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Bulk Coordination Polymerization of Dicyclopentadiene (DCPD) by Pd Complexes Containing β-Ketoiminate or β-Diketiminate Ligands

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Several palladium complexes containing β-ketoiminate and β-diketiminate ligands successfully produced poly(DCPD) possibly *via* vinyl addition. It was found that catalysts with β-diketiminate ligands containing bulkier aryl substituents showed the highest activity in the presence of MAO as a cocatalyst. Purity of DCPD is quite essential for the higher activity and small amount of organic solvent such as CH_2Cl_2 and toluene is required to reduce the viscosity of the reactant mixture for the higher activity. ^{1}H NMR spectra of produced polymers with *N,N*-dimethylanilinium tetra(pentafluorophenyl)borate (*N,N*-DAPFAr"$_4$) show that 5,6-double bond of DCPD is removed with 2,3-double bond remaining. Produced poly(DCPD) with MAO cocatalyst is quite rigid and insoluble in common organic solvents but rather brittle.

Key Words : Palladium complexes, β-Ketoiminate, β-Diketiminate, Vinyl addition polymerization, Poly(DCPD)

Introduction

Poly(DCPD) is a crosslinked thermosetting polymer with high impact strength and modulus well suited in a wide variety of applications such as production of large intricate objects through reaction injection molding (RIM) (Figure 1). RIM is a process for in-mold polymerization by mixing two or more reactive streams of low viscosity. The combined streams are then injected into a mold where they quickly set up into a solid infusible mass. Since this process requires low pressures, the molds are inexpensive and easily changed. No requirement of massive extruders and molds due to low viscous monomer leads to much less energy consumption than other molding techniques such as injection molding or compression molding.[1]

For a RIM system, following requirements should be met; (1) stable and long shelf-life of the individual streams under ambient conditions, (2) thorough mixing of the streams without setting up in the mixing head, (3) rapid formation of solid in the injection into the mold, (4) no interference of any selected additives in the polymerization reaction.[2(1)(c)]

Historically poly(DCPD) for a RIM process has been prepared by ring-opening metathesis polymerization (ROMP) catalyzed by Group 6 or 8 metal carbene complexes (A route in Figure 1).[3(a)] In many patents,[2] these carbene complexes were obtained *in-situ* during the process mainly due to economic reasons. However, presence of Lewis acid cocatalyst usually induces competitive side reactions with metathesis polymerization.[3(b)] In order to improve the performance of the process, several cocatalysts have been tested and optimization has been tried. However, Wagener[3(b)] claimed that real polymerization of DCPD proceeded *via* ROMP with a double bond in a six-membered ring (5,6-double bond) followed by vinyl addition (coordination) polymerization with a double bond in a five-membered ring (2,3-double bond) (B route in Figure 1). Therefore, vinyl addition polymerization using all the double bonds in the DCPD can proceed with an appropriate catalyst, if any. If this happens, new poly(DCPD) with different structure and properties could be obtained. Poly(DCPD) *via* ROMP would contain higher proportion of double bonds causing instability toward UV radiation, which requires hydrogenation for the further applications. There is another latent problem for the higher performance in the ROMP system. Catalyst precursors (*e.g.* MCl_6 or $MOCl_4$, M=Mo or W) in the ROMP are generally insoluble in DCPD or common organic solvents and generally small amounts of polar solvents, a possible catalyst poison, are added for the

