Polymer Bulletin 41, 433–440 (1998)

Polymer Bulletin

Transition metal catalyzed polymerisation of norbornene

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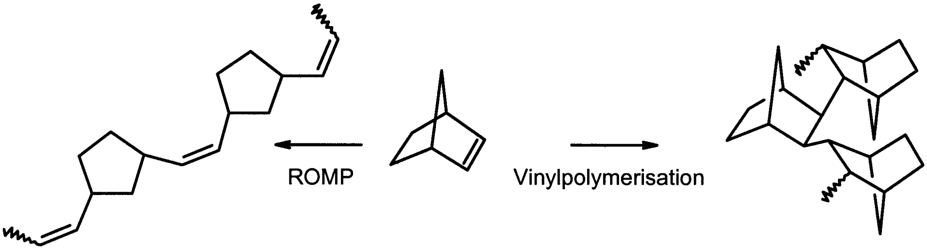
Received: 4 June 1998/Revised version: 28 July 1998/Accepted: 28 July 1998

Summary

Metallocene/methylaluminoxane and single component Pd(II)-catalysts are compared to methylaluminoxane activated Ni and Pd-catalysts for the vinylpolymerisation of norbornene. Ni(II), Ni(0) and Pd(II)-compounds were found to be orders of magnitude more active than metallocenes and produce polymers of much higher molecular weights. Polymerisation kinetics for these systems have been studied in detail and reflected high initial activity followed by significant catalyst deactivation. Based on NMR-spectroscopy and WAXS five types of polynorbornenes have been identified and structures are proposed.

Introduction

Transition metal catalysts may polymerise norbornene by ring opening metathesis (ROMP) or by addition to the double bond (vinyl polymerisation). Group 4 metallocenes in combination with methylaluminoxane promote the vinylpolymerisation (1) as well as L_2PdX_2 catalysts (2) which even tolerate functional groups or water as the reaction medium. Recently Risse (3) , Novak (4) and Goodall et al. (5) described a new class of catalysts based on Ni- and Pd-allyl compounds for the vinylpolymerisation of norbornene and derivatives.



In context with their invention we have studied the polymerisation of norbornene by Ni(II)- and Pd(II)-salts in combination with methylaluminoxane (mao) as a cocatalyst (6) and compared their catalytic performance to those of metallocene/mao and mao free Pd-catalysts.

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Experimental Part

Ni- and Pd-compounds used were commercial samples, while biscyclopentadienyl zirconium dichloride (Cp_2ZrCl_2), rac-ethylenebis(1,1'indenyl) zirconium dichloride (rac-$[C_2H_4(Ind)_2]ZrCl_2$), rac-ethylenebis(4,4',5,5',6,6',7,7'-tetrahydro-1,1'-indenyl) zirconium dichloride (rac-$C_2H_4(H_4Ind)_2]ZrCl_2$), rac and meso-dimethylsilyl(1,1'-indenyl) zirconium dichloride (rac- and meso- rac-$[Me_2Si(Ind)_2]ZrCl_2$), Isopropylidene(cyclopentadienyl)(9-flourenyl) zirconium dichloride ($[Me_2C(Cp)(Flu)]ZrCl_2$), and Diphenyl methylidene(cyclopentadienyl)(9-fluorenyl) zirconium dichloride $[Ph_2C(Cp)(Flu)]ZrCl_2$ were prepared according to the literature (7). Mao was purchased from Witco and used as a solid after removal of toluene and volatile trimethylaluminium. All manipulations were carried out in an Ar-atmosphere using Schlenk-techniques. All polymerisations were conducted in a total volume of 50ml and the polymers were isolated by precipitation from Ethanol and filtration. Polymers were dried in a vacuum oven at 60°C until no more loss of weight is observed. Kinetics were determined from the yield of parallel runs quenched at different times.

Molecular weights and molecular weight distributions were measured by GPC at 135°C in trichlorobenzene. CPMAS-spectra were measured at 100°C, pulse angle 90°, relaxation delay 3s using a Bruker MSL 300. WAXS was measured using a Siemens D500.

