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NEW MATERIALS BY POLYMERIZATION OF OLEFINS AND STYRENE BY METALLOCENE/MAO CATALYSTS

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Abstract: Metallocenes and other transition metal compounds comprise a new generation of single site catalysts for the production of precisely designed polyolefins and engineering plastics. The discovery of metallocene methylalumoxane (MAO) catalysts has opened a frontier in the area of polymer synthesis and processing. A great number of symmetric and chiral zirconocenes have been synthesized to give isotactic, syndiotactic, isoblock, or stereoblock polymers with increased impact strength and toughness, better melt characteristics or elasticity, and improved clarity in films. Cycloolefin copolymers (COC) and syndiotactic polystyrene can be produced by metallocene catalysts. These are new types of polymers with special properties and a high potential as engineering plastics. Norbornene-ethene copolymers are most interesting for technical uses because of the easily available monomers. Due to different incorporation values of the cyclic olefin in the copolymer, the glass transition temperature can vary over a wide range and reaches 180 ℃.

Key words: metallocene catalyst, polyolefin, polystyrene
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INTRODUCTION

Metallocenes in combination with methylalumoxane or perfluorinated borates as cocatalyst form extremely active catalysts for the polymerization of olefins , cycloolefins, styrene, and butadiene are now used in industrial processes (Scheirs et al., 2000; Kaminsky et al., 1997b; Bochmann, 1996; Fink et al., 1995). Supporting of the zirconocenes on silica decreases the necessary surplus of MAO and can change the tacticity.

Polyolefins, with different microstructures and characteristics, can be custom-made just by varying the ligands on the metallocene (Brintzinger et al., 1995; Sinn et al., 1980a; Kaminsky, 1996). By combining different olefins and cycloolefins with one another, the range of characteristics can be further broadened. The production of polyolefins with narrow molecular weight distributions ($M_w/M_n = 2$), of syndiotactic polymers and of chemically uniform copolymers has not yet been achieved by conventional Ziegler-Natta heterogeneous catalysts.

Using metallocene catalyst, it was possible for the first time to produce polyethylenes, polypropylenes and copolymers with narrow molecular weight distributions (Sinn et al;., 1980b), syndiotactic polypropylene (in technical scale amounts) (Ewen et al., 1988), syndiotactic polystyrene (Ishihara et al., 1988), cyclopolymerisates of 1, 5-hexadiene (Coates et al., 1991), cycloolefin copolymers (COC) with high catalytic activity (Kaminsky et al., 1989a), optically active oligomers (Kaminsky et al., 1989b) and composite materials of biomass, powdered metals with polyolefins (Dutschke et al., 1983). Organic or inorganic particles (starch, cellulose, quartz sand or powdered metal) can be coated with a hydrocarbon soluble metallocene catalyst and in turn, after polymerization, with a polyolefin film of variable thickness (Kaminsky et al., 1993).

The polymerizations can be controlled precisely by metallocene catalysts. To increase the activity and to make the metallocenes more stable for higher temperatures, [$PhMe_3PenFlu$] $ZrCl_2$ was synthesized (Kaminsky et al., 1999). This zirconocene is more stereorigid and shows high activities for the polymerisation of propene and the ethene norbornene copolymerisation. A strong dependence of the activity on the propene concentration is observed. The molecular weight of the polypropylene produced is two to four times higher than that synthesized with other C_1-compounds. Isotactic blocks in a hemiisotactic microstructure are observed which are responsible for elastomeric properties.

Metallocene catalysts are particularly important for the polymerization of cycloolefins (cyclopentene, norbornene and their substituted compounds). In this process, only the double bond is opened and not the ring. Crystalline polycycloolefins are rendered, that have extremely high melting points of at least 380 ℃, sometimes being higher than the decomposition temperature (Kaminsky et al., 1991)

While homopolymerization of cyclopentene results in 1, 3-enchainment of the monomer units, norbornene is inserted in 1, 2-enchainment as usual for olefin polymerization. The problems of processing that arise from the high melting temperatures of the homopolymers can be solved by copolymerizing cycloolefins with ethene (Cherdron et al., 1994; Herfert et al., 1993; Collins et al., 1992).

