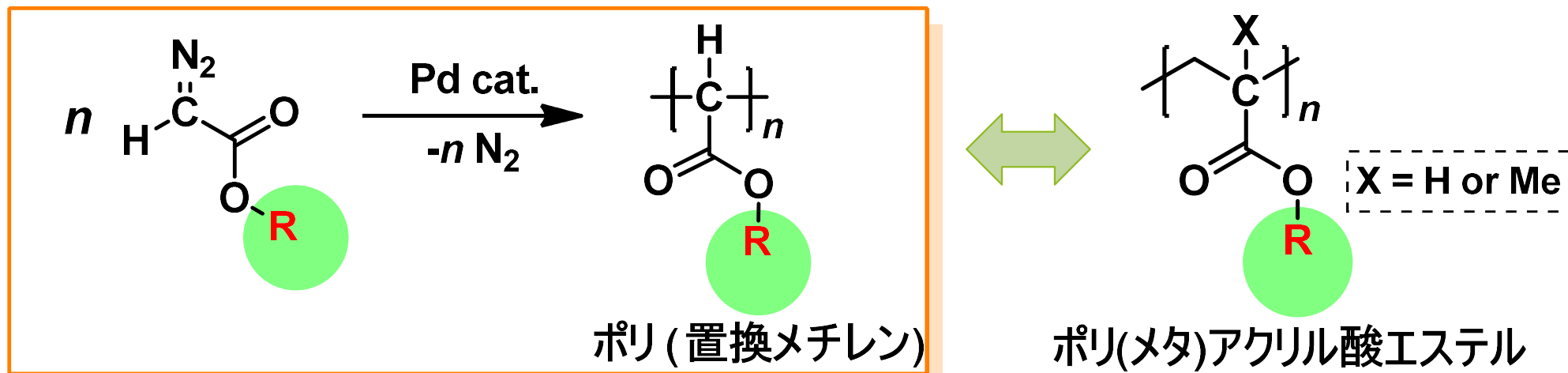


ジアミン配位子を有するPd錯体を用いたジアゾ酢酸エステルの重合

高分子化学研究室
寺岡一輝

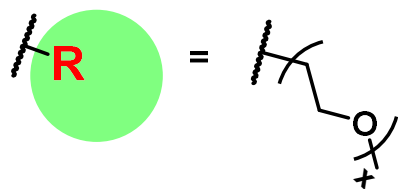
緒言

●ジアゾ酢酸エステルの重合



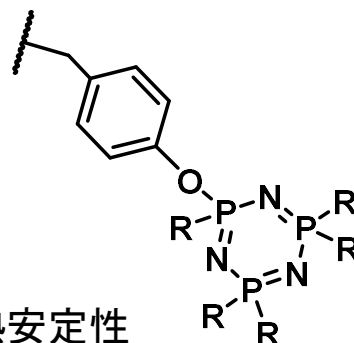
主鎖炭素すべてに置換基が存在

➤ 置換基集積効果の例



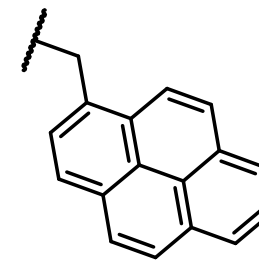
高い親水性、LCST
高いLiイオン伝導率

Polym. Chem. **6**, 8124 (2015)



高い熱安定性
制御重合

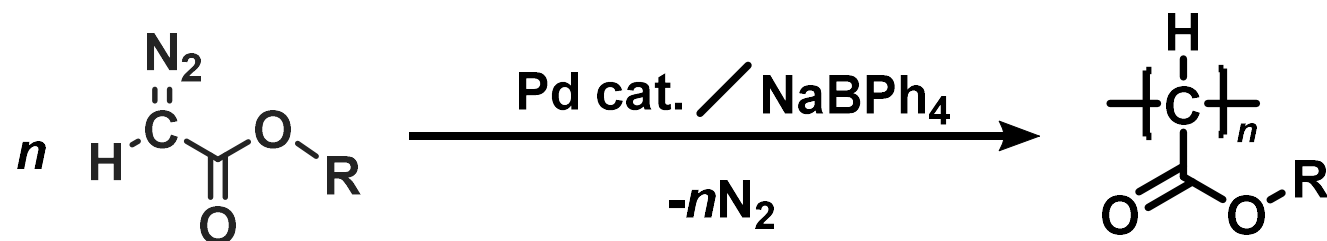
Polym. Chem. **6**, 4709 (2015)



高いエキシマー発光効率
Macromolecules. **51**, 5430 (2018)

