

N-HETEROCYCLIC CARBENE LIGANDS FOR NICKEL ETHYLENE
POLYMERIZATION CATALYSTS: TOWARD THE INCORPORATION
OF POLAR COMONOMERS

Thesis by

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Abstract

The development of a catalyst capable of incorporating vinyl-functionalized polar olefins (methyl acrylate, acrylonitrile) into a linear polyethylene backbone is one of the most prominent challenges in organometallic chemistry. Recent developments in group 10 catalysts (Ni and Pd) have shown promise; however, there remains no system capable of this goal. Our group has developed a series of neutral Ni complexes which are excellent catalysts for the polymerization of ethylene but are rapidly deactivated in the presence of methyl acrylate and other polar olefins. This thesis presents our studies toward the cause of catalyst deactivation by these olefins, and describes the design of novel Ni complexes based on the findings of the deactivation study.

To determine the cause of deactivation by polar olefins, our neutral Ni catalysts were allowed to react with methyl acrylate (MA). Examination of the products revealed that, upon coordination of MA, the catalysts form chelated enolate complexes which are susceptible to deactivating protonolysis across Ni-C bonds. Furthermore, it was determined that MA itself is a potential source of hydrogen atoms for this cleavage, implying protolytic deactivation is an unavoidable result whenever olefins capable of chelation are introduced to the catalysts. Therefore, it was decided that chelation should be made less favorable through the use of more electron-donating ligands. For this purpose, N-heterocyclic carbenes (NHCs) were chosen.

NHCs are stable carbenes which have found increasing use as electron-rich ligands for transition metals. In order to make viable catalysts, NHC ligands capable of chelation through a phenoxide moiety were required. An efficient synthesis of these ligands was developed, and they were successfully ligated to Pd. However, it was found

that upon attempted ligation to Ni, a series of unexpected and undesired compounds were obtained, one of which is the apparent result of an unprecedented C–N cleavage of the NHC heterocycle. Unfortunately, when a targeted Ni complex was finally synthesized, it proved inactive toward ethylene polymerization. Finally, it was shown that group 4 (Ti and Zr) complexes of the novel NHC ligands are good catalysts for ethylene polymerization, as well as the copolymerization of ethylene with other olefins.

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Abbreviations

acac	acetylacetonate
Ad	adamantyl
Ar	aryl
ATRP	atom transfer radical polymerization
<i>n</i> -BuLi	<i>n</i> -butyllithium
Bz	benzoyl
cod	cyclooctadiene
dme	dimethoxyethane
GC–MS	gas chromatograph–mass spectrometer
HDPE	high density polyethylene
IMesH ₂	1,3-dimesityl-4,5-dihydroimidazol-2-ylidene
KHMDS	potassium hexamethyldisilylazide
LDPE	Low Density Polyethylene
LLDPE	Linear Low Density Polyethylene
MA	methyl acrylate
MALDI/TOF	matrix assisted laser desorption ionization/time of flight (mass spectrometer)
MAO	methaluminoxane
MMA	methyl methacrylate
NHC	N-heterocyclic carbene
PCy ₃	tricyclohexylphosphine
PE	polyethylene
PEt ₃	triethylphosphine

Ph	phenyl
PPh ₃	triphenylphosphine
sal	salicylaldimine
SHOP	Shell Higher Olefin Process
THF	tetrahydrofuran
tmeda	<i>N,N,N',N'</i> -tetramethyl ethylenediamine