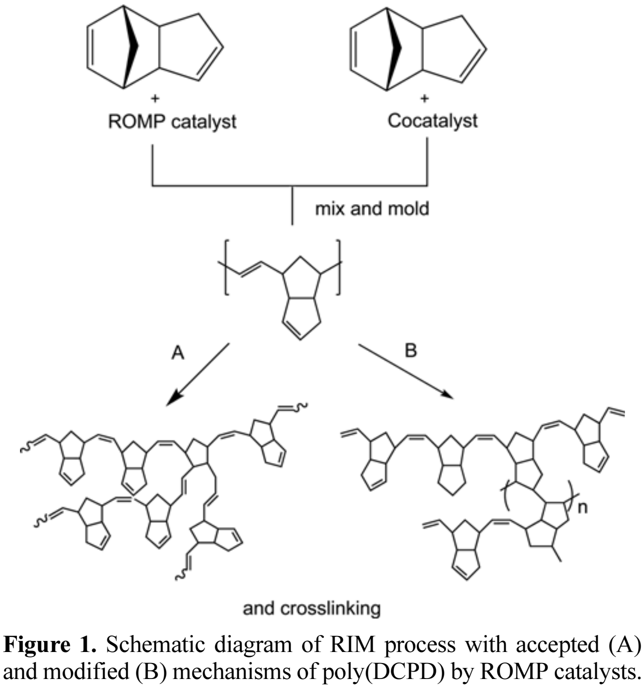

Figure 1. Schematic diagram of RIM process with accepted (A) and modified (B) mechanisms of poly(DCPD) by ROMP catalysts.

homogeneous dispersion of catalysts in the system.

However, it is found that coordination polymerization of DCPD is rare and comparison between ROMP and coordination polymerization has not been attempted. Many Ni or Pd complexes with β-ketoiminate or β-diketiminate ligands have been developed for the norbornene polymerization in our group[4] and these have proved to have higher shelf life and solubility in common organic solvents. Therefore, higher dispersion of catalytic system and exclusion of polar solvents, potential catalyst poisons, can be accomplished with these catalysts and higher catalytic activity and longer shelf life on storage would be expected.

Herein we report the successful coordination polymerization of DCPD catalyzed by Pd complexes containing β-ketoiminate or β-diketiminate ligands. Bulk polymerization of DCPD can be accomplished in less than 1 min at room temperature on mixing the two streams containing DCPD and a Pd complex and DCPD and a cocatalyst, respectively.

Experimental Section

All the works involving moisture-sensitive compounds were carried out using standard Schlenk or dry-box techniques. All reagents, purchased from Aldrich Chemical Co., were used as supplied commercially without further purification. 95% DCPD was supplied by Kolon and 100% DCPD was purchased from Aldrich. The distilled DCPD was obtained by the vacuum distillation of 95% one in the presence of CaH_2 at 80 °C. *N,N*-Dimethylanilinium tetra(pentafluorophenyl)borate (*N,N*-DAPFAr"$_4$) (98%) was purchased from Strem Co. and used as supplied. ^1H and ^{13}C NMR spectra were recorded by using 5 mm tube on a Varian Unity Inova 400 (400 and 100 MHz, respectively) spectrometer and were referenced to tetramethylsilane (TMS). ^{31}P NMR spectra were recorded on a Varian (162 MHz) FT-NMR spectrometer and were referenced to 85% H_3PO_4. All manipulations were conducted under an inert atmosphere. Elemental analyses were performed with EA-1110 (CE Instruments) in the Inha University.

Ligands **1-7**,[4] ligands for **8a**,[5] **8b**,[6] **8c**,[7] $[Pd(PPh_3)MeCl]_2$[8] $[Pd(PhCH_2NH_2)_2MeCl]$[4], $H(OEt_2)_2BAr'_4$ and $NaBAr'_4$ (Ar' = $3,5\text{-}(CF_3)_2C_6H_3$)[9] have been prepared according to literature procedures. MMAO (Tosoh Finechem Co., 5.7% Al content in toluene) was used as supplied.

(Ph)$_2$nacnacPd(PPh$_3$)Me (8a) (MW: 633.07). (Ph)$_2$nacnacH (0.25 g, 1 mmol) was dissolved in 20 mL dry hexanes and was added into NaH in 30 mL hexane (0.03 g, 1.2 mmol) dropwise. The resulting solution was stirred at room temperature for 4 h and then , the mixture was filtered through celite. $[Pd(PPh_3)MeCl]_2$ (0.51 g, 0.6 mmol) in 30 mL of dry Hexanes was added in this solution dropwise with continuous stirring at room temperature for 8 h, the mixture was filtered through celite and the filtrate was concentrated leading to crystallization at −20 °C. Yellow solids were collected on filtration and dried in vacuum to give a pale yellow solid (yield: 0.58 g, 87%).