The insertion of norbornene units into the growing polymer chain is very easy. As seen by the copolymerization parameter r_1, which is between 2.0 to 3.4 and shows how much faster ethene is inserted than norbornene when the previous insertion was ethene, it is easy to incorporate this huge monomer (Table 1).

Table 1 Copolymerization parameters r_1 and r_2 of ethene/cycloolefin copolymerizations with different metallocene/MAO catalysts

Cycloolefin	Catalyst	Temp. in ℃	r_1	r_2	$r_1 \cdot r_2$
Cyclopentene	$[\mathrm{En(IndH_4)_2}]\mathrm{ZrCl_2}$	0	1.9	< 1	~ 1
Cyclopentene	$[\mathrm{En(IndH_4)_2}]\mathrm{ZrCl_2}$	25	2.2	< 1	~ 1
Norbornene	$[\mathrm{Me_2Si(Ind)_2}]\mathrm{ZrCl_2}$	30	2.6	< 2	~ 1
Norbornene	$[\mathrm{Me_2C(Fluo)(Cp)}]\mathrm{ZrCl_2}$	30	3.4	0.06	0.2
Norbornene	$[\mathrm{Ph_2C(Fluo)(Cp)}]\mathrm{ZrCl_2}$	0	2.0	0.05	0.1
Norbornene	$[\mathrm{Ph_2C(Fluo)(Cp)}]\mathrm{ZrCl_2}$	30	3.0	0.05	0.15
Norbornene	$[\mathrm{Me_2C(Fluo)(t\text{-}BuCp)}]\mathrm{ZrCl_2}$	30	3.1	0	0
DMON	$[\mathrm{Ph_2C(Fluo)(Cp)}]\mathrm{ZrCl_2}$	50	7.0	0.02	0.14
DMON	$[\mathrm{Ph_2C(Ind)(Cp)}]\mathrm{ZrCl_2}$	50	6.4	0.10	0.64
DMON	$[\mathrm{Ph_2C(Fluo)(Cp)}]\mathrm{HfCl_2}$	50	7.1	0.04	0.28

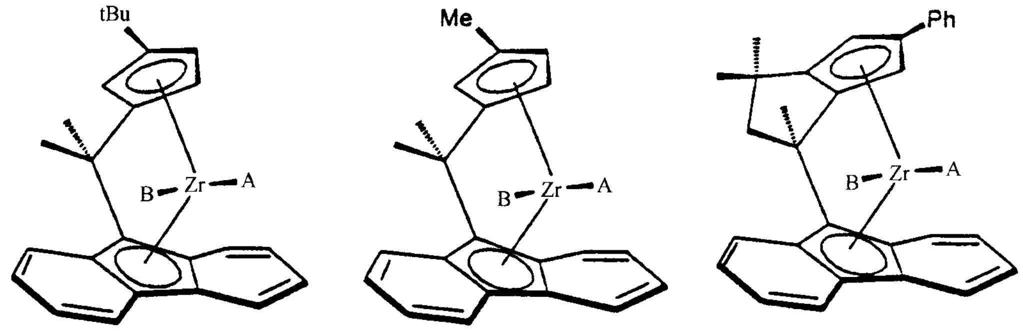
In most cases the r_1 parameter increases with the temperature and polymers with a statistical structure are obtained.

Such materials characteristically have an excellent transparency and a very high continuous service temperature. From cycloolefin insertion rates of 10 mol % upwards, these cycloolefin copolymers (COC) are no longer crystalline but amorphous.

ALTERNATING CYCLO OLEFIN COPOLYMERS

In general, metallocenes are more likely to form statistical to alternating copolymers. Alternating copolymers are of special interest because they could form semi-crystalline polymers (Arndt et al., 1998). Fig. 1 shows the types of structures used for the copolymerisation of cyclic olefins and ethene (Beulich, 1999). C_1-symmetric metallocenes should produce stereoregular alternating copolymers while meso-compounds should produce atactic alternating copolymers.