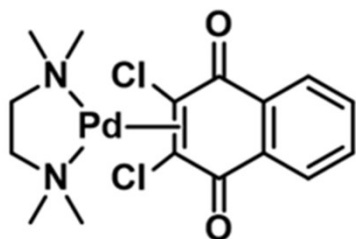
- ✓ 置換基集積効果による特徴的な機能の発現
- ✓ 生成ポリマーは剛直

緒言



Previous Work¹⁾

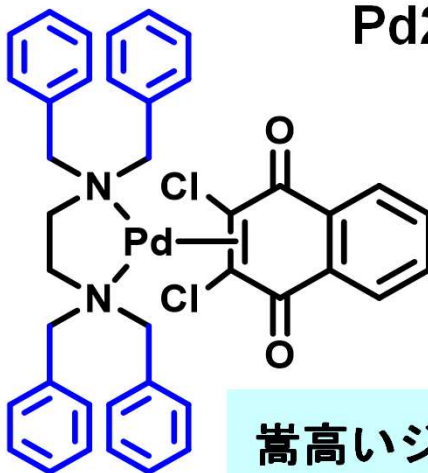
Pd1



- $M_n = 9000$
- yield = 58%
- syndiotactic-rich polymer

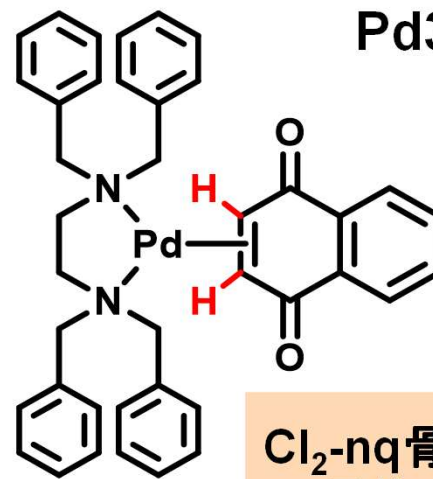
This Work

Pd2



嵩高いジアミン
配位子の導入

Pd3



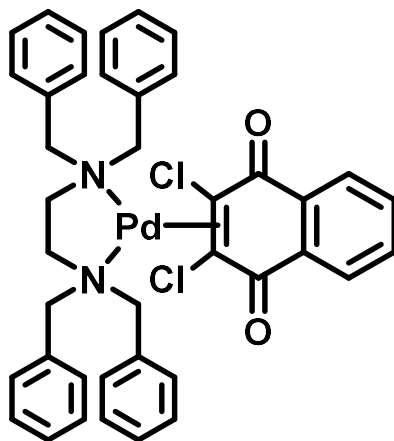
Cl₂-nq骨格から
nq骨格へ

高収率でポリマーを生成し、立体構造を高度に
シンジオタクチックに制御する新規Pd錯体の開発

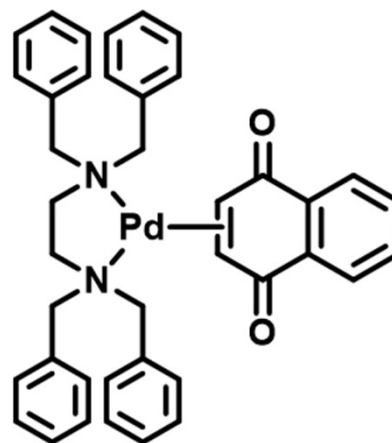
本日の内容

✓ 新規錯体Pd2、Pd3の合成

✓ Pd2、Pd3を用いた重合挙動の調査

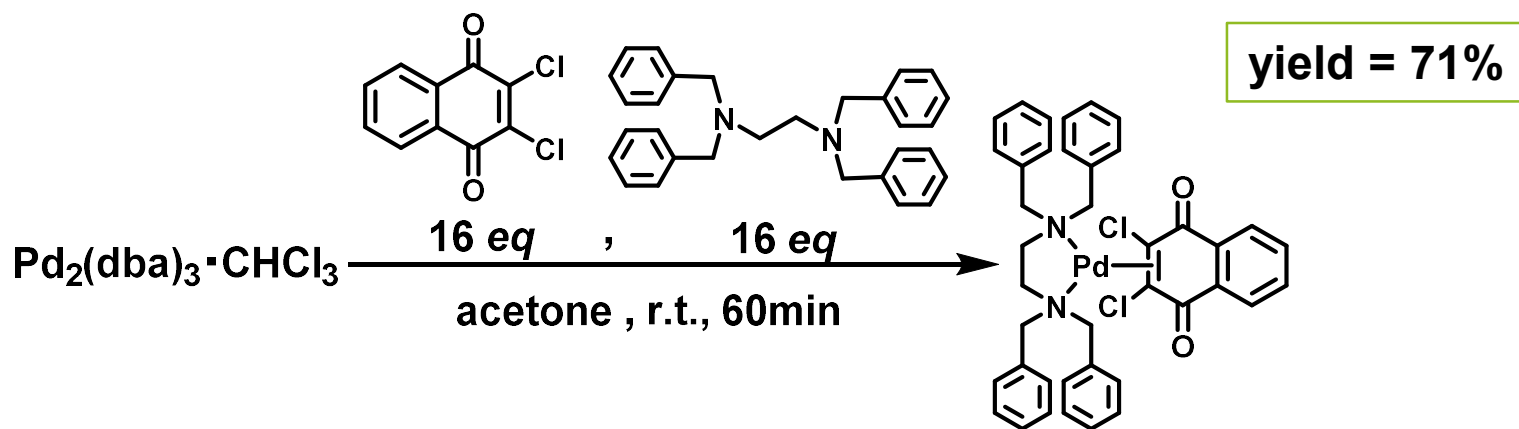


Pd2

