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Initiating abilities of diphosphine- and diamine-ligated Pd complexes/$NaBPh_4$ systems for C1 polymerization of diazoacetates†

Hiroaki Shimomoto, * Yuto Miyano, Kaito Kinoshita, Tomomichi Itoh and Eiji Ihara *

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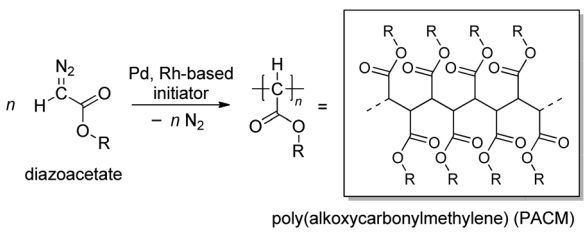
A series of well-defined Pd complexes bearing diphosphines or diamines and a dichloroquinone-derived unit as ligands were newly prepared and their initiating abilities in conjunction with $NaBPh_4$ for the C1 polymerization of diazoacetates were investigated. Among the (diphosphine)Pd(II)Cl(Cl-quinonyl) complexes examined here, square planar *cis* (diphosphine: diphenylphosphinoferrocene) and distorted square planar *trans* (diphosphine: xantphos) complexes with $NaBPh_4$ yielded highly syndiotactic polymers from ethyl diazoacetate despite low polymer yields. A series of Pd(0) complexes bearing a bidentate diamine such as *N*,*N*,*N*′,*N*′-tetramethyl-1,3-propanediamine and 2,3-dichloronaphthoquinone in conjunction with $NaBPh_4$ polymerized diazoacetates to afford moderately syndiotactic polymers in moderate yields, indicating that the (diamine)Pd(0)(dichloroquinone) framework could be a promising general platform for an initiating system with high activity and stereoselectivity for the C1 polymerization of diazoacetates.

Introduction

Polymerization of diazoacetates has been gaining recognition as an effective method for C–C main chain polymer synthesis with the development of effective initiating systems for the polymerization in the last two decades (Scheme 1).[1–7] The polymerization affording poly(alkoxycarbonylmethylene)s (PACMs) is classified as a member of "C1 polymerizations", where the C–C main chain of the products is constructed from "one carbon unit". In comparison with vinyl polymers obtained from "C2 polymerization", PACMs are expected to exhibit unique properties or functions derived from the structural feature of having an alkoxycarbonyl group (ester) on each of the main chain carbon atoms; indeed, enhancement in properties such as hydrophilicity, photophysical properties, and so on of PACMs has been observed,[8–25] because of the densely-packed ester substituents around the C–C main chain.

For the preparation of high M_n (>10 000) PACMs, initiators based on some Rh and Pd complexes have been demonstrated to be most effective: for example, de Bruin and coworkers have reported that Rh(diene) complexes can yield high M_n (>200000) polymers with high syndiotacticities,[26,27] and we and other groups have demonstrated that some Pd complexes with an η^3-anionic ligand are effective for yielding atactic polymers with a variety of ester substituents.[28–32] In addition, our recent finding revealed that two types of Pd complexes with naphthoquinone (nq)-based ligands can be utilized as effective initiators for diazoacetate polymerization in conjunction with $NaBPh_4$.[33] The first one is zero valent Pd(0)$(nq)_2$ **1**, which can afford high M_n polymers in high yields; as shown in Scheme 2, according to a previous literature report on the reactivity of a Pd(0) complex in an analogous system,[34] the initiating Pd–Ph group is proposed to be generated *via* oxidative transmetalation, where the transmetalation of the Ph group occurs from the borate to the Pd center and oxidation of Pd(0) to Pd(II) occurs at the same time; indeed, the high activity of the initiating species thus generated indicates the importance of the presence of an η^3-type anionic ligand for the initiator to be highly active.[35,36] The



Scheme 1 C1 polymerization of diazoacetates.

Department of Materials Science and Biotechnology, Graduate School of Science and Engineering, Ehime University, 3 Bunkyo-cho, Matsuyama 790-8577, Japan.
E-mail: shimomoto.hiroaki.mx@ehime-u.ac.jp, ihara@ehime-u.ac.jp;
Fax: +81-89-927-9949, +81-89-927-8547; Tel: +81-89-927-9949, +81-89-927-8547

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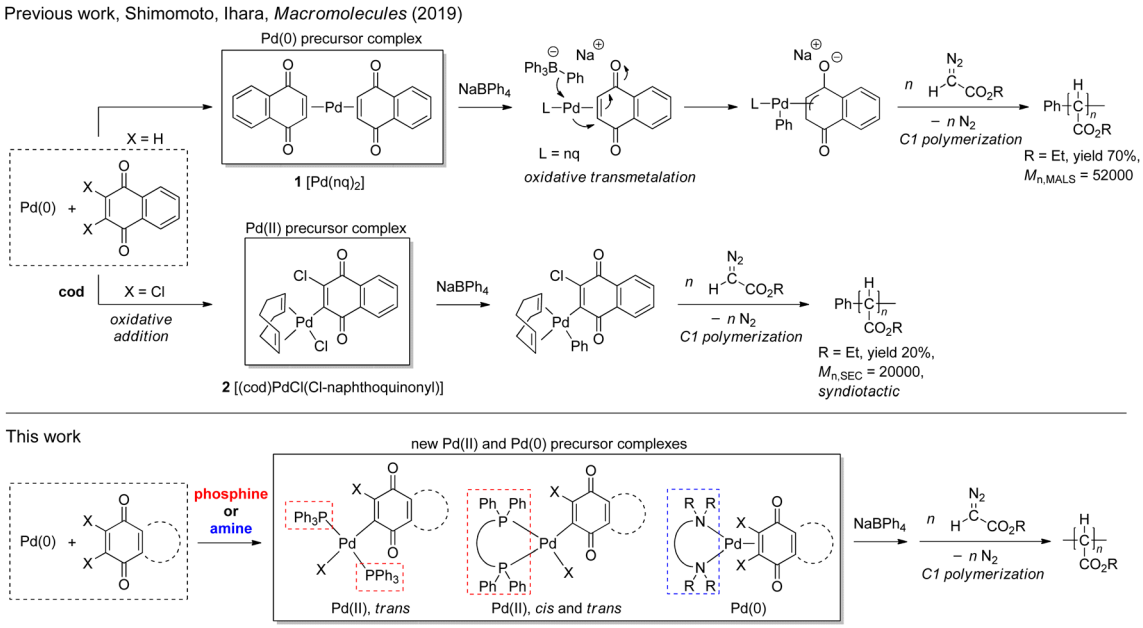


Scheme 2 Initiating systems with Pd complexes bearing naphthoquinone-based ligands.

second one is divalent (cod)Pd(II)Cl(Cl-naphthoquinonyl) **2** (cod: 1,5-cyclooctadiene) generated *via* the oxidative addition of one of the two Cl–C bonds of 2,3-dichloronaphthoquinone (dichlone) to the Pd(0) center, which generates an initiating Pd–Ph species *via* transmetalation with subsequent activation with $NaBPh_4$. Although the polymer yield with this initiating system was rather low (*ca.* 20%), it is noteworthy that the polymers obtained with this system are highly syndiotactic.

