Macromol. Symp. **2007**, 260, 74–79

DOI: 10.1002/masy.200751411

The Advantages of Metal Complexes as Catalysts toward Polyolefins - The Vinyl Polymerization of Norbornene

Qisong Shi,[1,2] *Suyun Jie,*[1] *Shu Zhang,*[1] *Haijian Yang,*[3] *Wen-Hua Sun**[1]

Summary: Various nickel complexes bearing [N,O], [P,N] ligands as well as the supported nickel complexes were prepared and showed moderate to high catalytic activities for vinyl polymerization of norbornene. The formed polynorbornenes (PNBs) are soluble for measuring both the molecular weights and the molecular weight distributions. Comparing the results in homogeneous catalysis, the PNBs produced by supported catalysts possessed higher molecular weights and slightly broader molecular weight distributions. The reactor fouling generally happens in homogeneous catalytic systems, while spherical polymer particle morphology could be obtained without reactor fouling by using $MgCl_2$-supported nickel catalysts.

Keywords: nickel catalyst; polynorbornene; vinyl polymerisation

Introduction

Polynorbornene (PNB) has attracted great attention for chemists and engineers because of their applications as thermostable, optical, dielectric and photoresist polymers. The ring-opening metathesis polymerization (ROMP) of norbornene was first reported by Andersen and Merckling[1] in the 1950s' and well investigated, and the achievement of metathesis reactions was awarded the Nobel Prize to Professors Yves Chauvin, Robert H. Grubbs and Richard R. Schrock in 2005. Another type of PNB through vinyl-polymerization of norbornene is a special polymer with constrained rings in each unit, and expected to possess interesting and unique properties, for instance, such as highly chemical resistance, low UV resistance, low dielectric constant, high glass transition temperature, excellent transparency, large refractive index and low birefringence.[2] There are two significant points in applying PNBs obtained through vinyl-polymerization: 1) understanding the properties of PNB with molecular weight and distribution, 2) development of practical catalytic systems. Five years ago, there were few reports considering the molecular weights of PNBs due to the solubility problem. However, this problem was solved with our works by using nickel complexes as catalysts.

The development of nickel-based complexes as catalysts for vinyl polymerization of norbornene attracted considerable attention due to their high catalytic activities and good property of resulting polynorbornenes (PNBs).[3–8] In attempting copolymerization of ethylene with norbornene in our group, the various nickel complexes were explored and found that nickel complexes bearing ligands of [N,O],[9–13] [O,N,O][14] and [P,N][15] showed high catalytic activity in vinyl polymerization of

---

[1] Key Laboratory of Engineering Plastics and Beijing National Laboratory for Molecular Sciences, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100080, China
Fax: (+86) 10 62618239; E-mail: whsun@iccas.ac.cn

[2] Department of Materials Science and Engineering, Beijing Institute of Petrochemical Technology, Beijing 102600, China

[3] Key Laboratory of Analytical Chemistry of the State Ethnic Affairs Commission, College of Chemistry and Materials Science, South-Central University for Nationalities, Wuhan 430074, China

norbornene. We could demonstrate that it is not difficult to have our resulting PNBs solved in aromatic hydrocarbons.

Though such homogeneous catalytic systems resulted in PNBs with serious fouling in the reactor, the soluble PNBs could be measured the molecular weight and distributions by GPC, and further consideration of the polymeric applications is thus possible. In general, reactor fouling could be overcome by supporting catalyst on suitable carriers. Following process in supporting catalysts for normal polyolefins (PE and PP), the nickel complex could be suitably supported on spherical $MgCl_2$ and heterogeneous catalytic systems gave good catalytic activities and especially polymer particles in spherical morphology without reactor fouling.[16] Therefore, the catalytic system would be considered for processing when the polynorbornenes are finally found for their true values in application.