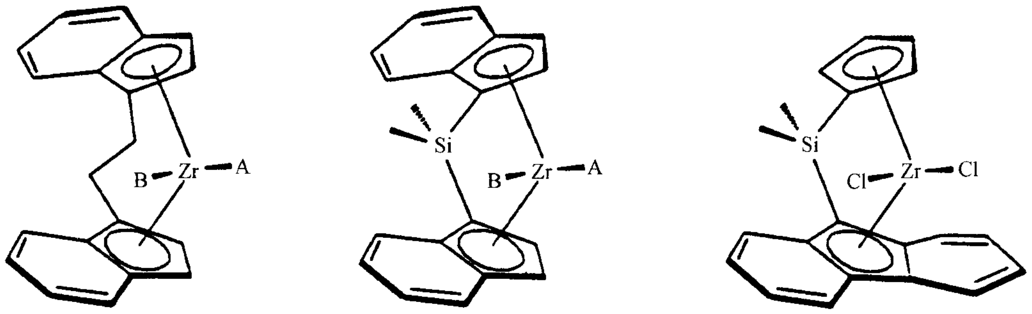
The steric demand of the two coordination sites A and B of a C_1-symmetric catalyst was exploited to control the distribution of monomers along the polymer chain and to generate a specific copolymerisation mechanism. In this way the formation of alternating copolymers was found. Table 2 shows the results of some catalysts in activities of the copolymerisation, incorporations of the cyclic olefin, and molecular weights of the copolymers.



tBuCpFlu
[Me$_2$C(3-tBuCp)(Flu)]ZrCl$_2$

MeCpFlu
[Me$_2$C(3-MeCp)(Flu)]ZrCl$_2$

DHPh
[Me$_3$PhPen(Flu)]ZrCl$_2$



meso EnInd2
meso-[En(Ind)$_2$]ZrCl$_2$

meso SiInd2
meso-[Me$_2$Si(Ind)$_2$]ZrCl$_2$

SiCpFlu
[Me$_2$Si(Cp)(Flu)]ZrCl$_2$

Fig. 1 Molecular structure of the used metallocenes and their terms

Table 2 Copolymerization of ethene and norbornene with different zirconocenes/MAO catalysts by 30 ℃ in toluene. [Zr] = 5 μmol/L, MAO = 2.5 g/L, [E] = 0.237 mol/L

Catalyst (see Fig. 1)	Norbornene in feed X_N	Norbornene in polymer X_N	Activity (kg Pol/mol Zr·h)	Molecular weight M_w
tBuCpFlu	0.23	0.055	1 850	230 000
	0.43	0.080	1 130	159 400
	0.69	0.220	360	89 800
	0.87	0.349	420	94 800
	0.97	0.445	30	
MeCpFlu	0.19	0.073	3 440	145 000
	0.37	0.150	3 270	87 000
	0.77	0.324	4 420	171 000
	0.89	0.407	5 720	252 000
	0.94	0.438	1 600	431 000
meso SiInd$_2$	0.31	0.096	650	12 600
	0.49	0.170	260	200 000
	0.70	0.299	27	222 000
meso EnInd$_2$	0.40	0.041	1 970	221 000
	0.68	0.098	1 080	211 000
	0.90	0.253	180	245 000
DH Ph	0.37	0.094		537 000
SiCpFlu	0.21	0.054	38 900	840 000
	0.57	0.184	30 200	808 000
	0.90	0.407	14 300	1 120 000
	0.99	0.644	430	190 000

In comparison to [Me_2C(3-tBuCp)(Flu)]$ZrCl_2$ and [Me_3PhPen(Flu)]$ZrCl_2$ the C_1-symmetric catalyst [Me_2C(3-MeCp)(Flu)]$ZrCl_2$ inserted norbornene slightly better. Only isolated and alternating norbornene sequences but no norbornene blocks were performed. Polymers containing more than 40 mol% of norbornene in the copolymer produced by [Me_2C(3-MeCp)(Flu)]$ZrCl_2$ featured norbornene blocks. At 99.8 mol% norbornene in the reactor copolymers contained up to 60 mol% norbornene. The molar masses of the copolymers produced by [Me_2C(3-MeCp)(Flu)]$ZrCl_2$ did not drop as strong with norbornene incorporation as those produced by [Me_2C(3-tBuCp)(Flu)]$ZrCl_2$. The alternating microstructure led to melting points from 240 to 273 ℃ with a norbornene content of 40 to 47 mol%. At higher contents the crystallinity was disturbed by norbornene blocks.

