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Concentration effects of methylalumoxane, palladium and nickel pre-catalyst and monomer in the vinyl polymerization of norbornene

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Summary

The vinyl polymerization of norbornene with di-μ-chloro-bis-(6-methoxybicyclo-[2.2.1]hept-2-ene-5σ,2π)-palladium(II), Ni(acetylacetonate)$_2$ and Ni(2-ethylhexanoate)$_2$ in combination with methylalumoxane (MAO) was investigated by varying the molar MAO:metal-complex ratio, the norbornene:metal ratio and the metal concentration. The effects on the catalyst activity could be explained with a complexation equilibrium for the active homogeneous complex. Activity data in combination with polymer analyses suggest that at low, yet economical Al(MAO):metal ratios of 100 the fraction of active metal centers is less than 15%. The turnover frequency for the monomer insertion was found to reach 50 s^{-1}. Polydispersities around $M_w/M_n = 2$ indicate a coordination polymerization with chain transfer and a single-site character of the active centers.

Introduction

Norbornene (**1**, NB) and its derivatives can be polymerized in three different ways (Figure 1). Each route leads to its own polymer type which is different in structure and properties from the other two.

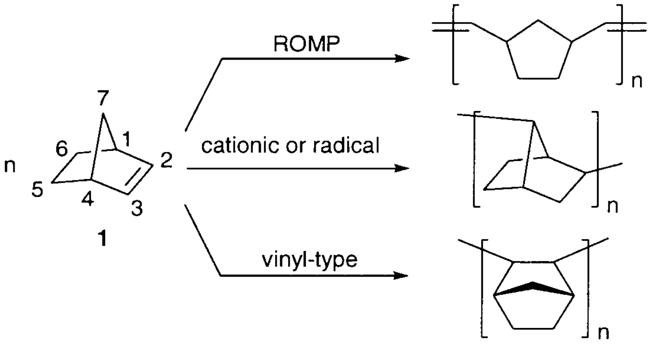

Figure 1. Schematic representation of the three different types of polymerization for norbornene.

The best known polymerization of norbornene is the ring-opening metathesis polymerization (ROMP) [1]. Little is known about the cationic and the radical polymerization of norbornene. The result is a low molar mass oligomeric material with 2,7-connectivity of the monomer. Initiators for the radical polymerization were, for example, azoisobutyronitrile (AIBN), tert-butyl peracetate or tert-butyl perpivalate. The cationic polymerization was started with $EtAlCl_2$ [2].

It is also possible to polymerize norbornene and to leave the bicyclic structural unit intact, i.e. to open only the double bond of the π-component. Such a polymerization which is akin to the classical olefin polymerization is termed a vinyl polymerization here. The product does not contain anymore double bonds. The vinyl polymerization of norbornene can take place as a homo- or as a copolymerization. The vinyl polymerization is much less developed for norbornene than ROMP [3].

The homopolymer vinyl-polynorbornene is a specialty polymer with good mechanical strength, heat resistivity, good solubility in organic solvents and optical transparency. Vinyl homo-polynorbornene is investigated *inter alia* as a deep ultraviolet photoresist and interlevel dielectric in microelectronics applications. High glass-transition temperature polynorbornenes exhibit many of the key performance criteria necessary for these demanding applications, which include good adhesion to a variety of films and substrates, thermal stability, high elongation-to-break values and low stress [4]. The vinyl norbornene polymer is also said to have a cost advantage over related materials [5]. Films made from norbornene vinyl-polymer are excellent in transparency and heat resistance and have unchanged viscoelastic and electric characteristics to markedly high temperatures. Such a film is suitable for a condensor or an insulator [6]. Homo-polynorbornene films are applied as cover layers for liquid-crystal displays. The polymer is developed by the B.F. Goodrich Corp. under the trade name Avatrel® dielectric polymer [4,5]. The sometimes poor adhesion of homo-polynorbornene can be improved by attaching triethoxysilyl groups to the polymer backbone. Alkyl groups on the backbone lower the rigidity of the system and result in higher elongation-to-break values and a decrease in residual stress [4].