^1H NMR (400 MHz, $CDCl_3$) δ 7.703 (d, 1H, *J* = 4.8 Hz), 7.355-7.187 (m, 17H), 7.019 (m, 3H), 6.660 (t, 2H, *J* = 5.2 Hz), 6.299 (d, 2H, *J* = 3.2 Hz), 4.709 (s, 1H), 1.883 (s, 3H), 1.650 (s, 3H), −0.424 (d, 3H, *J* = 4.4 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 179.456, 164.114, 151.485, 134.725, 134.603, 132.989, 132.034, 131.935, 131.821, 131.799, 129.903, 129.881, 128.448, 128.327, 128.092, 127.796, 127.690, 125.348, 123.460, 122.422, 96.580, 29.744, 26.772, 25.446, 2.083. ^{31}P-NMR (162 MHz, $CDCl_3$) δ 41.317. Anal. Calcd. For $C_{36}H_{35}N_2PPd$: C, 68.30; H, 5.57; N, 4.43; Found C, 68.70; H, 5.77; N, 3.90.

(dmp)$_2$nacnacPd(PPh$_3$)Me (8b) (MW: 689.18). (dmp)$_2$nacnacH (0.31 g, 1 mmol) was dissolved in 20 mL of dry hexane. This solution was added into NaH (0.03 g, 1.2 mmol) in 30 mL hexane dropwise. The resulting solution was stirred at room temperature for 4 h. The mixture was filtered through celite. $[Pd(PPh_3)MeCl]_2$ (0.51 g, 0.6 mmol) was taken in 30 mL of dry hexane and then added to this solution dropwise with stirring at −20 °C for 8 h, the mixture was filtered through celite and the filtrate concentrated leading to crystallization at −20 °C. The solids were collected on filteration and dried in vacuum to give a pale yellow solid (yield: 0.32 g, 45%).

^1H NMR (400 MHz, $CDCl_3$) δ 7.685 (t, 2H, *J* = 18.0 Hz), 7.533 (d, 2H, *J* = 8.0 Hz), 7.474-7.111 (m, 15H), 6.692 (t, 2H, *J* = 10.2 Hz), 4.813 (s, 1H), 2.276 (s, 6H), 2.034 (s, 6H), 1.686 (s, 3H), 1.638 (s, 3H), −0.814 (d, 3H, *J* = 4.4 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 179.248, 166.314, 154.418, 134.725, 134.803, 132.975, 132.134, 131.635, 131.521, 131.799, 129.803, 129.781, 128.408, 128.327, 128.092, 127.896, 127.390, 126.348, 124.480, 123.482, 94.390, 24.682, 24.194, 18.932, 18.786, 0.658. ^{31}P-NMR (162 MHz, $CDCl_3$) δ 43.278. Anal. Calcd. For $C_{40}H_{43}N_2PPd$: C, 69.71; H, 6.29; N, 4.06; Found C, 69.37; H, 5.83; N, 3.93.

Polymerization Condition. In an inert (N_2) atmosphere, 1 equivalent of catalyst and 300 equivalents of distilled DCPD were placed into a 10 or 20 mL vial containing a stirring bar and the vial was sealed with a rubber septum. To this, approximately 0.05 mL of toluene was added and the mixture was gently stirred to dissolve the solids. 100 equivalents of MMAO were added to this solution and the resulting solution was stirred until the stirring was stopped due to increased viscosity. The reaction was quenched with acidic methanol (methanol/conc. HCl = 50/1) and the solid was filtered and dried under vacuum at 60 °C for 12 h.

