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Bidentate [*N, N*] nickel complexes with salen type ligands for polymerization of methyl methacrylate

RAPID COMMUNICATION

Summary — Nickel complexes with bidentate [N,N] salen type ligands activated by different organoaluminium compounds, within which methylalumoxane (MAO) turned out to be the best, were studied in methyl methacrylate (MMA) polymerization. Activity of the investigated complexes was found to increase with increasing Al/Ni molar ratio. The studied catalytic systems were found to produce high molecular weight (M_w = 280 000—560 000) poly(methyl methacrylate) (PMMA) with rich syndiotactic microstructure. Activity of the catalyst as well as M_w and glass transition temperature (T_g) of poly(methyl methacrylate) (PMMA) are dependent on polymerization temperature and they reach maximum values for reaction temperature about 30 °C.

Key words: methyl methacrylate, polymerization, nickel complex, modified salen ligand, methylalumoxane.

DWUKLESZCZOWE [*N,N*] KOMPLEKSY NIKLU ZE ZMODYFIKOWANYMI LIGANDAMI SALENOWYMI JAKO KATALIZATORY POLIMERYZACJI METAKRYLANU METYLU

Streszczenie — Otrzymano kompleksy niklu [N,N]$NiBr_2$, które po aktywacji związkiem glinoorganicznym zastosowano w polimeryzacji metakrylanu metylu (MMA). Dwukleszczowe ligandy [N,N] uzyskano zastępując w ligandach salenowych grupy hydroksylowe podstawione do pierścieni fenylowych różnymi grupami alkoksylowymi (OMe lub $OCH_2C_6H_5$). Metyloalumoksan (MAO) okazał się skutecznym aktywatorem kompleksów niklu w polimeryzacji MMA. Same kompleksy bez aktywatora nie wykazywały żadnej aktywności. Stwierdzono, że aktywność badanych układów katalitycznych rośnie ze wzrostem stosunku molowego Al/Ni. W wyniku polimeryzacji w stosowanych warunkach otrzymano poli(metakrylan metylu) (PMMA) z przewagą triad syndiotaktycznych charakteryzujący się stosunkowo dużym ciężarem cząsteczkowym (M_w = 280 000—560 000) i rozkładem M_w/M_n od 6.07 do 7.53 oraz temperaturą zeszklenia (T_g) wynoszącą ok. 120 °C. Aktywność katalizatora oraz wartości M_w i T_g otrzymanych próbek PMMA były zależne od temperatury polimeryzacji i osiągały maksymalne wartości, gdy rekcję prowadzono w temp. ok. 30 °C.

Słowa kluczowe: metakrylan metylu, polimeryzacja, kompleks niklu, zmodyfikowany ligand salenowy, metyloalumoksan.

The highest global commercial production of plastics is recorded for polyolefins, and principally for polyethylene (PE). Huge volumes of these polymers are consumed worldwide due to attractive combination of their perfect chemical and physical properties with low production costs and good processing performance. Polyolefins can be synthesized using free-radical initiator (only PE) or organo-metallic catalyst, which include both early transition metal catalysts [1, 2] and late transition metal catalysts [3]. Despite numerous unquestionable advantages of polyolefins, their hydrophobic nature and hence incompatibility with other polar materials creates problems in the production of composite systems, while poor adhesion makes it hard to incorporate polar additives to the polymer. In order to improve applicability of polyolefins, polar functional groups are introduced to their structures, which impart chemical activity to polyolefins and improve their adhesion to and compatibility with other materials.

The method which is in common practice to functionalize hydrocarbon macromolecules (*i.e.* to incorporate polar functional groups to such molecules) is radical-induced grafting or the addition process of polar compounds to polyolefins in reactive processing (post-polymerization modification). Further to post-polymeriza-

