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A salicylaldiminate/Pd(trifluoroacetate)$_2$ [SalAld/Pd(tfa)$_2$] initiating system for C1 polymerization of diazoacetate: generation of an active initiator from ordinary reagents with facile procedures†

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Salicylaldiminate (SalAld)-ligated Pd complexes were generated by the reaction of SalAld with Pd(tfa)$_2$ in THF, and their initiating ability for C1 polymerization of diazoacetate was investigated. When a mixture of a series of SalAlds and Pd(tfa)$_2$ ([SalAld]/[Pd(tfa)$_2$] = 2 : 1–4 : 1) was employed for the polymerization of ethyl diazoacetate (EDA), polyEDA′ with a high number-average molar mass ($M_{n,SEC}$ = 20000–35 000) was obtained in moderate yield; the polymer yield became highest (50%) when the polymerization was conducted with a [SalAld]/[Pd(tfa)$_2$] ratio of 4 : 1 at 50 °C for 13 h. NMR analyses indicated that polyEDA′ had a syndiotactic-rich main chain stereo-structure. These results demonstrate that the SalAld/Pd(tfa)$_2$ system is a new effective initiating system for the C1 polymerization of diazoacetate, which can be generated from a combination of ordinary reagents with facile procedures.

Introduction

"C1 polymerization" has been gaining recognition as an effective method for preparing C–C main chain polymers, where, in contrast to conventional vinyl polymerization (C2 polymerization), the C–C main chain of the polymers is constructed from "one carbon units" derived from monomers such as sulfoxonium methylide and diazoacetate.[1–9] While the polymerization of sulfoxonium methylide affords polymethylene with a well-defined molar mass and chain-end structures, the polymerization of diazoacetate can yield polymers whose each main chain carbon atom has an alkoxycarbonyl group (ester); thus, the ester substituents of the resulting polymer should be densely packed around the C–C main chain. The structural characteristics of the polymers obtained by diazoacetate polymerization have been demonstrated to bring about enhanced properties derived from the densely packed substituents, compared to their vinyl polymer counterpart [poly(alkyl acrylate)] with the same ester substituent.[10–29]

For the C1 polymerization of diazoacetate, transition metal initiators based on Rh and Pd have been demonstrated to be effective for preparing high molar mass polymers, even in a highly stereoselective manner in some cases.[30–42] For example, Rh(diene)-based initiators can afford high number-average molar mass (M_n) polymers (M_n up to 200 000) with high syndioselectivity,[30–32] whereas some Pd-based initiating systems can afford atactic high M_n polymers (M_n of several tens of thousands) with a variety of ester substituents. In particular, we have succeeded in developing a series of initiating systems consisting of a combination of well-defined Pd complexes and $NaBPh_4$: (NHC)Pd(nq)/$NaBPh_4$ (NHC: N-heterocyclic carbene, nq: 1,4-naphthoquinone),[33] π-allylPdCl/$NaBPh_4$,[34,39] and (nq)$_2$Pd/$NaBPh_4$.[37] Although these Pd-based systems are indeed effective initiators for diazoacetate polymerization, in most cases, the active initiator should be generated at −78 °C under a strictly controlled N_2 atmosphere with careful handling of the Pd precursor and $NaBPh_4$. Therefore, initiating systems that can be generated from more ordinary reagents with more facile procedures are desired.

In that context, apart from the Pd-precursor complexes used for the reported polymerization, in this study we turned our attention to salicylaldiminate (SalAld)-ligated Pd complexes which can be generated *in situ*, because some SalAld-ligated transition metal complexes have been demonstrated to be extremely effective as highly active initiators for olefin polymerization.[43–48] As described in this paper, while investigating the initiating behavior of a mixture of SalAld and some Pd precursors for diazoacetate polymerization, we have found

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that a certain mixture of the combination can indeed exhibit activity for the polymerization, yielding high M_n polymers in moderate yield. Although the identity of the actual active species of this system is not clear at present, it is advantageous that the active species can be generated by just mixing SalAld formed using NaH as a base and commercially available Pd(trifluoroacetate)$_2$ [Pd(tfa)$_2$] as a Pd precursor.

