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Polymerization of Various Alkyl Diazoacetates Initiated with (*N*-Heterocyclic Carbene)Pd/Borate Systems

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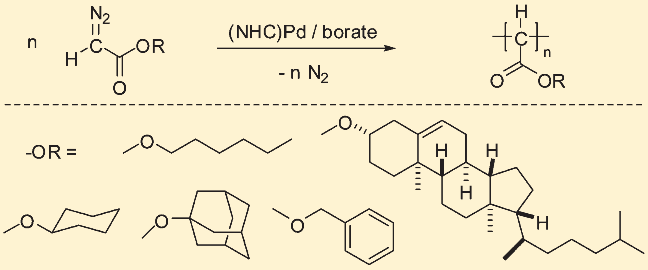
Supporting Information

ABSTRACT: (NHC)Pd/borate initiating systems (NHC = *N*-heterocyclic carbene) were applied for polymerization of alkyl diazoacetates with a variety of ester groups. The monomers with *n*-hexyl, cyclohexyl, benzyl, and cholesteryl group as an ester group were transformed into the corresponding poly(alkoxycarbonylmethylene)s with M_n > 10 000. On the other hand, the polymerization of 1-adamantyl diazoacetate afforded low-M_n polymers (M_n < 4000), probably because of steric reasons. Copolymerization of a few comonomer combinations also proceeded successfully to give copolymers with M_n > 20 000.



INTRODUCTION

C−C main chain polymers are obviously one of the most important classes of synthetic polymers. While they have most commonly been prepared by vinyl polymerization, an alternative method has been recognized for the synthesis, where the C−C main chain is constructed from one carbon unit.[1−3] In particular, recent progress in this field is represented by the polymerization of dimethylsulfoxonium methylide[3] and diazocarbonyl compounds,[1,2] and the latter polymerization is unique because it can afford polymers bearing a polar substituent such as alkoxycarbonyl groups at every main chain carbon atom. Whereas high molecular weight highly syndiotactic polymers (M_n > 200 000) have been prepared by de Bruin and co-workers with Rh-mediated stereospecific polymerization of ethyl and benzyl diazoacetates (EDA **1** and BnDA **2**, respectively),[4−7] our (NHC)Pd/borate (NHC = *N*-heterocyclic carbene) initiating system is able to afford atactic poly(ethoxycarbonylmethylene)s with M_n > 20 000 from EDA efficiently.[8] Although the polymerization has not been applied to a wide range of diazoacetates with respect to variation of the ester groups so far, polymers obtained from such monomers could be promising as new polymeric materials, for which peculiar properties can be expected based on the dense packing of the ester group around the C−C main chain. Herein, we will describe the polymerization behavior of various alkyl diazoacetates initiated with the (NHC)Pd/borate systems.

RESULTS AND DISCUSSION

Monomer Synthesis. Benzyl diazoacetate (BnDA, **2**), *n*-hexyl diazoacetate (*n*-HDA, **3**), cyclohexyl diazoacetate (*c*-HDA, **4**), and cholesteryl diazoacetate (ChDA, **5**) were prepared by a very convenient synthetic procedure for a variety of diazoacetates reported by Fukuyama and co-workers,[9] which utilizes a reaction of bromoacetate with *N*,*N*′-ditosylhydrazine. However, the method was not effective for the synthesis of 1-adamantyl diazoacetate (AdDA, **6**) in our attempt, which was thus prepared by using a conventional method with the use of glyoxylic acid chloride *p*-toluenesulfonylhydrazone.[10]

Homopolymerization of Alkyl Diazoacetates. As an alkyl diazoacetate with a longer linear alkyl chain than ethyl in EDA, *n*-hexyl diazoacetate (*n*-HDA, **3**) was subjected to the (NHC)Pd/borate-initiated polymerization in THF at room temperature (Scheme 1, Table 1). The (NHC)Pd/borate systems employed here consisted of a combination of $[\mathrm{IMesPd(NQ)}]_2$ or $[\mathrm{IPrPd(NQ)}]_2$ (NQ = naphthoquinone) and $NaBPh_4$ or $NaBAr^F{}_4$ [Ar^F = 3,5-$(CF_3)_2C_6H_3$], which were used in our previous study for EDA polymerization.[8] As shown in Table 1, the polymerizations with the (NHC)Pd/borate systems afforded poly(*n*-hexyloxycarbonylmethylene)s (poly**3**′s) with M_n = 25 000−37 000 in more than 50% yield when the [monomer]/[initiator] ratio was 100 (runs 1−4). The polymerization behavior was not much affected by the kind of (NHC)Pd complex or borate, as was observed for the polymerization of EDA.[8] M_n increased to 42 000 with the [monomer]/[initiator] feed ratio of 200 (run 5), and the initiator efficiencies for runs 4 and 5 are 42 and 47%, respectively, which are significantly higher than those for polymerization of EDA reported in our previous publication (ca. 30%) under similar conditions.[8] When the [monomer]/[initiator] feed ratio was further increased to 300, polymer yield diminished and M_n of

