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Preparation of rubbery polyethylene and polyethyelene wax using homogeneous late transition metal catalyst

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ABSTRACT

Rubber form polyethylene with crystallinity of about 1 to 14% was prepared using a late transition metal catalyst of bis(2,6-isopropyl phenyl) 1,4-diazobutadine Nickel(II) dibromide, $[(2,6\text{-i-prph})_2\ DABMe_2]NiBr_2$. Methylaluminoxan (MAO) and triisobuthylaluminum (TIBA) were used as cocatalyst and scavenger respectively. The optimum activity of the catalyst was observed at [Al]:[Ni]=3333:1 molar ratio and polymerization temperature of 25°C. Higher concentration of MAO than the optimum value not only decreased the activity of the catalyst but also produced polyethylene-wax (PE-Wax). The rate/time profile of the polymerization was a decay type with an acceleration period of about 60 min at polymerization temperature of 25°C. However, the higher the temperature to 65°C, the lower the acceleration period and the higher decay rate were observed. The polyethylene produced at temperature up to 55°C showed rubbery form while the reaction at 65°C produced PE-Wax. Activity of the catalyst was increased with monomer pressure to 5 bars. The viscosity average molecular weight (M_v) of the polymer obtained was 7.5×10^4 at the monomer pressure of 3 bars and 35°C temperature.

KEYWORDS

Rubbery form polyethylene;
Late transition metal catalyst;
Ni-catalyst;
Ethylene polymerization;
Solution polymerization.

INTRODUCTION

Although the industrial process of shell higher olefin process (SHOP) is an example to produce oligomers by using homogeneous chelate of Ni(II) complexes with very high activity[1,2] but the late transition metal catalyst systems of Fe, Co, Ni and Pd have developed since the mid-1990s when Brookhart and his group reported a family of new cationic Pd(II) and Ni(II) α-diimine catalyst for the polymerization of ethylene, α-olefins and even cyclic olefins[1,3-9]. Significant electronic effects were observed in a number of systems[10-12]. Many structural modification including steric tuning, changing the ligand backbone structure, and changing the heteroatom have been pursued with α-diimine ligands[1,7].

In general, the high productivity of these metals chelating catalysts are based upon N-N and N-O ligands in the polymerization of ethylene and the copolymerization of ethylene with α-olefins and even polar comonomers[1,13-15]. The α-diimine ligands are well-known to stabilize organometallic complexes and the catalyst bearing these ligands remain the most active for polymerization of ethylene[1].

Most late transition metal systems often dimerize or oligomerize olefins, due to competing β-hydride elimination with propagation reaction. However, the key to high molecular weight polymer is to use aryl-substituted α-diimine systems incorporation with bulky groups in the ortho positions[3]. The bulky groups favors insertion reaction over the transfer reaction[16,17]. The polymerization reaction is expected to have a cationic nature of the metal. The electrophilicity of the transition metal center in these complexes results in rapid rate of olefin insertion. The complexes of Ni and Pd which are the most active catalyst among the late transition metal catalyst bearing α-diimine ligands are the most thoroughly described in the literature[1]. In contrast to Pd(II) and Ni(II) catalysts which produce highly or moderately branched polyethylene, tridentate Fe(II) and Co(II) complexes with 2,6-alkyl phenyl diimino ligands produce linear and high density polyethylene[18,19].

The late transition metal catalysts are usually supported on inorganic or polymeric materials[20,21]. Among the support inorganic oxide particularly silica and $MgCl_2$ appears to be a support of choice. The supported catalysts produce better morphology of the polymer can be obtained with lower fouling[1,21-23].

In the present work, since the kind of produced polyethylene strongly affected with the structure of α-diimine ligand, two catalysts of [(2,6-i-prph)$_2$DABMe$_2$]NiBr$_2$ and [(2,4,6-trimethylph)$_2$DABMe$_2$]NiBr$_2$ were prepared and used for polymerization. Rubbery form polyethylene was prepared with the catalyst containing the bulky group ligand, while, an oily polymer was obtained using another catalyst.

