Novel Pd Catalysts with β-Diketiminates for Homopolymerization of Functionalized Norbornene Derivatives in Water/Organic Mixed Solvents

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Polynorbornenes prepared by vinyl addition pathway are known to have some desirable characteristics for wider application but they have some critical drawbacks such as brittleness, poor solubility and adhesion. In order to improve these drawbacks, extensive research for the successful homo- and copolymerization of polar functionalized norbornene with olefin has been carried out. Even though considerable advance has been achieved in the polymerization of polar functionalized monomers, successful catalytic systems for the homopolymerization of polar functionalized norbornene are rare. In this study, a novel successful catalytic system for the polymerization of polar functionalized norborene is proposed. This system employs Pd β-diketiminate/borate cocatalyst in water/organic mixed solvents and it is unique due to introduction of water as a component of solvents. Polymers obtained in this study show high Mw with narrow PDI. Effects of several reaction parameters to the polymer activity and properties are investigated and optimal catalytic system are proposed.

Key Words : Pd complexes, β-Diketiminate, Vinyl addition polymerization, Polar functionalized norbornene, Suspension polymerization

Introduction

One of Polynorbornenes (PNBEs), prepared by vinyl addition polymerization, has been attracted much attention due to some desirable properties for the application as an optical material.[1] Many metal complexes have been used for the synthesis of the vinyl addition PNBEs.[2] However, the PNBEs are known to have critical drawbacks such as brittleness, poor solubility and adhesion. Homo- and copolymerization of polar functionalized norbornenes with other olefins including norbornene have been suggested for the improvement of drawbacks[3] but polymerization of polar functionalized monomers, especially easily available monomers such as methyl acrylate (MA) and methyl methacrylate (MMA) *via* vinyl addition pathway has remained a great challenge.[4] In the initial efforts in this area, monomers with polar functional groups far from olefinic moiety have generally employed. Moreover, since metallocene complexes based on group 4 metals showed poor activity towards polar monomers due to well-known oxophilicity of early transition metal, research activities have shifted to the system based on late transition metals. After partial success in the incorporation of polar monomer in the polymer chain by using Ni-based complexes as a catalyst, Brookhart reported cationic Pd(II) α-diimine complexes with remarkable activities in the copolymerization of nonpolar olefins with polar vinyl monomers.[5] In 2002, Drent reported new system containing neutral Pd(II) complexes obtained *in situ* from phosphonium-sulfonate were active for the production of highly linear copolymers of ethylene with MA.[6] Extensive research efforts have been summarized in the recent review.[4]

Even though cyclic olefin copolymers (COC), especially ethylene/norbornene copolymer are one of the commercially important amorphous and transparent materials,[7] not many reports on homo- or copolymerization of functionalized norbornene have been published possibly due to expensive monomers. Sen claimed the first catalytic system employing Pd(cod)MeCl/PPh₃ with NaB[3,5-(CF₃)₂C₆H₃]₄ to produce homopolymers of polar functionalized norbornenes with MW of 6,000 to 20,000.[1(a)] He also found the active system with Pd(II) complex for the production of PMA.[8] In a series of research works, he concluded that catalytic activities of the catalytic system depend on the exo/endo ratio in the polar monomer, size of substituents and coordinating abilities of functionalities.[9] Among these extensive efforts,[1(a),7-10] it is worth mentioning that mixed solvents with toluene and water has been employed in the copolymerization of ethylene with functionalized norbornene.[9(b)] Even though water is used for dissolution of phosphine ligand, new solvent system, if only active, can bring green effect onto the environment due to less use of volatile organic compound.