Results

The Ni/ and Pd/mao catalysts were found to be orders of magnitude more active than the well known metallocene/mao and mao free Pd-catalysts. Due to the large difference of the activities it was not possible to compare the catalysts at the same catalyst concentrations and times of polymerisation. Conditions were chosen in order to keep the monomer conversion below 10% and to keep the system isotherm (with the highly active Ni- and Pd-catalysts higher catalyst concentrations lead to significant increase of the temperature). Besides the Ni(II)-salts, $Ni(acac)_2$ and $Ni(2\text{-ethylhexanoate})_2$, $(COD)_2Ni(0)$ was found to generate an active catalysts in combination with mao. A direct comparison shows $Pd(acac)_2$/mao-system to be much more active than the $Ni(acac)_2$/mao catalysts. While all Ni-catalysts produce polymers which are totally soluble in toluene Pd catalysis led to instantanous preciptation of the polymer. It is also possible to increase the productivity of $(CH_3CN)_2PdCl_2$ and $(CH_3CN)_4Pd(BF_4)_2$ by adding methylaluminoxane. The major disadvantage of these catalysts is the low solubility of the catalyst precursors in solvent like toluene.

In case of soluble polymers molecular weights and molecular weight distributions have been determined by means of gpc and viscosity measurements. The polymers generated by Ni-catalysts feature much higher molecular weights than those from metallocene/mao systems, while the narrow molecular weight distribution indicates a single active species.

Table 1: Comparison behavior of transition metal catalysts for the vinylpolymerisation of norbornene. All experiments were conducted at room temperature in toluene (total volume 50ml).

catalyst	mol Kat.	[Kat] mol/l	mg MAO	Al/Kat	tpol	g PN	kgPN/mol Mh	M_w g/mol	M_w/M_n	CPMAS-type	WAXS	
											r1	r2
Cp_2ZrCl_2	$3.5 \bullet 10^{-5}$	$7.1 \bullet 10^{-4}$	500	240	72	4.02	1.6	$9.3 \bullet 10^{3}$	2.0	I	1.00	0.60
rac-$[C_2H_4(Ind)_2]ZrCl_2$	$4.6 \bullet 10^{-5}$	$9.2 \bullet 10^{-4}$	1500	560	72	2.81	0.8	insoluble				
rac-$[C_2H_4(H_4Ind)_2]ZrCl_2$	$5.2 \bullet 10^{-5}$	$1.0 \bullet 10^{-3}$	1500	510	72	2.85	0.8	insoluble		III		
rac-$[Me_2Si(Ind)_2]ZrCl_2$	$2.2 \bullet 10^{-5}$	$4.4 \bullet 10^{-4}$	530	410	72	1.07	0.7	insoluble		II	1.01	0.57
meso-$[Me_2Si(Ind)_2]ZrCl_2$	$2.2 \bullet 10^{-5}$	$4.4 \bullet 10^{-4}$	600	470	72	1.16	0.7	insoluble		III	1.17	0.59
$[Me_2C(Cp)(Flu)]ZrCl_2$	$2.8 \bullet 10^{-5}$	$5.6 \bullet 10^{-4}$	550	340	72	1.77	0.9	$2.7 \bullet 10^{4}$	2.0	I	1.12	0.61
$[Ph_2C(Cp)(Flu)]ZrCl_2$	$2.2\ 10^{-5}$	$4.4 \bullet 10^{-4}$	520	410	72	3.45	2.2			I	1.10	0.59
$(CH_3CN)_2PdCl_2$ a)	$1.0 \bullet 10^{-4}$	$4.0 \bullet 10^{-3}$	0	0	1	1.93	38.7			III		
b)	$5.0 \bullet 10^{-7}$	$1.4 \bullet 10^{-5}$	0	0	72	traces	-					
b)	$5.0 \bullet 10^{-7}$	$1.4 \bullet 10^{-5}$	150	2600	0.25	0.46	4400					
$(CH_3CN)_4Pd(BF_4)_2$ a)	$1.0 \bullet 10^{-4}$	$4.0 \bullet 10^{-3}$	0	0	1	2.25	45.1			III	1.05	0.60
b),c)	$1.0 \bullet 10^{-6}$	$2.9 \bullet 10^{-5}$	0	0	0.08	0.22	2650	$6.1 \bullet 10^{5}$	2.3			
b),c)	$1.0 \bullet 10^{-6}$	$2.9 \bullet 10^{-5}$	150	5200	0.08	0.64	7710					
$Pd(acac)_2$	$1.0 \bullet 10^{-7}$	$2.0 \bullet 10^{-6}$	150	25000	0.5	1.36	27180	insoluble		III	1.03	0.60
$Ni(acac)_2$	$2.5 \bullet 10^{-7}$	$5.0 \bullet 10^{-6}$	150	10000	0.5	1.36	10880	$3.8 \bullet 10^{6}$	1.6	I	1.17	0.61
$Ni(2\text{-ethylhexanoate})_2$	$2.5 \bullet 10^{-7}$	$5.0 \bullet 10^{-6}$	150	10000	0.5	1.31	10470	$1.7 \bullet 10^{6}$	1.5	I	1.12	0.60
$(COD)_2Ni$	$2.5 \bullet 10^{-7}$	$5.0 \bullet 10^{-6}$	150	10000	0.5	0.48	3840	$1.6 \bullet 10^{6}$	1.7	I	1.15	0.60