Catalysts containing the metals titanium, zirconium [7], cobalt [8], chromium [9], nickel [10,11] and palladium [12] are described in the literature for the vinyl homo-polymerization of norbornene and strained cyclic olefins in general [13,14].

Our interest concerned the pre-catalysts di-μ-chloro-bis-(6-methoxybicyclo[2.2.1]-hept-2-ene-5σ,2π)-palladium(II) (**A**) [15] and the nickel complexes $Ni(acetylacetonate)_2$ [11] (**B**) and $Ni(2\text{-ethylhexanoate})_2$ [11] (**C**) (Figure 2). These complexes had only been briefly described in the literature concerning their behavior in the vinyl polymerization of norbornene. In view of the industrial importance of vinyl polynorbornene we report here on a more detailed polymerization investigation by varying the ratio of reactands.

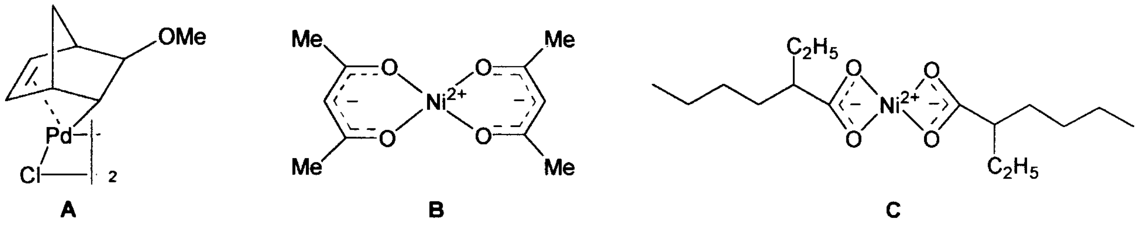

Figure 2. Schematic representation of the pre-catalysts di-μ-chloro-bis-(6-methoxybicyclo[2.2.1]hept-2-ene-5σ,2π)-palladium(II) (**A**), $Ni(acetylacetonate)_2$ (**B**) and $Ni(2\text{-ethylhexanoate})_2$ (**C**).

Experimental

Materials

Palladium(II) chloride (Acros), 2,5-norbornadiene (Lancaster), Ni(acetylacetonate)$_2$ (Merck), Ni(2-ethylhexanoate)$_2$ (Aldrich) and methylaluminoxane (MAO) (10% solution in toluene, Witco) was used as received. Toluene was dried over sodium. Methylene dichloride was dried over CaH$_2$. Methanol was dried over 4 Å molecular sieve and norbornene (Aldrich) was purified by distillation and used as a solution in toluene (c = 2.3 mmol/ml). All work involving air- and/or moisture-sensitive compounds was carried out by using standard vacuum, Schlenk or drybox techniques.
Di-μ-chloro-bis-(6-methoxybicyclo[2.2.1]hept-2-ene-5σ,2π)-palladium(II) (**A**) was synthesized by addition of sodium methoxide to bicyclo[2.2.1]-hepta-2,5-diene-dichloro palladium(II) [16] in methanol according to a procedure published by Green and Hancock [17] and stored under argon in a glove box.

Instruments

Gel permeation chromatography (GPC) analysis were performed on a 2-3g/mL polymer solution in 1,2,4-trichlorbenzene. The dried polymer samples were dissolved in 1,2,4-trichlorbenzene with a concentration of 2-3 g/mL. The polymer solution was filtered (Schleicher&Schuell, Rezist 30/0, 45 PTFE, 0.45 μm, Grünrand) and the clear solution stored at 4-6 °C in glass vials with a bakelite-sealing and a PTFE stopper. Filtration of the polymer solution should remove any catalyst residues for the protection of the GPC columns. The GPC was measured at 140°C with an injection volume of 200 μl and with a rate of 1 mL/min. The thermal properties of the polymer samples were investigated under nitrogen with a heating rate of 10 K/min by thermogravimetric analysis (TGA), differential thermal analysis (DTA) on a Netzsch STA 409 and by differential scanning analysis (DSC) on a Netzsch DSC 200.