While we and other research groups have established that the presence of an η^3-type anionic ligand on a Pd center is essential for the Pd-based system to have high initiating ability (Chart 1),[34,36–40] the results in this study demonstrate that SalAld-ligated Pd complexes can be another type of platform for initiator generation. The results reported here show the promising potential of SalAld-ligated Pd complexes as highly active initiators for diazoacetate polymerization. The details of this SalAld/Pd(tfa)$_2$ initiating system will be described in this paper.

Results and discussion

Effect of the SalAld structure, Pd precursor, and reaction conditions on the polymerization behavior of ethyl diazoacetate (EDA)

We have found that in some literature reports, a series of well-defined (SalAld)$_2$Pd(II), (SalAld)Pd(II)Cl, and (salen)Pd(II) type complexes were prepared by the reactions of Pd(OAc)$_2$ or PdCl$_2$ with neutral salicylaldimine in alcohol or acetonitrile as a solvent.[49–53] For employing this type of reaction for the *in situ* generation of SalAld-ligated Pd complexes, we attempted to react SalAld generated from salicylaldimine by using NaH as a base with Pd(OAc)$_2$ or Pd(trifluoroacetate)$_2$ [Pd(tfa)$_2$] as a Pd precursor in THF as a solvent, because THF is the most suitable solvent for the polymerization so far and the presence of alcohol will be disadvantageous for the polymerization with nucleophilic propagating species to proceed (Scheme 1).

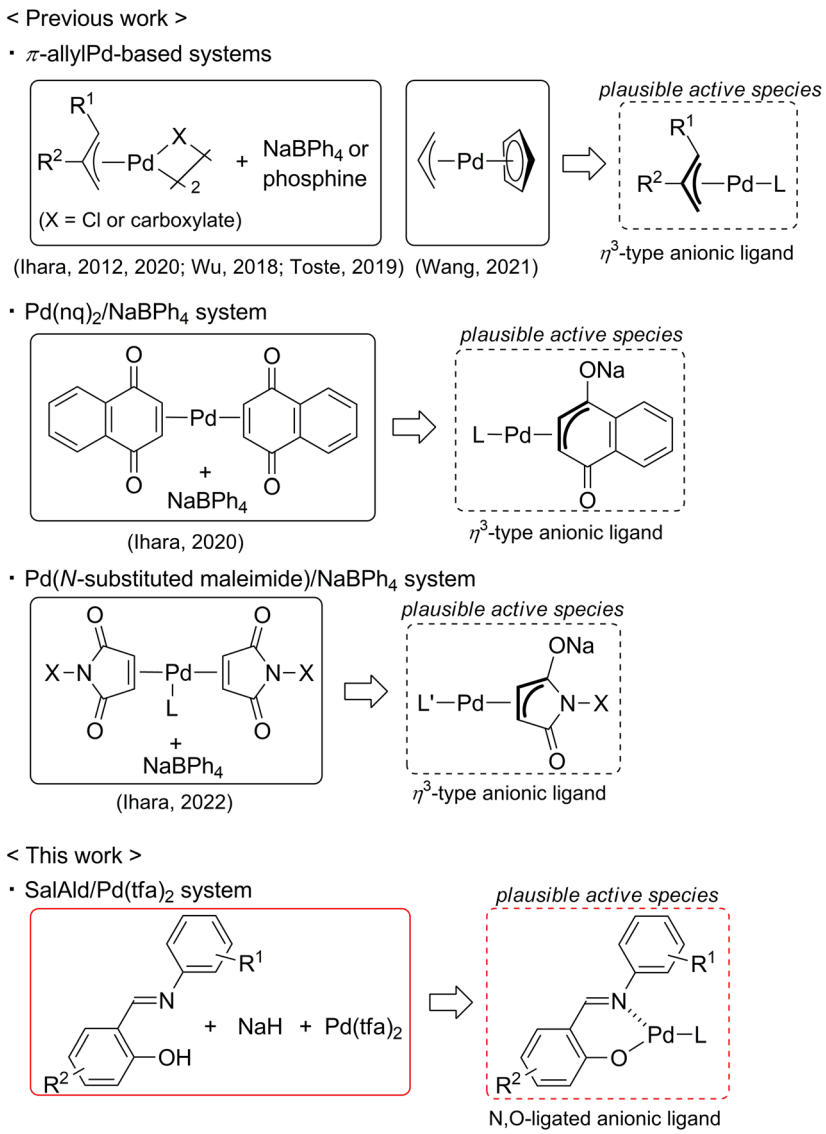
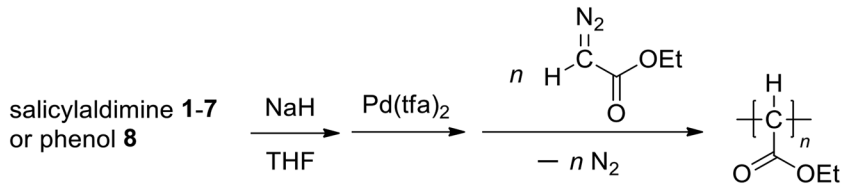