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tion modification method, which is applied directly after the polyolefin product has been obtained, functional groups may be added to the polymer chain at the polymerization stage, through copolymerization of olefins and polar monomer. Present-day commercial copolymerization processes of ethylene and polar monomers follow the high pressure route only with the use of radical initiators. This method is used to produce copolymers of ethylene with vinyl acetate or acrylates (methyl, ethyl and/or butyl acrylates). In the low pressure process which is generally employed worldwide for the synthesis of polyolefins, and which is definitely less energy-consuming, early transition metal complexes (*i.e.* both Ziegler-Natta catalysts and metallocene ones) are poisoned by polar monomers due to high oxophilicity of those metals and the tendency of polar groups to coordinate to the active species [4, 5]. On the other hand, rare earth metal initiators are effective for polymerization and copolymerization of polar monomers [6] but they are unsuitable for copolymerization of polar monomers with non-polar ones since the oxophilicity of rare earth metals is too high [7]. In recent years there has been increasing interest in the development of late transition metal complexes (Pd, Pt or Ni) which are less oxophilic than those of early transition metals and which potentially would not be poisoned by O-containing polar functionalities [5, 7, 8]. A catalyst which contained the α-diimino-Pd(II) complex, activated with methylalumoxane (MAO), was used in direct copolymerization of ethylene with acrylic monomers, and the structure of the resultant product was highly branched, with ester functional groups [4]. In turn, α-diimine Ni catalysts were used for co- and terpolymerization of unsaturated alcohols with ethylene and propylene [8]. Such complexes, however, are more commonly investigated in the homopolymerization processes of polar monomers. Thus, various nickel catalysts, which were resistant to moisture and stable during exposure to air and which contained sterically expanded N,O-chelate ligands, after activation with MAO, were successfully used in the synthesis of syndiotactic poly(methyl methacrylate) (PMMA) [5], while other bidentate, tridentate and tetradentate iron(II) and cobalt(II) complexes, with donor nitrogen atoms, were used for polymerization of methyl acrylate and *t*-butyl acrylate, as well as methyl methacrylate [9, 10].

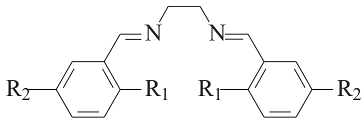
Our recent studies on the latest generation the post-metallocene systems, cover the synthesis and catalytic performance in ethylene polymerization of various new complexes of group 4 and 5 metals (Ti, V, Zr) with tetradentate salen ligands [O,N,N,O], which contain various substituents in aromatic rings and which are activated by various organoaluminum compounds [11, 12]. As the next stage, we decided to modify the structures of salen ligands by blocking phenyl ring hydroxyl groups, which led to the formation of ligands with two donor atoms of nitrogen; that might be used to prepare the complexes of metal of further groups in the periodic table of elements, as precursors of potential catalysts for polymerization and copolymerization of polar monomers. This paper presents the preliminary findings for polymerization of methyl methacrylate with the use of Ni complexes with bidentate type [N,N] ligands activated with various organoaluminum compounds.

EXPERIMENTAL

Materials

All operations were conducted under inert atmosphere (nitrogen) using the standard Schlenk and glove box techniques. Ethylene (PKN Orlen, Poland) and nitrogen (Messer) were used after having been passed through a column packed with sodium metal supported on alumina. CH_2Cl_2 and methyl methacrylate (MMA) (POCh Gliwice, Poland) were distilled from CaH_2 prior to use. Methylalumoxane (MAO) as a 10.0 wt. % solution in toluene (Witco), Et_2AlCl as 1M solution in toluene (Aldrich) and (1,2-dimethoxyethane)nickel(II) bromide [(DME)$NiBr_2$, Aldrich] were used without further purification. Pure toluene (POCh Gliwice, Poland) was distilled from sodium before use.

All ligands utilized in this study were synthesized by the research team of prof. W. Bukowski (Rzeszów Technical University) and their structures were shown by formula (I). The structures of presently employed ligands were close to those of salen ligands used in our earlier investigations [11, 12], except that the groups -OH at position R_1 were substituted by OMe or $OCH_2C_6H_5$ groups.



(I)

$R_1 = OCH_3$ or $OCH_2—C_6H_5$
$R_2 = OCH_3$ or H

Synthesis of Ni complexes

Nickel complexes with bidentate type [N,N] ligands were synthesized according to the well known method [13—15] based on the displacement of 1,2-dimethoxyethane (DME) from (DME)$NiBr_2$ by the respective ligand (L).

$$L + (DME)NiBr_2 \rightarrow LNiBr_2 + DME \tag{1}$$

The reaction was conducted in CH_2Cl_2 at room temperature (about 25 °C) for 20 hours with the use of equimolar amounts of nickel compound and ligand. The structures of D_1 and D_2 complexes (dependent on the ligands used) are described by formula (II). After filtration and washing with hexane, the solid complex D_1 was dried in vacuum. The resulting solution of D_2 complex was subjected to concentration, and then hexane was used to precipitate the solid product, which was filtered and dried under vacuum.

Polymerization reaction

Polymerization of MMA was conducted in a 100 ml glass flask, in a solvent (toluene or dichloromethane, 20 ml). The following components were then added to the flask: 5 ml of freshly distilled MMA, pre-defined amount of organoaluminum activator (MAO or Et_2AlCl), and finally the tested amount of nickel complex. The polymerization process was conducted at room temperature over 105 minutes, if not specified otherwise. After the assumed time has passed, the reaction was stopped by the addition of acidic methanol solution. The polymer was subsequently filtered off, washed several times with methanol and dried in vacuum.