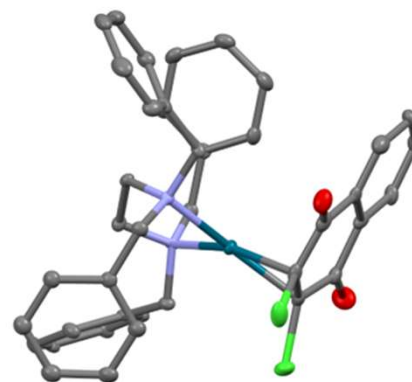


Pd3

Pd2の合成

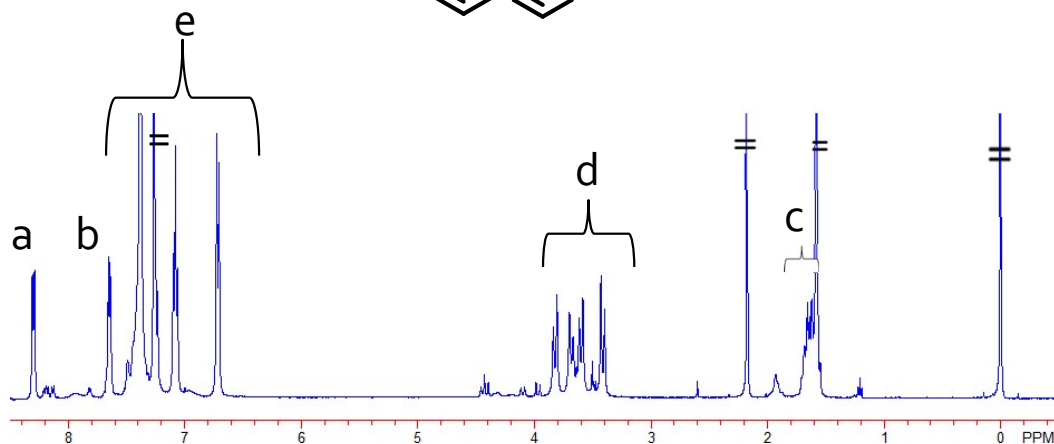
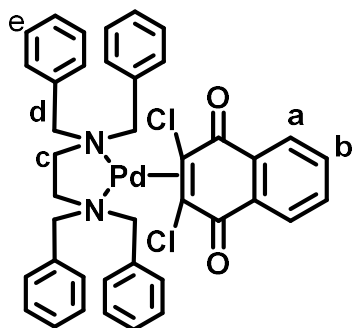


〈単結晶X線構造解析〉



$2(\text{C}_{40}\text{H}_{36}\text{Cl}_2\text{N}_2\text{O}_2\text{Pd}), \text{C}_3\text{H}_6\text{O}$
 FW = 1566.09, monoclinic, P
 $2_1/c,$
 $a = 22.7656(5) \text{ \AA},$
 $b = 9.27461(18) \text{ \AA},$
 $c = 17.8844(4) \text{ \AA},$
 $\alpha = 90, \beta = 110.785(3), \gamma = 90,$
 $V = 3530.39(15) \text{ \AA}^3,$
 $Z = 2, R1 = 0.0659,$
 $wR2 = 0.1511,$
 $\text{GOF} = 1.219$

