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(*N*-Heterocyclic Carbene)Pd/Borate Initiating Systems for Polymerization of Ethyl Diazoacetate

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Introduction. Constructing a C−C main chain of polymers from one carbon unit [poly(substituted methylene) synthesis] could become a general strategy for polymer synthesis, particularly being valuable for making C−C main chain polymers, which cannot be obtained by vinyl polymerization.[1,2] For the strategy, diazocarbonyl compounds can be a promising monomer candidate if their diazo-bearing carbons can be connected linearly after the release of N_2. Actually, recent studies have demonstrated that alkyl diazoacetates can be converted to poly(alkoxycarbonylmethylene)s, which have an ester group on all main chain carbons by the initiation with B-,[3] Cu-,[4] Pd-,[5] and Rh-based[6,7] initiating systems. In particular, the Rh(diene)-initiated polymerization[6,7] was highly effective to afford high-molecular-weight polymers (M_n > 200 000) in a stereospecific (syndiotactic) manner, whereas other metal-based systems gave rather low-molecular-weight products with M_n of several thousand at the most. After we found that $PdCl_2$ was effective for the polymerization of not only alkyl diazoacetates[5] but also some diazoketones[8,9] and diazoacetamides,[10] we have been trying to find an effective initiating system for preparing higher-molecular-weight polymers from diazocarbonyl compounds. As a result, we have found that Pd(0) complexes with *N*-heterocyclic carbene (NHC) ligand [(NHC)Pd] in conjunction with tetraarylborate [(NHC)Pd/borate systems] are capable of transforming ethyldiazoacetate (EDA) into poly(ethoxycarbonylmethylene)s with M_n > 20 000.

Results and Discussion. After examining various Pd-based complexes for the initiation of EDA, we found that a mixture of the commercially available zerovalent (NHC)Pd complexes[11−13] **2** {$[IMesPd(NQ)]_2$ (NQ = naphthoquinone)} and **3** {$[IPrPd(NQ)]_2$} with sodium tetraarylborate **4** ($NaBPh_4$) or **5** ($NaBAr^F{}_4$) was effective to give high-molecular-weight polymers (Scheme 1). The polymerization was initiated by the addition of a dichloromethane or 1,1,2-trichloroethane solution of EDA (1.66 to 3.33 M) to a mixture of the (NHC)Pd and the borate ([**4** or **5**]/[Pd] = 1.1 to 1.4; [Pd] = 2[**2** or **3**]) in THF. The crude product obtained after the removal of volatiles from the reaction mixture was purified by using preparative recycling GPC to give a colorless solid. Control experiments reveal that the presence of all three components (NHC ligand, Pd, and borate) is essential for the preparation of high-molecular-weight poly(ethoxycarbonylmethylene)s (poly**1′**s). As shown in run 1 in Table 1, when the polymerization was conducted at room temperature with a feed ratio of [**1**]/[Pd] = 20, poly**1′** with M_n = 7800 was obtained in high yield (82.3%). Although M_n of the poly**1′** became higher with the increase in the feed ratio to [**1**]/[Pd] = 200, M_n did not linearly correspond with the feed ratio, and yields gradually decreased with higher feed ratios, suggesting the instability of the propagating species and the occurrence of termination (runs 2−4). However, compared with other Pd-based initiating systems we examined including $PdCl_2$ [M_n of poly**1′** < 1000 (GPC)], the (NHC)Pd/borate system is apparently very effective to afford high-molecular-weight poly**1′**s. The reactivity of the initiating system was maintained at 50 °C (run 5), whereas it was drastically diminished at 0 °C (run 6). Another (NHC)Pd/borate system **3**/**4** with diisopropylphenyl-substituted NHC exhibited similar initiating behavior (runs 7−10). The use of CF_3-substituted borate **5** instead of **4** did not improve the initiating performance (runs 11−14).