Methods of testing

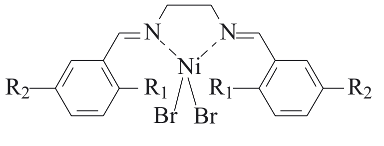
Elemental analyses of $[N,N]NiBr_2$ complexes were performed using elemental analyzer Vario ELIII. Molecular weight ($\overline{M}_w$) values and molecular weight distribution ($\overline{M}_w/\overline{M}_n$) were determined by gel permeation chromatography (GPC) at 35 °C, with the use of tetrahydrofuran (THF) as a solvent and standard polystyrene as the reference.

The PMMA microstructure was analysed by ^1H NMR method. Polymer samples (10 mg) were prepared in the form of solutions in $CDCl_3$ (0.6 ml).

The polymer glass transition temperature (T_g) was determined by differential scanning calorimetry (DSC) analyses, using a 2010 DSC calorimeter from TA Instruments.

RESULTS AND DISCUSSION

The ligands in obtained complexes [formula (II)] had different substituents on aromatic rings at positions R_1 and R_2. The complex D_1 had OMe groups at both those positions, while the complex D_2 had only one big substituent $OCH_2C_6H_5$ at R_1 in the phenyl ring. The complex D_1 was obtained as a powder which was light-green with yellow tinge, at the yield of about 60 %, while the complex D_2 was violet-coloured and the synthesis reaction yield approached 73 %.



(II)

Complex D_1: $R_1 = R_2 = OCH_3$
Complex D_2: $R_1 = OCH_2{-}C_6H_5$, $R_2 = H$

T a b l e 1. Elemental analyses data of $[N,N]NiBr_2$ complexes in comparison with calculated data

Complex	C, wt. %		N, wt. %		H, wt. %	
	exp.	calc.	exp.	calc.	exp.	calc.
D_1	38.78	41.78	4.79	4.87	4.24	4.21
D_2	50.25	54.02	4.25	4.20	4.22	4.23

The measured C, H, N contents in investigated complexes and calculated by their structural formula are presented in Table 1. Crude complexes were used in polymerization processes.

Polymerization of methyl methacrylate

The preliminary tests demonstrated that none of the catalyst components can by itself initiate the methyl methacrylate polymerization process. The experimental results of activity of used for polymerization catalysts activated with organoaluminum compounds, were presented in Table 2. Polymerization process was carried out in toluene and nickel concentration in all cases was [Ni] = 0.75 mmol/dm^3. Et_2AlCl in composition with selected nickel complexes gave no polymer, while the presence of MAO proved catalytic activity for the MMA polymerization process. It was also found that, irrespective of the complex structure, activity of the complex which involved MAO was improving with the increasing amount of the organoaluminum activator in the reaction medium, *i.e.* with the growing Al/Ni molar ratio.

T a b l e 2. Effect of organoaluminum activator on the catalyst activity

Complex	Al activator	Al/Ni molar ratio	Activity, kg PMMA/mol Ni
D_1	MAO	150	3.3
		450	15.3
D_2	Et_2AlCl	150	—
	MAO	75	5.3
		150	22.0
		300	32.7
		450	40.7

Attention should be given to the fact that clearly superior activity is offered by a nickel compound D_2 with the ligand which incorporates a more sterically expanded alkyl substituent ($CH_2C_6H_5$) in the alkoxy group at position R_1, in relation to the complex which contains a relatively small group OMe in that place (D_1).

Table 3. Effect of solvent on D_2/MAO catalyst activity in MMA polymerization

Solvent	Reaction time min	Activity kg PMMA/mol Ni
toluene	105	22.0
CH_2Cl_2		5.3
toluene	1200	49.3
CH_2Cl_2		29.3

The effect of solvent type on the yield of the polymerization process was also verified for the more active complex D_2 activated with MAO. For these investigation constant values of [Ni] = 0.75 mmol/dm^3 and ratios Al/Ni = 150 was employed. Two solvents with different polarities were used (toluene and dichloromethane). The results are listed in Table 3. The studied catalytic system appeared to be clearly more active in toluene than in dichloromethane, irrespective of the adopted reaction conditions.

The temperature effect on efficiency of MMA polymerization was studied, too. Activity data for the catalyst D_2/MAO obtained for reaction temperatures within 5 to 60 °C were illustrated in Figure 1.