EXPERIMENTAL

Dichloromethane, methanol, 4-toluenesulfonic acid, diacetyl (2,3- butanedione) and aniline derivatives were supplied by Merck Chemical (Darmstadt, Germany) and were used as received. Toluene was obtained from the Merck Chemicals, n- hexane was supplied by Arak Petrochemical Co (Arak, Iran), the chemicals were prepared from distilling over sodium wire, stored over 13X and 4A activated molecular sieves and degassed by bubbling with dried nitrogen gas before use. Polymerization grade ethylene (purity 99.9%) was supplied by Iranian Petrochemical (Tehran, Iran). Nitrogen gas (purity 99.99%) was supplied by Roham (Tehran Iran). The gases were purified as explained elsewhere[24,25]. Methylaluminoxane (MAO) (10% solution in toluene) and nickel(II) bromide ethylene glycol dimethyl ether [(DME)NiBr$_2$] (purity 97%) were purchased from Sigma Aldrich Chemicals (Steinheim, Germany). Triisobutylaluminm (T1BA) (purity 93%) was supplied by Sigma Aldrich Chemicals (Steinheim, Germany) and used as 1 molar solution in n-hexane.

Catalyst handling and polymerization procedures were carried out in 1-L stainless steel Buchi reactor (bcp 250) equipped with controllers systems as previously described[24-26]. Toluene (250 ml) was used as solvent. TIBA was used as scavenger and added to the reactor before addition of the MAO. For the polymerization carried out using 50 ml toluene a three necked flask was used with the same control system used for the Buchi reactor. At the end of the polymerization acidic methanol was added to the resulting dark-blue solution as antisolvent. The polymer was precipitated and dried at 70°C for overnight. Differential scanning calorimetry (DSC) (Universal V4IDTA) with a rate of 10°C/min instrument was used for polymer characterization. The viscosity average molecular weight of some the polymer was determined according to refs 25 and 28.

Dibromo[N,N'-bis(2,6-diisopropylphenyl)-2,3-butanediimine]nickel(II) (Catalyst A)

The ligand was synthesized through the reaction of 2,3-butanedione (5.0 mmol, 0.43 mL in 15 ml methanol), 2,6-diisopropylaniline (10.0 mmol, 1.88 mL) and in the presence of trace amount of 4-toluenesulfonic acid as a catalyst. The solution was stirred for 24 h at 40 °C. A yellow solid was obtained by solvent removing method. The solid was washed and crystallized with coldmethanol and dried. The yield of the reaction was about 85 %; mp: 100 °C. ^{1}HNMR (CDCl$_3$, 100MHz): δ 7.05–7.30 (m, 6 H, Ar-H), 2.72 (septet, 4 H, CH–(Me)$_2$), 2.24 (s, 6 H, N=C–CH$_3$), 1.24, 1.17 (d, 24 H, CH–(CH$_3$)$_2$). ^{13}C NMR (CDCl$_3$, 100.6 MHz): δ 167.2 (C=N), 146.7, 135.1, 123.9, 123.2 (Ar-C), 28.5 (CH–(Me)$_2$), 23.6, 23.1 (CH–(CH$_3$)$_2$), 16.8 (CH$_3$–C=N). EI-MS: m/z 404 [M$^+$]. Anal. Calc. for $C_{28}H_{40}N_2$:

C, 83.11; H, 9.96; N, 6.93. Found: C, 83.07; H, 10.02; N, 6.88.

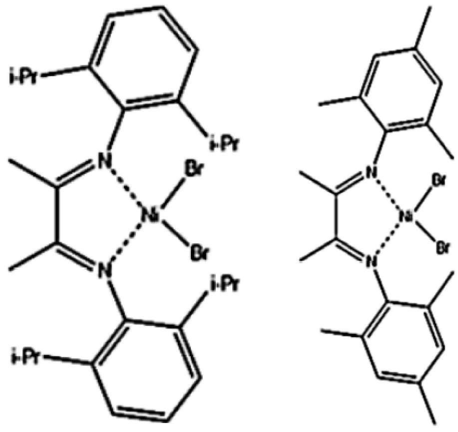
(DME)NiBr$_2$ (1.2 mmol, 0.37 g) and ligand 1 (1.2 mmol, 0.48 g) were combined in a Schlenk flask under a nitrogen atmosphere to prepare catalyst A. Ethylene chloride (25 ml) was added to the solid mixture. The produced suspension was stirred for 24 h at room temperature. Solvent removal of the suspension resulted brown solid. The solid was washed with pure Et$_2$O several times and dried in vacuum. The yield of the reaction was about 71 %; mp: > 300 °C. EIMS: m/z 543 [M$^+$–Br], 463 [M$^+$–2Br], 404 [M$^+$–NiBr$_2$]. Anal. Calc. for $C_{28}H_{40}N_2NiBr_2$: C, 53.97; H, 6.47; N, 4.49. Found: C, 53.76; H, 6.53; N, 4.45