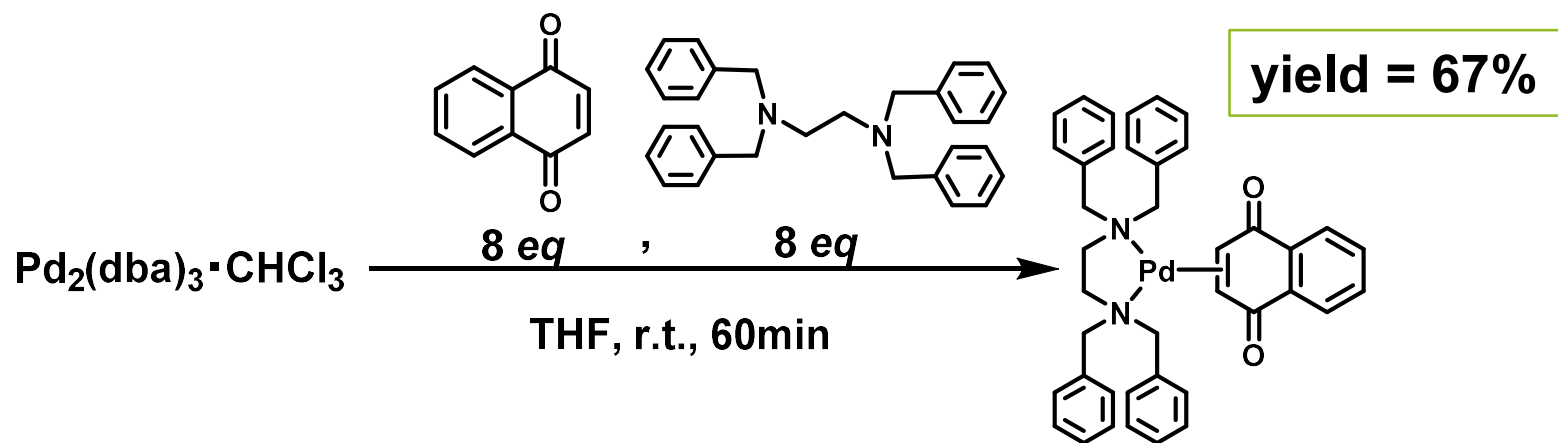
〈¹H NMR〉



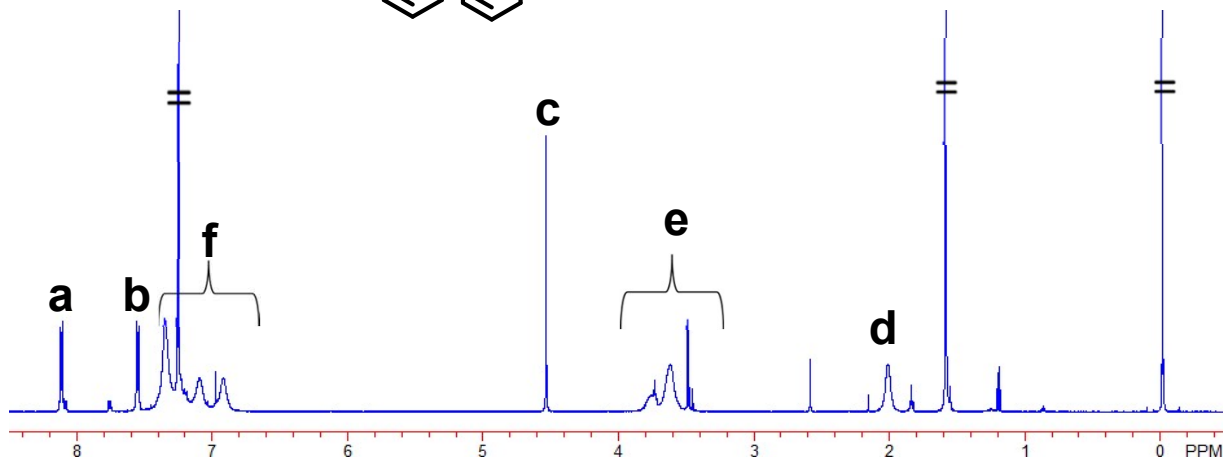
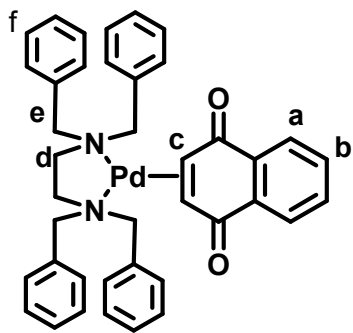
〈元素分析〉