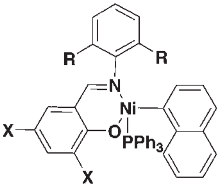
The Determination of the Molecular Weight and the Molecular Weight Distribution of Polynorbornenes

There was no report of the molecular weight and molecular weight distribution of resulting polynorbornene before the year of 2002. It was assumed that the PNBs without functional group could not be fully dissolved;[17] and no stable composite polymers could be obtained for their application, especially for PNBs without melting points. With bias for synthesis, we have developed numerous nickel complexes as catalysts to vinyl-polymerize norbornene with good to high activity in the presence of MAO. Blessed, the resulted PNBs could be well solved; therefore their molecular weights and distributions could be measured. Those works were done in 2001, with considering their applications, several Chinese patents were applied in June through July of 2002, and now authorized (ZL 02 1 23213.X, ZL 02 1 26318.3, ZL 02 1 26507.0, ZL 02 1 26508.9 and ZL 021 26509.7). The key issue of the new observation is to measure the molecular weights and distributions of PNBs obtained. With that, the formed polymeric properties could be measured and repeated through controlling molecular weights of PNBs. Followings will discuss various nickel complexes as catalysts and the supported catalysts.

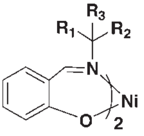
Nickel Complexes Bearing [N,O] Ligands

Salicylaldiminato Nickel Complexes: Neutral salicylaldiminato Ni(II) complexes system **1**[9] showed high catalytic activities for vinyl-polymerization of norbornene in the presence of MAO, which could be reached up to 2.86×10^8 g PNB/(mol Ni $\cdot$ h) and provided polymers with high molecular weights up to 2.0×10^6 g/mol. The complexes with more electron-withdrawing chloro-substituents on the ligands showed higher activity than those with less electron-withdrawing iodo-substituents. Furthermore, various reaction parameters would affect the catalytic activity, conversion yield and polymer with different molecular weight and molecular weight distribution. For example, the catalytic activity increased from 4.70×10^5 g PNB/(mol Ni $\cdot$ h) to 2.65×10^8 g PNB/(mol Ni $\cdot$ h) by increasing the monomer concentration (from the M:Ni ratio of 2500 to 20000), meanwhile the molecular weight varied from 2.92×10^5 g/mol to 1.95×10^6 g/mol.

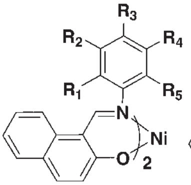
The bis-[*N*-(substituted methyl)-salicylideneiminato]nickel/MAO systems **2**[10] showed high catalytic activities up to 4.23×10^8 g PNB/(mol Ni $\cdot$ h) with M_w up to 3.26×10^6 g/mol. The ligand environment and reaction parameters also had great effect on the catalytic activity and properties of obtained polynorbornene. Different from the catalytic behavior of **1**, catalytic systems of **2**/MAO were greatly affected by the ligand environment. The higher steric hindrance, the better catalytic activity.



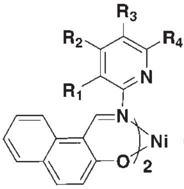
1



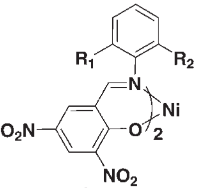
2



3a

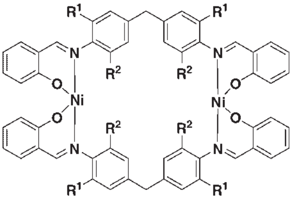


3b

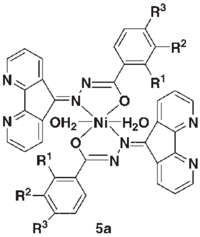


3c

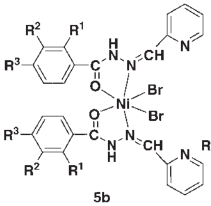
Bis(1-Aryliminomethyl-naphthalen-2-oxy)Nickel Complexes: The bis(1-Aryliminomethyl-naphthalen-2-oxy)nickel **3a,3b**/MAO system[11] exhibited relatively lower activities than the salicylaldiminato nickel complexes **1** and **2**, however, the catalytic activities could still reached up to 6.70×10^5 g PNB/(mol Ni·h) with M_w up to 1.8×10^6 g/mol. In addition, complexes **3b** which contain a pyridinyl group showed somewhat higher catalytic activities than the aryl analogue-substituted complexes **3a** and the generated polynorbornenes exhibited narrower molecular weight distributions. Analogous nickel complex (**3c**) reported by Carlini group[18] displayed a similar activity with respect to the nickel complexes **3a,3b**.