Dibromo[N,N'-bis(2,4,6-trimethylphenyl)-2,3-butanediimine]nickel(II) (Catalyst B)

The ligand was prepared as yellow crystals similar to above mentioned procedure (75% yield). mp: > 300 °C. EIMS: m/z 459 [M$^+$–Br], 379 [M$^+$–2Br], 320 [M$^+$–NiBr$_2$]. Anal. Calc. for $C_{22}H28N_2NiBr_2$: C, 82.45; H, 8.81; N, 8.74. Found: C, 82.28; H, 8.86; N, 8.81

RESULT AND DISCUSSION

Solution polymerization of ethylene was carried out using the prepared catalyst (a) at different conditions in toluene. The catalyst productivity, Rp(average), is expressed in term of g PE (mmol Ni.h)$^{-1}$ was determined after polymerization for 30 min for each run. TlBA (2 mmol) as scavenger was added prior to addition of MAO, the cocatalyst.



cat (a) cat (b)

Figure 1 : Structures of the nickel complex catalysts

The polymerization activity increased with addition of MAO to a maximum activity of 5.1×10^3 g PE/(mmol Ni.h) following to a slightly decrease at higher molar ratio than [MAO]:[Ni] = 3333:1 (Figure 2). The polyethylene obtained up to [MAO]:[Ni] molar ratio of 3333:1 was rubbery form while the polymer obtained at the ratio of 5000:1 was a waxy form polymer (TABLE 1). This behavior could be as a result of high chain transfer reactions at the presence of high amount of MAO which leads to production of low molecular weight polyethylene.

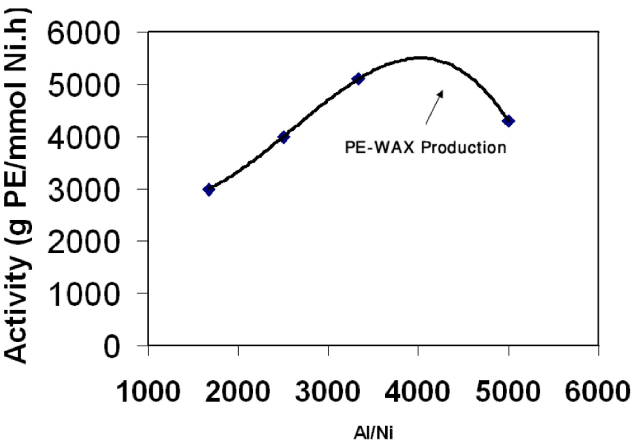


Figure 2 : Effect of MAO concentration on the average rate of polymerization (cat a). Polymerization conditions: temp=25°C, polymerization time=30 min, monomer pressure=1 bar, [Ni]=0.9×10^{-3} mmol, toluene=50 ml.

The highest activity of the catalyst was obtained at about 35 °C (Figure 3). Higher temperatures promote easier monomer transfer to the catalytic active centers. It has also been reported that there is a little abatement of interaction between the Ni atom and the π-electron of ethylene monomer by the bulkier group cause deceleration of chain propagation in ethylene polymerization or oligomerization[31].