	C (%)	H (%)	N (%)
実測値	63.70	4.84	3.55
理論値	63.71	4.81	3.72

Pd3の合成



〈 $^1\text{H NMR}$ 〉



〈単結晶X線構造解析〉

※粉末状のため、測定不可

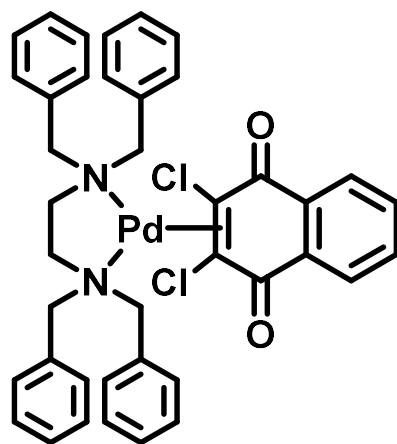
〈元素分析〉

	C (%)	H (%)	N (%)
実測値	69.21	5.29	3.80
理論値	70.12	5.59	4.09

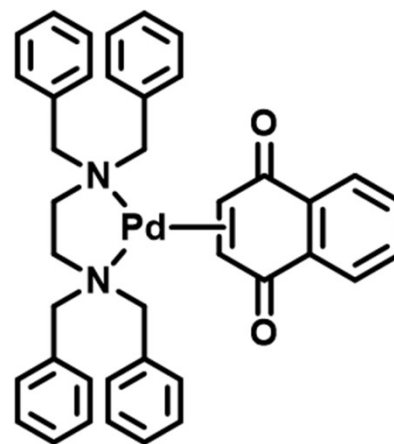
本日の内容

✓ 新規錯体Pd2、Pd3の合成

✓ Pd2、Pd3を用いた重合挙動の調査



Pd2



Pd3

Pd2、Pd3を用いた重合 ([EDA]/[Pd] = 100)

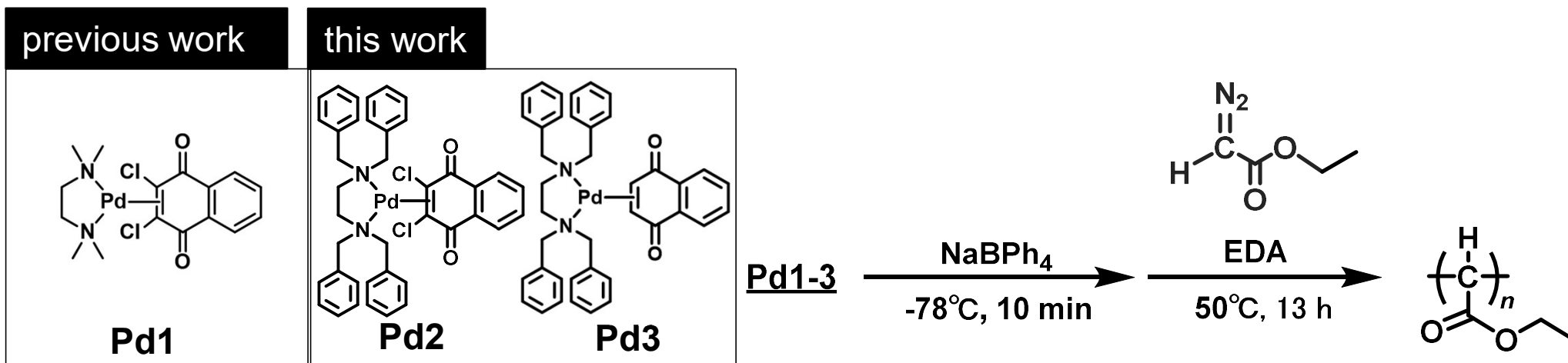


Table 1. Polymerization of EDA with Pd/borate system

run	Pd	yield(%)	M_n	M_w/M_n
1	Pd1	58	9000	1.90
2	Pd2	34 ▼	22600 ▲	1.86
3	Pd3	26 ▼	8500 ▼	2.00

In THF (3.0 ml). M_n and M_w/M_n were obtained by GPC calibration using standard PMMAs in CHCl_3 solution.

Pd1との比較

Pd2

- ・ 分子量は**増加**
- ・ 収率は**低下**

Pd3

- ・ 分子量は**低下**
- ・ 収率は**低下**

[EDA]/[Pd]の変更

this work

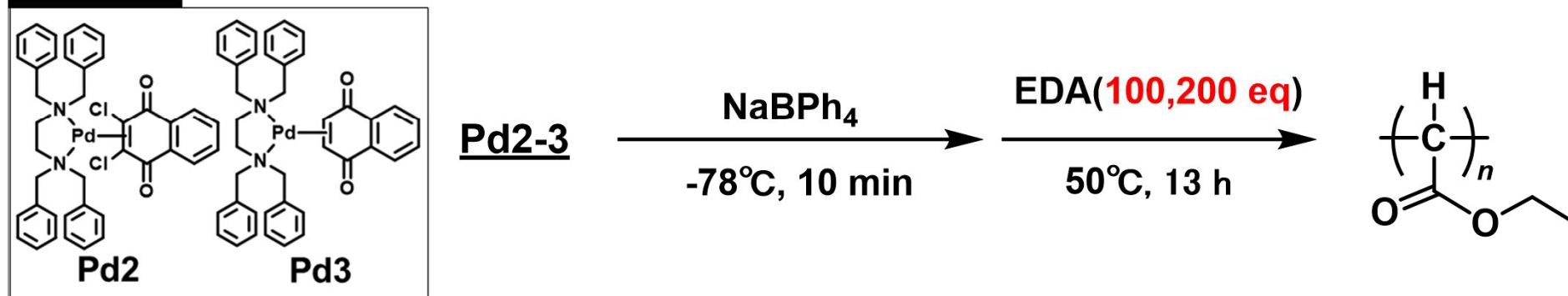


Table 2. Polymerization of EDA with Pd/borate system

run	Pd	[EDA]/[Pd]	yield(%)	M_n	M_w/M_n
1	Pd2	100	34	22600	1.86
2		200	32	32700	1.95
3	Pd3	100	26	8460	2.00
4		200	23	10800	1.80