Polymerization

General procedures for the homopolymerization of norbornene with the catalysts **A**, **B** and **C**: A 50 mL Schlenk-flask was charged with the norbornene solution and the MAO-solution was added. The flask was emersed in a water bath to ensure a constant temperature during the reaction. After 1 min. the solution of the catalyst was added via syringe and the mixture was stirred with a magnetic stirrer. The polymerization was stopped through the addition of 40 mL of a 10:1 methanol/conc. HCl mixture. The precipitated polymer was filtered, washed with methanol and dried *in vacuo* for 5 h.

Results and Discussion

The vinyl polymerization of norbornene (NB) with the complexes **A**, **B**, and **C** in combination with methylalumoxane (MAO) has been carried out under various conditions. Experiments, conditions and results are summarized in Table 1 and 2.

Table 1. Polymerization activity as function of the molar Pd : Al ratio for the catalyst system **A**/MAO

Molar ratio Pd : Al	Yield [%]	Activity [g PNB/mol Pd·h]
1 : 200	97	$4.2\cdot10^6$
1 : 100	87	$3.7\cdot10^6$
1 : 60	75	$3.2\cdot10^6$
1 : 30	40	$1.7\cdot10^6$

Pd : NB= 1 : 760; n(Pd) = $10.5\cdot10^{-3}$ mmol; n(NB) = 8.1 mmol; time = 1 min; room temperature.

Table 2. Polymerization activity as function of the molar metal:norbornene ratio (M : NB) for catalysts **A**, **B** and **C** in combination with MAO

Cat.	Molar ratio M : NB	Yield [%]	Activity [g PNB/ mol M·h]	M_w [g·mol^{-1}]	M_w / M_n
A	1 : 770	75 [a]	$3.2\cdot10^6$	not soluble	
A	1 : 1540	46 [a]	$4.0\cdot10^6$	not soluble	
A	1 : 2300	41 [a]	$5.3\cdot10^6$	not soluble	
A	1 : 3070	27 [a]	$4.6\cdot10^6$	not soluble	
B	1 : 770	47 [a]	$2.0\cdot10^6$	$4.0\cdot10^5$	3.1
B	1 : 2020	44 [b]	$2.5\cdot10^6$	not measured	
B	1 : 3040	37 [b]	$3.2\cdot10^6$	$7.4\cdot10^5$	2.4
B	1 : 4050	35 [b]	$4.0\cdot10^6$	not measured	
B	1 : 5060	24 [b]	$3.4\cdot10^6$	$7.7\cdot10^5$	2.1
C	1 : 770	27 [a]	$1.2\cdot10^6$	$7.3\cdot10^5$	3.2
C	1 : 2020	31 [b]	$1.7\cdot10^6$	$9.8\cdot10^5$	2.2
C	1 : 3040	30 [b]	$2.5\cdot10^6$	$1.1\cdot10^6$	1.9
C	1 : 4050	22 [b]	$2.5\cdot10^6$	$1.1\cdot10^6$	2.1
C	1 : 5060	20 [b]	$2.9\cdot10^6$	$1.2\cdot10^6$	1.9

molar ratio Pd : Al = 1 : 60; Ni : Al = 1 : 100; n(cat) = $10.5\cdot10^{-3}$ mmol; room temperature.
[a] time = 1 min; [b] time = 2 min.