Polymerization activity was rise to a maximum values within 60 min of the reaction time following to slow decrease of the activity at 25°C (Figure 4). Generally, a decay type profile with different acceleration period was observed which was depended on polymerization temperature. The maximum activity of the catalyst was observed after 60, 10 and 5 min of the polymerization for the reaction carried out at 25, 45 and 55°C respectively. The rate/time profiles are compared in Figure 4. As can be seen from the profiles, the higher temperature of the reaction the lower the acceleration period

TABLE 1 : Effect of MAO, the cocatalyst, concentration on the polymerization behaviour. Polymerization conditions as in Figure 2.

no	MAO (mmol)	[Al]:[Ni] Molar ratio	Yield g PE	Activity (g PE/mmol Ni.h)	Kind of resulting polymer
1	1.5	1666.6:1	1.37	3.0×10^3	Rubber form
2	2.25	2500.0:1	1.78	4.0×10^3	Rubber form
3	3	3333:1	2.3	5.1×10^3	Rubber form
4	4.5	5000:1	1.92	4.3×10^3	Wax form

and the higher decay behavior were obtained. The formation of PE-wax obtained at 65 °C and also at high concentration of the MAO could be as a result of β-hydride elimination which is facilitated by the temperature as well as cocatalyst concentration respectively[32] (TABLE 2).

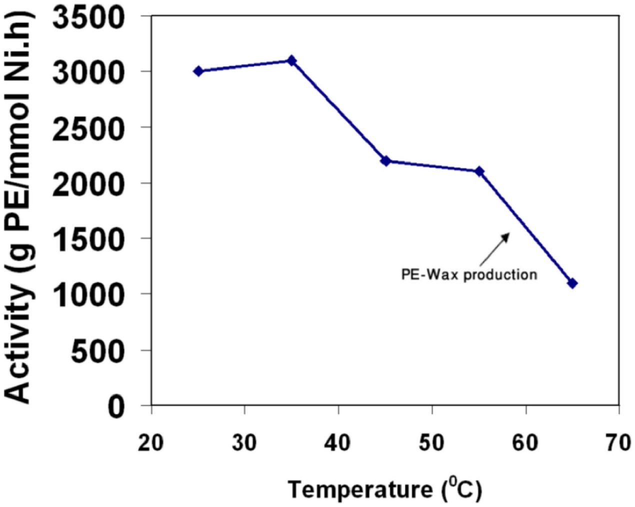


Figure 3 : Effect of temperature on the average rate of polymerization. Polymerization conditions: [MAO]=1.5 mmol, other conditions as in Figure 2.

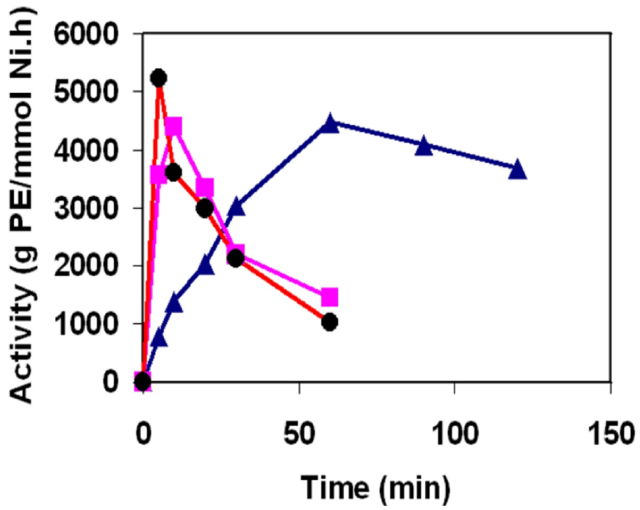


Figure 4 : Plot of R_p versus time. Polymerization conditions: monomer pressure=1 bar, [Al]:[Ni]=1666:1, [Ni]=0.9×10^{-3} mmol, toluene=50 ml, (▲) 25°C, (■) 45°C, (•) 55°C.

TABLE 2 : Effect of temperature on the polymerization behaviour. Polymerization conditions as in Figure 4.

no	Temperature (⁰C)	yield (g PE)	Activity (g PE/mmol Ni.h)	Kind of resulting polymer
1	25	1.37	3.0×10^3	Rubber form
2	35	1.40	3.1×10^3	Rubber form
3	45	0.99	2.2×10^3	Rubber form
3	55	0.97	2.1×10^3	Rubber form
4	65	0.50	1.1×10^3	Wax form