a) solvent 1,2-dichloroethane, 0.03 mol norbornene, total volume 25ml; b) solvent 1,2-dichloroethane, 0.03 mol norbornene, total volume 35ml; c) the catalyst was dissolved in 1ml of a a toluene/nitromethane 1/1 mixture.

For the new catalysts Ni(2-ethylhexanoate)$_2$, Ni(acac)$_2$ and Pd(acac)$_2$ polymerisation kinetics have been studied in detail. Plotting conversion versus time shows that the three catalysts show a rather high initial activity followed by a rapid decrease.

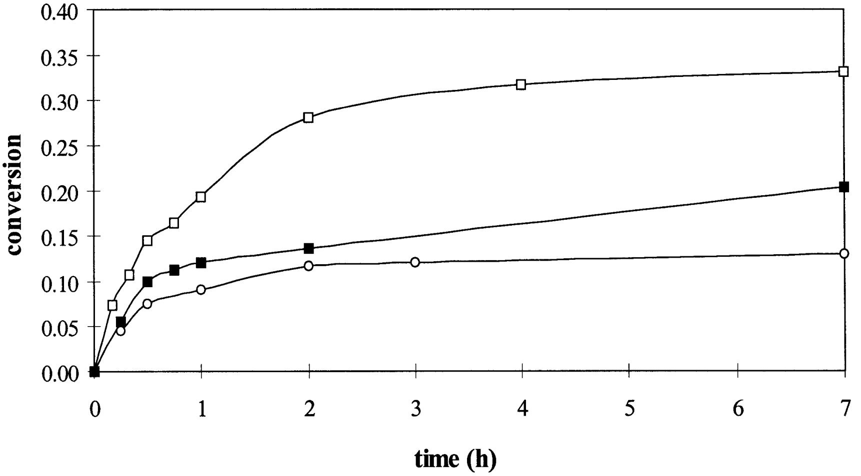


Fig.1: Kinetics of the norbornene polymerisation at 22°C. All experiments were conducted using 150mg mao and 0.1 mol norbornene in toluene (total volume 50ml). (□) 5•10^{-6} mol/l Ni(acac)$_2$, (■) 5•10^{-6} mol/l Ni(2-ethylhexanoate)$_2$, (O) 2•10^{-6} mol/l Pd(acac)$_2$.

Although the rate profiles are similar, Ni(acac)$_2$ is found to be more active than Ni(2-ethylhexanoate)$_2$. The difference of the two catalysts systems is also reflected if additional catalyst (5• 10^{-6} mol) is added after 19.5h of polymerisation. While in case of Ni(acac)$_2$ conversion did not significantly change within the next 2 hours for Ni(2-ethylhexanoate)$_2$ it increased from 28 to 40%. In order to study the activation in more detail the Al/Ni ratio has been changed by varying the Ni concentration at a constant Al concentration and vice versa. While the rate of the Ni(acac)$_2$/mao catalysed polymerisation of norbornene was found to be first order, the problem of deactivation Ni(2-ethylhexanoate)$_2$ is reflected in a mutual reaction order of four with respect to Ni and the fact that, contrary to the Ni(acac)$_2$ system, at a given Ni-concentration the activity is not enhanced by increasing the Al/Ni ratio above 10 000.