Results and Discussion

Since many palladium alkyl complexes are known to catalyze olefin polymerization *via* vinyl addition,[10] polymerization of DCPD by Pd alkyl complexes containing β-ketoiminate and β-diketiminate ligands have drawn our attention due to difference in the polymerization mechanism generally accepted in the RIM process. After the initial tests, it is found that polyDCPD has been successfully obtained with various Pd complexes (**3a**, **4a**, and **5a**). It also found that the complexes with β-ketoiminate, phosphine and Me ligands (complex **a** in Figure 2) are more active than ones with β-ketoimine and

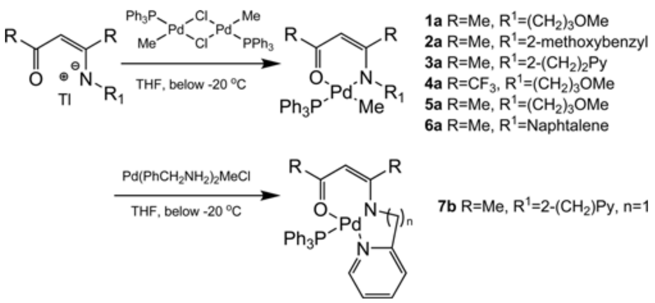

Figure 2. Synthesis of Pd(II) β-ketoiminate complexes.

Me ligands (without phosphines) (complex **b** in Figure 2) even though it appears these have the same 4-coordinated square planar structures. This is rather surprising because pyridine is expected to be coordinated to the metal weaker than phosphine. Displacement of phosphine with pyridine may cause change of bonding modes of β-ketoimine (4σ to 6π) or structure of catalysts (planar to boat conformation) with reduced steric and electronic effects around the metal center as indicated by Collins[11] and Pörschke.[12]

DCPD with only one component of the catalytic system (catalysts/cocatalysts) shows no change up to 12 h, which is the prerequisite property for the RIM process. For the substituent effect, β-ketoiminate complexes with Me substituent **5a** are more effective than ones with CF_3 substituent **4a**. MAO (methylaluminoxane) is more effective than $HBAr'_4$ as a cocatalyst in every catalyst. However, it is worth mentioning that both cocatalysts are very active toward norbornene polymerization.

For the feasibility of industrial grade (95%) DCPD as a feedstock, polymerization of 95% and 100% DCPD with new catalysts, developed in this study, has been tried and the results are summarized in Table 1. The yield increases with the reaction time but activity decreases rapidly, indicating the decomposition of active species. The purity of DCPD is important for the higher polymerization activity. The analysis of gas chromatography showed that the impurities present in the 95% DCPD supplied by the manufacturer (Kolon Industries, Inc.) are mainly cyclopentadiene (Cp) and moisture. To confirm the effect of Cp content on the polymerization activity, polymerization has been tried with DCPD containing various amounts of Cp. As shown in Table 2, activity decreases slowly with the content of Cp up to 7% and reduces rapidly over 10% contents. Easier access of less bulky Cp to the metal center than DCPD would be the reason. However, the decrease in the activity with 95% DCPD is much more than those with the increase of Cp. Therefore, we conclude that the moisture, even though it is small, is the main cause for the decrease of the activity with the 95% DCPD as a feedstock.

Table 1. Effects of Reaction Time and Purity of DCPD on Yields with Pd Complexes (**1a**, **2a**, **5a** and **6a**)

Entry	DCPD Purity	Catalyst	Reaction Time (min)	Yield (%)	Activity (kg/pd.mol·h)
1	95%	**1a**	5	33	158.4
2	95%	**1a**	10	33	79.2
3	95%	**1a**	30	37	29.6
4	95%	**1a**	60	47	18.8
5	95%	**1a**	180	49	6.5
6	95%	**1a**	360	51	3.4
7	95%	**2a**	30	24	95.2
8	100%	**2a**	30	66	264.8
9	95%	**5a**	30	24	94.8
10	100%	**5a**	30	77	308.4
11	95%	**6a**	5	30	144.0
12	95%	**6a**	10	42	100.8
13	95%	**6a**	30	42	33.6
14	95%	**6a**	60	47	18.8
15	95%	**6a**	180	49	6.53
16	95%	**6a**	360	70	4.67

Conditions: [MAO]/[Pd] = 100, 20 °C, [DCPD]/[Pd] = 300.