The influence of monomer pressure in the range 1 to 5 bars on the polymerization behavior was investigated. The higher the pressure of the monomer, the higher the activity obtained. The behavior is mainly due to higher concentration of the monomer close to the active centre[32]. In the presence of enough solvent, the activity linearly increased with increasing monomer pressure in the range studied. The polymerization behavior is shown in Figure 5. The polymerization was carried out at [Al]:[Ni] = 1667: 1 and temperature of 25°C. Due to the rubbery form of the resulted polymer, the solvent used was trapped in the polymer formed and prevent the polymerization to carry out further, when 250 ml of toluene was used. Due to the exothermic nature of the reaction, a sudden increase in temperature from 25 to 35°C, particularly at the beginning of the reaction was observed. The increase was very tedious at higher pressure and low amount of the solvent used (250 ml). Increasing the solvent to 500 ml could overcome the problem (Figure 5).

Polymerization of ethylene using the catalysts [(2,4,6-trimethyl-ph)$_2$DABMe$_2$]NiBr$_2$ produced oily form polymer even at 30°C polymerization temperature which not further study.

Polymer characterization

The melting point (Tm) and crystallinity of the polyethylene sample were determined using the DSC technique (TABLE 3). The crystallinity of the polyethylene

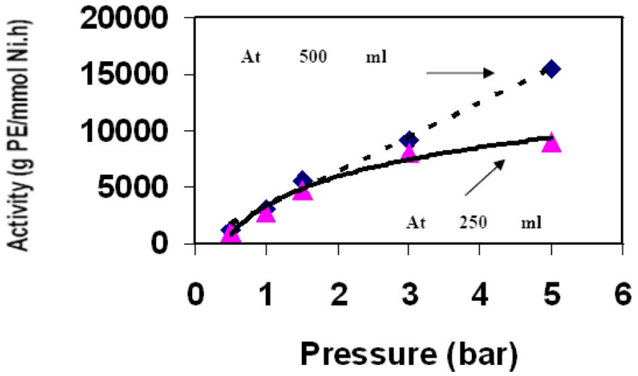


Figure 5 : Influence of monomer pressure on the average rate of polymerization. Polymerization conditions: temp=25°C, polymerization time=30 min, [Al]:[Ni]=1667:1, [Ni]=0.9×10^{-3} mmol.

TABLE 3 : Effect of polymerization conditions on characteristic of the polymer obtained.

Pressure (bar)	Time (min)	ΔH_{Cry} (Cal/g)	Crystallinity %	T_m (^{0}C)	$\overline{MV}$
1	5	8.54	14	110	-
1	10	4.27	7	108	-
1	30	0.61	1	107	-
3	30	5.49	9	115	7.5×10^4
5	30	5.49	9	115	8.3×10^4

was between 1 to 14% indicating of rubbery amorphous polymer produced. The higher crystalline polymer was formed at the early stages of the polymerization. However, as the polymerization proceeds, the crystallinity began to decrease. It has been reported that mass transfer limitation could produce amorphous polymer[5]. Due to the rubbery form of the polymer produced, it is expected that by progress of the polymerization, the catalytic active centers encapsulated and prevent the monomer to rich the active centers somewhat. The behavior could produce amorphous polymer due to mass transfer limitation[5], which confirmed by the following results of high crystallinity obtained at higher monomer pressure. High pressure of monomer could enhance the crystallinity of the polymer obtained. The crystallinity of the polymer was about 1% and 9% for the polymer produced at 1 and 5 bar pressure respectively (TABLE 3). Furthermore, it is conceivable copolymerization of ethylene with produced higher carbon alpha-olefins provides rubbery polyethylene. Moreover, SEM micrograph of the obtained polymer indicated the polymer obtained has a amorphous and porous character (Figure 6).

The ($\overline{MV}$) of the polymer obtained at 35°C and the monomer pressure of 3 bar was about 7.5×10^4. The molecular weight was increased with the monomer pressure (TABLE 3). Therefore low molecular weight polymer belongs to the nature of Ni-based catalyst to