Scheme 1. Polymerization of EDA with (NHC)Pd/Borate Systems

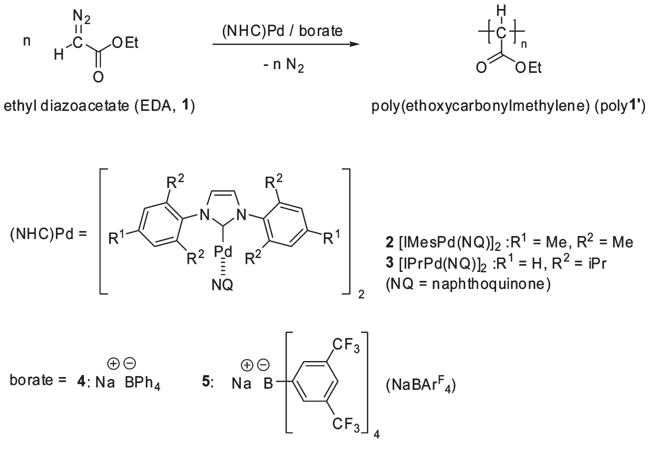

Table 1. Polymerization of Ethyl Diazoacetate (1) with (NHC)Pd/Borate Systems[a]

run	(NHC)Pd	borate	[**1**]/[Pd][b]	temp	yield (%)	M_n[c]	M_w/M_n[c]
1	**2**	**4**	20	r.t.	82.3	7800	1.19
2	**2**	**4**	50	r.t.	52.5	12 200	1.20
3	**2**	**4**	100	r.t.	49.3	15 100	1.36
4	**2**	**4**	200	r.t.	34.9	20 700	1.50
5	**2**	**4**	100	50 °C	52.3	16 500	1.40
6	**2**	**4**	100	0 °C	7.3	4100	1.20
7	**3**	**4**	20	r.t.	74.5	9900	1.32
8	**3**	**4**	100	r.t.	34.0	24 000	1.53
9	**3**	**4**	100	50 °C	57.3	19 800	1.70
10	**3**	**4**	100	0 °C	9.1	400	1.15
11	**2**	**5**	20	r.t.	57.5	5600	1.26
12	**2**	**5**	100	r.t.	56.6	17 600	1.67
13	**3**	**5**	20	r.t.	59.6	11 000	1.45
14	**3**	**5**	100	r.t.	40.8	20 400	1.62

[a] In THF (2 mL) for 13 h; EDA **1** = 0.30 to 1.76 mmol (1.66 to 3.33 M solution in CH_2Cl_2 or Cl_2HCCH_2Cl). [b] [Pd] = $2[(NHC)Pd(NQ)]_2$. [c] M_n and M_w/M_n were obtained by GPC calibration using standard PMMAs and dibutyl sebacate in THF solution.

Figure 1 shows ^1H and ^{13}C (carbonyl region, insets) NMR spectra (in $CDCl_3$) of poly**1′** obtained by **2**/**5** (run 12 in Table 1) (a) and **3**/**5** (run 14) (b) initiating systems. Interesting to note is that the appearance of CH signals of the poly**1′**s slightly differs between the two ^1H NMR spectra. The

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CH signals split into three peaks centered at 3.4, 3.2, and 3.0 ppm, which can probably be ascribed to triads for the main chain structure. By comparing a ^{1}H NMR spectrum of our poly**1**′ measured in tetrachloroethane-d_2 with that of a syndiotactic poly**1**′ in the solvent reported by de Bruin et al.,[6] we can estimate that the signal at 3.2 ppm in Figure 1 should be derived from the *rr* triad. It is apparent that the *rr* signal is more intense in Figure 1b than in Figure 1a. In accord with the appearance in the ^{1}H NMR spectra, one of the carbonyl-C signals in the inset of Figure 1b is clearly more enhanced than that in Figure 1a, and the chemical shift of the enhanced signal (107.8 ppm) indeed corresponds to that of the syndiotactic poly**1**′ reported in the literature.[7] The difference of the signal intensity of these spectra suggests that the tacticity of the poly**1**′ could be influenced by the structure of the substituents on the NHC ligand, thus indicating the possibility of stereo regulation of the polymerization in these (NHC)Pd/borate systems by changing the structure of NHC ligands.

