were prepared in Schlenk tubes under a nitrogen atmosphere. Each Schlenk tube contained about 1 mL (2.2 μmol mL^{-1}) of catalyst solution. These solutions were exposed to UV light (UV lamp or sunlight) for times varying from 0 to 600 min. These solutions were then used for propylene polymerization. MAO (8 mL of a 10 % solution in toluene) was added to each of the catalyst solutions that had been prepared and then these solutions were allowed to react for 15 min before mixing the catalyst solution, toluene and monomer. The polymerization reactions were carried out in a stainless steel autoclave with two inlets and a pressure gauge. Polymerization temperature was 25 °C, and reaction times were set at 2 h. Reactions were terminated by venting the reactor and then adding acidic methanol (10 % HCl). Polymers were precipitated in methanol, washed and dried under reduced pressure.

Polymers were characterized by high temperature GPC, ^{13}C NMR (120 °C on a Varian VXR 300 MHz spectrometer, using a 9 : 1 mixture of 1,2,4-trichlorobenzene and C_6D_6 as solvent), DSC and Crystaf. Preparative Temperature Rising Elution Fractionation (prep-TREF) was carried out on a instrument built in-house [16]. Typically the polymer was crystallized onto an inert support from xylene solution. The temperature was lowered from 130 °C to 25 °C at 1 °C per h. The fractions were then eluted at selected temperatures, isolated and characterized.

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