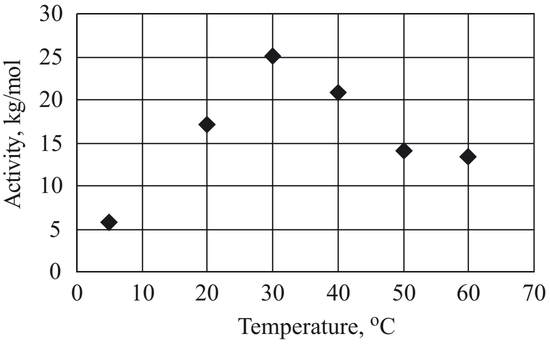


Fig. 1. Temperature dependence of D_2/MAO catalytic system activity in MMA polymerization; polymerization conditions: [MMA] = 2.2 mol/dm^3, Al/Ni = 290, reaction time 180 min

The catalyst activity versus temperature function was found to pass through its maximum value at about 30 °C. A similar temperature profile, but with the maximum value at 50 °C, was also observed for MMA polymerization with the use of other nickel complexes which contained N,O-chelate ligands [5]. The declining activity of a tested complex at higher temperatures may be caused by its low thermal stability. That is confirmed by a dark deposit which precipitates directly after both catalyst components are mixed together at higher temperatures. Low stability of nickel complexes is known from literature reports, and it was demonstrated in [16] that dialkyl-(2,2′-bipyridyl)nickel compounds are decomposed by addition of trialkylaluminum compounds with separation of elemental nickel.

Properties of PMMA

The polymers were isolated as white solids, and they were characterized by GPC, DSC and ^{1}H NMR analytical methods. The properties determined are listed in Table 4. Most of those polymers appeared to be insoluble in THF at room temperature or at elevated temperature (30—50 °C) which suggested their high M_w values. For the polymers obtained with the catalyst D_2/MAO, values of M_w in the range of 280 000—560 000 were found, while their distribution M_w/M_n were from 6.07 up to 7.53. T_g of the produced PMMA was about 120 °C. The data collected in Table 4 demonstrate that the products obtained at the temperature close to the optimum (from the reaction yield view point) show the highest values of the properties analyzed herein at the same time.

^{1}H NMR spectra of the samples, which were soluble at the adopted conditions, were similar. A typical spectrum presented in Figure 2 demonstrates that the stu-

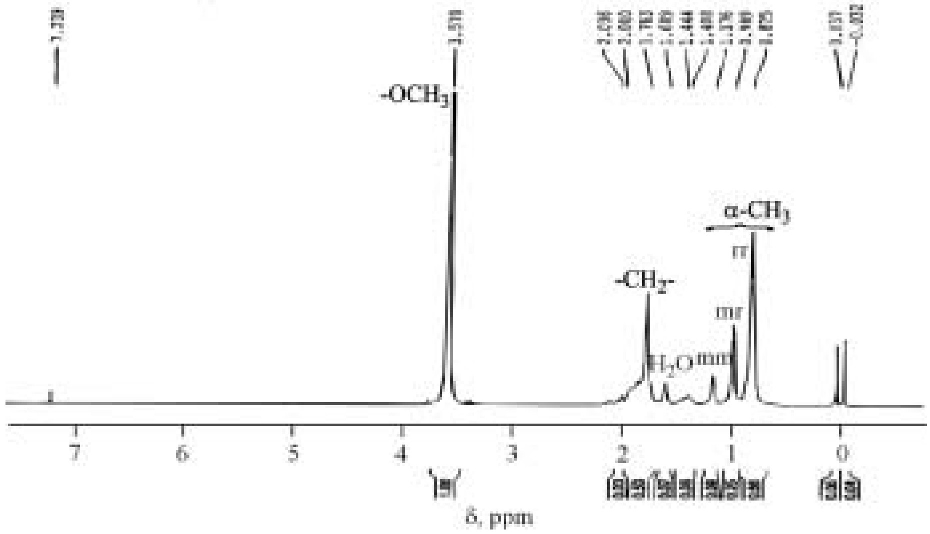


Fig. 2. Typical ^{1}H NMR spectrum of PMMA sample

died catalytic systems initiate MMA polymerization to PMMA with rich syndiotactic microstructures (syndiotactic triads — rr are definitely dominant in the spectrum, with a very low part of isotactic triads — mm).

Table 4. Molecular weights (M_w) and glass transition temperatures (T_g) of obtained PMMA samples

Catalyst	Polymerization conditions		M_w g/mol	M_w/M_n	T_g, °C
	time, min	temp., °C			
D_1	105	20	—	—	118.7
D_2	105	20	—	—	124.4
	180	5	283 800	6.07	113.2
		20	434 400	6.54	124.3
		30	—	—	124.0
		40	559 300	7.53	125.1
		50	—	—	123.0
		60	495 400	7.40	125.9

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