In addition to these efforts, new efficient catalytic systems for the ethylene/norbornene,[11] norbornene/functional norbornene,[12] norbornene/polar monomer copolymerization[13] have been reported and most of them are based on the group 10 metals, especially Ni or Pd. Most complexes are found to have N^N, N^O, and P^O type ligands. Recently, copper complexes containing β-ketoiminate ligands have been utilized for the catalytic polymerization of norbornene or MA in the presence of methylaluminoxane (MAO).[14]

We have improved the preparative procedures of β-ketoimine and β-diketimine and developed several applications where metal complexes with these ligands are key compounds.[15] Collins reported high catalytic activities of zirco-

nium β-diketiminate complexes toward ethylene polymeri-zation[16] and many complexes containing N^N, and N^O ligands, especially Ni or Pd complexes with β-ketoiminate ligands,[15(c),(d),17] were found to be active in the homo and copolymerization of norbornene derivatives or polar mono-mers (*vide supra*). Therefore, the outcome would be interesting if Pd complexes with β-diketiminates were tested for the polymerization of norbornene with polar substituents.

In this article, we report that much improved homopoly-merization of functionalized norbornenes catalyzed by Pd complexes with β-diketiminates has carried out in water/ organic mixed solvents successfully.

Experimental Section

All the experimental works involving moisture-sensitive compounds have been done using standard Schlenk or dry-box techniques under an inert atmosphere. All reagents including [Pd(acac)$_2$], purchased from Aldrich Chemical Co., were used as supplied without further purification. ^{1}H and ^{13}C NMR spectra were recorded by using 5 mm tube on a Varian Unity Inova 400 (400.265 and 100.657 MHz, respectively) or Varian Gemini 2000 (199.976 and 50.289 MHz, respectively) spectrometer and were referenced to tetramethylsilane (TMS). ^{31}P NMR spectra were recorded on a Varian (162.027 MHz) FT-NMR spectrometer and were referenced to 85% H$_3$PO$_4$. GPC analyses of the polymers in 1,2,4-trichlorobenzene (TCB) as an eluent were performed on a PL-GPC 220 instrument with mixed-D column at 130 ^{o}C and referenced with standard polystyrene.

Ligands for **1a** and **1b**, complexes **1a** and **2a**, [Pd(PPh$_3$)-MeCl]$_2$, H(OEt$_2$)$_2$BAr'$_4$ and NaBAr'$_4$ (Ar' = 3,5-(CF$_3$)$_2$C$_6$H$_3$) have been prepared according to literature procedures.[15(d)] MMAO (Tosoh Finechem Co., 5.7% Al content in toluene) was used as supplied. Dicyclopentadiene (DCPD, 95%) was supplied by Kolon and used as supplied.

Preparation of Monomers. Diels-Alder reactions em-ploying dicyclopentadiene (DCPD, 95%) and appropriate β-olefins were carried out in a 100 mL pressure reactor. 1 equivalent of DCPD and 2 equivalents of β-olefin were introduced in a autoclave and the reactor was flushed with N$_2$. After sealing the reactor, the temperature was increased up to 200 ^{o}C (polar functionalized norbornene) or 240 ^{o}C (nonpolar functionalized norbornene) and maintained for 2 h. After cooling to room temperature, the produced mixture was transferred to the vacuum fractional distillation apparatus. The mixture was heated to the predetermined temperature (polar functionalized norbornene: 120 ^{o}C, polar functionalized tetracyclododecene (TCD): 215 ^{o}C, nonpolar functionalized norbornene: 95 ^{o}C, respectively) and the product was collected at the following temperature; polar norbornene, 76 ^{o}C, polar TCD, 157 ^{o}C, nonpolar norbornene, 36 ^{o}C.

In Table 1, prepared functionalized norbornenes and TCDs are summarized.