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Scheme 1. Polymerization of Various Alkyl Diazoacetates with (NHC)Pd/Borate Systems

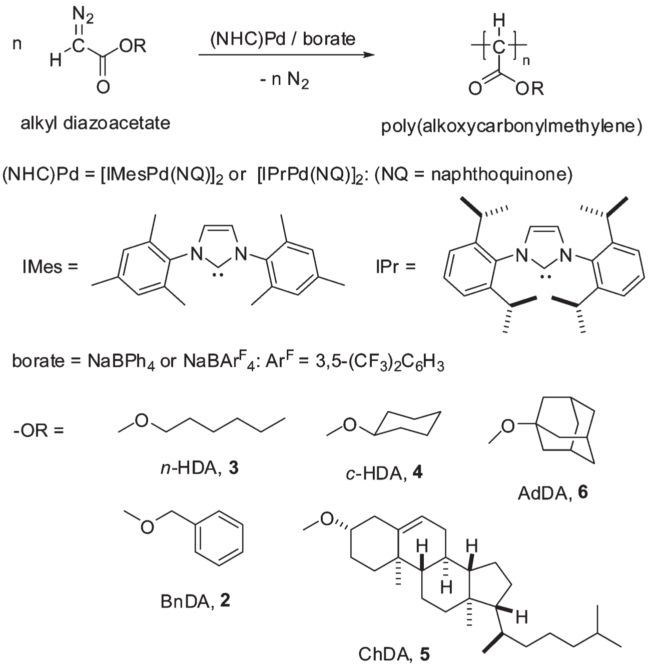


Table 1. Polymerization of Alkyl Diazoacetate (2−6) with (NHC)Pd/Borate Systems[a]

run	monomer (M)	(NHC) Pd	borate	[**1**]/[Pd][b]	yield (%)	M_n[c]	M_w/M_n[c]
1	*n*-HDA, **3**	IPrPd	$NaBPh_4$	100	54.4	35 600	1.63
2	*n*-HDA, **3**	IPrPd	$NaBAr^F_4$	100	52.7	37 000	1.94
3	*n*-HDA, **3**	IMesPd	$NaBPh_4$	100	68.3	26 000	1.57
4	*n*-HDA, **3**	IMesPd	$NaBAr^F_4$	100	75.1	25 200	1.39
5	*n*-HDA, **3**	IMesPd	$NaBAr^F_4$	200	69.5	42 000	1.39
6[d]	*n*-HDA, **3**	IMesPd	$NaBAr^F_4$	300	42.7	22 800	1.78
7	*c*-HDA, **4**	IPrPd	$NaBPh_4$	100	25.4	11 000	1.74
8	*c*-HDA, **4**	IPrPd	$NaBAr^F_4$	100	13.6	11 800	1.59
9	*c*-HDA, **4**	IMesPd	$NaBPh_4$	100	36.7	12 000	1.41
10	*c*-HDA, **4**	IMesPd	$NaBAr^F_4$	100	41.0	13 600	1.61
11[d]	*c*-HDA, **4**	IMesPd	$NaBAr^F_4$	100	52.6	8 200	1.70
12[d]	*c*-HDA, **4**	IMesPd	$NaBAr^F_4$	300	10.9	12 100	1.71
13	AdDA, **6**	IMesPd	$NaBPh_4$	100	13.2	3 600	1.59
14	AdDA, **6**	IMesPd	$NaBAr^F_4$	100	11.5	3 000	1.23
15	BnDA, **2**	IPrPd	$NaBAr^F_4$	100	27.3	23 000	1.95
16	BnDA, **2**	IMesPd	$NaBAr^F_4$	100	62.6	18 000	1.74
17	ChDA, **5**	IPrPd	$NaBAr^F_4$	100	6.9	15 600	1.32
18	ChDA, **5**	IMesPd	$NaBAr^F_4$	100	23.4	18 900	1.34