Investigations of the temperature dependence of the conversion showed a rather linear decrease of conversion for the Ni(2-ethylhenanoate)$_2$ system while the Ni(acac)$_2$ catalyst showed a small increase of conversion between -20 and 30°C and a plateau above 30°C. Pd(acac)$_2$ shows an optimum activity at about 30°C and a significant decrease of activity at lower and higher temperatures.

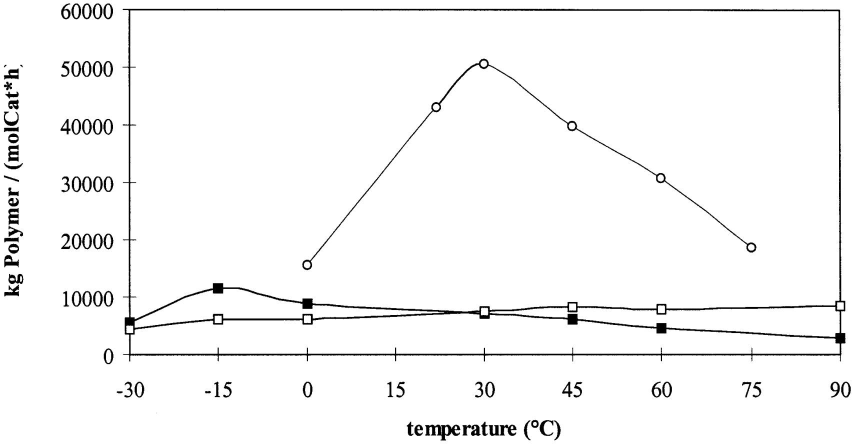


Fig.2: Temperature dependece of the activity of the Ni- and Pd/mao catalysts. All experiments were conducted using 150mg mao and 0.1 mol norbornene in toluene (total volume 50ml). (□) $5 \cdot 10^{-6}$ mol/l $Ni(acac)_2$, (■) $5 \cdot 10^{-6}$ mol/l Ni(2-ethylhexanoate)$_2$, (○) $1 \cdot 10^{-6}$ mol/l $Pd(acac)_2$.

Polymerisation by $Ni(acac)_2$/mao in different solvents shows that more polar solvents like 1,2-dichloroethane enhance the reaction significantly (again the catalyst concentration had to be lowered in order to work isotherm), while the rate profile did not change. In contrast the polymerisation in hexane resulted in polymer precipitation and the system is totally inactive after a few minutes.

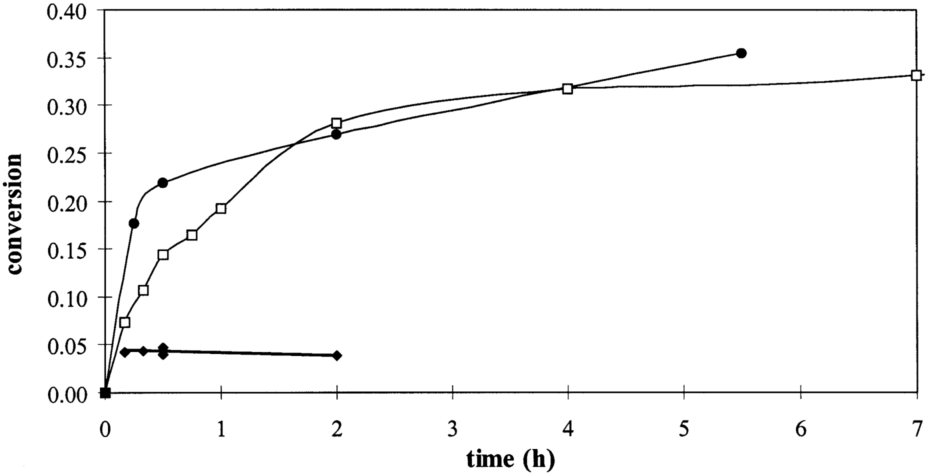
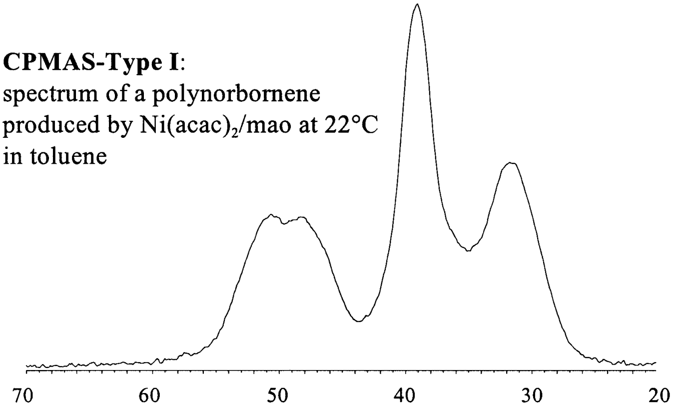
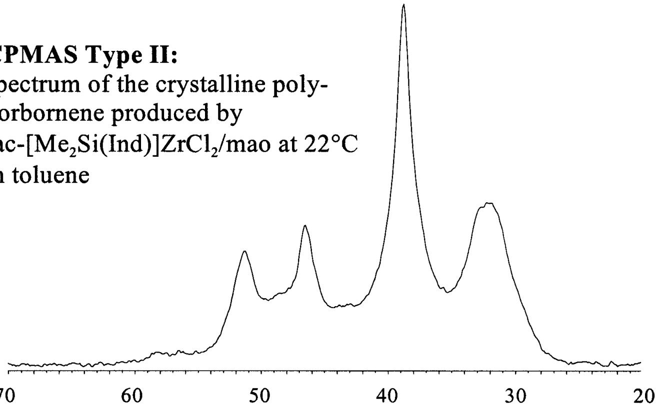