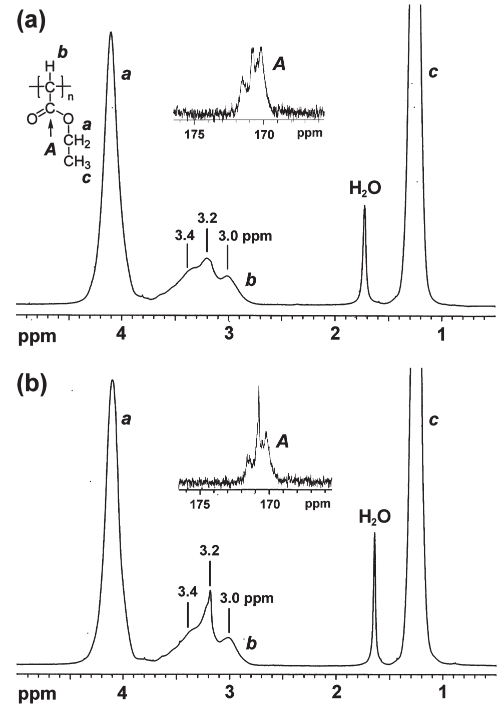


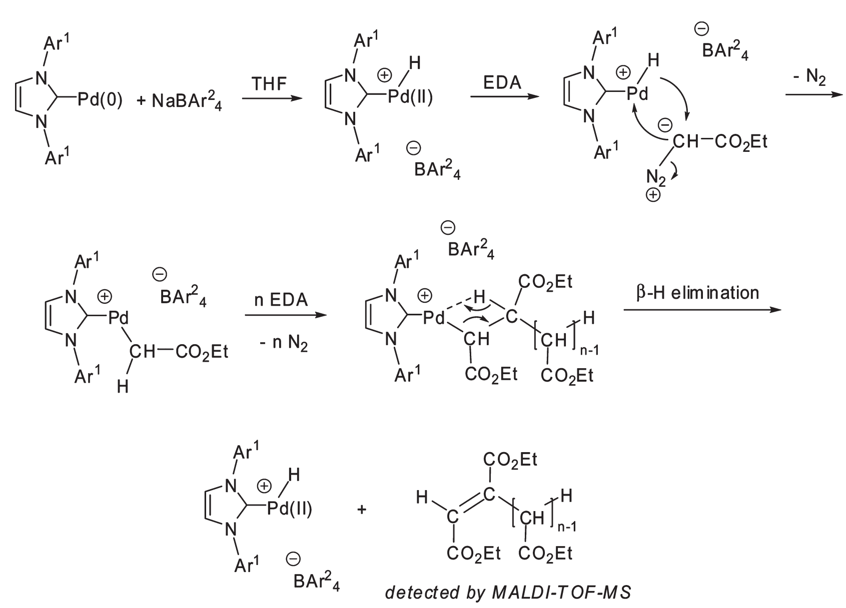
Figure 1. ^{1}H and ^{13}C (carbonyl region, insets) NMR spectra of poly1′ obtained by (a) 2/5 (run 12 in Table 1) and (b) 3/5 (run 14) in $CDCl_3$ at 50 °C (^{1}H) or 25 °C (^{13}C).

In MALDI-TOF-MS analysis of poly**1**′s obtained by the (NHC)Pd/borate system (Figures 5−8 in the Supporting Information), we observed three main sets of the signals whose intervals corresponded to the MW of the repeating unit derived from EDA (86.1). In addition, the analysis in reflector mode with higher resolution revealed that the signal set with the lowest relative *m*/*z* value could be ascribed to Na adducts of poly**1**′ with a structure having H and C=C at chain ends, H[CH(C=O)OEt]$_n$CH[(C=O)OEt]CH-(C=O)OEt (e.g., *m*/*z* of a parent peak in the isotopic distribution = 625.3 for $n = 5$). Accordingly, for the polymers exhibiting the identified signal set, we can propose a mechanism for their generation, as described in Scheme 2: (1) generation of a cationic $[(NHC)Pd(II)H]^+$ as an initiating species by the reaction of (NHC)Pd(0) with the borate in THF,[14] (2) insertion of EDA into Pd−H (initiation) and Pd−C (propagation) accompanied by release of N_2, and (3) termination via β−H elimination affording the initiating Pd(II)−H species and a polymer with H and C=C at chain ends.

As for the other two sets of signals observed in the MS spectra whose *m*/*z* values are 12 and 26 higher than that of the above-described signal set (Supporting Information), we cannot identify their structures at present. Furthermore, the complexity of the MS charts apparently indicates the nonuniformity of the (NHC)Pd/borate system with respect to the initiation and termination, thus, leading to the aforementioned low controllability of the polymerization with respect to the molecular weight of products. Our further investigation using better-defined initiating systems based on the (NHC)−transition metal complexes will clarify the mechanistic issue,[14] along with the possibility of tacticity control.