According to the literature, complex **A** is already weakly active without MAO as a cocatalyst. A competitive polymerization activity of **A** requires, however, the presence of MAO. A large excess of MAO is normally employed with the molar ratio of Al to transition metal in the range of 200:1 to 10^3:1 [18]. Our results for **A** show that the MAO excess can be lowered considerably without a significant loss in activity (Figure 3). Only when the Al:Pd ratio drops below a value of 30 does a significant decrease in activity occur. This decrease in activity may be explained by an equilibrium in the formation of the active complex (equation 1) or by an increasing influence of impurities at a smaller MAO excess. A related complexation equilibrium has been suggested for the olefin polymerization with metallocene(zirconocene)-MAO catalysts [19].

$$\begin{array}{ccccc} \text{inactive} & & & & \text{active} \\ \text{pre-catalyst} & & \text{cocatalyst} & & [\text{pre-catalyst-cocatalyst-adduct}]^{\ddagger} \\ ML_n & + & MAO & \rightleftharpoons & [ML_n{\bullet}MAO]^{\ddagger} \text{ or } \{[ML_{n-m}]^{m+}\}^{\ddagger}\,[L_m\text{-}MAO]^{m-} \end{array} \qquad (1)$$

Our results are in agreement with the literature where monomer conversions up to 98% and catalysts activities typically on the magnitude of 10^6 g PNB/mol Pd·h were reported. Only with large Al:Pd ratios of 6000:1 did the activities increase to 10^8 g PNB/mol Pd·h [18]. A similar curve of activity (or yield) versus Al:M ratio was found for M = Ni with **B**/MAO [20].

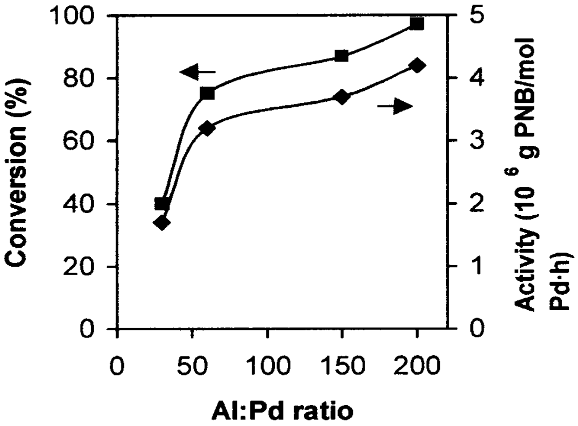

Figure 3. Monomer conversion and polymerization activity as function of the molar Al : Pd ratio for the catalyst system **A**/MAO [n(Pd) = $10.5 \cdot 10^{-3}$ mmol, n(NB)= 8.1 mmol; reaction time = 1 min.; room temperature, PNB = polynorbornene].

An increase in the monomer:metal ratio (NB:M) usually leads to an increase in activity. For catalysts **A**/MAO and **B**/MAO the activity passed through a maximum for NB:M at about 2300 and 4100, respectively. An further increase of NB:M lowered the activity again (Figure 4). This may be explained by impurities which are contained in the monomer and eventually decrease the number of active centers. Alternatively, we may invoke again the activation equilibrium between the pre-catalyst and MAO to give the active catalyst. The increase in monomer leads to a concomittant dilution of the metal and MAO content. The total reaction volume increased from 6 to 28 mL. An increased dilution leads to a higher degree of dissociation for the active complex according to the law of mass action. It can be noted that the maximum in Figure 4 is shifted to higher NB:M ratios with a lower activity of the complex. The maximum of the least active complex **C** has, thus, not been reached at the highest NB:M ratio of 5000. In the literature, a steady linear increase in activity has just been reported for **B**/MAO in the range of NB:Ni = 1500:1 to 6000:1. At the same time, the activity was between $2.4 \cdot 10^4$ and $1.1 \cdot 10^5$ g PNB/mol Ni·h [20]. This is much less than the activities found by us on the order of $2\text{-}4 \cdot 10^6$ g PNB/mol Ni·h for **B**/MAO and NB:Ni between 770 and 5000:1 (see Table 2). Generally it is difficult to compare polymerization results for the same catalyst with values from literature sources. A sizable number of parameters enter in a polymerization reaction and can considerably affect the activities, e.g. temperature, solvent, catalyst-cocatalyst activation time, age of MAO, relative ratios of catalyst:cocatalyst:monomer, concentrations. With respect to concentrations we have found in comparative experiments with **B**/MAO that an increase of the reaction volume from 10 mL to 30 mL resulted in a sizable decrease of the polymerization activity by factor 30.

