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Styrene polymerization using nickel(II) complexes as catalysts

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Abstract

Styrene polymerization is investigated with neutral and cationic Ni(II) complexes, i.e. Ni(bipy)Me_2, **1**, Ni(bipy)Br_2, **2**, Ni(phen)Br_2, **3**, or Ni(Me_2phen)Br_2, **4**, Ni(acac)$_2$, **5**, (bipy = 2,2′-bipyridine, phen = phenanthroline, Me_2phen = 2,9-dimethyl-1,10-phenanthroline, acac = acetylacetonate), activated by $[NHMe_2Ph][B(C_6F_5)_4]$ or $B(C_6F_5)_3$ as cocatalysts, in the presence of $AlMe_3$. The influence on the polystyrene features and the reaction kinetics of the nickel complex and boron activator, the Al/Ni or B/Ni molar ratios as well as the monomer concentration are studied. Catalytic systems derived from **2**, **3** or **5** and $[NHMe_2Ph][B(C_6F_5)_4]$ at a Ni:B:Al ratio of 1:1:5 are the most efficient at room temperature.

Keywords: Boron; Kinetics; Nickel; Polymerization; Styrene

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1. Introduction

Interest in late transition metal (groups VIII–X) catalysts for olefin polymerization, has been growing over the last decade since the discovery by Brookhart of (α-diimine)nickel(II) catalysts leading to high molar mass polyethylene [1]. Novel catalytic systems involving mono-anionic or neutral, bidentate or tridentate, oxygen-, nitrogen-, or phosphorous-containing chelating ligands have been recently described for ethylene polymerization and are still being investigated [2,3].

Styrene polymerization from such late transition metal catalysts has been the subject of numerous studies. The activity of nickel dichloride towards styrene polymerization has been described despite its heterogeneous character. Use of ligands such as bidentate nitrogen moieties (1,10-phenanthroline (phen), substituted 2,2′-bipyridine,...) to form soluble $NiCl_2$ derivatives noticeably alters the catalytic activity and the polymer molar mass [4]. In the same way, organophosphorous ligands also reduce the activity: the more bulky the PR_3 groups, the lower the yield and the polystyrene molar mass [5].

Some early reports deal with the catalytic activity of organometallic type nickel derivatives such as $Ni(\eta^5\text{-}C_5H_5)_2$ or $[Ni(\eta^3\text{-methyl-2-allyl})(\eta^4\text{-cycloocta-1,5-diene})][PF_6]$ [5a,6]. In situ substitution of the weaker cyclo-octadiene group by phosphorous(III) ligands (phosphine or phosphite) gives bis(phosphine) precursors which exhibit enhanced catalytic activity. This was explained by a favorable compromise between the steric stabilization of the active species by the bulky phosphines and their lability which favors their dissociation from the nickel coordination sphere. Sterically demanding phosphine

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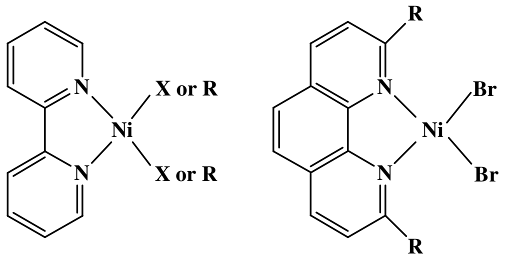

1: R = CH_3
2: X = Br

3: R = H
4: R = CH_3

Scheme 1.

ligands such as P(cyclohexyl)$_3$ or P(*o*-tolyl)$_3$ thus afford highly isospecific nickel catalyst for styrene polymerization [6a,6b,6c].

Numerous studies also concern bis(acac)nickel derivatives/MAO systems (acac = acetylacetonate, MAO = methylaluminoxane) [5]. Styrene polymerization catalyzed by Ni(acac)$_2$/MAO were investigated in details; changes in the solvent polarity and reaction temperature were found to affect the polymer molar mass, yield and isotacticity [5a,5b]. The catalyst productivity was improved with higher Al/Ni molar ratios (60–90) at the expense of the isotacticity [5c]. Subsequent studies highlighted the close relationship between the trimethylaluminium (TMA) amount in MAO and the polystyrene stereoregulation; the lower the TMA content, the greater the isotacticity of polystyrene [5b, 5c,5d]. Addition of an amine such as NEt_3 to the homogeneous Ni(acac)$_2$/MAO polymerization system was also shown to improve the isotacticity [5e].