Table 2. Effect of Cp Contents on the Activity of DCPD Polymerization

Entry	Cp Content (%)	Yield (%)	Reaction time (Sec)	Activity (kg/pd.mol·h)
1	0	97.6	2	70300
2	1	96.3	3	46200
3	5	95.95	5	27600
4	7	94.1	11	12300
5	10	88.85	16	8000
6	12	62.25	23	3900
7	15	56.5	38	2140
8	17	45.65	80	820
9	20	40.9	150	390

Conditions: **2a**, [MAO]/[Pd] = 100, toluene (1 mL), distilled DCPD ([DCPD]/[Pd] = 300).

In order to find the better catalyst for the DCPD polymerization, β-ketoiminate ligands was replaced with β-diketiminate ones and the activities of the new complexes have been investigated. After the initial tests, these β-diketiminate complexes with MAO showed almost the same activities towards DCPD polymerization as the corresponding β-ketoiminate ones.

As shown in Table 3, detailed experiments showed that the catalyst with a bulkier substituent (**8b** in Figure 3) polymerized with higher activity even though the differences were not great. Another merit of β-diketiminate complexes is higher solubility in common organic solvents over β-ketoiminate ones. Since RIM process requires higher miscibility of catalysts or cocatalysts with monomers throughout the polymer body in a mold, this property would be helpful for the higher quality of the product. As temperature increases up to 50 °C, the activity increases but it decreases rapidly up to 80 °C probably due to decomposition of the active species.

The effects of DCPD amount and solvent were investigated and the results are summarized in Table 4. The activity decreases with the amount of DCPD possibly due to increase of viscosity. However, introduction of small volume (1 mL) of solvent such as methylene dichloride or toluene has been

Table 3. Effects of Substituent of the β-Diketiminate Ligand, Temperature, and Cocatalysts on the Yields of DCPD Polymerization

Entry	DCPD ([DCPD]/[catalyst])	Catalyst	Cocatalyst ([Cocat]/[cat])	Reaction Temp (°C)	Yield (%)	Activity (kg/Pd.mol·h)
1	100% (300)	**8b**	MAO (100)	20	66	1.6×10^3
2	100% (300)	**8b**	MAO (100)	50	72	1.7×10^3
3	100% (300)	**8b**	MAO (100)	80	20	0.48×10^3
4	100% (300)	**8b**	$HBAr'_4$ (2)	20	-	-
5	100% (300)	**8b**	$AlEt_3$ (50)	20	-	-
6	100% (300)	**8b**	$AlEt_2Cl$ (50)	20	-	-
7	100% (300)	**8a**	MAO (100)	20	45	1.1×10^3
8	Distilled (300)	**8a**	MAO (100)	20	95.8	13×10^3
9	Distilled (300)	**8a**	$AlEt_2Cl$ (50)	20	-	-
10	Distilled (300)	**8a**	$AlEt_3$ (50)	20	5.3	4

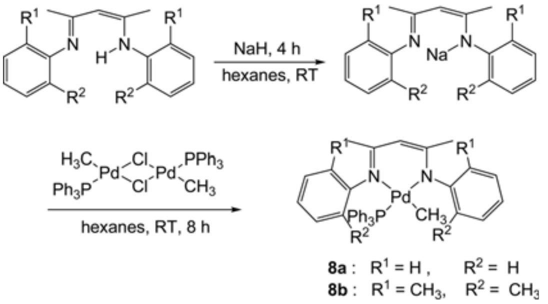

Figure 3. Synthesis of Pd(II) β-diketiminate complexes.

Table 4. Effects of DCPD Amounts and Solvent on the Activity of DCPD Polymerization

Entry	([DCPD]/ [catalyst])	Solvent (1 mL)	Yield (%)	Reaction Time (sec)	Activity (kg/pd.mol·h)
1	300	-	95.8	10	13000
2	600	-	80.3	20	5760
3	1200	-	67.9	35	2800
4	300	Dichloromethane	50.3	16	4500
5	600	Dichloromethane	64.2	14	6600
6	1200	Dichloromethane	43.1	12	5400
7	2400	Dichloromethane	18.9	210	130
8	300	Toluene	40	32	1800
9	600	Toluene	39.4	11	5400
10	1200	Toluene	31.6	15	3000
11	2400	Toluene	20.1	120	240

Conditions: **8a**, [MAO]/[Pd] = 100, 20 °C, distilled DCPD.