The best alternating microstructures of ethene norbornene copolymers were obtained by [Me_2C(3-tBuCp)(Flu)]$ZrCl_2$. Fig. 2 shows the concentration of the alternating pentade and pentades with short ethene blocks in dependence of the norbornene molar ratio in the polymer.

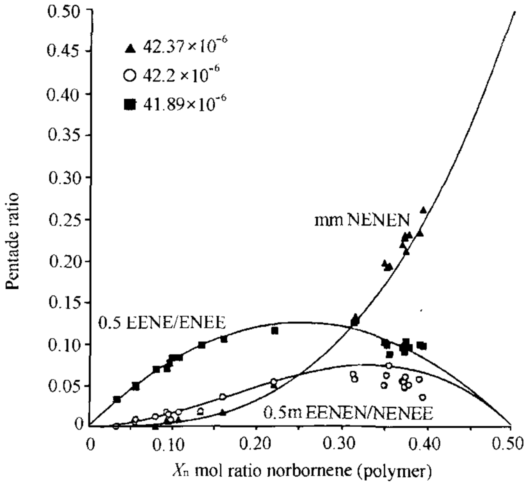


Fig. 2 **Copolymerization of ethene and norbornene with [Me_2C(3-tBuCp)(Flu)]$ZrCl_2$/MAO by 30 ℃ in toluene. ^{13}C-NMR spectroscopic measured pentads vs the molar ratio of norbornene in the obtained polymer**

In comparison to copolymers obtained by [Me_2C(3-MeCp)(Flu)]$ZrCl_2$ copolymers produced by [Me_2C(3-tBuCp)(Flu)]$ZrCl_2$/MAO showed melting points of up to 320 ℃ at 50 mol% norbornene in the polymer (Fig. 3). The melting point of the alternating copolymer depends on the molar ratio of norbornene units in the polymer while the glass transition temperature is nearly independent of that. Crystallinity of these copolymers is detected using wide angle X-ray scattering of films. The degree of crystallinity is about 22 % for copolymers containing 49 mol% of the cycloolefin.

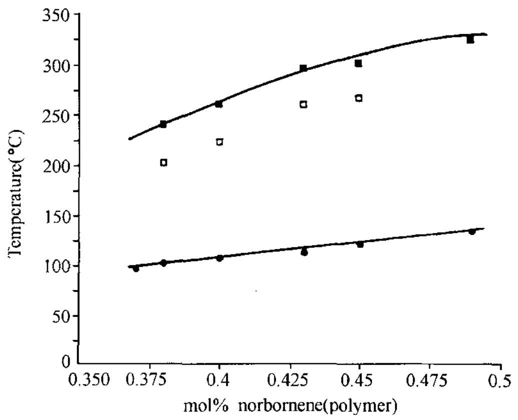


Fig. 3 **Melting points (▪) and crystallization temperatures (□) and glass transition temperature (•) of ethane/norbornene copolymers containing alternating sequences; produced by [Me_2C(3-tBuCp)(Flu)]$ZrCl_2$ measured at (heat) cooling rate of 40 °/min**

The systems [Me_2Si(Ind)(Flu)]$ZrCl_2$/MAO, meso[$Me_2Si(Ind)_2$]$ZrCl_2$/MAO, meso-[En$(Ind)_2$]$ZrCl_2$/MAO and meso-[$Me_2Si(THInd)_2$]$ZrCl_2$/MAO inserted norbornene poorly into the polymer chain, nevertheless norbornene blocks were formed. The activity of these systems and the molar masses of the produced copolymers were very low. Polymer mixtures were formed by [Me_2Si(Ind)(Flu)]ZrCl, meso[$Me_2Si(Ind)_2$]$ZrCl_2$ and meso-[$Me_2Si(THInd)_2$]$ZrCl_2$.