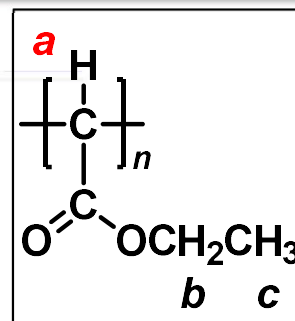
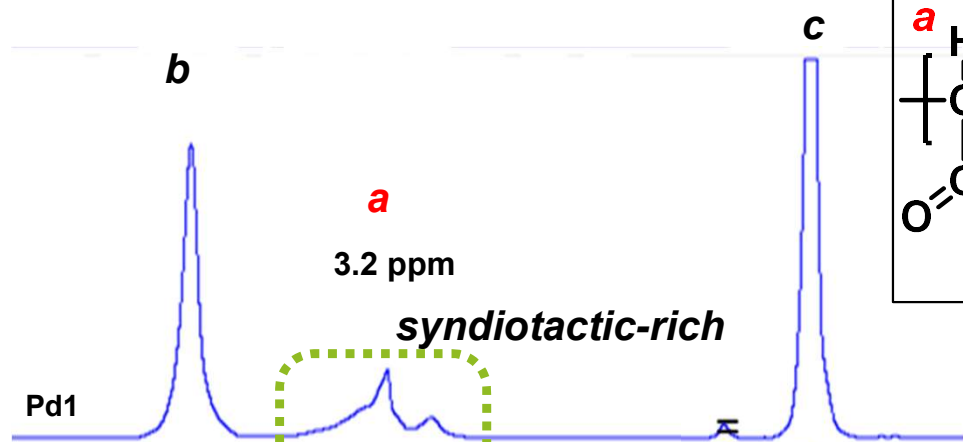
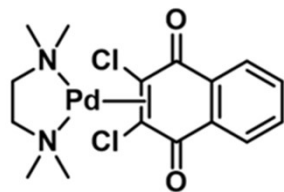
In THF (3.0 ml). M_n and M_w/M_n were obtained by GPC calibration using standard PMMAs in $CHCl_3$ solution.

当量を増加させると M_n も増加した

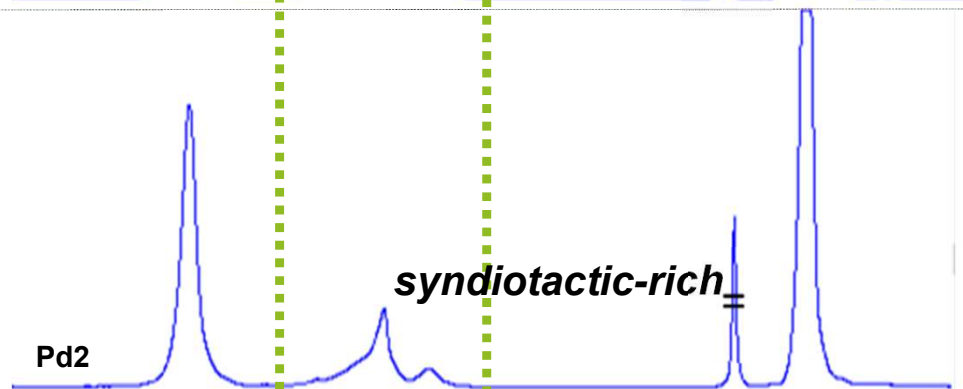
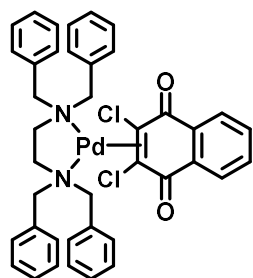
立体規則性の調査

used complexes

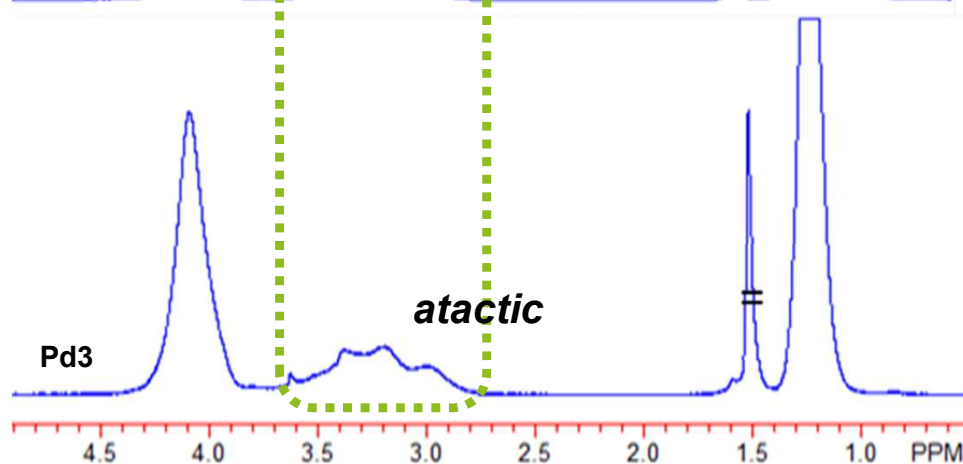
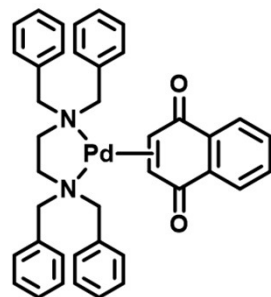
previous
work