Fig.3: Kinetics of the norbornene polymerisation using $Ni(acac)_2$/mao in different solvents at 22°C. All experiments were conducted using 150mg mao and 0.1 mol norbornene in a total volume of 50ml. (□) $5 \cdot 10^{-6}$ mol/l $Ni(acac)_2$ in toluene, (●)$1.25 \cdot 10^{-6}$ mol/l $Ni(acac)_2$ in 1,2-dichloroethane, (◆) $5 \cdot 10^{-6}$ mol/l $Ni(acac)_2$ in hexane.

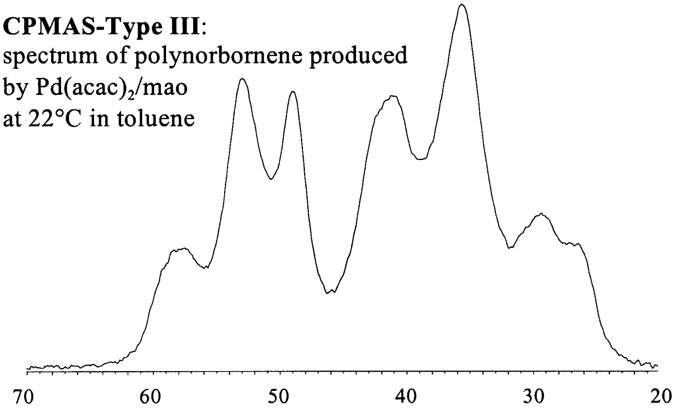
Generally polynorbornenes may be grouped into those soluble in toluene and those precipitating during the polymerisation. WAXS and ^{13}C-CPMAS investigations as well as high temperature high resolution ^{13}C-NMR investigations of the soluble polymers confirm the different structures of the polymers and enable a further classification. CPMAS-investigations showed 3 basic types of spectra:



CPMAS-Type I:
spectrum of a polynorbornene produced by Ni(acac)$_2$/mao at 22°C in toluene



CPMAS Type II:
spectrum of the crystalline polynorbornene produced by rac-[Me$_2$Si(Ind)]ZrCl$_2$/mao at 22°C in toluene



CPMAS-Type III:
spectrum of polynorbornene produced by Pd(acac)$_2$/mao at 22°C in toluene

For CPMAS-type I (and the closely related type II) assignements have been made before[1] while type III represents a new class of polynorbornene. Among the soluble polymers the products generated by the three Ni-catalysts show no significant differences in their WAXS and ^{13}C-NMR spectra. $[Me_2C(Cp)(Flu)]ZrCl_2$ and $[Ph_2C(Cp)(Flu)]ZrCl_2$ in combination with mao also yield soluble polymers showing CPMAS spectra almost identical (CPMAS-type I) to those of the Ni-products and only small differences may be found by comparison of the WAXS and the ^{13}C-NMR spectra in solution. We have previously investigated the microstructure of norbornene oligomers produced by $[Me_2C(Cp)(Flu)]ZrCl_2$/mao and deduced a erythrodisyndiotactic microstructure of low stereoregularity for the polymer. Therefor we also propose a microstructure of low disyndiotacticity for the products generated by the Ni-catalysts.