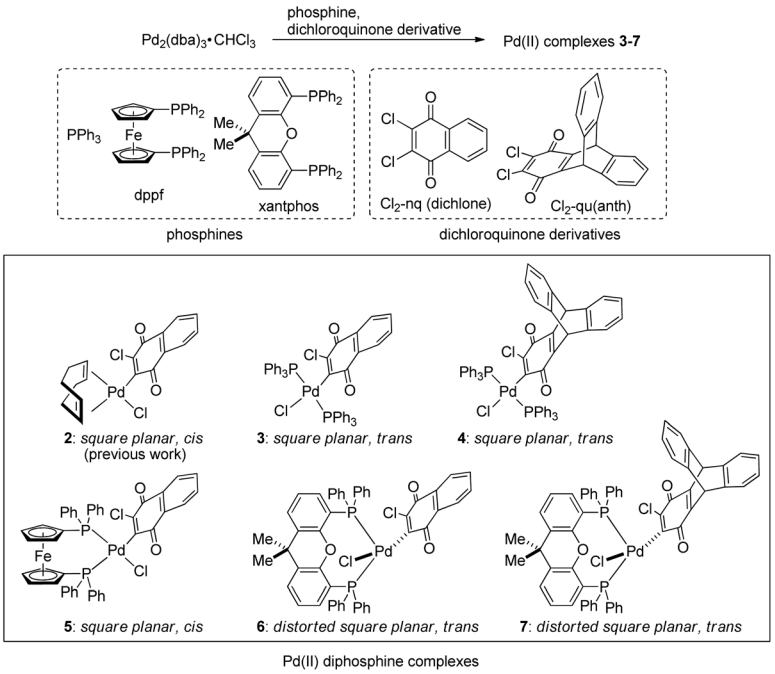
With these results in mind, our next strategy examined here for further improving the initiating ability with respect to the polymer yield and M_n and tacticity control is the replacement of the neutral ligands, nq and cod in **1** and **2**, respectively, with other neutral ligands in order to affect the reactivity and stereoselectivity of the Pd-containing initiating and propagating species. Thus, as candidates for such neutral ligands, we chose a series of phosphines and amines and attempted to prepare new well-defined Pd precursor complexes with these ligands and investigate the initiating ability of the resulting systems activated with $NaBPh_4$ for diazoacetate polymerization. In the course of the investigation, we have succeeded in finding (*N*,*N*,*N*′,*N*′-tetramethyl-1,3-propanediamine)Pd(0)(dichlone)/$NaBPh_4$ as a new effective initiating system, which possesses advantages of both systems based on **1** and **2** and can afford polymers with moderate syndioselectivity in moderate yields. The details of the investigation will be described in this paper.

Results and discussion

Preparation of Pd(II) complexes with diphosphine and quinonyl anions as ligands

First of all, we attempted to investigate the possibility of using phosphine as a ligand in place of cyclooctadiene (cod) in the (cod)Pd(II)Cl(Cl-naphthoquinonyl) (**2**)/$NaBPh_4$ system. For this purpose, we employed three phosphines,[37] triphenylphosphine (PPh_3), 1,1′-bis(diphenylphosphino)ferrocene (dppf), and 4,5-bis(diphenylphosphino)-9,9-dimethylxanthene (xantphos), and two dichloroquinones, 2,3-dichloronaphthoquinone (dichlone) and 14,15-dichloro-9,10-[1,2]benzenoanthracene-13,16(9*H*,10*H*)-dione [Cl_2-qu(anth)],[38] which was prepared by 2 + 4 addition of anthracene and 1,4-benzoquinone followed by chlorination, and some combinations of these reagents were employed for the syntheses of new Pd(II) complexes following the standard procedure for the preparation of **2** (Scheme 3). Thus, a starting material, $Pd(0)_2(dba)_3{\cdot}CHCl_3$, was reacted with an excess amount of phosphine and dichloroquinone in acetone (PPh_3 and dppf) or THF (xantphos) at room temperature for 1 h, and as a result of the oxidative addition of a Cl–C bond of dichloroquinone to Pd(0), the expected Pd(II) complexes **3**–**7** were obtained as air-stable solids, which were identified by NMR and elemental analyses (see the ESI†).

Except for **4**, solid-state structures of these complexes were identified by X-ray crystal analyses, among which the structures of **3**, **5**, and **6** are shown in Fig. 1 (for detailed data including the structure of **7**, see the ESI†). The Pd center of bis(triphenylphosphine) complex **3** adopts a square planar configuration with two phosphines coordinated in a *trans* form. In accordance with the solid-state structure, the ^{31}P NMR spectrum of **3** exhibits only one P signal at 22.8 ppm. Although single crystals suitable for X-ray analysis were not obtained for **4**, the ^{31}P NMR spectrum of the complex shows only one signal at 22.8 ppm, indicating that **4** also adopts a similar square planar *trans* configuration to that of **3**. Meanwhile, the Pd center in the dppf complex **5** adopts a square planar configuration with the two P atoms coordinated in a *cis* form as



Scheme 3 Synthesis of (diphosphine)Pd(II)Cl(Cl-quinonyl) complexes.

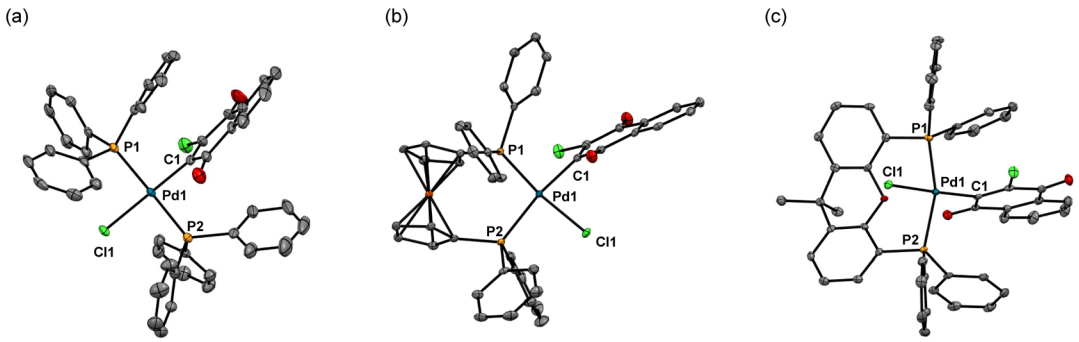


Fig. 1 X-ray structures of (a) **3**, (b) **5**, and (c) **6** with 50% thermal ellipsoids. Hydrogen atoms and solvents have been omitted for clarity. Selected bond lengths (Å) and angles (°): (a) **3**: Pd1–P1 = 2.323(1), Pd1–P2 = 2.309(1), Pd1–C1 = 1.991(4), Pd1–Cl1 = 2.370(2), P1–Pd1–P2 = 176.68(4), C1–Pd1–Cl1 = 179.9(1), P1–Pd1–Cl1 = 90.63(4); (b) **5**: Pd1–P1 = 2.2448(9), Pd1–P2 = 2.3650(9), Pd1–C1 = 2.029(4), Pd1–Cl1 = 2.356(1), P1–Pd1–P2 = 98.94(4), C1–Pd1–Cl1 = 82.5(1), P1–Pd1–Cl1 = 170.49(4); (c) **6**: Pd1–P1 = 2.3261(7), Pd1–P2 = 2.3230(8), Pd1–C1 = 2.013(2), Pd1–Cl1 = 2.4070(7), P1–Pd1–P2 = 150.80(3), C1–Pd1–Cl1 = 174.65(7), P1–Pd1–Cl1 = 87.90(2).

revealed by X-ray analysis. Accordingly, the ^{31}P NMR spectrum of **5** contains two signals at 31.0 and 13.7 ppm, reflecting the presence of two P atoms in different environments. On the other hand, xantphos complexes **6** and **7** adopt a distorted square planar configuration, two P atoms being located in *trans* positions as confirmed by X-ray analysis. Whereas the C–Pd–Cl angles (174.7° for **6** and 175.7° for **7**) are close to the ideal value (180°) for the square planar configuration, the P–Pd–P bite angles of 150.8° and 152.6° for **6** and **7**, respectively, are much smaller than the ideal value. In accordance with the solid-state structures, the ^{31}P spectra of **6** and **7** exhibit only one signal at 6.3 ppm. With these Pd(II) complexes ligated with phosphine and oxidatively added dichloroquinone derivatives in hand, we can investigate the relationship of the structures of the Pd(II) complexes and the initiating ability for diazoacetate polymerization with the activation with $NaBPh_4$, hopefully leading to the development of highly active initiating systems for the polymerization.