Chart 1 Pd-based initiating systems for the C1 polymerization of diazoacetate.



Scheme 1 Polymerization of EDA with SalAld/$Pd(tfa)_2$ initiating systems.

The results using a variety of salicylaldimine, **1**–**7** and a related phenol **8** (Chart 2) are summarized in Table 1, where the neutral ligand precursor was first reacted with NaH in THF for 1 h at room temperature, and then the resulting SalAld was reacted with a Pd precursor for 3 h at room temperature, followed by the addition of 100 equiv. of EDA (CH_2Cl_2 solution, *ca.* 1–2 M) and polymerization for 13 h at room temperature. In this table, the [SalAld]/[Pd] ratio was fixed to 2 : 1, because no polymerization occurred with the ratio of 1 : 1.

With the use of salicylaldimine **1** without any substituent on the two phenyl rings, the attempt for polymerization using $Pd(OAc)_2$ as a Pd precursor afforded a trace of a polymeric product (run 1). On the other hand, the use of $Pd(tfa)_2$ in place of $Pd(OAc)_2$ under the same conditions yielded a high M_n polymer (SEC-estimated $M_{n,SEC}$ = 35 000) in a low yield of 15% (run 2). The results suggest that SalAld ligation on $Pd(tfa)_2$ is more efficient than on $Pd(OAc)_2$. Under the same conditions as that in run 2, a series of salicylaldimines **2**–**5** with different substitution modes on the two phenyl rings on the salicylaldimine framework were employed (runs 3–7); as a result, SalAld derived from **4** with 2,6-diisopropyl substitution on the aniline-derived ring afforded polyEDA' in the highest yield of 30% (run 5), while the $M_{n,SEC}$s of polyEDA's obtained with these SalAlds were in the range of 24 000–36 000, which is relatively high for polyEDA' obtained with Pd-initiated polymerization (as described later, M_n determined with MALS ($M_{n,MALS}$) is 1.8 times higher than the $M_{n,SEC}$; thus, the number-average-degree of polymerization of polyEDA's typically obtained here exceeds 500). When the monomer concentration was increased from the standard value of 0.5 M to 1.3 M, the polymer yield decreased to 16% (run 6). The use of other solvents than THF, such as 1,4-dioxane, Et_2O, and DMF failed to give polymers.