In this paper, new insights into the polymerization of styrene using various Ni(II) precursors are presented; the successful impact provided by the associated boron based co-catalysts is also discussed. Both neutral and cationic nickel(II) systems are evaluated; these include Ni(bipy)Me$_2$, **1**, Ni(bipy)Br$_2$, **2**, Ni(phen)Br$_2$, **3**, and Ni(Me$_2$phen)Br$_2$, **4**, Ni(acac)$_2$, **5**, (bipy = 2,2′-bipyridine, phen = phenanthroline, Me$_2$phen = 2,9-dimethyl-1,10-phenanthroline, acac = acetylacetonate) complexes (Scheme 1) activated by [NHMe$_2$Ph][B(C_6F_5)$_4$] or B(C_6F_5)$_3$ in presence of $AlMe_3$. The influence of various reaction parameters on the catalytic activity as well as on the reaction kinetics and the polystyrene characteristics is presented.

2. Experimental

2.1. Materials

All operations were conducted under inert atmosphere (nitrogen or argon, less than 5 ppm of oxygen and water) using standard Schlenk, vacuum line and glove box techniques [7a]. Solvents were thoroughly dried and deoxygenated by standard methods and distilled immediately prior to use [7b]. $CDCl_3$ was dried over molecular sieves and THF-d_8 over a sodium mirror. All commercial reagents were purchased from Aldrich or Strem. Styrene (Styr) was dried over CaH_2, stored over dibutylmagnesium and freshly distilled. $AlMe_3$ (2 M in toluene), (DME)NiBr$_2$ (DME = dimethoxyethane), Zr(acac)$_4$, Pd(acac)$_2$, [NHMe$_2$Ph][B(C_6F_5)$_4$], B(C_6F_5)$_3$ were used directly without further purification. Ni(acac)$_2$, 2,2′-bipyridine (bipy), 1,10-phenanthroline (phen), 2,9-dimethyl-1,10-phenanthroline (Me$_2$phen) were dried under vacuum prior to use.

2.2. Instrumentation and measurements

^{1}H (200 MHz) and ^{13}C (50 MHz) NMR spectra were recorded on a Bruker AC200 instrument. Molar masses and polydispersity indices (PDI = $\overline{M}_w/\overline{M}_n$) were determined by size exclusion chromatography (SEC) using THF (1 mL/min) as eluent at 25 °C, on a Varian 5500 apparatus equipped with a refractive index detector and high-speed PSS–SDV linear M column; the polymer samples were dissolved in THF (2 mg/mL). Average molar mass values were calculated from the polystyrene calibration curve. EI mass spectra (EIMS) were recorded on a Micromass AUTOSPEC apparatus in positive mode with a beam energy of 70 keV.

2.3. Synthesis of (bipy)NiMe$_2$, *1*

THF (60 ml) was condensed into a flask containing Ni(acac)$_2$ (0.519 g, 2.0 mmol) and 2,2′-bipyridine (0.821 g, 5.26 mmol). The suspension was stirred over 1.5 h at room temperature, then cooled to −25 °C prior to addition of MeMgBr (3 M in Et_2O; 2.1 ml, 6.3 mmol) upon which it immediately turned dark green. After 2 h of stirring at −25 °C, the mixture was warmed to room temperature and then filtered. Drying of the filtrate, washing the resulting solid with ether and finally drying it under vacuum gave Ni(bipy)Me$_2$, **1**, as a dark green solid in 89%. ^{1}H NMR (THF-d_8, δ): 9.05 (d, 2H, bipy), 8.04 (m, 4H, bipy), 7.48 (m, 2H, bipy); −0.04 (6H, Me). EIMS (*m*/*z*, relative intensity): 281 (1.3), 229 ((bipy)-NiMe,1.0) 214 ((bipy)Ni, 7.1), 170 (1.3), 156 (bipy, 100.0), 128 (31.2), 103 (5.3), 78 (28.2), 58 (Ni, 1.1), 51 (23.6), 39 (4.1), 28 (6.3).

2.4. Synthesis of Ni(bipy)Br$_2$, *2*, Ni(phen)Br$_2$, *3*, Ni(Me$_2$phen)Br$_2$, *4*

Complexes **2–4** were synthesized following the same procedure. Typically, Ni(DME)Br$_2$ (0.45 g, 1.45 mmol) and phen (0.31 g, 1.7 mmol) were stirred in CH_2Cl_2 over 24–48 h until the suspension became light green for bipy and phen, or yellow-pinkish for Me$_2$phen. The solid