Polymerization of ethyl diazoacetate with (diphosphine)Pd(II)Cl(Cl-quinonyl)/$NaBPh_4$ systems

Following our previous publication on diazoacetate polymerization with **2**/$NaBPh_4$,[33] polymerization of ethyl diazoacetate (EDA) with **3**–**7**/$NaBPh_4$ was conducted using THF or 1,4-dioxane as the solvent (Table 1). For the effective initiation, one of the Ph groups on the borate should be transferred to Pd, leading to a Pd–Ph initiating species [activation of the Pd(II) precursor], into which carbenes generated from diazoace-

Table 1 Polymerization of EDA initiated with (diphosphine)Pd(II)Cl(Cl-quinonyl)/$NaBPh_4$ systems[a]

Run	Pd(II)	Solvent	Temperature	Yield[b] (%)	M_n [c]	$Đ$[c]	Syndiotacticity[d]
1[e]	**2**	THF	50 °C	20	20 500	1.46	High
2	**3**	THF	RT	1.2	11 300	1.46	Moderate
3	**3**	THF	50 °C	17	7600	1.58	Moderate
4	**3**	1,4-Dioxane	50 °C	24	8100	2.08	Moderate
5	**3**	1,4-Dioxane	70 °C	28	10 800	2.39	Moderate
6	**3**	1,4-Dioxane	90 °C	38	8100	1.83	Moderate
7	**4**	THF	50 °C	1.6	12 100	1.63	Low
8	**5**	THF	50 °C	5.7	12 000	2.13	High
9	**5**	1,4-Dioxane	70 °C	18	10 600	2.39	High
10	**6**	THF	RT	3.2	40 600	1.62	Very high
11	**6**	THF	50 °C	21	9700	2.14	High
12	**6**	1,4-Dioxane	70 °C	9.1	13 500	2.23	High
13	**7**	THF	50 °C	4.1	8700	1.62	Low

[a] Pd = 0.01 mmol, THF or 1,4-dioxane = 3 mL, polymerization time = 13 h, [EDA]/[Pd] = 100, [$NaBPh_4$]/[Pd] = 1.1; EDA was used as a CH_2Cl_2 solution with a concentration of 1.5–2.3 M. [b] After purification with preparative SEC to remove dimers and oligomers. [c] Determined by SEC using PMMA standards. [d] Estimated by NMR measurements (Fig. 2).[39] [e] Quoted from our previous work.[33]

tates will be inserted efficiently after N_2 elimination, resulting in the formation of polymers with a Ph group at the α-chain end. The transmetalation was carried out at −78 °C or 0 °C in THF or 1,4-dioxane respectively. Then, an EDA solution in CH_2Cl_2 was added to the mixture at a low temperature, followed by polymerization at each temperature mentioned in Table 1.

The square planar *trans*-bis(triphenylphosphine) Pd(II) complex **3** with $NaBPh_4$ gave polyEDA′ in a very low yield (1.2%) at room temperature (run 2). The polymer yield increased to the same level (17%) as that with **2**/$NaBPh_4$ in the polymerization at 50 °C (run 3). A further increase in the polymer yield was observed in the polymerization at a higher temperature with 1,4-dioxane as the solvent (24–38%) (runs 4–6). Polymer tacticity was evaluated from the peak positions of the main chain methine signals in ^{1}H NMR spectra of polyEDA′s (Fig. 2).[39] Although the polymer prepared with the **3**/$NaBPh_4$ system (run 5) exhibits a dominant peak at the same position (3.2 ppm) as those for highly syndiotactic polymers obtained with **2**/$NaBPh_4$, the presence of relatively large peaks on both sides of the dominant peak suggests that the stereoregularity is not so high (moderate). Another square planar *trans*-bis(triphenylphosphine) Pd(II) complex **4** with a bulky chloroquinonyl moiety with $NaBPh_4$ was much less active for the polymerization, affording a polymer in a very low yield (1.6%) in the polymerization at 50 °C (run 7). A broad methine proton signal was observed for the product obtained with **4**/$NaBPh_4$, suggesting the stereoselectivity of the product is low. These results indicated that the use of two PPh_3 groups in a square planar configuration with a *trans* coordination instead of *cis* coordinated cod significantly diminishes the syndioselectivity for the polymerization.

Then, the square planar Pd(II) complex with a *cis* coordinated bidentate phosphine (dppf) **5** with $NaBPh_4$ was employed for EDA polymerization. Polymerization in THF at 50 °C afforded polyEDA′ in a much lower yield (5.7%) compared to that observed with **2**/$NaBPh_4$ under the same conditions, while the same level of syndiotacticity as **2**/$NaBPh_4$ was observed for the product (run 8, Fig. 2). In addition, the higher syndiotacticity of the product compared with those for the polymers obtained with **3**/$NaBPh_4$ and **4**/$NaBPh_4$ was maintained for the polymerization in 1,4-dioxane at 70 °C with an increasing polymer yield of 18% (run 9). These results suggest that the *cis* configuration of a bidentate ligand plays an important role in the syndioselective propagation of EDA.

On the other hand, the distorted square planar *trans* Pd(II) complex with a xantphos ligand **6** with $NaBPh_4$ afforded polyEDA′ in THF at 50 °C in a similar yield (21%) to that observed with **2**/$NaBPh_4$, despite slightly lower syndioselectivity (run 11 in Table 1, Fig. 2); polymerization in 1,4-dioxane at 70 °C resulted in a lower yield of polyEDA′ (9.1%) with the same level of syndioselectivity as that obtained with THF (run 12). Interestingly, the EDA polymerization with **6**/$NaBPh_4$ at room temperature afforded polyEDA′ with a slightly higher syndioselectivity than that observed with **2**/$NaBPh_4$, although the polymer yield diminished significantly (3.2%) (run 10 in Table 1, Fig. 2). A xantphos ligated Pd(II) complex **7** with a bulky chloroquinone with $NaBPh_4$ afforded polyEDA′ with a low stereoselectivity in a lower yield (4.1%) in THF at 50 °C (run 13 in Table 1, Fig. 2), probably because the bulky chloroquinonyl moiety would sterically prevent the polymerization and exert a negative effect for the stereoselectivity. These results indicated that the distorted square planar *trans* configuration brought about by the xantphos ligand was not effective for increasing the polymer yield, although under specific conditions a very small amount of a highly syndioselective initiator can be generated.

On the basis of the results described above, although the use of phosphine as a ligand in place of cod in **2**/$NaBPh_4$ for diazoacetate polymerization is not so effective for increasing the polymer yield, the same level of activity and syndioselectivity as those of **2**/$NaBPh_4$ was observed in some cases. In addition, we can confirm that the steric environment around the Pd center can strongly affect the initiating ability with

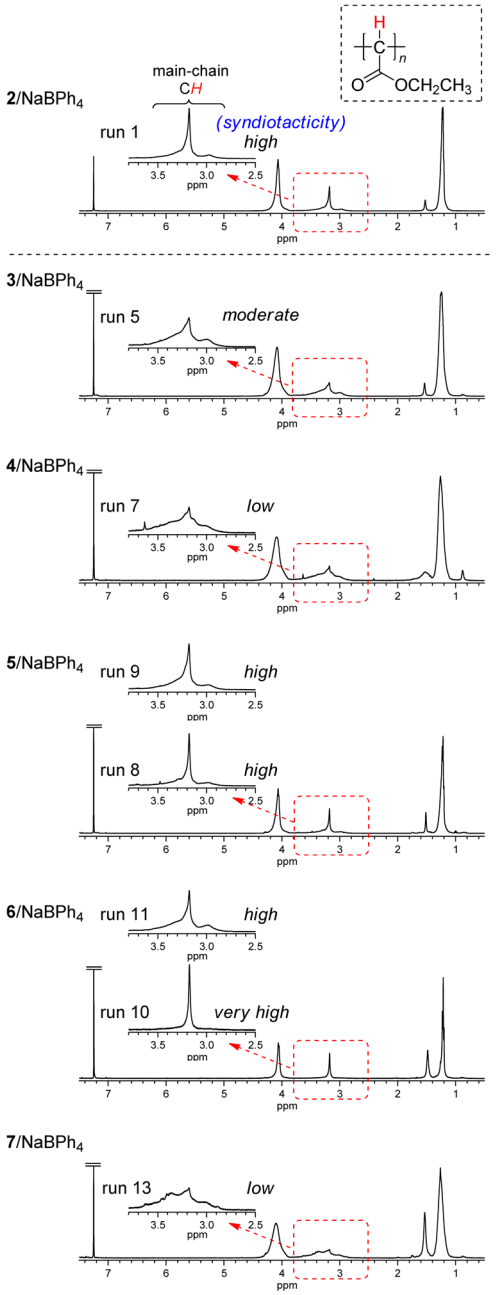


Fig. 2 ^{1}H NMR spectra of polyEDA's obtained with **2**/$NaBPh_4$, **3**/$NaBPh_4$ (run 5 in Table 1), **4**/$NaBPh_4$ (run 7 in Table 1), **5**/$NaBPh_4$ (runs 8 and 9 in Table 1), **6**/$NaBPh_4$ (runs 10 and 11 in Table 1), and **7**/$NaBPh_4$ (run 13 in Table 1), recorded in $CDCl_3$ at 50 °C.

respect to the polymer yield and stereoselectivity in these systems.