To test the validity for our repeated assumption of an activation equilibrium we have varied the concentration for catalyst **B**/MAO at constant ratios of Al:Ni = 100 and NB:Ni = 1000 at n(Ni) = $10.5 \cdot 10^{-3}$ mmol. The activity dropped upon dilution by more than one order of magnitude from $2.6 \cdot 10^6$ g PNB/mol Ni·h at a reaction volume of 10 mL to $7.8 \cdot 10^4$ g PNB/mol Ni·h at a reaction volume of 30 mL.

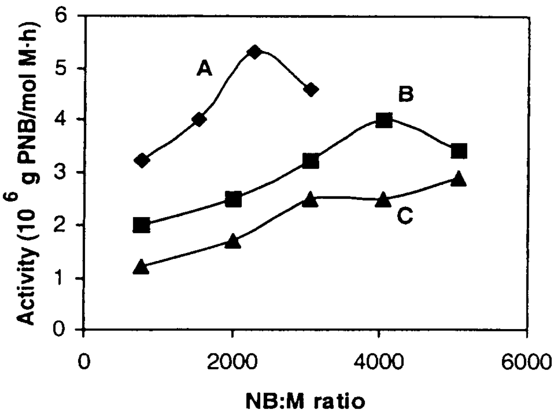

Figure 4. Polymerization activity as function of the molar norbornene:metal ratio (NB:M) for catalysts **A**, **B** and **C** in combination with MAO [n(M) = $10.5 \cdot 10^{-3}$ mmol; Al:M ratio = 60 for **A** and 100 for **B** and **C**; reaction time = 1 min for **A** and 2 min for **B** and **C**; room temperature].

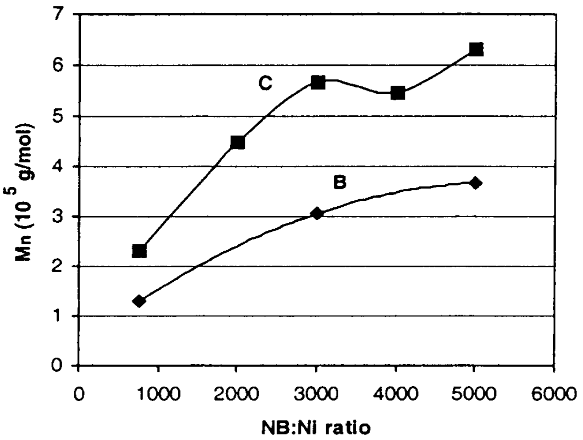

Figure 5. Molar mass (M_n) as a function of the molar norbornene:nickel ratio (NB:Ni) for catalysts **B** and **C** in combination with MAO [n(Ni) = $10.5 \cdot 10^{-3}$ mmol; Al:Ni ratio = 100; reaction time = 2 min; room temperature; conversion between 20 and 36%].