this
work



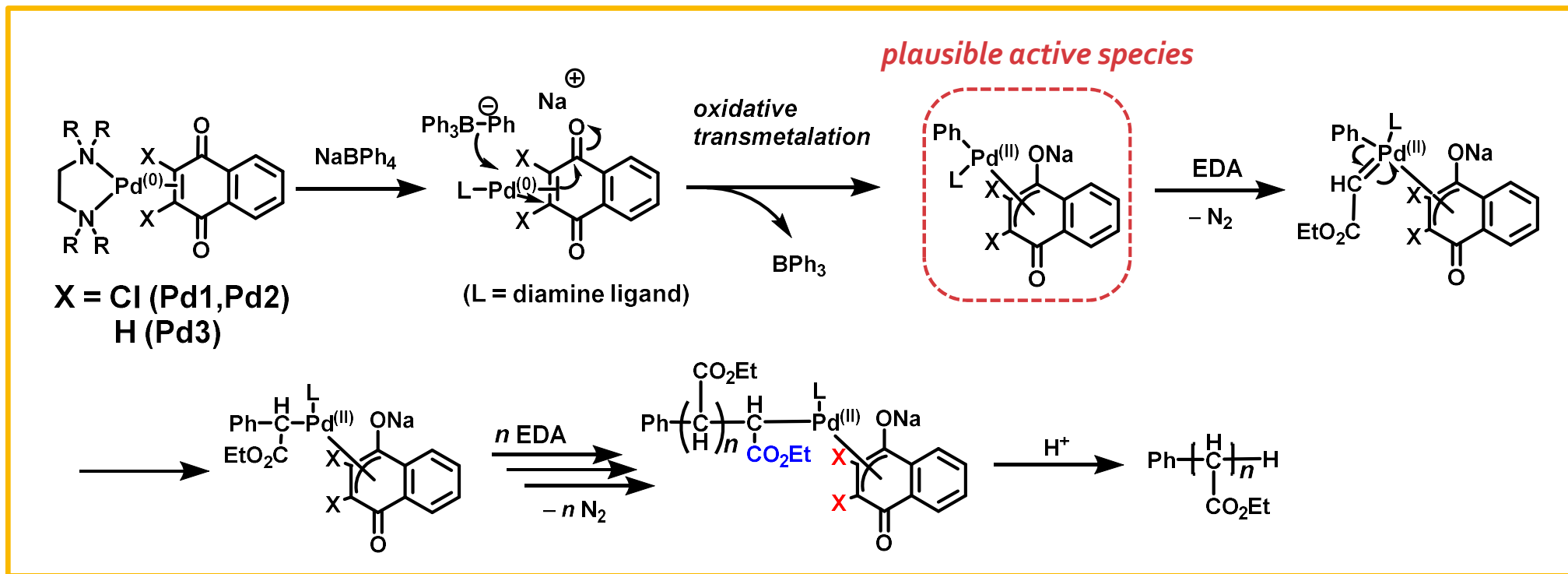
Pd1と立体規則性はほとんど同じ



立体規則性は低い

推定される重合機構

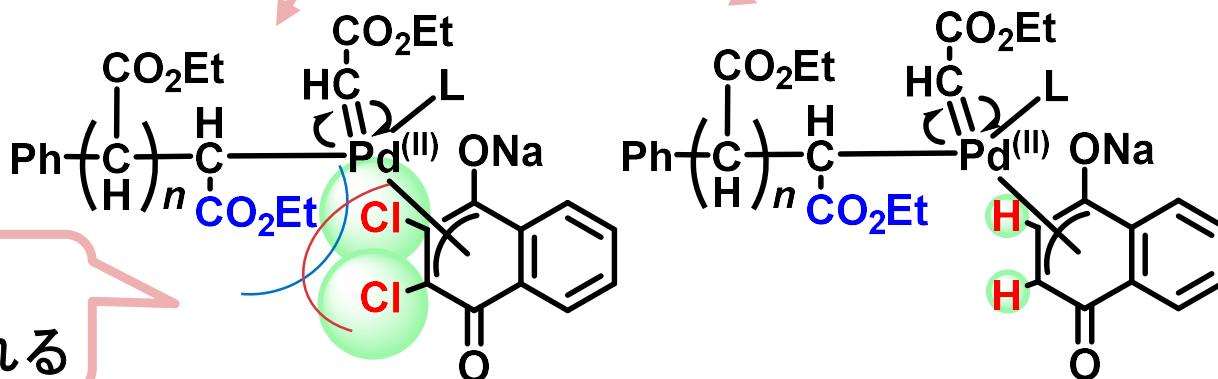
重合機構



used complexes

Pd1, Pd2

Pd3



Clの立体障害により
立体規則性が制御される

開始剤効率による考察

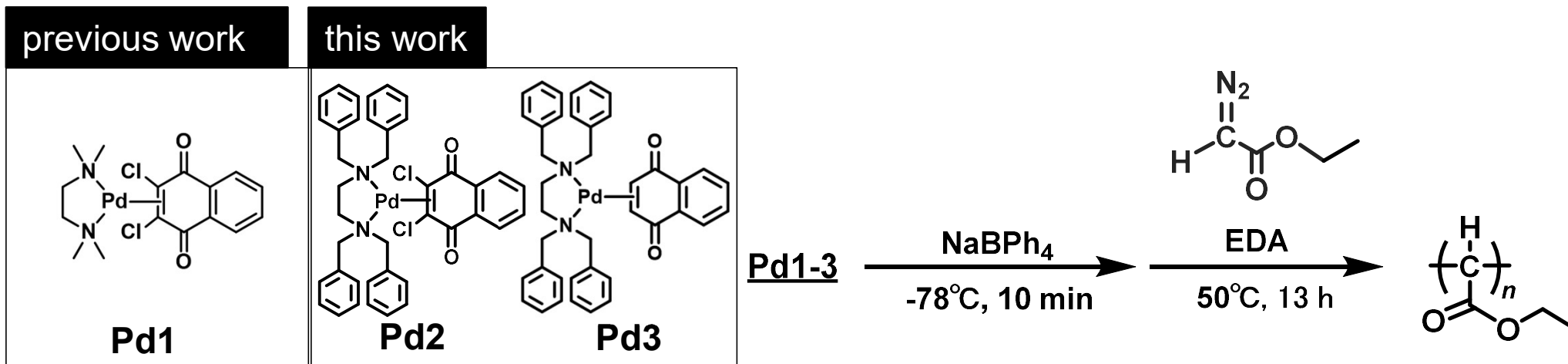


Table 4. Polymerization of EDA with Pd/borate system

run	Pd	yield(%)	M_n	M_w/M_n	IE(%)
1	Pd1	58	9000	1.90	55
2	Pd2	34 ▼	22600 ▲	1.86	13 ▼