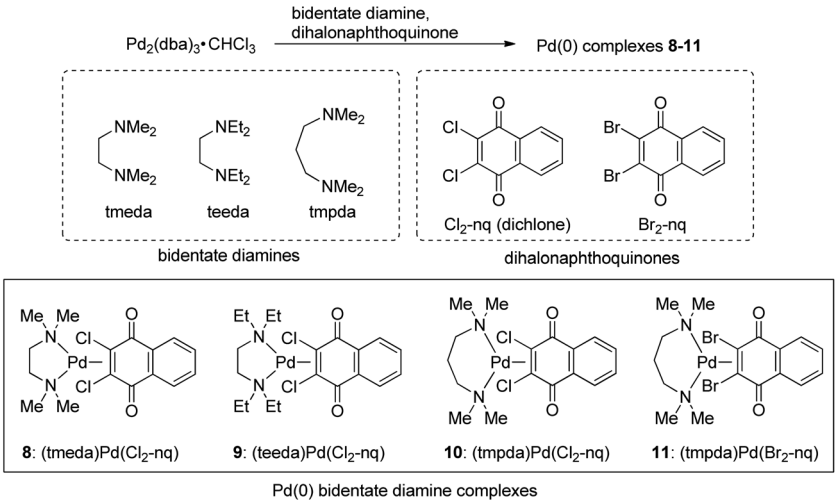
Preparation of Pd(0) complexes with bidentate diamine ligands

Next, we attempted to employ bidentate diamines as a ligand in place of cod and phosphine in the above-described Pd complexes. *N*,*N*,*N*′,*N*′-tetramethylethylenediamine (tmeda), *N*,*N*,*N*′,*N*′-tetraethylethylenediamine (teeda), and *N*,*N*,*N*′,*N*′-tetramethyl-1,3-propanediamine (tmpda) were chosen as bidentate diamines in conjunction with dichlone and its dibromo analogue. For the preparation of Pd complexes, $Pd_2(dba)_3CHCl_3$ was reacted with excess diamine and dihalonaphthoquinone in acetone (tmeda) or THF (teeda and tmpda) at room temperature for 1 h using a similar procedure employed for the synthesis of phosphine complexes described above (Scheme 4). To our surprise, the products obtained here were not Pd(II), but Pd(0) complexes with a dihalonaphthoquinone moiety coordinated to a Pd center in an η^2-mode without the oxidative addition of an X–C bond (X = Cl or Br), as unambiguously identified by X-ray analyses as shown in Fig. 3 for complexes **8** and **10** (for the structure of **11**, see the ESI†). The solid-state structures were also supported by ^{1}H NMR, where only two aromatic signals were observed with an equal intensity for two sets of equivalent 2Hs (see the ESI†), indicating that the dihalonaphthoquinones were coordinated in a symmetrical manner in these Pd(0) complexes including **9**, whose suitable crystals for X-ray analysis were not obtained. These results indicate that, in contrast to diphosphine ligands, the bidentate diamine ligands render the oxidative addition of an X–C bond in the dihalonaphthoquinones unfavorable. This phenomenon can be reasonably explained by a possible lower electron density on the Pd center in **8**–**11** than that in the aforementioned diphosphine complexes, owing to less effective electron donation from the two nitrogen atoms in diamines than the phosphorus atoms in diphosphines, because the higher electron density on Pd should be more favorable for the oxidative addition of the X–C bond to proceed.

According to the mechanism for the formation of the initiating Pd–Ph species described in the Introduction, the unexpectedly obtained Pd(0) complexes with a bidentate diamine would be transformed into an active initiator for the diazoacetate polymerization *via* a pathway involving the oxidative transmetalation of one of the Ph groups in $NaBPh_4$ to the Pd center, where at the same time an η^3-type anionic ligand derived from the dihalonaphthoquinone moiety should be attached as an effective ligand to Pd. In that case, we can expect a high polymer yield as that obtained in the polymerization with the **1**/$NaBPh_4$ system, and hopefully, stereoselectivity would be imparted to the polymerization because of the steric effect of the bidentate diamine ligand on the Pd center and additional two Cl atoms on the anionic naphthoquinonyl ligand.

Polymerization of diazoacetates with (diamine)Pd(0)(dihalonaphthoquinone)/$NaBPh_4$ systems

The results of polymerization of EDA with **8**–**11** in conjunction with $NaBPh_4$ are presented in Table 2. While the polymerization with the Pd(0) complex with tmeda **8** with $NaBPh_4$ at room temperature gave polyEDA′ in a very low yield (2.4%), raising the polymerization temperature to 50 °C resulted in a higher polymer yield of 58% (runs 4 and 5); SEC-estimated M_ns of the polyEDA′s were about 10 000. The Pd(0) complex with a teeda ligand **9** with $NaBPh_4$ exhibited a similar initiating ability under similar conditions (runs 7 and 8).



Scheme 4 Synthesis of (diamine)Pd(0)(dihalonaphthoquinone) complexes.

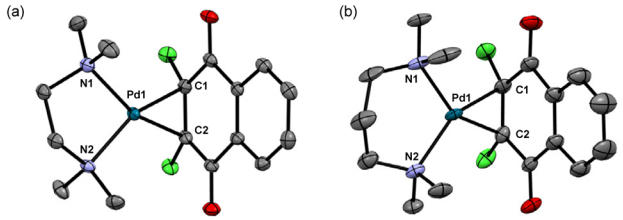


Fig. 3 X-ray structures of (a) **8** and (b) **10** with 50% thermal ellipsoids. Hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (°): (a) **8**: Pd1–N1 = 2.166(2), Pd1–N2 = 2.165(2), Pd1–C1 = 2.074(2), Pd1–C2 = 2.074(2), N1–Pd1–N2 = 83.08(8). (b) **10**: Pd1–N1 = 2.177(4), Pd1–N2 = 2.182(3), Pd1–C1 = 2.063(3), Pd1–C2 = 2.078(4), N1–Pd1–N2 = 95.7(1).

Polymerization in 1,4-dioxane yielded polyEDA′ with the same level of M_n and yield as in THF at the same temperature (run 9). A further increase in the polymer yield was not observed in the polymerization at a higher temperature of 70 °C (run 10). On the other hand, the tmpda-ligated Pd(0) complex **10** with $NaBPh_4$ afforded polyEDA′ in a higher yield of 34% at room temperature compared to that afforded by **8** and **9** with $NaBPh_4$ (run 11), while at 50 °C the **10**/$NaBPh_4$ system showed a similar activity to that exhibited by **8** and **9** with $NaBPh_4$ (run 12). To further confirm the higher activity of **10**/$NaBPh_4$, the activities of **8**/$NaBPh_4$ and **10**/$NaBPh_4$ were compared with the polymerization conducted for 1 h at 50 °C (runs 6 and 13); as a result, while the polymerization with **10**/$NaBPh_4$ conducted for 1 h afforded polyEDA′ in a similar yield (49%) to that for 13 h,

Table 2 EDA polymerization with (diamine)Pd(0)(dihalonaphthoquinone)/$NaBPh_4$ systems[a]

Run	Pd(0)	[EDA]/[Pd]	Solvent	Temperature	Period (h)	Yield[b] (%)	M_n[c]	$Đ$[c]	Syndiotacticity[d]
1[e]	**2**	100	THF	50 °C	13	20	20 500	1.46	High
2[e]	**1**	100	THF	RT	13	63	17 200	1.27	(Atactic)
3[e]	**1**	100	THF	50 °C	13	72	17 200	1.42	(Atactic)
4	**8**	100	THF	RT	13	2.4	11 000	1.42	Moderate
5	**8**	100	THF	50 °C	13	58	9000	1.90	Moderate
6	**8**	100	THF	50 °C	1	27	10 700	2.20	Moderate
7	**9**	100	THF	RT	13	3.3	12 000	1.93	Moderate
8	**9**	100	THF	50 °C	13	45	12 100	2.09	Moderate
9	**9**	100	1,4-Dioxane	50 °C	13	47	13 600	2.67	Moderate
10	**9**	100	1,4-Dioxane	70 °C	13	42	11 800	2.92	Moderate
11	**10**	100	THF	RT	13	34	17 100	2.06	Moderate
12	**10**	100	THF	50 °C	13	48	10 800	2.16	Moderate
13	**10**	100	THF	50 °C	1	49	13 900	2.25	Moderate
14	**10**	200	THF	50 °C	13	51	13 500	2.08	Moderate
15	**10**	300	THF	50 °C	13	44	21 300	2.26	Moderate
16	**10**	400	THF	50 °C	13	36	28 100 (37 100)	2.13 (1.54)	Moderate
17	**11**	100	THF	50 °C	13	6.2	9400	1.53	High

[a] Pd = 0.01 mmol, THF or 1,4-dioxane = 3 mL, [$NaBPh_4$]/[Pd] = 1.1; EDA was used as a CH_2Cl_2 solution with a concentration of 1.4–2.5 M. [b] After purification with preparative SEC to remove dimers and oligomers. [c] Determined by SEC using PMMA standards (values in parentheses were determined by SEC-MALS). [d] Estimated by NMR measurements (Fig. 4).[39] [e] Quoted from our previous work.[33]

the yield with **8**/$NaBPh_4$ (27%) was much lower in the 1 h reaction period.