[a] In THF (2.5 mL) at room temperature for 14 h; monomer = 0.212−1.31 mmol; (NHC)Pd = $[IPrPd(NQ)]_2$ or $[IMesPd(NQ)]_2$ × 1/2 (NQ = naphthoquinone); $NaBAr^F_4$ = $NaB[3,5\text{-}(CF_3)_2C_6H_3]_4$. [b] [Pd] = $2[(NHC)Pd(NQ)]_2$; [borate] = 1.2[Pd]. [c] M_n and M_w/M_n were obtained by GPC calibration using standard PMMAs and dibutyl sebacate in THF solution. [d] Polymerization time = 38 h.

the resulting polymer did not increase even with a longer reaction period of 38 h (run 6). The products of the reactions in Table 1 always contained a significant amount of oligomers, probably including a small amount of an unreacted monomer, and the side products and remaining monomer were removed by using preparative recycling GPC. The initiator for the undesirable oligomer formation would be different from that produces the desirable high molecular weight polymers. We assume the following two reasons for the inability of the (NHC)Pd/borate systems to afford higher molecular weight poly(alkoxycarbonylmethylene)s (e.g., M_n > 100 000): (1) there exists inherent termination that occurs at some point during the propagation, and (2) the oligomer-forming undesirable initiator consumes a significant amount of monomer. Solubility of the polymers is not relevant to the former point because all the polymerizations in this study proceeded homogeneously throughout the reaction period and the obtained polymers were soluble in common organic solvents such as THF and $CHCl_3$. As for the mechanism for the polymerization giving high molecular weight polymers, we have proposed one that includes cationic divalent Pd complex with a NHC ligand possibly generated by the reaction of the zerovalent (NHC)Pd precursor complexes with THF in the presence of borate,[8] whereas de Bruin and co-workers recently presented some experimental data that suggested the involvement of *lower-valent* Pd species [Pd(0) or Pd(I)] as the actual initiator of the (NHC)Pd/borate system.[11] The mechanistic issue for the Pd-initiated polymerization should be clarified by further investigation.

When cyclohexyl diazoacetate (*c*-HDA, **4**) was used as a secondary ester monomer, M_n and yield of the resulting polymers significantly diminished as shown in runs 7−10 in Table 1. The longer reaction period and higher [monomer]/[initiator] feed ratio did not improve the M_n and yield of the poly**4′** (runs 11 and 12). The polymerization behavior indicates that the sterically bulkier cyclohexyl group in **4** prevents the efficient progress of the polymerization, resulting in the formation of lower M_n polymers in lower yields because of slower propagation and predominance of the oligomer formation. In addition, interesting to note is that the yields of polymers obtained with IMesPd bearing the smaller NHC ligand were higher than those with IPrPd. Such difference of the reactivity between IMesPd and IPrPd was not observed for the polymerization of *n*-HAD (runs 1−4), suggesting that the combination of steric bulkiness of the monomer and NHC ligand brought about the negative effect for the progress of the polymerization.

The steric effect was further enhanced for the polymerization of a monomer with a tertiary ester group, 1-adamantyl diazoacetate (AdDA, **6**), where only low-M_n polymers (M_n < 3600) were obtained in low yields by the IMesPd-based initiating system (Table 1, runs 13 and 14). The IPrPd-based system with the bulkier substituent on NHC-nitrogen was no longer able to give polymeric products, probably because the steric environment around the Pd center with the bulky NHC and AdDA is too crowded for the initiation and/or propagation to take place. Because the polymerization in runs 13 and 14 proceeded homogeneously and the obtained polymers were soluble in THF and $CHCl_3$, the solubility of the product is not the reason for the inefficient progress of AdDA polymerization. This is in contrast to the Rh-mediated polymerization of *tert*-butyl diazoacetate, where insoluble stereoregulated polymer precipitated during the polymerization and the poor solubility of the polymer is assumed to be a main reason for the inefficient progress of the polymerization.[7]

When benzyl diazoacetate (BnDA, **2**), whose ester group is primary but bulkier than that of *n*-HDA or EDA, was used as a