The copolymerisation of ethene and dimethanooctahydronaphthalene (DMON) by [Me_2C(3-tBuCp)(Flu)]$ZrCl_2$/MAO and [Me_2C(3-MeCp)(Flu)]$ZrCl_2$/MAO yielded semi-crystalline alternating copolymers with melting points at 380 ℃.

Statistical ethene/norbornene copolymers were produced by Cs-symmetric metallocenes [Me_2C(Cp)(Flu)]$ZrCl_2$/MAO and [Me_2Si(Cp)(Flu)]$ZrCl_2$/MAO. The microstructure of ethene/norbornene copolymers containing norbornene diblocks besides isolated and alternating sequences was measured by ^{13}C-NMR spectroscopy. The signals were assigned in comparison with the signals of alternating ethene/norbornene copolymers and the resonances of norbornene hydrodi-and trimers to rac-and meso-bonded norbornene units. In these polymers the diad distribution and the distribution of norbornene centred triads could be calculated (Arndt et al., 1996).

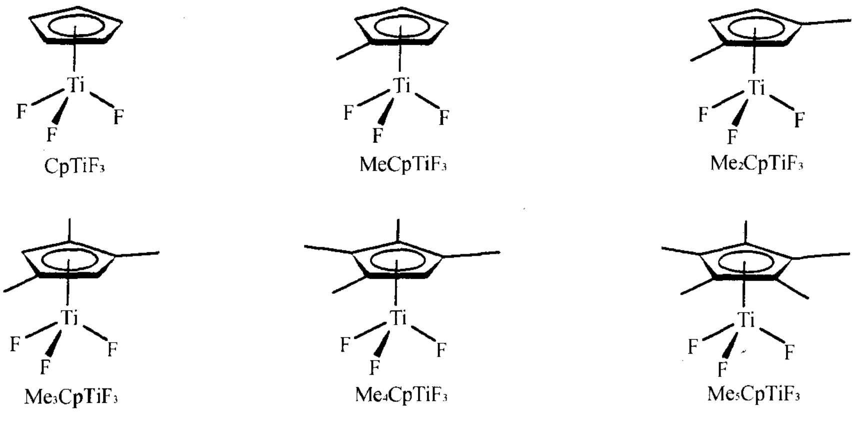
[Me_2-C(Cp)(Flu)]$ZrCl_2$/MAO inserted into norbornene very well, followed by [Me_2Si(Cp)(Flu)] $ZrCl_2$/MAO which yielded by far the highest activities and the highest molar masses, more than 400.000 g/mol at contents of up to 40 % in the polymer.

Depending on the metallocene used, the mechanism of the ethene/norbornene copolymerisation changed. While a chain migratory insertion with both coordination sites was present in the case of the tertbutyl substituted system [Me_2C(3-tBuCp)(Flu)]$ZrCl_2$ at T_P = 30 ℃ (alternating mechanism: $r_E^A = 3.08$, $r_N^A = 0$, $r_E^B = 500$, $r_N^B = 0$), monomers inserted only into one site (retention mechanism: $r_E = 3.3$, $r_N = 0.001$) in the case of the methyl substituted catalyst at low norbornene excesses ($x_N < 0.93$, $X_N < 0.46$). At high norbornene excess in the reactor ($x_N > 0.98$) norbornene blocks were formed and the mechanism changed. The insertion mechanism of the copolymerisation proceeded with control of the penultimate monomer unit in the case of C_s-symmetric metallocenes [Me_2C(Cp)(Flu)]$ZrCl_2$ and [Me_2Si(Cp)(Flu)]ZrCl_2, which meant it could be described by a 2nd order Markovian model. Ethene is inserted three times faster than norbornene. No higher blocks as diblocks were formed (CCpFlu: $r_{EE} = 2.40$, $r_{EN} = 4.34$, $r_{NE} = 0.33$, $r_{NN} = 0$). This explained the maximum content of 66 mol% of norbornene in the copolymer at comonomer content of 98 mol% in the reactor. Since only meso-[En(Ind)$_2$]$ZrCl_2$, of all the investigated meso-compounds, formed monomodal molar mass distributions as normal for a single site catalyst, the mechanism was investigated. The copolymerisation parameter were calculated by the 1st order Markovian model to be $r_E = 18.1$ and $r_N = 0.007$. Norbornene inserted badly compared to the other systems.