The above-described difference in the activity between **8** and **9** bearing a CH_2CH_2 spacer with $NaBPh_4$ and **10** bearing a $CH_2CH_2CH_2$ spacer with $NaBPh_4$ should be ascribed to the structural difference in the Pd(II) active species during the initiation and propagation. On comparing the crystal structures of the precursors **8** and **10**, the major difference is found to be in the bite angle of N–Pd–N, which is 83.1° and 95.7° for **8** and **10**, respectively; other structural parameters being almost the same.

Initiating mechanisms with these **8–11**/$NaBPh_4$ systems should be discussed on the basis of the comparison of the polymer yield and tacticity with the polymerization results with **2** and **1** with $NaBPh_4$ as presented in runs 1–3 in Table 2. As described in the Introduction, initiation mechanisms for the two naphthoquinone-based Pd complexes **2** and **1** with $NaBPh_4$ are entirely different.[33] In the case of **2**, a Ph anion derived from $NaBPh_4$ nucleophilically replaces Cl at the Pd center, resulting in the formation of the Pd–Ph initiating species where the chloronaphthoquinonyl group is attached to Pd with a σ-bond as an anionic ligand. On the other hand, in the case of **1**, oxidative transmetalation from $NaBPh_4$ to Pd yields the Pd–Ph initiating species where an η^3-type anionic ligand derived from naphthoquinone is attached to Pd. The former system has been revealed to afford highly syndiotactic polymers in low yields, while the latter to afford atactic polymers in high yields as clearly demonstrated in runs 1–3 in Table 2. Even though the polymer yields obtained with **8–10**/$NaBPh_4$ systems were lower than that obtained with **1**/$NaBPh_4$, moderate yields of polyEDA's and the isolation of Pd(0) complexes without the oxidative addition of a Cl–C bond in **8–10** indicate that the polymerization with these systems should be initiated *via* oxidative transmetalation in a manner similar to that of **1**/$NaBPh_4$. On the other hand, the appearance of signals of main chain CHs and carbonyl C=Os in ^1H and ^{13}C NMR spectra, respectively, shown in Fig. 4 indicates that the syndiotacticities of the polyEDA's obtained with **8–10**/$NaBPh_4$

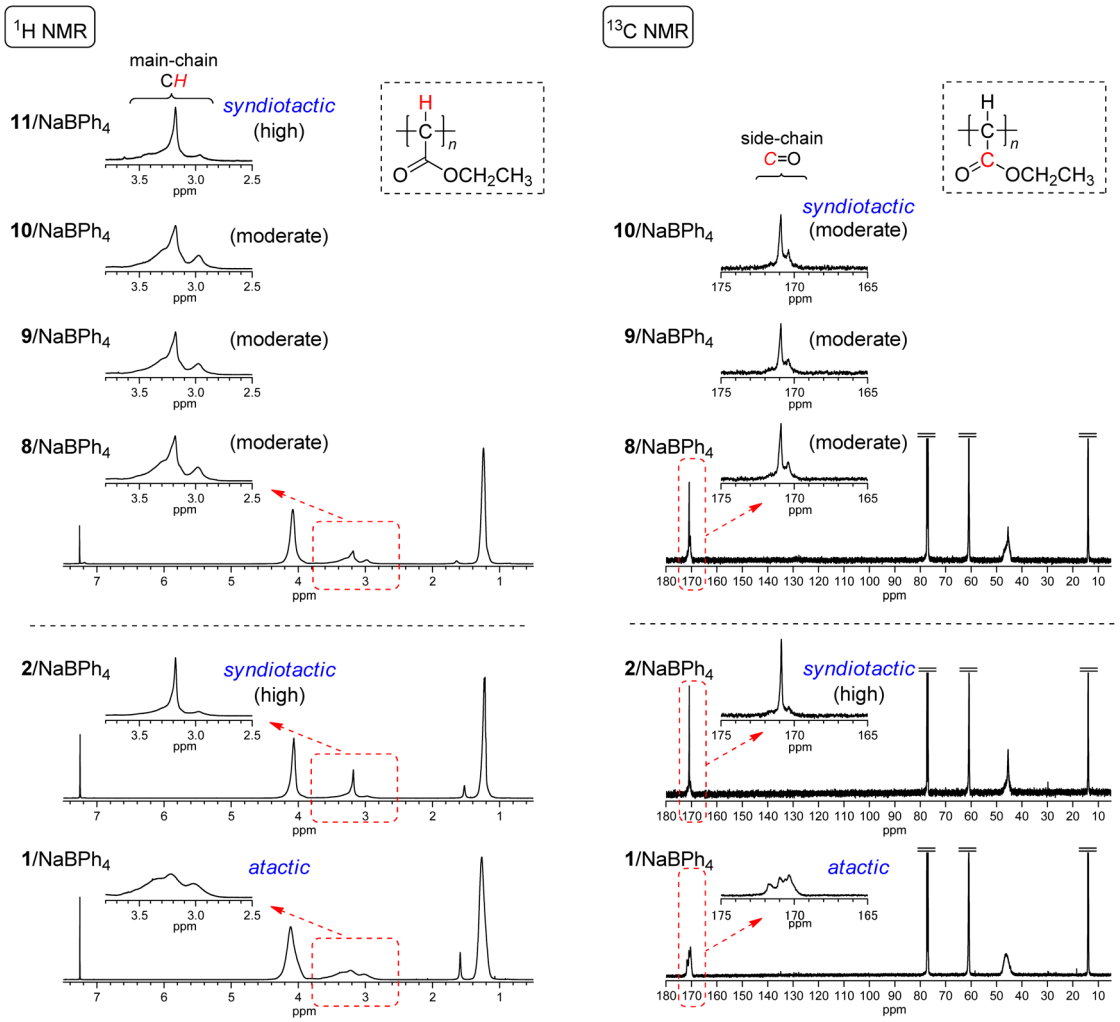


Fig. 4 ^1H and ^{13}C NMR spectra of polyEDA's obtained with **8**/$NaBPh_4$ (run 5 in Table 2), **9**/$NaBPh_4$ (run 8 in Table 2), **10**/$NaBPh_4$ (run 12 in Table 2), and **11**/$NaBPh_4$ (run 17 in Table 2), and with **2**/$NaBPh_4$, and **1**/$NaBPh_4$, recorded in $CDCl_3$ at 50 °C (^1H NMR) or room temperature (^{13}C NMR).