Polymerization Conditions. In an inert (N$_2$) atmosphere, 1 equivalent of catalyst and various equivalents of each monomer were placed into a 30 or 40 mL vial containing a

Table 1. Monomers used in this study

Abbrevia-tion	Full Name	Structure	Yield (%)^a
AANB	Allyl acetate norbornene		65
AATCD	Allyl acetate tetracy-clododecene		58
VATCD	Vinyl acetate tetracy-clododecene		53
TESNB	Triethoxy silyl norbornene		61
BANB	Butyl acrylate norbornene		48
VANB	Vinyl acetate norbornene		51
BuNB	Butyl nor-bornene		68
HxNB	Hexyl nor-bornene		70

^{a}Preparative yields of monomers

stirring bar and the vial was sealed with a rubber septum. 2 equivalents of DAPFAr'$_4$ (*N,N*-dimethyl anilinium tetra-(pentafluorophenyl)borate) or other cocatalysts were added to this solution and the resulting solution was stirred for 24 h or until stirring stops due to increased viscosity of the solution. The reaction was quenched with methanol (50 mL) and the solid was filtered and dried under vacuum at 60 ^{o}C for 12 h.

Results and Discussion

Homopolymerization of Polar Functionalized Norbor-nene. As described in the experimental section, polar functionalized norbornenes are prepared by corresponding Diels-Alder reactions in a pressure reactor with moderate yields. The results are summarized in Table 1. Although Pd complexes containing β-diketiminates are very active towards norbornene polymerization with MAO, homopolymerization

of polar functionalized norbornenes by the same complexes did not proceed very well as expected.

However, it was found that these complexes are very soluble in common organic solvents (even in hexane) and pretty stable in air and water. As proved in the series of Sen's papers,[9] exo norbornene derivatives are more active than endo ones towards polymerization. In other words, if the polar substituents are located far from the active metal center, the possibility of deactivation of active center for polymerization becomes less. It is well known that surfactants with polar groups at the end of long nonpolar chains help dissolving nonpolar compounds in water by forming the micelle. Also Sen[9(b)] reported the successful polymerization in the toluene/water mixed solvents (*vide supra*).

We performed the polymerization of polar functionalized norbornene with a hope that polar group of the monomer would align toward the water layer and far from the metal center dissolved in organic solvent. As shown in Table 2, these trials were successful even though no polymerization is detected in some cases. Norbornene derivatives with a Si(OEt)$_3$ group generally show the highest yield among monomers tested. Yields obtained in methylene dichloride/water solvents are higher than those in toluene/water or toluene/methylene dichloride/water systems.

Several characters of these catalytic system may be reasons for the successful polymerization; high solubility in organic solvent, and relatively high stability in water. Choice of cocatalyst is important because MAO or alkyl aluminums, sensitive to the moisture, cannot use in these mixed solvents and several borate compounds are adopted as a cocatalyst.

As summarized in Table 3, most of the monomers show higher activities at higher temperatures but TESNB show maximum activity at 40 °C and then lower activity with increase of the temperature possibly due to hydrolysis of monomers to produce OH terminal group. Combined with this, it is worth mentioning that no activity in all over the temperature ranges was observed with MeOHNB, which cannot be rationalized yet.

In Table 4, the effect of cocatalyst was monitored and it is found that polymerization activity depends on the type of cation in cocatalyst and functionality of monomer. Generally, functional groups with heteroatoms in the β position from the norbornene (VA, TES, BA) favor trityl cation (cocatalyst A) but one with heteroatoms (except Si) in the α position

Table 4. Effect of cocatalyst on the polymerization of polar functioalized norbornene in dichloromethane/water

Entry	Monomer (1000 equiv.)	Yield (%)	
		Cocat. A	Cocat. B
1	AANB	38.0	73.6
2	VATCD	40.3	No reaction
3	AATCD	No reaction	83.3
4	TESNB	79.3	No reaction
5	BANB	56.2	35.3
6	MeOHNB	No reaction	No reaction

Catalyst = 1a. Cocat. A = (*N,N*-Dimethyl anilinium tetra(pentafluorophenyl)borate) (2 equiv.). Cocat. B = Trityl tetra(pentafluorophenyl)-borate (2 equiv.). Solvent = Dichloromethane (10 mL) + H$_2$O (10 mL). Reaction Temperature = Room temp., Reaction time = 12 h

Table 2. Polymerization results of polar functioalized norbornene in the water/organic mixed solvents