When 2,6-difluoroaniline derived salicylaldimines **6** and **7** were used, the polymer yield significantly decreased (runs 8 and 9), suggesting that electron donation from the aniline derived moiety is important for the high initiating ability. The use of an anion derived from sterically demanding phenol **8** in place of salicylaldimine with $Pd(tfa)_2$ yielded polyEDA' in a very low yield (run 10), indicating that the chelating coordination of O and N to Pd is essential for the initiating ability. We also confirmed that the reaction of EDA either with Pd $(tfa)_2$ alone (run 11), SalAld **4** alone (run 12), or NaH/$Pd(tfa)_2$ without salicylaldimine (run 13) did not afford a polymeric product. In addition, the reaction of EDA with a mixture of salicylaldimine **4** with $Pd(tfa)_2$ in the absence of NaH (run 14) did not afford a polymeric product, indicating that SalAld is required for the generation of the active initiator. Furthermore, we newly prepared and isolated $(SalAld)_2Pd$

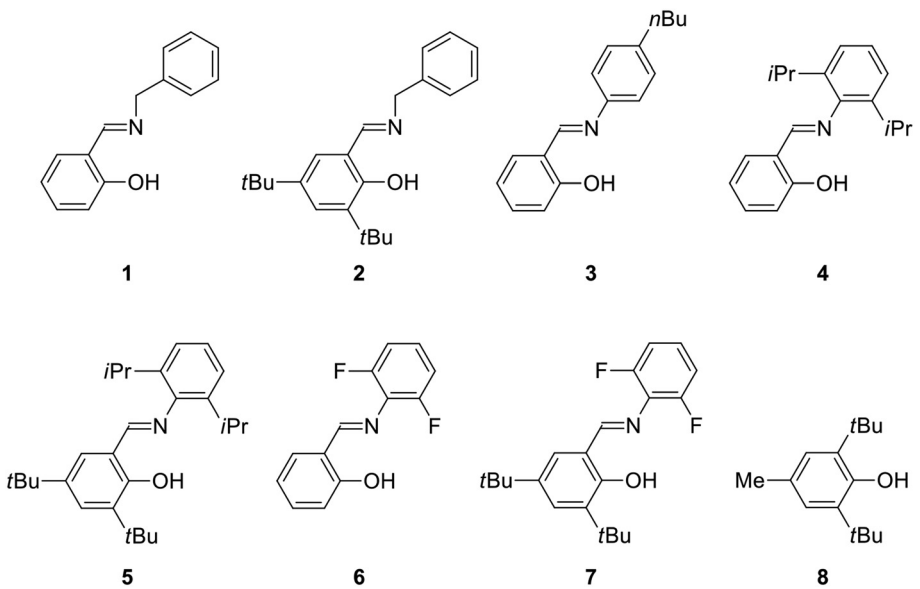


Chart 2 Salicylaldimines **1**–**7** and phenol **8** used in this study.

Table 1 Polymerization of EDA with SalAld/Pd initiating systems[a]

			Complexation		Polymerization				
Run	Ligand precursor/base	Pd	Temp.	Time	Temp.	Time	Yield[b] (%)	$M_{n,SEC}$[c]	$Đ$[c]
1	**1**/NaH	$Pd(OAc)_2$	RT	3 h	RT	13 h	Trace		
2	**1**/NaH	$Pd(tfa)_2$	RT	3 h	RT	13 h	15	35 000	1.98
3	**2**/NaH	$Pd(tfa)_2$	RT	3 h	RT	13 h	14	36 000	1.73
4	**3**/NaH	$Pd(tfa)_2$	RT	3 h	RT	13 h	10	24 000	1.61
5	**4**/NaH	$Pd(tfa)_2$	RT	3 h	RT	13 h	30	34 000	1.89
6	**4**/NaH	$Pd(tfa)_2$	RT	3 h	RT	13 h	16	33 000	1.88
7	**5**/NaH	$Pd(tfa)_2$	RT	3 h	RT	13 h	27	35 000	2.16
8	**6**/NaH	$Pd(tfa)_2$	RT	3 h	RT	13 h	2.7	20 000	1.72
9	**7**/NaH	$Pd(tfa)_2$	RT	3 h	RT	13 h	9.5	32 000	2.12
10	**8**/NaH	$Pd(tfa)_2$	RT	3 h	RT	13 h	2.3	36 000	1.47
11	None/none	$Pd(tfa)_2$	RT	3 h	RT	13 h	No polymerization		
12	**4**/NaH	None	RT	3 h	RT	13 h	No polymerization		
13	None/NaH	$Pd(tfa)_2$	RT	3 h	RT	13 h	No polymerization		
14	**4**/none	$Pd(tfa)_2$	RT	3 h	RT	13 h	No polymerization		
15	$(SalAld)_2Pd$ (SalAld of **4**)		—	—	RT	13 h	No polymerization		
16	**4**/NaH	$Pd(tfa)_2$	RT	9 h	RT	13 h	35	31 000	1.75
17	**4**/NaH	$Pd(tfa)_2$	−10 °C	3 h	RT	13 h	6.6	22 000	2.72
18	**4**/NaH	$Pd(tfa)_2$	50 °C	3 h	RT	13 h	15	18 000	2.64