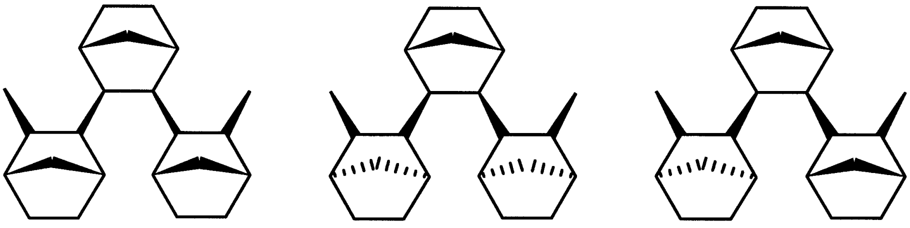

rr-triad mm-triad mr-triad

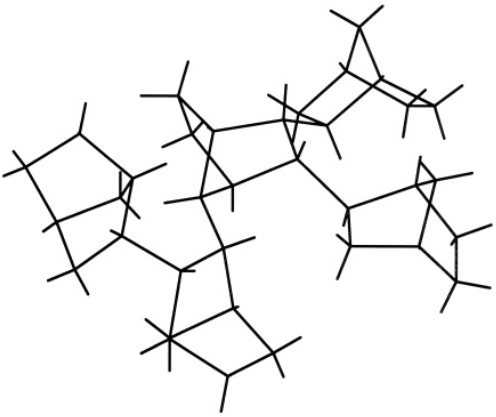
Fig.4: Stereochemistry of the 3 triads of an erythroditactic polynorbornene

Cp_2ZrCl_2/mao is another catalyst producing a soluble polynorbornene again the CPMAS is similar to the ones described above (type I), but there is a significant difference in the WAXS and the high resolution ^{13}C-NMR spectra. Again based on oligomerisation experiments a microstructure containing rather no rr-triads has been proposed for this polymer (the polymerstructure is placed between heterotactic and isotactic).

Among the insoluble polymers three subtypes are found: rac-$[Me_2Si(Ind)_2]ZrCl_2$ is the only catalyst producing a semicrystalline polymer (CPMAS-type II) as reflected by the WAXS. Based on our oligomerisation experiments an erythrodiisotactic microstructure is proposed.

The products made by the Pd-catalysts, rac-$[C_2H_4(IndH_4)_2]ZrCl_2$, and meso-$[Me_2Si(Ind)_2]ZrCl_2$ show an increased number of resonances in the CPMAS spectra which may be interpreted in terms of significant changes of the microstructure (CPMAS-type III). These changes are most probably caused by crosslinks.

We were able to isolate a pentamer from a hydrooligomerisation of



norbornene catalyzed by rac-[C_2H_4(lndH$_4$)$_2$]ZrCl$_2$ and the X-ray structure shows a trisubstituted norbornene unit. All norbornene-norbornene linkages show a meso arrangement of the monomer units.

WAXS as well as the intensity distribution of the CPMAS show a difference between the products generated by the Pd-catalysts and the meso metallocene. While WAXS of the "Pd-products" are similar to the ones found for the more or less „isotactic“-working metallocenes rac-[Me$_2$Si(Ind)$_2$]ZrCl$_2$ and Cp$_2$ZrCl$_2$, the one of the polymer produced by meso-[Me$_2$Si(Ind)$_2$]ZrCl$_2$ corresponds to the „atactic“ polynorbornenes produced by the Ni-catalysts and [R$_2$C(Cp)(Flu)]ZrCl$_2$/mao (R=Me,Ph). Therefore we propose and atactic, crosslinked structure for the polynorbornene generated by the meso-metallocene and an diisotactic,crosslinked structure for the ones from Pd-catalysts.

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