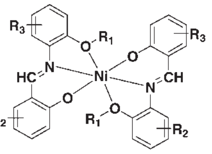
4



5a



5b



6

For all the above systems, the polymers obtained are soluble in halo-benzene and stable up to 450 °C. Catalytic activity, conversion yield, polymer molecular weight and molecular weight distribution could be controlled over a wide range.

Bis-[4,4′-methylene-bis[2,6-dialkyl-*N*-(2-phenylmethylene)-anil]]Nickel Complexes: The catalytic activities of **4**/MAO systems[12] were greatly affected by the ligand environment. Different from the catalytic behavior of **2**, the complexes with smaller steric hindrance exhibited better activities. The complexes with methyl substituents on the ligands showed the highest activity, which could be reached up to 1.92×10^6 g PNB/(mol Ni·h).

Acylhydrazone nickel complexes: The bis[4,5-diazafluorene-9-one-benzoylhydrazone]nickel and bis[N-(pyridine-2-carboxaldehyde-benzoylhydrazone)] nickel(II) dibromide **5**[13] exhibited high catalytic activities up to 5.68×10^6 g PNB/(mol Ni·h) with MAO as cocatalyst. In addition, PNBs produced by complexes **5b** exhibited lower molecular weight than those generated by complexes **5a** containing diazafluorene analogues.

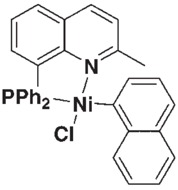
Bis-[2-[[(2-Alkoxyphenyl)imino]methyl]-phenolato-O,N,O]Nickel Complexes

The steric and electronic effects always play major roles, and it will be helpful in designing active center through understanding the nature of ligands and its coordination environment. The salicylideneminato compounds as bidentate ligands can easily coordinate with nickel and form four-coordinated nickel complexes.[10–12] The alkyoxy group on *o*-position of salicylidene to imine gave an additional coordinative site and result in [2-[[(2-alkoxyphenyl)-

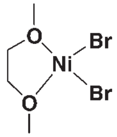
imino]methyl]-phenol to coordinate with nickel as tridentate ligands. The six-coordinated nickel complexes have similar catalytic activities for norbornene polymerization to their corresponding four-coordinated ones, which could reached up to 6.11×10^6 g PNB/(mol Ni · h). The steric hindrance and the electronic effect of ligands affect their catlytic activities without apparent regularity.

Nickel Complexes Bearing [N,P] Ligands

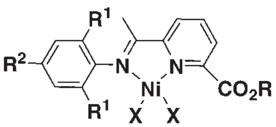
[2-Methyl-8-(diphenylphosphino)quinolino]nickel dichloride **7**/MAO system[15] showed high activity up to 1.70×10^8g PNB/(mol Ni · h) for vinyl-polymerization of norbornene. The resultant polynorbornenes possessed high molecular weights ($M_w < 2.08 \times 10^6$ g/mol) with wide molecular weight distributions ($M_w/M_n < 19.20$), and were soluble, showing no crystallinity in the solid state. The catalytic activities, yields, molecular weights and molecular weight distributions could be modified by adapting the reaction parameters. Properly designed N-P nickel complexes could open new perspectives for further development of vinyl-type norbornene polymerization.



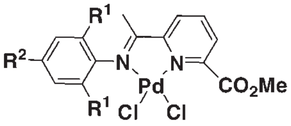
7



8



9



10

Metal Complexes Bearing [N,N] Ligands

In general, nickel complexes showed moderate to high activities for vinyl-polymerization of norbornene. Following the above works, the commercially available (DME)$NiBr_2$ (DME = 1,2-dimethoxyethane) **8** and nickel complexes **9**[19] bearing N^N ligands were investigated. At the conditions as norbornene monomer, nickel precursors and MAO (as M/Ni/Al in 5000:1:1000) in toluene, the high activity was observed up to 10^7 g PNB/(mol Ni · h) for **8**, meanwhile moderate activities for **9** with 10^5 g PNB/(mol Ni · h). However, the tridentate nickel complexes bearing 2-imino-1,10-phenanthrolines[20] showed very low activity. We kept those data in hands without publication because we turned our interests to understand the reason of not measuring molecular weights of PNB in past, in addition, there is no clear application of those PNB produced by vinyl-polymerization.