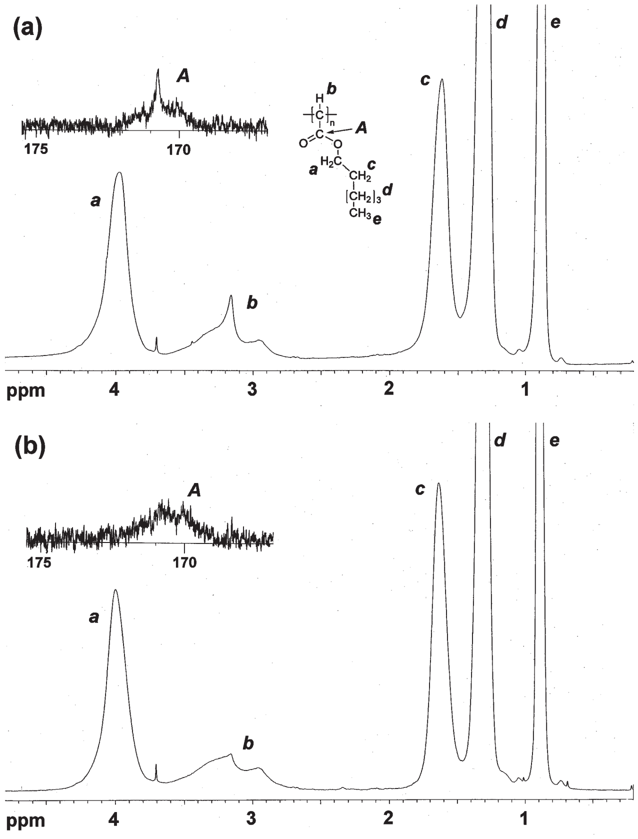


Figure 1. ^{1}H and ^{13}C (inset; carbonyl region) NMR spectra of poly**3**′ obtained with IPrPd/NaBAr$^F{}_4$ (M_n = 56 200, M_w/M_n = 2.85) (a) and IMesPd/NaBAr$^F{}_4$ (M_n = 25 500, M_w/M_n = 1.55) (b).

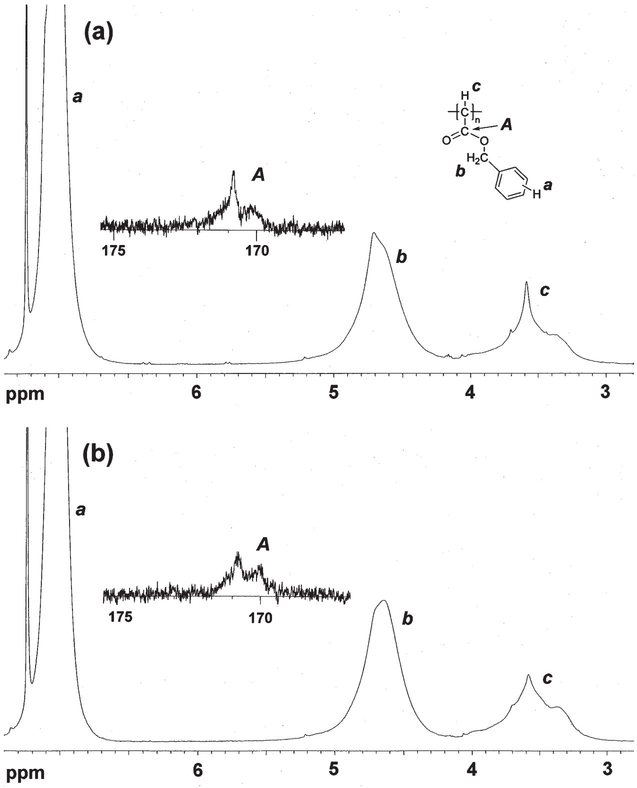


Figure 2. ^{1}H and ^{13}C (inset; carbonyl region) NMR spectra of poly**2**′ obtained with IPrPd/NaBAr$^F{}_4$ (M_n = 23 100, M_w/M_n = 1.91) (a) and IMesPd/NaBAr$^F{}_4$ (M_n = 22 900, M_w/M_n = 1.60) (b).

monomer, poly**2**′s with M_n = 18 000−23 000 were obtained as shown in runs 15 and 16 in Table 1. The steric effect of NHC ligand on the polymerization behavior described above is also observed for the BnDA polymerization, where polymer yield is much higher with IMesPd than with IPrPd.

In runs 17 and 18 in Table 1, a cholesteryl-substituted diazoacetate (ChDA, **5**) was used as a monomer. Although the ester group as a whole has a very large size, the polymerization proceeded to give polymers with M_n > 15 000 as expected for a monomer with a secondary ester group, although in rather low yields. Again, the IMesPd-based system with a smaller NHC ligand gave polymers with both higher M_n and yield, whereas IPrPd-based one afforded a polymer in a very low yield.