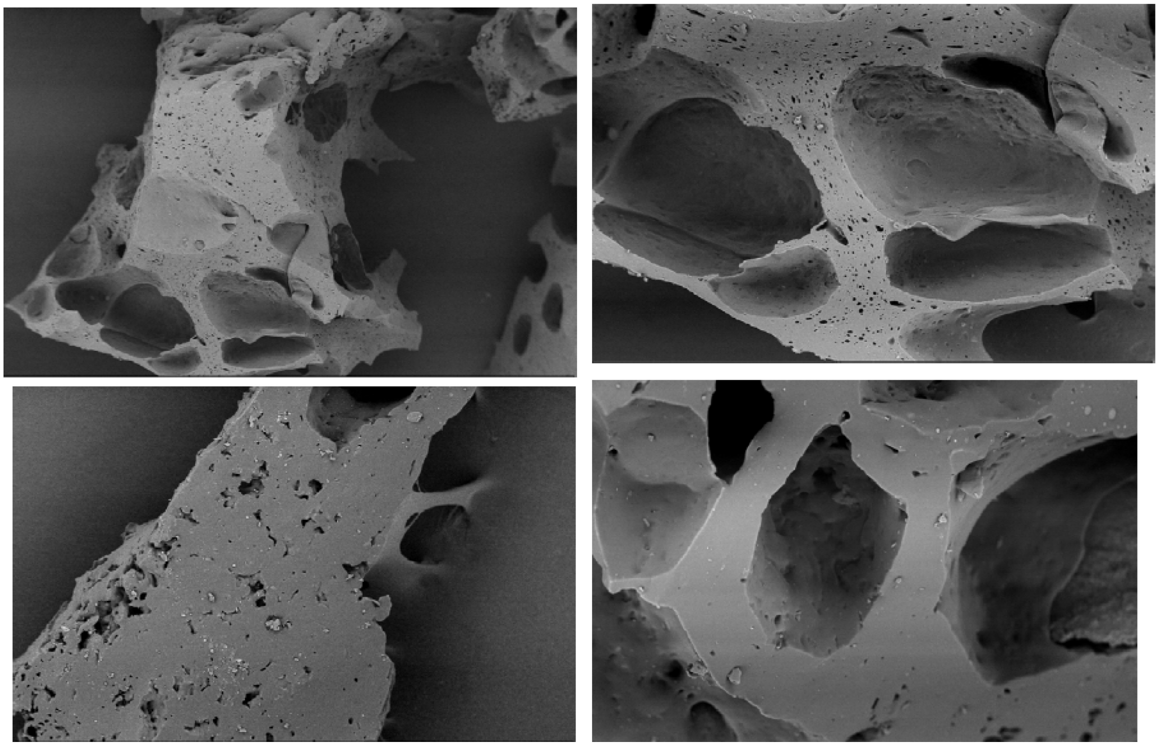


Figure 6 : SEM micrograph of the polyethylene obtained using homogeneous catalyst (a) magnification 10000x

produce[1].

CONCLUSION

The conclusion obtained from the polymerization of ethylene using the [(2,6-i-prph)$_2$DABMe$_2$]NiBr$_2$/TIBA/MAO catalyst system are as follows;

1 The prepared catalyst of [(2,6-i-prph)$_2$DABMe$_2$]NiBr$_2$ was quite an active catalyst. The catalyst with the bulky substituted ligand groups produces high rubbery form polyethylene, while, the catalyst of [(2,4,6-trimethylph)$_2$DABMe$_2$]NiBr$_2$ with less bulky substituted ligand produced oligomer of oily form polyethylene.

2 There is an optimum molar ratio of [MAO]:[Ni] = 3333:1 to obtain the highest yield of the polymer. This ratio is quite high for the catalytic polymerization.

3 At high temperature and high concentration of MAO, the cocatalyst, a waxy form polyethylene was obtained.

4 The optimum activity of the catalyst was obtained at 35°C. However, a linear increase of the activity was observed with increasing the monomer pressure up to 5 bar which studied.

5 Rate/time behaviour of the catalyst was a decay type with different acceleration period which was depends on the polymerization condition. The higher, the temperature used, the lower of the acceleration period observed. An acceleration period of about 60, 10 and 5 min was observed for the polymerization temperature of 25, 45 and 55°C respectively.

6 The polymer obtained has low crystallinity of about 1 to 14% depend on polymerization conditions used.

7 A viscosity average molecular weight polymer of 7.5×10^4 was obtained using 35°C temperature and monomer pressure of 3 bar. The molecular weight was increased with the monomer pressure.

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