Palladium complexes containing 2-methoxycarbonyl-6-iminopyridines system **10**[21] bearing N^N ligands also showed good activity for norbornene vinyl-polymerization. The complexes containing the ligand with electron-withdrawing halides exhibited higher catalytic activities than those of other complexes, the complexes with more electron-withdrawing fluoro-substituents on the ligands showed the highest activity up to 1.05×10^6 g PNB/(mol Pd · h). In addition to the electronic effect, less bulky substitutents provide the favorable environmental insertion of norbornene, and therefore, result in higher catalytic activity. Unlike the PNBs obtained in nickel catalytic systems, the PNBs obtained by palladium complexes could not be measured for their molecular weights and molecular weight distributions because they could not be fully soluble. At this moment, it was realized that it was used to report PNBs without measuring their molecular weights; that was caused by

Table 1.
Vinyl polymerization of Norbornene by complexes **1–7**

Complex	Activity (g PNB/(mol Ni · h))	Mw (g/mol)
1	2.86×10^8	2.0×10^6
2	4.23×10^8	3.26×10^6
3a	6.70×10^5	1.8×10^6
4	1.92×10^6	
5a	5.68×10^6	2.4×10^6
6	6.11×10^6	
7	1.70×10^8	2.08×10^6

commonly using palladium catalysts. To the best of our knowledge, the first vinyl polymerization of norbornene and substituted norbornene derivatives was mentioned in 1966 using $PdCl_2$,[22,23] rather earlier than the nickel catalysts for vinyl polymerization of norbornene. And the problem for PNBs with measuring their molecular weights was solved with finding the good activities by the nickel complexes as catalysts.

In general, most nickel complexes performed positive influence on vinyl polymerization of norbornene in the presence of cocatalyst. Their various catalytic activities and the molecular weights of PNBs obtained are summarized in Table 1.

Nickel Catalysts Supported and Polymerization Process

Considering the applicaion of PNBs in the future, the industrial process could not rely on the homogeneous catalytic system because the serious reactor fouling always happened. To avoid that, the nickel precursors **2** and **3a**[10,11] were supported on spherical $MgCl_2$ and SiO_2.[16] Spherical polymer particle morphology was achieved, without reactor fouling. The supported catalysts had fine morphology and similar catalytic activity. The PNBs produced with supported catalyst had higher molecular weight and slightly broader molecular weight distribution than those produced in homogeneous system. In case the PNBs were found to be useful materials, the process with supported catalysts will be ready for commercialization.

Application Scope of Polynorbornene

Where and what are PNBs used? As PNBs are not melted before going to be decomposed, their solutions were used for preparing membranes and fiber. Their membranes are highly transparent for UV lights. To get their fibers, the electrospinning process is used to produce fine fibers in nano-diameters with high surface. The diameters of the fibers were greatly relied on the molecular weights of PNBs, electric potential, solution concentration, screen distance and surface tension. On the bases of the results, Chinese patents were applied in September of 2003, and now authorized (ZL 03 1 57536). Currently the investigation of PNBs' properties and their potential applications is progressed instead of exploring any new model of catalysts in our group.

Conclusion

In the chemistry of vinyl-polymerization of norbornene, the nickel complexes played an important role because the produced PNBs could be measured for their molecular weights and molecular weight distributions. The nickel catalysts performed moderate to high activities, and resultant PNBs could be controlled for molecular weights by using different catalysts and adapting their reaction conditions. Homogeneous catalytic systems resulted in reactor fouling. The supported catalysts could keep their good activities without reactor fouling; therefore the industrial catalysts could be prepared with supported technology. There are some ways to go for finding the real applications of PNBs. The properties such as thermostable, optical, dielectric and photoresist will be promising for these new polymeric materials.