Tacticity of Poly(*n*-hexyloxycarbonylmethylene) (Poly2′) and Poly(benzyloxycarbonylmethylene) (Poly3′). In our previous publication,[8] we reported that the appearance of the main chain CH signals in ^{1}H NMR spectra of poly(ethoxycarbonylmethylene)s (poly**1**′s) differed depending on the structure of NHC ligand (IPr or IMes) employed for the polymerization. The CH peak was split into three signals centered at 3.0, 3.2, and 3.4 ppm possibly according to triad of the main chain, where the intensity of the signal at 3.2 ppm is more enhanced for the polymer obtained with IPrPd than that with IMesPd. Bacause the highly syndiotactic poly**1**′ prepared by Rh(diene)-initiators has been reported to exhibit the signal at 3.2 ppm exclusively,[4,5] we assumed that the structure of NHC ligand affected the tacticity of the resulting polymers, with IPr enhancing the syndiotactic selectivity. The analysis was also supported by ^{13}C NMR,[8] where the signal enhancement in the spectrum of IPrPd-obtained poly**1**′ was observed for the peak at 171 ppm, which was assigned to a carbonyl carbon of highly syndiotactic poly**1**′.[4,5] Figure 1 shows ^{1}H NMR spectra of poly(*n*-hexyloxycarbonylmethylene)s (poly**3**′s) obtained with IPrPd (M_n = 56 200, M_w/M_n = 2.85) (a) and IMesPd (M_n = 25 500, M_w/M_n = 1.55) (b). As observed in the ^{1}H NMR spectra of poly**1**′s, the appearance of CH signals differs between the two spectra, where the signal intensity at 3.2 ppm in Figure 1a is slightly enhanced compared to that in Figure 1b. On the assumption that the same assignment can be applied for the CH signals as poly**1**′, the main chain of poly**3**′ obtained with IPrPd should be slightly enriched with syndiotactic structure, compared to that with IMesPd. The assessment can be supported by comparison of the carbonyl carbon peaks in ^{13}C NMR spectra of poly**3**′s (insets in Figure 1), where the signal at 171 ppm assignable to syndiotactic sequence[4,5] is more enhanced in (a) compared to that in (b). Similar analyses were conducted for poly(benzyloxycarbonylmethylene)s (poly**2**′s) as shown in Figure 2, where a rather small enhancement of signal intensity can be recognized for a polymer prepared with IPrPd (M_n = 23 100, M_w/M_n = 1.91) at 3.6 ppm (^{1}H) and 171 ppm (^{13}C), compared to that with IMesPd (M_n = 22 900, M_w/M_n = 1.60) (b). Highly syndiotactic poly**2**′ has been reported to exhibit these signals exclusively in its ^{1}H and ^{13}C NMR spectra.[7]

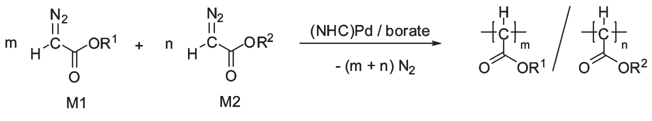
We cannot rule out the possibility that small amount of highly syndiotactic polymers was obtained along with the atactic polymers, although polymers obtained with IPrPd show monomodal charts in their GPC measurements, and in any of our polymerization, we have not realized the presence of a polymeric product with lower solubility, which might suggest the generation of

Table 2. Copolymerization of Alkyl Diazoacetate with IMesPd/borate Systems[a]

run	monomer M1	monomer M2	copolymer composition [M1′]/[M2′]	yield (%)	M_n[b]	M_w/M_n[b]
1	*n*-HDA, **3**	BnDA, **2**	1:1.25	61.9	26 000	1.53
2	EDA, **1**[c]	ChDA, **5**	1.44:1	62.7	23 000	1.53

[a] In THF (3.0 mL) at room temperature for 14 h; monomer (M1 + M2) = 0.658 mmol; ([M1] + [M2])/[Pd] = 100, [Pd] = 2[IMesPd(NQ)]$_2$; borate = NaB[3,5-(CF$_3$)$_2$C$_6$H$_3$]$_4$; [borate] = 1.2[Pd]. [b] M_n and M_w/M_n were obtained by GPC calibration using standard PMMAs and dibutyl sebacate in THF solution. [c] EDA **1** was used as a 4.36 M solution in CH$_2$Cl$_2$.