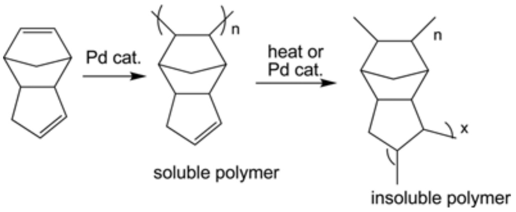

Figure 4. Proposed vinyl addition polymerization mechanism of DCPD.

tried to reduce the viscosity but the significant decrease of activity was observed. The reason is not clear but decreased concentration of monomer around the active catalytic center may be one reason of the reduction of activity. However, addition of methylene dichloride accompanied with increase of DCPD from 300 to 600 or 1200 equivalents induced higher activity, indicating dissipation of reaction heat becomes more important with the increase of DCPD amount than the reduction of monomer concentration around active centers. Reduced yields with more monomer concentration still cannot be explained reasonably but unequal distribution of catalysts and slower diffusion of monomers due to increased viscosity may be the reason. Generally yield and activity reach maximum at [DCPD]/[Pd] = 600 and then decrease slowly beyond that point. Also, in the presence of 2400 equivalents of monomer, much less activities were observed with addition of solvents. However, as Wagener pointed out, observed reduced yields may be resulted from the formation of soluble linear polymer. He argued that the heat released during the polymerization or Lewis acid cocatalysts caused crosslinking with remaining double bonds.[3(b)] It is well recognized that reactivity of 5,6-double bond in the DCPD is higher than that of 2,3-double bond.[13] Therefore, as described in Figure 4, the 2,3-double bond of DCPD would remain after the initial vinyl addition of DCPD and then crosslinked products could be obtained by further vinyl addition of remaining 2,3-double bond. Initial polymer would be a soluble linear polymer and it may be lost after the work-up procedure with organic solvents.

Fortunately, we recently found that *N,N*-Dimethylanilinium tetra(pentafluorophenyl)borate (***N,N*-DAPFAr"$_4$**) could be used as a cocatalyst for DCPD polymerization but it is much less active than MAO. The produced polymer is partially soluble in $CDCl_3$. In Table 5, DCPD polymerization results with this cocatalyst were summarized. It is found that almost quantitative polymerization with 4 equivalents of this cocatalyst was done after 12 h. The yields are proportional to the amount of cocatalysts. However, the yields decreased with the amount of solvent, toluene. For [Cocatalyst]/[Pd] = 2 and 4 with 5 mL of toluene, the products were solidified to stop the stirring after 6 and 3 h, respectively. With 10 mL of toluene, maximum yield was obtained. Under these conditions, it is believed that crosslinking can be effectively block-

Table 5. Effect of Cocatalyst, *N,N*-DAPFAr'$_4$ and Solvent on the Yields of DCPD Polymerization with β-Diketiminate Complexes

Entry	Cocatalyst *N,N*-DAPFAr"$_4$ ([cocat]/[cat])	Reaction Time (h)	Solvent Volume	Yield (%)	
				Solid	Liquid
1	0.5	12 h	1 mL	10.5	1.5
2	0.5	12 h	2 mL	6.3	0.8
3	0.5	12 h	3 mL	0.4	-*
3	1	12 h	5 mL	15	-
4	1	12 h	10 mL	8.3	-
5	1	12 h	30 mL	3.2	-
6	2	12 h	1 mL	85-	-
7	2	12 h	2 mL	84	-
8	2	12 h	3 mL	81	-
9	2	6 h	5 mL	84.1	-
10	2	12 h	10 mL	85.6	-
11	2	12 h	30 mL	17.4	-
12	4	12 h	1 mL	99.5	-
13	4	12 h	2 mL	98	-
14	4	12 h	3 mL	92	-
15	4	3 h	5 mL	60	-
16	4	12 h	10 mL	95.9	-
17	4	12 h	30 mL	39.4	-

Conditions: 20 °C, **8a**, distilled DCPD ([DCPD]/[Pd]) = 1000), toluene. entry 9 and 15: stirring stopped after 6 and 3 h, respectively.