Entry	Monomer (1000 equiv.)	Yield (%)		
		Dichloromethane (10 mL) + H$_2$O (10 mL)	Toluene (10 mL) + H$_2$O (10 mL)	Toluene (5 mL) + Dichloromethane (5 mL) + H$_2$O (10 mL)
1	AANB	38	24.8	No reaction
2	VATCD	40.3	No reaction	4.2
3	BANB	No reaction	No reaction	No reaction
4	TESNB	79.3	76.8	66
5	AATCD	56.2	No reaction	10.8
6	MeOHNB	No reaction	No reaction	No reaction

Catalyst = 1a, Cocat. A = (*N,N*-Dimethylanilinium tetra(pentafluorophenyl)borate) (2 equiv.). Reaction time = 12 h. Reaction temperature = Room temp.

Table 3. Effect of temperature on the polymerization of polar functioalized norbornene in toluene/water

Entry	Monomer (1000 equiv.)	Yield (%)				
		20 °C	40 °C	60 °C	80 °C	100 °C
1	AANB	24.8	trace	28	36	
2	VATCD	No reaction	trace	68.6	78	99.2
3	BANB	No reaction	trace	16.2	35	
4	TESNB	76.8	92.5	71	76	65
5	AATCD	No reaction	trace	70.8	80	
6	MeOHNB	No reaction	No reaction	No reaction	No reaction	No reaction

Cat. = 1a, Cocat. A = (*N,N*-Dimethyl anilinium tetra(pentafluorophenyl)borate) (2 equiv.). Reaction time = 12 h. Solvent = Toluene (10 mL) + H$_2$O (10 mL)

Table 5. GPC data of polar functionalized polynorbornenes

Entry	Monomer	Solvent	Temp.	Yield (%)	Mw (10^3)	PDI
1	TESNB	M.C (10 mL) + H$_2$O (10 mL)	Room Temp.	79.3	181	2.83
2				76.8	381	3.32
3	AANB			28	7.09	1.69
4	VATCD		60 °C	68.6	2.40	1.79
5	BANB	Toluene (10 mL) + H$_2$O (10 mL)		16.2	18.6	1.84
6	TESNB			71	10	1.67
7	VATCD			78	1.57	1.58
8	BANB		80 °C	35	6.82	2.11
9	TESNB			76	16.5	2.11

Catalyst: 1a, Cocatalyst: *N,N*-Dimethyl anilinium tetra(pentafluorophenyl)borate. Reaction time: 12 h. Only polynorbornenes soluble in organic solvent were analyzed. Nonpolar functionalized polynorbornenes were not soluble in organic solvent.

(AA) favors anilinium cation (cocatalyst B).

GPC analysis has been done from only part of polymers produced in this study due to solubility and the results are listed in Table 5. Generally PNBEs with nonpolar functionalized groups are not soluble in common organic solvents. Poly(TESNB) obtained at room temperature showed the highest Mw (up to 381,000) but wide PDI (> 2). Polymer with higher Mw with wider PDI was obtained in toluene/water system. Mw and PDI decrease rapidly with the increase of temperature due to fast termination but yields decreases slowly, which shows rather high stability of the catalyst up to 80 °C. Poly(VATCD) and poly(BANB) also showed decreased Mw with increase of temperature but yields improved with similar PDI.

In order to show the positive and steric effect of β-diketiminate ligand, Pd(acac)$_2$ and **2a** were employed as a catalyst and the results are summarized in Table 6. As shown, **1a** is the best catalyst toward polymerization of polar functionalized norbornene and TCD. This might be due to

Table 6. Effect of catalyst on the polymerization of polar functioalized norbornene

Catalyst	Monomer (300 equiv.)	Yield (%)		
		Dichloromethane (20 mL)	Dichloromethane (10 mL) + H$_2$O (10 mL)	Toluene (5 mL) + Dichloromethane (5 mL) + H$_2$O (10 mL)
Pd(acac)$_2$	AANB	trace	trace	
	AATCD	trace	trace	
	VATCD	trace	trace	
	TESNB	trace	10.8	
	BANB	trace	trace	
2a	AANB		19.2	No reaction
	VATCD		15.2	9.2
	TESNB		62	48
	BANB		No reaction	No reaction