Scheme 2. Copolymerization of Various Alkyl Diazoacetates with (NHC)Pd/Borate System



(NHC)Pd = [IMesPd(NQ)]$_2$: borate = NaBAr$^F{}_4$: Ar^F = 3,5-(CF$_3$)$_2$C$_6$H$_3$: [M1]/[M2] = 1:1

M1 = *n*-HDA **3**, M2 = BzDA **2** (Table 2, run 1)
M1 = EDA **1**, M2 = ChDA **5** (Table 2, run 2)

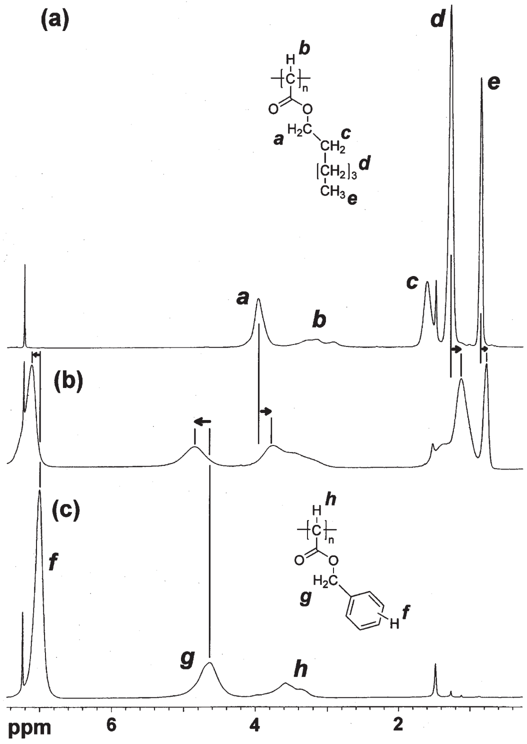


Figure 3. ^{1}H NMR spectra of poly**3**′ (run 3 in Table 1) (a), copolymer from **3** and **2** (run 1 in Table 2), and poly**2**′ obtained with IMesPd/NaBAr$^F{}_4$ (M_n = 17 800, M_w/M_n = 1.45).

highly stereo-regulated polymers. Although the variation of tacticity brought about by the NHC structure is in a small extent at present, we think that these phenomena would lead to the tacticity control by a proper choice of a ligand employed for the metal complex initiators for the polymerization in the near future.

Copolymerization of Alkyl Diazoacetates. Random copolymerizations with two monomer combinations of **3** + **2** and **1** + **5** were examined using the IMesPd-based system (Table 2, Scheme 2). As a result, both copolymerizations gave copolymers with M_n > 23 000 in good yields, whose GPC charts were monomodal. Formation of the random copolymer from **3** and **2** can be confirmed from its ^{1}H NMR spectrum in Figure 3, where some signals of the repeating units are different from those of each homopolymer as observed in Rh-mediated random copolymerization of EDA (**1**) and **2**;[7] downfield shift of peak tops for signals of aromatic-Hs (7.01−7.14 ppm) and benzylic-Hs (4.64−4.87 ppm) derived from **2** and upfield shift for signals of OCH$_2$ (4.00−3.78 ppm), (C*H*$_2$)$_3$CH$_3$ (1.31−1.16 ppm), and CH$_3$ (0.90−0.81 ppm) from **3** were clearly observed. These peak shifts could be ascribed to the ring current effect of the phenyl ring in the repeating unit from **2**. Accordingly, without an aromatic ring in the repeating units, such shift of the signals is not observed in the spectrum of copolymers from **1** and **5**, where same signals as those of each homopolymer appear.

Compositions of the two repeating units calculated from the signal intensity are listed in Table 2, where the two comonomers were reacted in a 1:1 molar ratio for both runs. For the copolymerization of **3** and **2** in run 1, the composition of [**3**′]/[**2**′] = 1:1.25 indicates that the reactivities for the monomers with primary ester groups were comparable, with **2** being slightly more reactive. The composition of the polymer in run 2 ([**1**′]/[**5**′] = 1.44:1) shows that **1** with a primary and smaller ester group is much more reactive than **5** with a secondary and bulkier ester group, as expected.

Differential scanning calorimetric (DSC) measurements were carried out for some homo- and copolymers obtained by these (co)polymerizations. Whereas glass transition temperature (T_g) for poly**2**′ obtained with IMesPd (M_n = 22 900, M_w/M_n = 1.60) was observed at 14 °C, T_g was not observed for a poly**3**′ obtained with IMesPd (M_n = 25 500, M_w/M_n = 1.55) with a heating scan from −100 °C. The comparison of T_gs of the atactic poly**2**′ and a syndiotactic poly**2**′ obtained with Rh-complex (52 °C; M_n = 154 000, M_w/M_n = 1.60)[7] clearly shows an effect of tacticity on the thermal behavior. A copolymer from **3** and **2** (M_n = 18 400, M_w/M_n = 1.46, composition of [**3**′]/[**2**′] = 1:1.17) exhibited only one T_g at −10 °C, indicating that it was a random copolymer. Poly**5**′ (M_n = 9900, M_w/M_n = 1.20) and a copolymer from EDA (**1**) and **5** (M_n = 18 700, M_w/M_n = 1.44, composition of [**1**′]/[**5**′] = 1.36:1) did not show T_g with a heating scan up to 150 °C, at which point decomposition of the polymers starts. Because an atactic poly**1**′ (M_n = 19 300, M_w/M_n = 1.37) shows T_g at 6 °C, which was lower than that of an syndiotactic poly**1**′ (22 °C; M_n = 42 000, M_w/M_n = 3.6),[7] the absence of T_g for the copolymer from **1** and **5** supports the progress of random copolymerization of **1** and **5**.