3	Pd3	26 ▼	8500 ▼	2.00	26 ▼

In THF (3.0 ml). M_n and M_w/M_n were obtained by GPC calibration using standard PMMAs in CHCl₃ solution.

Pd1との比較

Pd2

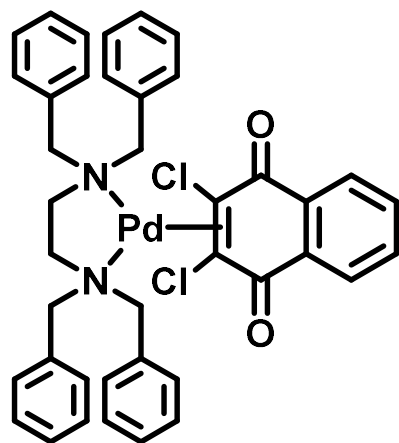
- ・ 分子量は**増加**
- ・ 収率は**低下**

Pd3

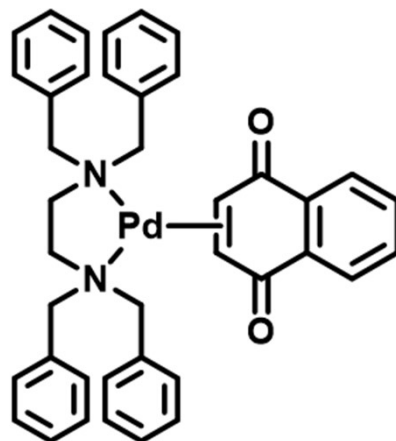
- ・ 分子量は**低下**
- ・ 収率は**低下**

結言

- ✓ 新規錯体Pd2、Pd3の合成に成功した
- ✓ どちらのPd錯体もEDAの重合に対し活性を示した



Pd2



Pd3

- Pd2は、高分子量でシンジオタクチックなポリマーを与えた
- Pd3はアタクチックなポリマーを与えた