Both nickel catalysts **B** and **C**/MAO exhibit an steady increase of molar mass with increasing monomer:metal ratio (Figure 5). At the same time the molar mass (M_n) is rather high, when taking into account the NB:Ni ratio. With M_{NB} = 94.16 g/mol an M_n of $5.5 \cdot 10^5$ g/mol (cf. **C** in Figure 5) corresponds to a chain of about 5800 monomer units. At the same time, the preset molar NB:Ni ratio is around 3500 (cf. **C**) and the average conversion was 25% only. The conversion dropped somewhat from 30-36% at the low end of the NB:Ni ratio to 20-26% at the high end. This implies that only a fraction of the metal atoms is catalytically active. If we assume that each active metal center gives rise to only one chain than the fraction of active metal atoms is about 15% at the above NB:Ni ratio. If an average chain length of 5800 monomer units is reached after 2 min (120 s) at the most than this translates into a turnover frequency of about 50 s^{-1}. The fraction of active metal centers will be halfed and the turnover frequency doubled when two chains are formed by each active catalyst molecule. The rather narrow and close to a value of 2 (Figure 6). A value of 2 is the theoretical dispersity for a Schulz-Flory type distribution which arises from an ideally behaved polymerization reaction with a chain-termination reaction. The value of $Q \approx 2$ indicates a single-site character, i.e. highly homogeneous structure of the active catalyst species.

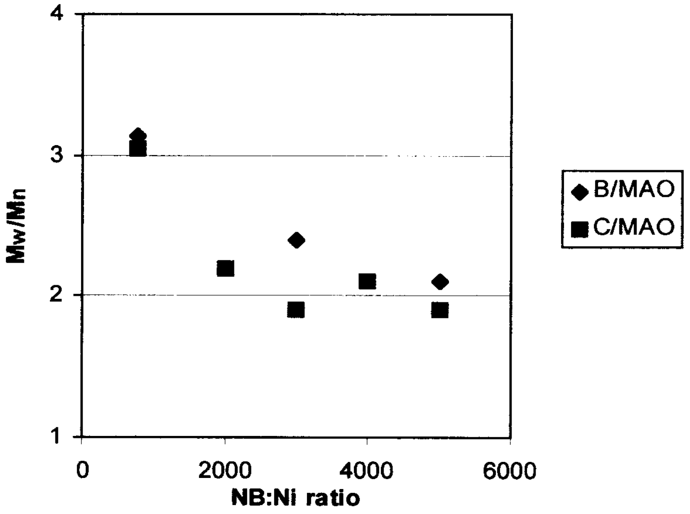

Figure 6. Dispersities for polymers obtained at different molar norbornene:nickel ratios (NB:Ni) in correspondence to Figure 5.

Selected polymer samples were investigated by thermogravimetric analysis (TGA), differential thermal analysis (DTA), and differential scanning analysis (DSC). TGA studies showed that the polymer samples were very stable up to about 400°C (under nitrogen). A more accurate decomposition temperature was obtained with DTA. Slight differences were seen from DTA depending on the pre-catalyst: Polymer from **A**/MAO decomposition at 395°C, **B**/MAO 438°C and **C**/MAO 463°C. Heating under air showed an earlier onset of decomposition around 250 to 300 °C. The determination of the glass transition temperature (T_g) for vinyl homo-polynorbornene is described as difficult since it is apparently located close to the temperature range where decomposition tends to set in. Our DSC studies did not show an endothermic signal upon heating up to 390 °C. Possibilities to determine a glass transition temperature involved the extrapolation of the glass transition temperatures of copolymers towards the one of the homopolymer (by DSC) and the measurement of thermal density fluctuations through absolute small angle X-ray scattering (SAXS) [21].

Conclusions

The vinyl polymerization of norbornene with a palladium and two nickel complexes in combination with methylalumoxane has been investigated. The effects in catalyst activity from variation of the molar MAO:metal-complex ratio, the norbornene-monomer:metal ratio and the metal concentration are explained with a complexation equilibrium for the active homogeneous complex. At an economical Al(MAO):metal ratio of 100 the fraction of active centers is on the order of 15% of all metal atoms according to the polymer analysis. Thus, attempts should also be made to increase the number of active centers. The turnover frequency for the monomer insertion was found to reach 50 s^{-1}. Polydispersities around $M_w/M_n = 2$ indicated a coordination polymerization with chain transfer and a single-site character of the active centers.

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