Despite our expectation that the ChDA-containing homopolymer and copolymer with EDA may exhibit unique optical properties due to the presence of cholesteryl groups around the polymer main chain, both polymers did not show any birefringence when observed on an optical microscope equipped with a hot stage.[12] This result is in contrast to the recently reported liquid crystallinity of highly syndiotactic poly**1**′[7] and demonstrate the importance of the highly stereo-regulated main chain structure for the physical properties of poly(substituted methylene)s to appear.

In conclusion, we have demonstrated that the (NHC)Pd/borate initiating systems are effective for polymerization of alkyl diazoacetates bearing various ester groups, affording poly(alkoxycarbonylmethylene)s with a variety of side chain ester groups. Substituents on NHC nitrogens are revealed to affect the initiating ability, particularly for monomers with a relatively bulky ester group. Attempts to further extend the monomer variation and to achieve controlled and/or stereoselective polymerization with a proper choice of transition-metal-based initiating systems is now underway in our laboratory.

EXPERIMENTAL SECTION

Materials. THF was dried over Na/K alloy and distilled before use. $[\mathrm{IMesPd(NQ)}]_2$ (Aldrich), $[\mathrm{IPrPd(NQ)}]_2$ (Aldrich), and $\mathrm{NaBPh_4}$ (Kanto Chemical, >99.5%) were used as received. EDA (4.63 M solution in $\mathrm{CH_2Cl_2}$)[13] and $\mathrm{NaBAr^F{}_4}$[14] were prepared according to the literature. BnDA **2**, *n*-HDA **3**, *c*-HDA **4**, and ChDA **5** were prepared according to the general procedure reported by Fukuyama and co-workers, and characterization data for **2** and **5** were described in the literature.[9] AdDA **6** was prepared according to the literature.[10] The characterization data for **3**,[15] **4**,[15] and **6**[16] were reported in the literatures. ***Caution!*** Extra care must be taken for preparation and handling of the diazoacetates because of their potential explosiveness.

Measurements. ^{1}H (400 MHz) and ^{13}C NMR (100 MHz) spectra were recorded on a Bruker Avance 400 spectrometer using tetramethysilane as an internal standard in chloroform-*d* ($\mathrm{CDCl_3}$) at 50 °C.

Molecular weights (M_n) and molecular weight distributions (M_w/M_n) were measured by means of gel permeation chromatography (GPC) on a Jasco-ChromNAV system equipped with a differential refractometer detector using tetrahydrofuran as eluent at a flow rate of 1.0 mL/min at 40 °C, calibrated with poly(MMA)s. The column used for the GPC analyses was a combination of Styragel HR4 (Waters; 300 mm × 7.8 mm i.d., 5 μm average particle size, exclusion molecular weight of 600K for polystyrene) and Styragel HR2 (Waters; 300 mm × 7.8 mm i.d., 5 μm average particle size, exclusion molecular weight of 20K for polystyrene), and poly(MMA) standards (Shodex M-75, M_n = 200 000, M_w/M_n = 1.05, M_n = 47 300, M_w/M_n = 1.02, M_n = 21 700, M_w/M_n = 1.02, M_n = 5220, M_w/M_n = 1.06, M_n = 2190, M_w/M_n = 1.08) and dibutyl sebacate (MW = 314.5) were used for the calibration.

Purification by preparative recycling GPC was performed on a JAI LC-918R equipped with a combination of columns of a JAIGEL-3H (600 mm × 20 mm i.d., exclusion molecular weight of 70K for polystyrene) and a JAIGEL-2H (600 mm × 20 mm i.d., exclusion molecular weight of 20K for polystyrene) using $\mathrm{CHCl_3}$ as eluent at a flow rate of 3.8 mL/min at 25 °C. The sample solution (3 mL containing ca. 0.3 g of the crude product) was injected and recycled before fractionation.

DSC measurements were performed on a Seiko DSC 6200 under a nitrogen atmosphere at a 10 °C/min heating rate. Elemental analyses were performed on a YANAKO MT-5 analyzer at the Integrated Center for Science (INCS) in Ehime University.