As for the CH contents in the elemental analysis results of the sample obtained in run 1 in Table 1, the observed values (C: 55.30, H: 7.04) agreed well with the expected ones for the repeating unit of [CH(C=O)OEt] (C: 55.81, H: 7.02, calcd for $C_4H_6O_2$) without considering the presence of any polymer chain end group. The result also shows that azo group (−N=N−) incorporation into the polymer main chain

Scheme 2. Probable Polymerization Mechanism Based on the Observation in MALDI-TOF-MS Analysis



often observed in the Pd-mediated polymerization of diazoketones[8,9] does not occur at all here.

In conclusion, we have demonstrated that (NHC)Pd/borate initiating systems can afford high-molecular-weight polymers (M_n > 20 000) from EDA. Along with the Rh(diene)-initiated stereospecific polymerization,[6,7] our findings will extend the generality of the polymerization of diazocarbonyl compounds as a practical method for polymer synthesis. Further investigation into the unique initiating systems is underway in our laboratory.

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Supporting Information Available: Representative procedure for polymerization of EDA with (NHC)Pd/borate systems, full ^{13}C NMR spectra for poly**1**′s in runs 12 and 14 in Table 1, and MALDI-TOF-MS spectra for poly**1**′s. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) Shea, K. J. *Chem.—Eur. J.* **2000**, *6*, 1113–1119.

(2) Noels, A. F. *Angew. Chem., Int. Ed.* **2007**, *46*, 1208–1210.

(3) Bai, J.; Burke, L. D.; Shea, K. J. *J. Am. Chem. Soc.* **2007**, *129*, 4981–4991.

(4) Liu, L.; Song, Y.; Li, H. *Polym. Int.* **2002**, *51*, 1047–1049.

(5) Ihara, E.; Haida, N.; Iio, M.; Inoue, K. *Macromolecules* **2003**, *36*, 36–41.

(6) Hetterscheid, D. G. H.; Hendriksen, C.; Dzik, W. I.; Smits, J. M. M.; van Eck, E. R. H.; Rowan, A. E.; Busico, V.; Vacatello, M.; Van Axel Castelli, V.; Segre, A.; Jellema, E.; Bloemberg, T. G.; de Bruin, B. *J. Am. Chem. Soc.* **2006**, *128*, 9746–9752.

(7) Jellema, E.; Budzelaar, P. H. M.; Reek, J. N. H.; de Bruin, B. *J. Am. Chem. Soc.* **2007**, *129*, 11631–11641.

(8) Ihara, E.; Fujioka, M.; Haida, N.; Itoh, T.; Inoue, K. *Macromolecules* **2005**, *38*, 2101–2108.

(9) Ihara, E.; Hiraren, T.; Itoh, T.; Inoue, K. *J. Polym. Sci., Part A: Polym. Chem.* **2008**, *46*, 1638–1648.

(10) Ihara, E.; Hiraren, T.; Itoh, T.; Inoue, K. *Polym. J.* **2008**, *40*, 1094–1098.

(11) Jackstell, R.; Andreu, M. G.; Frisch, A.; Selvakumar, K.; Zapf, A.; Klein, H.; Spannenberg, A.; Röttger, D.; Briel, O.; Karch, R.; Beller, M. *Angew. Chem., Int. Ed.* **2002**, *41*, 986–989.

(12) Selvakumar, K.; Zapf, A.; Spannenberg, A.; Beller, M. *Chem.—Eur. J.* **2002**, *8*, 3901–3906.

(13) Frisch, A.; Zapf, A.; Briel, O.; Kayser, B.; Shaikh, N.; Beller, M. *J. Mol. Catal. A: Chem.* **2004**, *214*, 231–239.

(14) One plausible mechanism for the formation of the cationic Pd(II) active species is that (NHC)Pd(0) reacted with THF with or without the assistance of borate to afford a series of neutral divalent complexes, (NHC)Pd(II)XY (X, Y = H, etc.), which should be converted to $[(NHC)Pd(II)X]^+[BAr_4]^-$ by the reaction (abstraction of Y from Pd center) with borate.