[1] A. W. Andersen, N. G. Merkling, *U.S. Patent* 2721189, **1954** to DuPont, Chem. Abstr. *50*: 3008i.

[2] [2a] C. Janiak, P. G. Lassahn, *J. Mol. Catal. A: Chem.* **2001**, *166*, 193;[2b] B. S. Heinz, F. P. Alt, W. Heiz,

Macromol. Rapid Commun. **1998**, *19*, 251;[2c] F. P. Alt, W. Heiz, *Macromol. Chem. Phys.* **1998**, *199*, 1951; [2d] C. Janiak, P. G. Lassahn, *Polym. Bull.* **2002**, *47*, 539.

[3] C. Mast, M. Krieger, K. Dehnicke, A. Greiner, *Macromol. Rapid Commun.* **1999**, *20*, 232.

[4] B. Berchtold, V. Lozan, P.-G. Lassahn, C. Janiak, *J. Polym. Sci. Part A: polym. Chem.* **2002**, *40*, 3604.

[5] S. Rush, A. Reinmuth, W. Risse, *Macromolecules* **1997**, *30*, 7375.

[6] T. J. Deming, B. M. Novak, *Macromolecules* **1993**, *26*, 7089.

[7] X.-F. Li, Y.-S. Li, *J. Polym. Sci. Part A: polym. Chem.* **2002**, *40*, 2680.

[8] Y.-Z. Zhu, J.-Y. Liu, Y.-S. Li, Y.-J. Tong, *J. Organomet. Chem.* **2004**, *689*, 1295.

[9] W.-H. Sun, H. Yang, Z. Li, Y. Li, *Organometallics* **2003**, *22*, 3678.

[10] H. Yang, W.-H. Sun, F. Chang, Y. Li, *Appl. Catal. A: Gen.* **2003**, *252*, 261.

[11] F. Chang, D. Zhang, G. Xu, H. Yang, J. Li, H. Song, W.-H. Sun, *J. Organomet. Chem.* **2004**, *689*, 936.

[12] D. Zhang, S. Jie, T. Zhang, J. Hou, W. Li, D. Zhao, W.-H. Sun, *Acta Polym. Sin.* **2004**, *5*, 758.

[13] J. Hou, W.-H. Sun, D. Zhang, L. Chen, W. Li, D. Zhao, H. Song, *J. Mol. Catal. A: Chem.* **2005**, *231*, 221.

[14] D. Zhang, S. Jie, H. Yang, F. Chang, W.-H. Sun, *Chin. J. Polym. Sci.* **2005**, *23*, 619.

[15] H. Yang, Z. Li, W.-H. Sun, *J. Mol. Catal. A: Chem.* **2003**, *206*, 23.

[16] J. Hou, S. Jie, W. Zhang, W.-H. Sun, *J. Appl. Polym. Sci.* **2006**, *102*, 2233.

[17] B.-G. Shin, M.-S. Jang, D. Y. Yoon, W. Heitz, *Macromol. Rapid Commun.* **2004**, *25*, 728.

[18] C. Carlini, M. Martinelli, A. M. R. Galletti, G. Sbrana, *J. Polym. Sci. Part A: polym. Chem.* **2006**, *44*, 1514.

[19] X. Tang, W.-H. Sun, T. Gao, J. Hou, J. Chen, W. Chen, *J. Organomet. Chem.* **2005**, *690*, 1570.

[20] W.-H. Sun, S. Zhang, S. Jie, W. Zhang, Y. Li, H. Ma, J. Chen, K. Wedeking, R. Fröhlich, *J. Organomet. Chem.* **2006**, *691*, 4196.

[21] W. Zhang, W.-H. Sun, B. Wu, S. Zhang, H. Ma, Y. Li, J. Chen, P. Hao, *J. Organomet. Chem.* **2006**, *691*, 4759.

[22] R. G. Schultz, *Polym. Lett.* **1966**, *4*, 541.

[23] J. E. Mckeon, P. S. Starcher, Patent US 3330815 **1967**, UnionCarbide Corp. (US), Chem. Abstr. 67 (1967) 64884g.