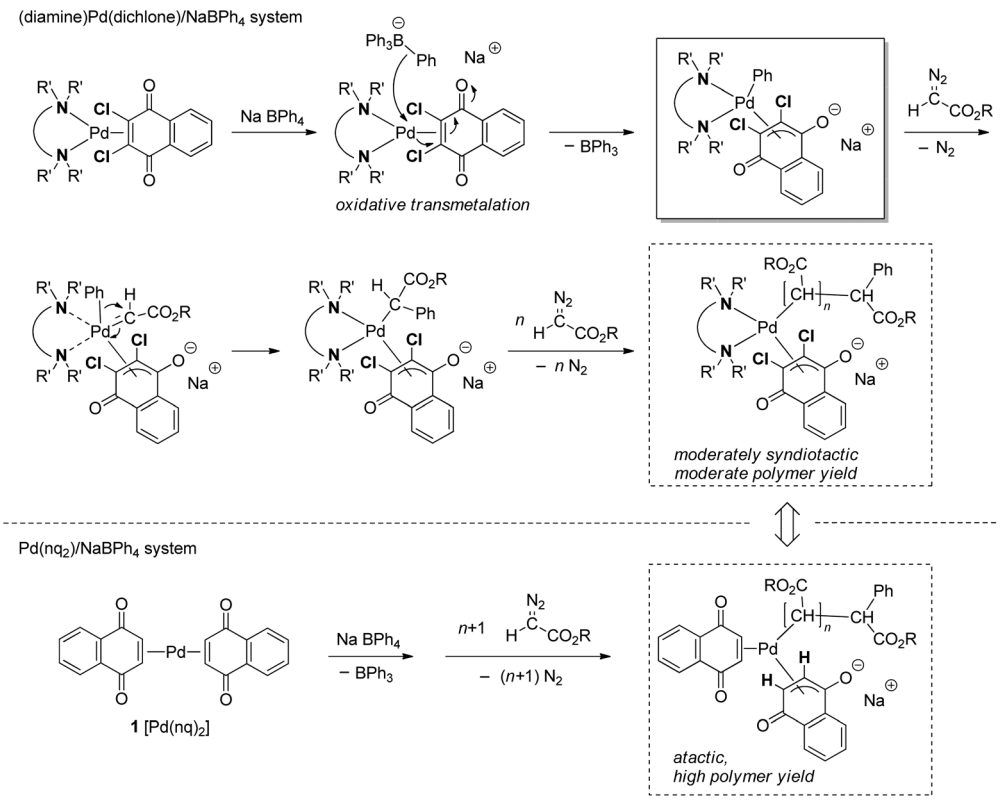
systems are apparently higher than those of the atactic polymers obtained with **1**/$NaBPh_4$ even in a small extent, suggesting that the coordination of a bidentate diamine ligand and two Cl atoms attached to the naphthoquinone-derived framework of the anionic ligand exert a certain steric effect favorable for the syndioselective propagation (Scheme 5).[41]

The results obtained with the dibromonaphthoquinone-ligated Pd(0) complex **11** with $NaBPh_4$ are noteworthy, where EDA polymerization furnished a polymer with much lower yield (6.2%) and higher syndiotacticity than those obtained with **8–10**/$NaBPh_4$ systems (run 17 in Table 2 and Fig. 4). These results suggest that the polymerization with **11**/$NaBPh_4$ proceeded *via* the same mechanism as that with **2**/$NaBPh_4$; thus, we can suppose that the weaker Br–C bond in the dibromonaphthoquinone in **11** resulted in the oxidative addition in the reaction mixture before the polymerization was initiated, even though in isolated **11** in the solid state, the oxidative addition of the Br–C bond did not yet occur; the lower polymer yield than that obtained with **2**/$NaBPh_4$ could be ascribed to the steric effect of the larger size of the Br atom in the bromonaphthoquinonyl ligand. However, an alternative possibility that cannot be ruled out here is that oxidative transmetalation occurs for the initiation with **11**/$NaBPh_4$ as that with **8–10**/$NaBPh_4$ systems, and the larger Br atoms on the η^3-type anionic ligand derived from the dibromonaphthoquinone moiety causes the lower polymer yield and higher syndioselectivity.

In any case, the newly developed (diamine)Pd(0)(dichlone)/$NaBPh_4$ system is a unique initiating system for EDA polymerization, which possesses both advantages of **2**/$NaBPh_4$ and **1**/$NaBPh_4$, affording moderately syndiotactic polymers in moderate yields. Further modification of the structure of the Pd(0) complex will improve both the polymer yield and tacticity.

Runs 14–16 along with run 12 show the relationship between [EDA]/[Pd] feed ratios and M_n of the products in the EDA polymerization with **10**/$NaBPh_4$. While the increase of M_n with the increase in the feed ratio was observed to a certain extent, the increase in M_n was not proportional to the feed ratio, and the polymer yield decreased gradually. The highest M_n with the [EDA]/[Pd] feed ratio of 400 was 28 100 achieved with SEC and 37 100 achieved with SEC-MALS analysis.

The relatively poor controlled behavior of the polymerization with respect to M_n suggested that some undesirable side reactions occurred during the polymerization of EDA with the system, which was confirmed by MALDI-TOF-MS analysis as shown in Fig. 5 for a polyBDA′ sample (BDA: benzyl diazoacetate, M_n = 5200, $Đ$ = 2.24) obtained by BDA polymerization with the **10**/$NaBPh_4$ system using a low [BDA]/[Pd] feed ratio of 10 (for BDA polymerization results, see below). The MALDI-TOF-MS spectrum clearly indicates that the chain end structures of the predominant polymer chain are those with Ph and H at α- and ω-chain ends, respectively, which should be generated by the expected initiation with the Pd–Ph species and termination of the propagating chain end with an acidic



Scheme 5 The proposed mechanism for C1 polymerization of diazoacetates by the (diamine)Pd(0)(dichlone)/$NaBPh_4$ system.

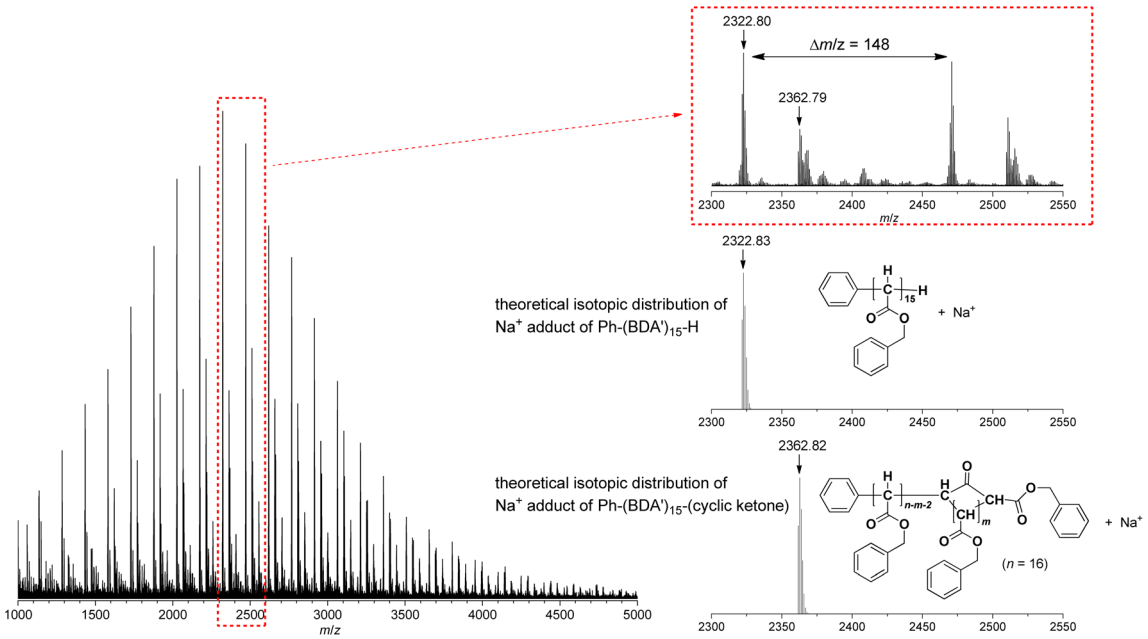


Fig. 5 MALDI-TOF-MS spectrum of polyBDA′ obtained with the **10**/$NaBPh_4$ initiating system (M_n = 5200, $Đ$ = 2.24).

quencher. Meanwhile, we identified the second largest signal of a polymer structure with chain ends bearing Ph and cyclic ketone frameworks derived by backbiting, at α- and ω-chain ends, respectively. In addition, there appear some minor signals, whose origin cannot be identified. Thus, the MALDI-TOF-MS results agree with the relatively poor controllability of the polymerization because of some undesirable side reactions occurring during the polymerization.

Polymerization of diazoacetates other than EDA, namely benzyl (BDA), cyclohexyl (*c*-HDA), and 1-naphthylmethyl ($NpCH_2DA$) diazoacetates was conducted with the (diamine)Pd(0)(dichlone)/$NaBPh_4$ system, and the results were presented in Table 3. As shown in runs 3, 6, and 7, Pd(0) complexes **8**–**10** in conjunction with $NaBPh_4$ initiated BDA polymerization in a similar efficiency to that with **1**/$NaBPh_4$ with respect to M_n and yields of the products. A higher [BDA]/[Pd] ratio of 200 with **10**/$NaBPh_4$ as an initiator yielded polyBDA′ with higher M_n ($M_{n,SEC}$ = 35 000, $M_{n,MALS}$ = 66 500) despite a lower yield (32%, run 8), indicating that the side reactions, as mentioned above, with the MALDI-TOF-MS analysis prevented the high yield synthesis of a polymer with high M_n. In addition, as ^1H and ^{13}C NMR spectra shown in Fig. 6 indicates, the syndiotacticity of the resulting polyBDA′ is apparently higher than that obtained with **1**/$NaBPh_4$, even though it is lower than that obtained with **2**/$NaBPh_4$. Thus, the (diamine)Pd(0)(dichlone)/$NaBPh_4$ system is again considered to possess the advantages of both **2**/$NaBPh_4$ (syndioselectivity) and **1**/$NaBPh_4$ (high polymer yield).