ed not to be solidified. With 30 mL of toluene, significant reduction in yields was observed. As discussed above, it is expected dissipation of reaction heat and reduced viscosity (increased diffusion rate) would induce higher yield but in fact lower yields obtained. Therefore, the possible removal of soluble polymer during work up is again proposed. Small amount of liquid products were obtained only in entry 1 and 2 after filtration of solid product and evaporation of solvent. In Figure 5, clear differences around $\delta = 6$ can be seen in the spectra of solid and liquid products, indicating one double bond in DCPD have been removed and it supports vinyl addition polymerization with 2,3-double bond remaining. However, in the liquid spectra, there are still peaks in the same region possibly due to presence of unreacted DCPD. In other words, partial removal of more reactive 5,6-double bond by initial polymerization cannot be fully concluded. Also some solid not dissolved in the NMR solvent completely prevents from full characterization.

In order to remove some problems mentioned above, controlled polymerization with catalyst poison EtOH has been done with hope of obtaining only soluble polymers, which may be induced by reduced activity. As expected, the yields are very low (less than 10%) and the solids are soluble in the NMR solvent, $CDCl_3$. As the amount of EtOH increase, the yields drop rapidly. However, all the ^{1}H NMR spectra of these solids are same and a doublet in $\delta = 6$ due to 5,6-double bonds was not removed and integration ratios of the peaks at 6 and 5.4 ppm were almost same as DCPD even with variation of EtOH amounts. NMR experiments with diluted monomer concentrations (10 equivalents) also fail to show significant change in the integration ratios. Therefore, discrimination of vinyl addition sites in DCPD polymerization is not accomplished with these catalytic systems.

The mechanical properties of the resulting poly(DCPD) are under investigating right now but it is found that the polymer is rigid but rather brittle. This indicates significant second step crosslinking occurs during the vinyl polymerization as described in Figure 3.

Conclusion

Coordination polymerization of DCPD has been successfully achieved with new Pd(II) β-ketoiminate or β-diketiminate complexes as expected. It was found that The DCPD polymerization activities of Pd(II) β-diketiminate complexes are higher than those of Pd(II) β-ketoiminate ones and they increase with the bulkiness of the substituent of the β-diketiminate ligands. The polymerization activity decreases with the amount of monomer and it is sensitive to the impurities such as moisture and Cp. It is also found that MAO is the most efficient cocatalyst for DCPD polymerization. Several trials for soluble linear polymer only have failed but ^{1}H NMR spectra of the solid polymer indicated that 5,6-double bond is removed with 2,3-double bond remaining. Unfortunately, obtained poly(DCPD) with MAO is brittle and insoluble in common organic solvents even though it is quite rigid.

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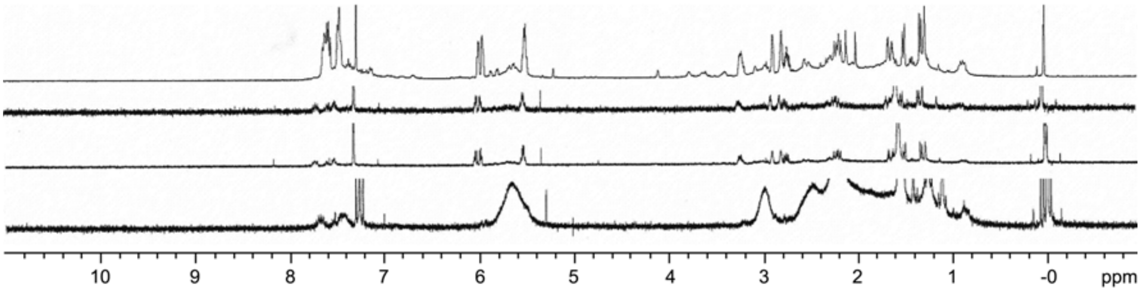

Figure 5. ^{1}H NMR spectra of polymerization products; solid (entry 2) and liquid (entries 1, 2 and 3). Bottom: Solid. Bottom to Top: Liquid (entries 1, 2 and 3).

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