SYNDIOTACTIC POLYSTYRENE

Half sandwich complexes such as $CpTiCl_3$, Cp* $TiCl_3$ or alkoxy complexes can polymerize styrene in combination with MAO affording a highly syndiotactic polymer with a melting point of 270 ℃ (Ishihara et al., 1988). The activity can be increased if fluorinated half sandwich titanocenes are used (Kaminsky et al., 1997)

The substitution of the cyclopentadienyl ligand plays an important role in the activity and molecular weight of the obtained polystyrene. Fig. 4 shows the synthesized and used fluorinated half sandwich titanium complexes.



CpTiF₃ MeCpTiF₃ Me₂CpTiF₃

Me₃CpTiF₃ Me₄CpTiF₃ Me₅CpTiF₃

Fig.4 Different methyl substituted cyclopentadienyl titanium trifluorides used for the polymerisation of styrene

The polymerisations were carried out in a temperature range of 10 – 70 ℃. Figure 5 shows the fluorinated and chlorinated compounds activities in dependence on the Al(MAO)/Ti molar ratio. The fluorinated complexes are much more active at low Al/Ti ratios. An optimum is given by a value of Al/Ti = 150 to 300. The chlorinated catalysts maximize at Al/Ti ratio of 1000.

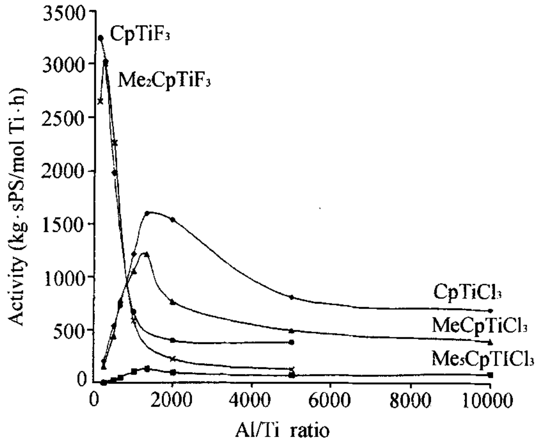


Fig.5 Dependence of the styrene polymerisation activity on the Al/Ti ratio
Polymerization temperature: 30 ℃

The activities, molecular weights and melting points of the obtained syndiotactic polystyrenes are given in Table 3.

Under those conditions the unsubstituted $CpTiF_3$ is the most active system. By higher polymerization temperatures the substituted complexes are more stable and therefore more active. The molecular weight increases with the substitution. Me_4CpTiF_3 gives a polystyrene with the highest molecular weight of 421 000 and a melting point of 273 ℃.

The catalyst Me_5CpTiF_3 is highly active at temperatures up to 70 ℃, producing syndiotactic polystyrene with a very high melting point of 277 ℃ and a high molecular weight of 660 000. The chlorinated analogue's strongly reduced activity at this temperature lowers the molecular weight of the resulting polymer.

EXPERIMENTAL DETAILS

Experiments were performed in an inert gas atmosphere using Schlenk techniques or a drybox. Toluene that was used as solvent was purified by refluxing over sodium-potassium alloy followed by distillation. Norbornene and styrene were commercially obtained from Fluka and dried over calcium hydride for 5 days and distilled under reduced pressure. Methylaluminoxane was purchased from Witco. The fluorinated titanium compounds were prepared from the chlorinated ones by the research group of Prof. Roesky according to the literature (Herzog et al., 1994).