Cocat. A = (*N,N*-Dimethyl anilinium tetra(pentafluorophenyl)borate) (2 equiv.). Reaction Temperature = Room temp., Reaction time = 12 h

Table 7. Polymerization of non-polar functionalized norbornene

Entry	Monomer (1000 equiv.)	Yield (%)		
		Bulk polymerization	Dichlomethane (30 mL)	Toluene (30 mL) + H$_2$O (10 mL)
1	BuNB	No reaction	Oligomer	Oligomer
2	BuTCD	99.3	Oligomer	Oligomer
3	HxNB	98	58.6	Oligomer

Cat. = 1a. Cocat. = MAO (methylaluminoxane) (300 equiv.). Reaction Temperature = Room temp. Reaction time = 12 h

Table 8. Effect of cocatalyst on the polymerization of nonpolar functioalized norbornene

Cocatalyst	Solvent	Yield (%)		
		BuNB	BuTCD	HxNB
AlEt$_2$Cl (100 equiv.)	No Solvent	No reaction	No reaction	No reaction
Cocat. C (2 equiv.)	Dichloromethane (30 mL)	52.4	No reaction	35.5
	Toluene (30 mL)	No reaction	No reaction	No reaction
Cocat. A (2 equiv.)	Dichloromethane (30 mL)	79.6	63.6	85.0
	Toluene (30 mL)	84.4	14.5	91.5

Cocat. = AlEt$_2$Cl (100 equiv.). Cocat. C = Sodium tetrakis[3,5-bis(trifluoromethyl)phenyl]borate. Cocat. A = (*N,N*-Dimethylanilinium tetra(pentafluorophenyl)borate). Reaction Temperature = Room temp., Reaction time = 12 h

lower solubility of Pd(acac)$_2$ in organic solvent and steric bulkiness of substituents of β-diketiminate in **2a**.

In Table 7 and 8, the results obtained from the polymerization of nonpolar functionalized norbornene are summarized. At first, MAO was chosen as a cocatalyst in the polymerization of nonpolar functionalized norbornenes because we thought that these monomers are not quite different from normal norbornene. However, as shown in Table 7, the reactivity of nonpolar functionalized norbornene is different from one of norbornene. Under the same reaction condition, PNBE can be obtained instantly. It is rather surprising that polyBuNB cannot be obtained in the bulk polymerization while polyHxNB is prepared almost quantitatively. From the Table 8, it can be concluded that cocatalyst A is the best for the polymerization of nonpolar functionalized norbornene except MAO.

Even though successful polymerization of polar and nonpolar functionalized norbornene and TCD with high Mw and low PDI in the water/organic mixed solvents, the solubility of the polymer is not sufficient for the wider application and reaction rate is not fast enough for the economic production of these polymers. However, this new system will contribute green effect onto the environment by using less organic solvent and cocatalyst.

Our efforts to increase the polymerization rate, yield and processility are still under way.

Conclusion

In order to improve the drawbacks of polynorbornene, polymerization of polar functionalized norbornene has been tried. Even though polymerization of every functionalized norbornene cannot be achieved, partial success in the polymerization of polar and nonpolar functionalized norbornene and TCD can be carried out by adopting new catalytic system. This system is quite unique because water is used as one component of solvents. This unique system can be adopted successfully by taking advantage of the uncommon characteristics of Pd β-diketiminate complexes such as high solubility in common organic solvents and high stability towards heat and moisture. Successful polymerization of polar functionalized norbornene catalyzed by Pd β-diketiminate/borate cocatalyst in water/organic mixed solvents has been done to produce polymers with high Mw but narrow PDI. This process is green in nature because less organic solvent and cocatalyst are used in the polymerization.

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