[a] Conditions: solvent = THF, [salicylaldimine]/[NaH]/[$Pd(tfa)_2$] = 2.0 : 2.0 : 1.0, $[EDA]_0$ = 0.5 M (1.3 M for run 6), $[EDA]_0$/[Pd] = 100; EDA was used as a CH_2Cl_2 solution with a concentration of 0.8–2.1 M. [b] After purification with preparative SEC to remove oligomers. [c] Determined by SEC using PMMA standards.

(SalAld: **4**) by the reaction of salicylaldimine with $Pd(OAc)_2$ in MeOH, following the reported procedures for the preparation of analogous complexes (see the ESI†),[52,53] and examined the reactivity of this complex with EDA. As a result, no polymerization occurred as shown in run 15, indicating that the outcome of the reaction of the Na salt of salicylaldimine with $Pd(tfa)_2$ in THF [the SalAld/$Pd(tfa)_2$ system] is totally different from that of the reaction of salicylaldimine with $Pd(OAc)_2$ in MeOH; in the former case, the presence of THF as a solvent and Na-tfa could play a crucial role in the generation of the active species for the EDA polymerization.

The above-described results suggest that even though the active species producing high M_n polymers was actually generated, the relative amount of the active species with respect to the $Pd(tfa)_2$ employed was not enough to give polyEDA' in a higher yield. Therefore, in order to improve the efficiency of initiator generation, the effect of the reaction conditions of SalAld with $Pd(tfa)_2$ on the polymerization behavior was examined. When the reaction period was extended from 3 h to 9 h, the polymer yield slightly increased to 35% (run 16). The reactions at −10 °C and 50 °C were found to result in lower polymer yields of 6.6% (run 17) and 15% (run 18), respectively. These results indicate that the ligand substitution on Pd occurred at room temperature and the reaction for 3 h is almost enough for the generation of the initiator.

Effect of [SalAld]/[Pd] and [EDA]/[Pd] ratios and polymerization temperature and period on the polymerization behavior