Although **8**/$NaBPh_4$ was not effective for *c*-HDA polymerization probably because the secondary cyclohexyl ester is too bulky for this initiator; $NpCH_2DA$ with a larger primary ester than BDA can be successfully polymerized with **8**/$NaBPh_4$ (run 5) and **10**/$NaBPh_4$ (run 9) to give polymers in moderate yields.

Table 3 Polymerization of benzyl, cyclohexyl, 1-naphthylmethyl diazoacetates with (diamine)Pd(0)(dihalonaphthoquinone)/$NaBPh_4$ systems[a]

Run	Pd(0)	Monomer	[monomer]/[Pd]	Yield[b] (%)	M_n[c]	$Đ$[c]	Syndiotacticity[d]
1[e]	**2**	BDA	100	26	11 900	2.31	High
2[e]	**1**	BDA	100	73	20 900	1.57	(Atactic)
3	**8**	BDA	100	72	11 600	2.49	Moderate
4	**8**	*c*-HDA	100	2.2	5600	1.67	n.d.
5	**8**	$NpCH_2DA$	100	64	8900	2.40	n.d.
6	**9**	BDA	100	59	17 600	2.31	Moderate
7	**10**	BDA	100	74	15 100	2.45	Moderate
8	**10**	BDA	200	32	35 000 (66 500)	1.65 (1.34)	Moderate
9	**10**	$NpCH_2DA$	100	59	12 500	2.30	n.d.

[a] At 50 °C in THF (3 mL) for 13 h, Pd = 0.01 mmol, [$NaBPh_4$]/[Pd] = 1.1. [b] After purification with preparative SEC to remove dimers and oligomers. [c] Determined by SEC using PMMA standards (values in parentheses were determined by SEC-MALS). [d] Estimated by NMR measurements (Fig. 6).[39] [e] Quoted from our previous work.[33]

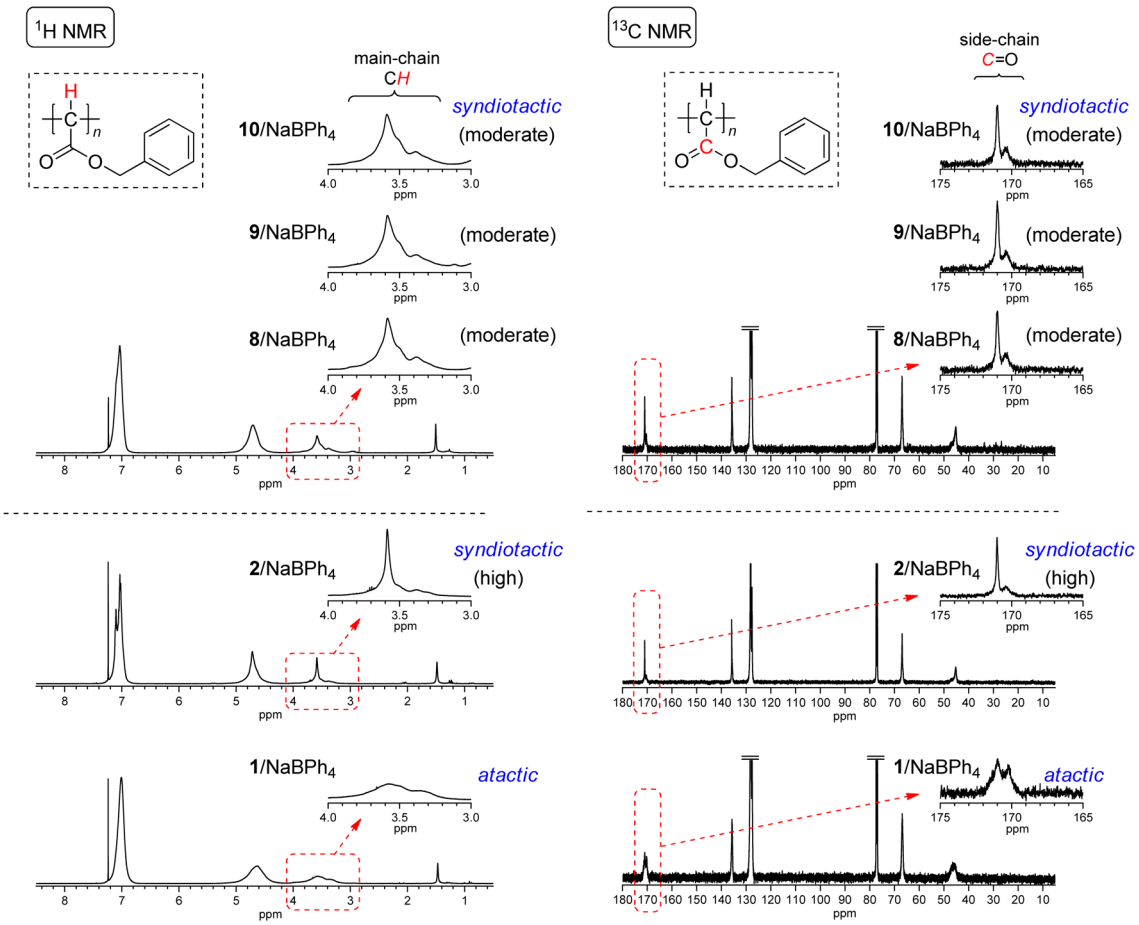


Fig. 6 ^{1}H and ^{13}C NMR spectra of polyBDA's obtained with **2**/$NaBPh_4$, **1**/$NaBPh_4$, **8**/$NaBPh_4$ (run 3 in Table 3), **9**/$NaBPh_4$ (run 6 in Table 3), and **10**/$NaBPh_4$ (run 7 in Table 3), recorded in $CDCl_3$ at 50 °C (^{1}H NMR) or room temperature (^{13}C NMR).

Conclusions

We have demonstrated that diphosphine- and diamine-ligated Pd complexes with a quinone-derived additional ligand can be used in conjunction with $NaBPh_4$ as initiating systems for the C1 polymerization of diazoacetates. As for the (diphosphine)Pd(II)Cl(Cl-quinonyl)-based system, it is significant to find that the steric environment around the Pd center strongly affects the polymerization behavior of diazoacetate; initiating systems with dppf- and xantphos-ligated Pd complexes can yield highly syndiotactic polymers despite low polymer yields. With much improved polymer yields, the (diphosphine)Pd-based system will develop into a highly active initiating system realizing stereospecific polymerization of diazoacetates. On the other hand, (diamine)Pd(0)(dichlone)/$NaBPh_4$ systems have been revealed to be effective initiators for diazoacetate polymerization, yielding moderately syndiotactic polymers in moderate yields; the results support our proposition that the η^3-type anionic naphthoquinonyl ligand is essential for achieving high activity. In addition, the moderate syndioselectivity of the resulting polymers suggests that the modification of the diamine structure will further improve the stereoselectivity of the polymerization. We believe that these fundamental investigations and findings hereby reported in this paper are quite important for the development of highly effective initiators for this relatively new and general polymerization.

Conflicts of interest

There are no conflicts of interest to declare.