Table 3 Polymerization of styrene to syndiotactic polystyrene by fluorinated titanium complexes and MAO as cocatalyst. Polymerization temperature = 30 ℃, **Al : Ti ratio** = 500, **solvent** = **toluene**

Catalyst	Activity(kg sPS/mol Ti·h)	Molecular weight of sPS	Melting point of sPS (℃)
$CpTiF_3$	3 100	186 000	264
$MeCpTiF_3$	3 050	258 000	270
Me_2CpTiF_3	2 700	321 000	273
Me_3CpTiF_3	830	397 000X	272
Me_4CpTiF_3	460	421 000	272
Me_5CpTiF_3	350	388 000	273

Copolymerization of ethene and norbornene was carried out in a 1 dm^3 autoclave (Büchi), polymerisation of styrene in a 0.2 dm^3 thermostated glass reactor equipped with a magnetic stirrer by introducing successively toluene, a solution of MAO in toluene, 20 mL of styrene, and titanium or zirconium compound dissolved in toluene. The total volume of the polymerization mixture was filtered out, washed with ethanol, and dried in vacuo at 60 ℃. The molecular masses and molecular weight distributions were measured at 135 ℃ by GPC (Waters 150-CALC/GPC) using trichlorobenzene as solvent. ^{13}C-NMR spectra were recorded on a Bruker AM 300 spectrometer.

CONCLUSIONS

The company Ticona has since September 2000 been running the first commercial plant for the production of COC materials. Syndiotactic polystyrene will be produced by a joint venture of Idemitzu and Dow. Other engineering plastics produced by metallocene or single site catalysts are scheduled for industrial production.

The development of metallocene catalysts is ongoing and for certain processes, such as the isotactic polymerisation of propene, only temporary optimum values have been reached. The future will certainly yield further custom-made structures and a whole string of new polymers and oligomers; the catalysts involved will have metallocenes as their main component. Other single site catalysts may also be used.

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NEWS

China-Germany Symposium on Organometallic Catalysts and Olefin Polymerization in Hangzhou

In line with increasing academic contacts and friendly cooperations between China and Germany, and supported by the National Natural Science Foundation of China (NSFC) and China Petrochemical Corporation(SINOPEC) and the German Science Foundation, the first China-Germany Symposium on organometallic catalysts and olefin polymerization was successfully held at Zhejiang University in Hangzhou on 9, 10 and 11 October 2000. About 80 participants from Germany, UK, and China (including Hongkong and Taiwan) attended the meeting. This symposium focused on:

1. Synthesis and characterization of organometallic catalysts;
2. Olefin polymerization by homo- and heterogeneous organometallic catalysts;
3. Functionalized polyolefins produced by organometallic catalysts;
4. New developments in organometallic catalysts in the polyolefin industry.

Prof. Dr. W. Kaminsky showed in his report many new results of Ziegler-Natta catalysts, especially from metallocene catalysts. The discovery of metallocene/methylaluminoxane (MAO) catalyst has opened a frontier in the area of polymer synthesis and processing. A great number of symmetric and chiral zirconocenes have been synthesized to give isotactic, syndiotactic, isoblock, or stereoblock polymers with increased impact strength and toughness, better melt characteristics or elasticity, and improved clarity in films. Some plastics made by metallocene catalysts are already on the market. He predicted that there will be a rapid increase in the next year.

Prof. Dr. Hong Dingyi, reviewed the great progress and brilliant prospects in development and application of metallocene catalyst for polyolefins in China. Since the early 1990's, a series of metallocene catalysts such as ansa-$(Ind)_2ZrCl_2$, $Ph_2CH_2(FluCp)ZrCl_2$, $CpTi(OPh)_3$, $Cp^*Ti(OPh)_3$ and etc., have been synthesized and applied successfully to prepare precisely designed PE, iPP, sPP, aPP and sPS. Some industrialized results have been achieved from the gas-phase fluidized bed PE, batch plant in Qilu, Liaoyang and Phillips respectively.

Prof. H. Schumann (TU Berlin), Prof. G. Erker (University Muenster), Prof. G. Fink (Max-planck-Institut fuer Kohlenforschung), Prof. M. Bochmann (University of East Anglia, UK) and Prof. HuYouliang (Beijing Institute of Chemistry, Chinese Academy of Sciences), Prof. Huang Baotong (Changchun Institute of Applied Chemistry, Chinese Academy of Sciences), Prof. Lin Shang'an (Zhongshan University), Prof. Shen Zhiquan (Zhejiang University) and others reported their new results in synthesis of new lanthanocene, tin-or germa-bridged metallocenes, polymerized metallocene, novel ehylene polymerization in water medium and polymerization mechanisms.