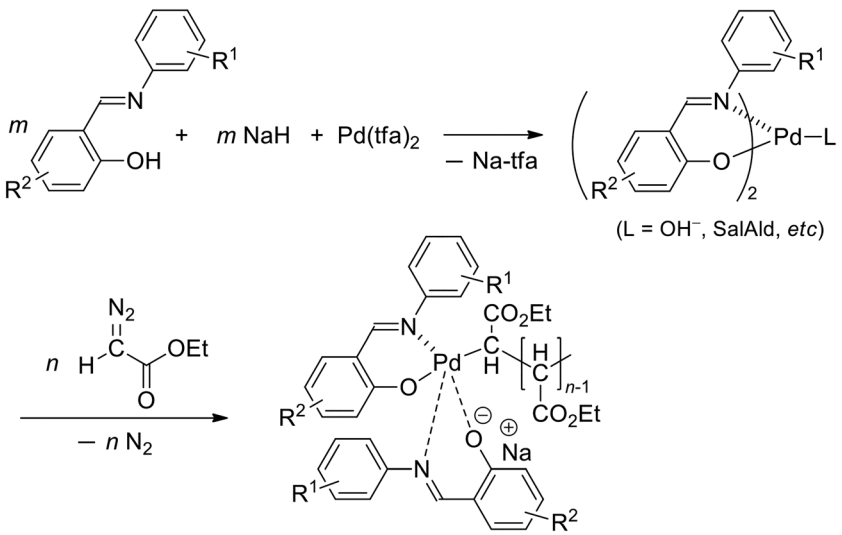
On the basis of the above-described investigation, the reaction of SalAld derived from **4** with $Pd(tfa)_2$ is most suitable for the initiator generation for obtaining high M_n polyEDA's in moderate yield (run 5 in Table 1). Next, we tried to examine the effect of equivalents of SalAld used for the initiator generation and the polymerization temperature on the polymerization behavior. Table 2 summarizes the results of polymerization at room temperature and 50 °C with a series of SalAld equivalents [2–4 equiv. to $Pd(tfa)_2$]. Interestingly, with the increase in the [SalAld]/[Pd] ratio, although the polymer yield upon polymerization at room temperature remained nearly constant at about 30% (runs 1–3), the yield increased for the polymerization at 50 °C (runs 4–6) up to 50% with the use of 4 equiv. of SalAld (run 6). On the basis of these results, we think that at least two equiv. of SalAld were required for the generation of the active initiating and propagating species with two SalAlds associated with the Pd center as illustrated in Scheme 2. As for the initiation, after the reaction of 2 equiv. of SalAld with $Pd(tfa)_2$, a certain nucleophilic species namely OH^- or SalAld would be associated with the Pd center and initiate the polymerization; the originally existing tfa with low nucleophilicity would not be the initiating species, although it is possible that the Na-tfa generated by the ligand substitution would play a crucial role in the generation and stabilization of the active initiating species (we failed to identify the initiating chain end with MALDI-TOF-MS analyses so far). The presence of the additional SalAld in the system would also contribute to the stabilization of the active species in a certain manner. For the polyEDA' sample obtained in run 6 with $M_{n,SEC}$ = 25 000, we measured M_n using a MALS detector, resulting in the value of $M_{n,MALS}$ = 45 000 (number-average degree of polymerization = 520).

Then, using the optimized conditions of [SalAld]/[$Pd(tfa)_2$] = 4 : 1 at 50 °C, the polymerization of EDA was conducted with a

Table 2 Polymerization of EDA with SalAld/Pd initiating systems under various conditions[a]

			Polymerization						
Run	[SalAld]/[Pd]	[EDA]/[Pd]	Temp.	Period	Yield[b] (%)	$M_{n,SEC}$[c]	$M_{n,MALS}$[d]	$Đ$[c]	IE[e] (%)
1	2	100	RT	13 h	30	34 000		1.89	7.6
2	3	100	RT	13 h	30	36 000		1.69	7.2
3	4	100	RT	13 h	25	29 000		1.93	7.4
4	2	100	50 °C	13 h	22	25 000		1.91	7.6
5	3	100	50 °C	13 h	39	31 000		2.01	11
6	4	100	50 °C	13 h	50	25 000	45 000	1.85	17
7	4	50	50 °C	13 h	44	22 000		2.02	8.6
8[f]	4	100	50 °C	13 h	50	25 000	45 000	1.85	17
9	4	200	50 °C	13 h	25	27 000		2.45	15
10	4	300	50 °C	13 h	27	28 000		2.50	26
11	4	100	50 °C	1 h	18	30 000		1.47	5.2
12	4	100	50 °C	3 h	32	26 000		1.92	11
13[f]	4	100	50 °C	13 h	50	25 000	45 000	1.85	17

[a] Conditions: solvent = THF, salicylaldimine = **4**, $[EDA]_0$ = 0.5 M; EDA was used as a CH_2Cl_2 solution with a concentration of 1.3–3.2 M. [b] After purification with preparative SEC to remove oligomers. [c] Determined by SEC using PMMA standards. [d] Determined by SEC-MALS. [e] Calculated based on the polymer yield and $M_{n,SEC}$. [f] The same data as those in run 6.