Acknowledgements

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References

1 E. Ihara, *Adv. Polym. Sci.*, 2010, **231**, 191–231.
2 E. Jellema, A. L. Jongerius, J. N. H. Reek and B. de Bruin, *Chem. Soc. Rev.*, 2010, **39**, 1706–1723.
3 N. M. G. Franssen, A. J. C. Walters, J. N. H. Reek and B. de Bruin, *Catal. Sci. Technol.*, 2011, **1**, 153–165.
4 C. R. Cahoon and C. W. Bielawski, *Coord. Chem. Rev.*, 2018, **374**, 261–278.
5 E. Ihara and H. Shimomoto, *Polymer*, 2019, **174**, 234–258.
6 H. Shimomoto, *Polym. J.*, 2020, **52**, 269–277.
7 F. Li, L. Xiao, B. Li, X. Hu and L. Liu, *Coord. Chem. Rev.*, 2022, **473**, 214806.
8 E. Ihara, R. Okada, T. Sogai, T. Asano, M. Kida, K. Inoue, T. Itoh, H. Shimomoto, Y. Ishibashi and T. Asahi, *J. Polym. Sci., Part A: Polym. Chem.*, 2013, **51**, 1020–1023.
9 M. Tokita, K. Shikinaka, T. Hoshino, K. Fujii, J. Mikami, N. Koshimizu, K. Sakajiri, S. Kang, J. Watanabe and K. Shigehara, *Polymer*, 2013, **54**, 995–998.
10 N. M. G. Franssen, B. Ensing, M. Hegde, T. J. Dingemans, B. Norder, S. J. Picken, G. O. R. Alberda, E. R. van Ekenstein, H. van Eck, J. A. A. W. Elemans, M. Vis, J. N. H. Reek and B. de Bruin, *Chem. – Eur. J.*, 2013, **19**, 11577–11589.
11 H. Shimomoto, E. Itoh, T. Itoh, E. Ihara, N. Hoshikawa and N. Hasegawa, *Macromolecules*, 2014, **47**, 4169–4177.
12 H. Shimomoto, H. Asano, T. Itoh and E. Ihara, *Polym. Chem.*, 2015, **6**, 4709–4714.
13 H. Shimomoto, K. Shimizu, C. Takeda, M. Kikuchi, T. Kudo, H. Mukai, T. Itoh, E. Ihara, N. Hoshikawa, A. Koiwai and N. Hasegawa, *Polym. Chem.*, 2015, **6**, 8124–8131.
14 N. Koshimizu, Y. Aizawa, K. Sakajiri, K. Shikinaka, K. Shigehara, S. Kang and M. Tokita, *Macromolecules*, 2015, **48**, 3653–3661.
15 H. Shimomoto, A. Oda, M. Kanayama, T. Sako, T. Itoh, E. Ihara, N. Hoshikawa, A. Koiwai and N. Hasegawa, *J. Polym. Sci., Part A: Polym. Chem.*, 2016, **54**, 1742–1751.
16 H. Shimomoto, T. Uegaito, S. Yabuki, S. Teratani, T. Itoh, E. Ihara, N. Hoshikawa, A. Koiwai and N. Hasegawa, *Solid State Ionics*, 2016, **292**, 1–7.
17 H. Shimomoto, M. Kikuchi, J. Aoyama, D. Sakayoshi, T. Itoh and E. Ihara, *Macromolecules*, 2016, **49**, 8459–8465.
18 H. Shimomoto, T. Kudo, S. Tsunematsu, T. Itoh and E. Ihara, *Macromolecules*, 2018, **51**, 328–335.
19 K. Shikinaka, K. Suzuki, H. Masunaga, E. Ihara and K. Shigehara, *Polym. Int.*, 2018, **67**, 495–499.
20 T. Takaya, T. Oda, Y. Shibazaki, Y. Hayashi, H. Shimomoto, E. Ihara, Y. Ishibashi, T. Asahi and K. Iwata, *Macromolecules*, 2018, **51**, 5430–5439.
21 D. S. Tromp, M. Lankelma, H. de Valk, E. de Josselin de Jong and B. de Bruin, *Macromolecules*, 2018, **51**, 7248–7256.
22 X. Li, Y. Sun, J. Chen, Z. Wu, P. Cheng, Q. Li, J. Fang and D. Chen, *Polym. Chem.*, 2019, **10**, 1575–1584.
23 X. Li, B. Mu, C. Chen, J. Chen, J. Liu, F. Liu and D. Chen, *Macromolecules*, 2019, **52**, 6913–6926.
24 H. Shimomoto, T. Yamada, T. Itoh and E. Ihara, *Polym. J.*, 2020, **52**, 51–56.
25 H. Shimomoto, R. Hohsaki, D. Hiramatsu, T. Itoh and E. Ihara, *Macromolecules*, 2020, **53**, 6369–6379.
26 D. G. H. Hetterscheid, C. Hendriksen, W. I. Dzik, J. M. M. Smits, E. R. H. van Eck, A. E. Rowan, V. Busico, M. Vacatello, V. V. A. Castelli, A. Segre, E. Jellema, T. G. Bloemberg and B. de Bruin, *J. Am. Chem. Soc.*, 2006, **128**, 9746–9752.
27 E. Jellema, P. H. M. Budzelaar, J. N. H. Reek and B. de Bruin, *J. Am. Chem. Soc.*, 2007, **129**, 11631–11641.
28 E. Ihara, M. Akazawa, T. Itoh, M. Fujii, K. Yamashita, K. Inoue, T. Itoh and H. Shimomoto, *Macromolecules*, 2012, **45**, 6869–6877.
29 H. Shimomoto, M. Nakajima, A. Watanabe, H. Murakami, T. Itoh and E. Ihara, *Polym. Chem.*, 2020, **11**, 1774–1784.
30 J.-H. Chu, X.-H. Xu, S.-M. Kang, N. Liu and Z.-Q. Wu, *J. Am. Chem. Soc.*, 2018, **140**, 17773–17781.
31 A. V. Zhukhovitskiy, I. J. Kobylianskii, A. A. Thomas, A. M. Evans, C. P. Delaney, N. C. Flanders, S. E. Denmark, W. R. Dichtel and F. D. Toste, *J. Am. Chem. Soc.*, 2019, **141**, 6473–6478.
32 X.-Q. Yao, Y.-S. Wang and J. Wang, *Macromolecules*, 2021, **54**, 10914–10922.
33 H. Shimomoto, S. Ichihara, H. Hayashi, T. Itoh and E. Ihara, *Macromolecules*, 2019, **52**, 6976–6987.
34 Y. Yamamoto, *Adv. Synth. Catal.*, 2010, **352**, 478–492.
35 A. J. C. Walters, O. Troeppner, I. Ivanović-Burmazović, C. Tejel, M. Pilar del Río, J. N. H. Reek and B. de Bruin, *Angew. Chem., Int. Ed.*, 2012, **51**, 5157–5161.
36 A. J. C. Walters, J. N. H. Reek and B. de Bruin, *ACS Catal.*, 2014, **4**, 1376–1389.
37 When 1,2-bis(diphenylphosphino)ethane (dppe) was employed as a bidentate phosphine, well-defined Pd complexes could not be isolated in our attempts.
38 I. Pochorovski, C. Boudon, J.-P. Gisselbrecht, M.-O. Ebert, W. B. Schweizer and F. Diederich, *Angew. Chem., Int. Ed.*, 2012, **51**, 262–266.
39 Quantitative evaluation of the tacticity for PACMs is not possible at present, because the assignment of NMR signals to the stereoregularity has not yet been established. However, on the basis of de Bruin's reports (ref. 26, 27 and 40) on syndiospecific polymerization, signals at 3.2 ppm in ^{1}H NMR and 171 ppm in ^{13}C NMR have been assigned to the syndiotactic structure of polyEDA′; likewise, signals at 3.6 ppm (^{1}H) and 171 ppm (^{13}C) have been assigned to syndiotactic polyBDA′. Accordingly, the degree of syndiotacticity in this study is qualitatively evaluated to be either very high, high, moderate, or low, depending on the appearance of methine-H signals in ^{1}H NMR and carbonyl-C signals in ^{13}C NMR. With DSC analyses of samples of moderately syndiotactic polyEDA′ and polyBDA′ (Fig. S13

in the ESI†), T_gs of these polymers were observed in the temperature range between T_gs of highly syndiotactic and atactic polymers, demonstrating that the qualitative assessment of the syndiotacticity employed in this study is indeed relevant.

40 E. Jellema, A. L. Jongerius, G. A. van Ekenstein, S. D. Mookhoek, T. J. Dingemans, E. M. Reingruber, A. Chojnacka, P. J. Schoenmakers, R. Sprenkels, E. R. H. van Eck, J. N. H. Reek and B. de Bruin, *Macromolecules*, 2010, **43**, 8892–8903.

41 As shown in Scheme 5, although the Pd-carbene species generated during the propagation has formally 20 electrons in the Pd center, we think that weak electron-donation from the diamine ligand or temporary detachment of one of the nitrogen atoms from the Pd center would enable the transient species to exist.