Scheme 2 Proposed mechanism for EDA polymerization with the SalAld/$Pd(tfa)_2$ system.

series of feed ratios of [EDA]/[Pd] from 50 to 300 as listed in runs 7–10. Regardless of the feed ratio, the $M_{n,SEC}$ of the product remains in a certain range of 20 000–30 000, and the apparent initiation efficiency (IE) of $Pd(tfa)_2$ based on the polymer yield and $M_{n,SEC}$ has an increasing trend with the feed ratio. In addition, when the polymerization was intentionally terminated after 1 and 3 h, it was found that regardless of the reaction period, $M_{n,SEC}$ reached the range of 20 000–30 000, and a gradual increase in the polymer yield and IE was observed. These results suggest that the initiating species were gradually and continuously generated for a period of several hours, and once the initiation started, the propagation rapidly ensued until completion as typically observed in the conventional radical polymerization of vinyl monomers.

Tacticity of polyEDA' obtained with the SalAld/$Pd(tfa)_2$ system

Fig. 1 shows the ^1H and ^{13}C NMR spectra of the polyEDA' sample obtained in run 6 in Table 2, and for comparison, the spectra of atactic and syndiotactic-rich polyEDA' obtained with $(nq)_2Pd/NaBPh_4$ and (cod)PdCl(Cl-naphthoquinonyl) (cod: 1,5-cyclooctadiene) systems,[37,42] respectively, are shown. According to the publications by de Bruin and coworkers, a highly syndiotactic polyEDA' exhibits its main chain ^1H and carbonyl ^{13}C NMR signals at 3.2 ppm and 171 ppm, respectively.[30–32] The comparison in these spectra indicates that the polymer obtained with the SalAld/$Pd(tfa)_2$ system has a syndiotactic-rich structure probably because the highly sterically demanding structure of the propagating Pd complex

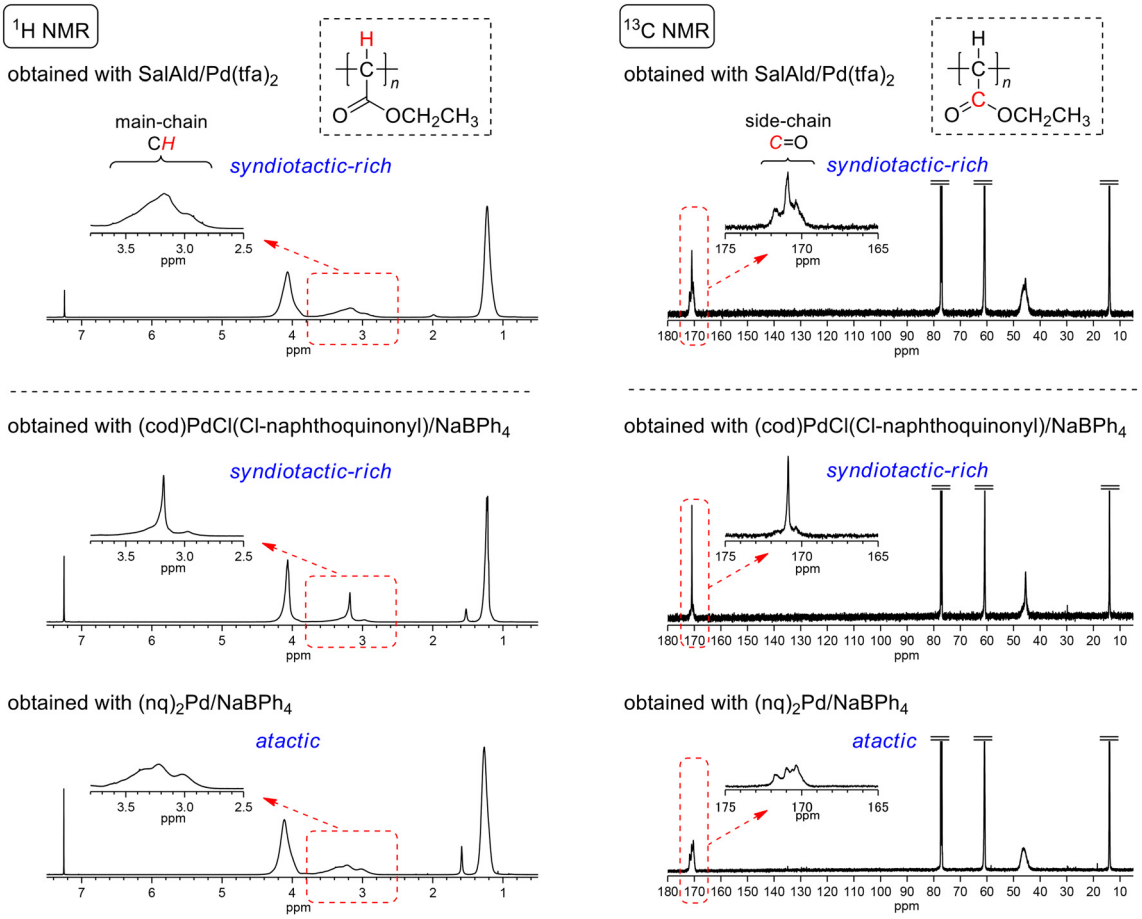


Fig. 1 ^{1}H and ^{13}C NMR spectra of the polyEDA's obtained with SalAld/Pd(tfa)$_2$, (cod)PdCl(Cl-naphthoquinonyl)/NaBPh$_4$, and (nq)$_2$Pd/NaBPh$_4$ systems.

would regulate the stereochemical course of the propagation to a certain degree, affecting the preference of Pd-carbene prochiral faces [Pd=CH(CO_2Et)] reacting with the growing chain end carbon atom.[31] PolyEDA' obtained by using other SalAld with different modes of substitution on the ligand framework exhibited similar tacticity based on their ^{1}H NMR spectra (see the ESI†).

Reactivity of other diazoacetates than EDA under the optimized conditions

Finally, polymerization of other diazoacetates, such as methyl diazoacetate (MDA), benzyl diazoacetate (BDA), and cyclohexyl diazoacetate (*c*HDA), was conducted under the optimized conditions (Table 3). While MDA was polymerized to give a high M_n polymer in a lower yield compared to that of EDA (run 1), BDA (run 2) and *c*HDA (run 3) afforded polymers in trace yields. These results suggest that because of the coordination of two SalAlds and a propagating chain, the propagating Pd center is sterically crowded and can only accommodate and polymerize sterically non-demanding EDA and MDA.

Table 3 Polymerization of various diazoacetates with SalAld/Pd initiating systems[a]

Run	Monomer	Yield[b], %	$M_{n,SEC}$[c]	$Đ$[c]
1	MDA	27	23 000	1.56
2	BDA	2.7	9300	2.1
3	*c*HDA	4.6	21 000	4.6

[a] Conditions: solvent = THF, salicylaldimine = **4**, [monomer]$_0$ = 0.5 M, [monomer]$_0$/[Pd] = 100; MDA was used as a CH_2Cl_2 solution with a concentration of 1.86 M. [b] After purification with preparative SEC to remove oligomers. [c] Determined by SEC using PMMA standards.

Conclusions

We have demonstrated that SalAld/Pd(tfa)$_2$ is an effective initiating system for diazoacetate polymerization, yielding high M_n polymers in moderate yield (*e.g.*, a polymer with $M_{n,MALS}$ = 45 000 in 50% yield). Compared to other Pd-based initiating systems we have developed so far, the important advantage of this system is that it does not need the addition of NaBPh$_4$ and the active species can be generated from relatively ordin-

ary reagents [salicylaldimine, NaH, and $Pd(tfa)_2$] using facile procedures, although polymerizable monomers are limited to EDA and MDA so far and the polymer yield should be improved significantly. In addition, another important finding in this study is that SalAld can be an effective ligand for the Pd complex to be active for the C1 polymerization of diazoacetates, suggesting the possibility for the development of *in situ*-generated or well-defined highly active initiating systems using this type of ligand. Further investigation along this line is now underway in our laboratory.

Conflicts of interest

The authors declare no competing financial interest.

Acknowledgements

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