Polymerization. As a representative procedure for the polymerization of alkyl diazoacetate with (NHC)Pd/borate systems, the procedure for run 4 in Table 1 is described as follows.

Under a nitrogen atmosphere, $[\mathrm{IMesPd(NQ)}]_2$ (4.29 mg, 3.28×10^{-3} mmol) and $\mathrm{NaBAr^F{}_4}$ (6.98 mg, 7.87×10^{-3} mmol) were placed in a Schlenk tube, and 0.5 mL of THF was added to the mixture to give a reddish-orange suspension at room temperature. A THF solution (2 mL) of *n*-HDA **3** (100 mg, 0.657 mmol) was added to the suspension, and the mixture was stirred at room temperature for 14 h. After the volatiles were removed under reduced pressure, 20 mL of 1 N HCl/MeOH, 20 mL of 1 N HCl aqueous solution, and 20 mL of $\mathrm{CHCl_3}$ were added to the residue. The $\mathrm{CHCl_3}$ phase was separated using a separatory funnel, and the aqueous phase was extracted with 30 mL of $\mathrm{CHCl_3}$. The combined $\mathrm{CHCl_3}$ phase was washed with 50 mL of 1 N HCl aqueous solution and 50 mL of water, dried over $\mathrm{Na_2SO_4}$, filtered, and concentrated under reduced pressure to afford a crude product. Purification with preparative recycling GPC gave poly**3′** (62.7 mg, 75.1%) as a colorless solid. For copolymerization, THF/$\mathrm{CH_2Cl_2}$ (**1** + **5**) or THF (**3** + **2**) solution of a mixture of the two monomers were used in place of the THF solution of **3** in the above procedure. Poly**3′**: ^{1}H NMR (400 MHz, $\mathrm{CDCl_3}$, δ): 3.8–4.2 (2nH, $-\mathrm{OCHH_2}-$), 2.8–3.6 (1nH, main chain CH), 1.5–1.8 (2nH, $-\mathrm{OCHH_2}C\mathrm{H_2}-$), 1.2–1.5 (6nH, $-[C\mathrm{H_2}]_3\mathrm{CH_3}$), 0.8–1.0 (3nH, $-\mathrm{CH_3}$). ^{13}C NMR (100 MHz, $\mathrm{CDCl_3}$, δ): 169–172 (C═O), 64–67 ($\mathrm{OCH_2}$), 44–49 (CH), 32 ($\mathrm{CH_2}$), 28 ($\mathrm{CH_2}$), 26 ($\mathrm{CH_2}$), 23 ($\mathrm{CH_2}$), 14 ($\mathrm{CH_3}$). Anal. Calcd for $\mathrm{C_8H_{14}O_2 \cdot 0.2H_2O}$ (without considering polymer chain ends): C, 65.90; H, 9.95. Found: C, 65.98; H, 9.76. Poly**4′**: ^{1}H NMR (400 MHz, $\mathrm{CDCl_3}$, δ): 4.6–5.0 (1nH, $-$OCHH), 2.6–3.8 (1nH, main chain CH), 1.0–2.4 (10nH, $-[\mathrm{CH_2}]_5-$). Anal. Calcd for $\mathrm{C_8H_{12}O_2 \cdot 0.4H_2O}$ (without considering polymer chain ends): C, 65.19; H, 8.75. Found: C, 64.07; H, 7.86. Poly**6′**: ^{1}H NMR (400 MHz, $\mathrm{CDCl_3}$, δ): 1.9–2.6 (9nH, $\mathrm{CH_2}$ and CH in adamantyl), 1.5–1.9 (6nH, $-\mathrm{CH_2}-$). Resonance for main chain CH was not observed. Anal. Calcd for $\mathrm{C_{12}H_{16}O_2 \cdot 1.1H_2O}$ (without considering polymer chain ends): C, 67.96; H, 8.65. Found: C, 67.65; H, 8.27. Poly**2′**: ^{1}H NMR (400 MHz, $\mathrm{CDCl_3}$, δ): 6.6–7.4 (5nH, Ph–*H*), 4.2–5.2 (2nH, $-\mathrm{OCHH_2}-$), 3.1–4.0 (1nH, main chain CH). ^{13}C NMR (100 MHz, $\mathrm{CDCl_3}$, δ): 169–172 (C═O), 135–137 (Ph), 127–130 (Ph), 66–68 ($\mathrm{CH_2}$), 44–49 (CH). Anal. Calcd for $\mathrm{C_9H_8O_2 \cdot 0.2H_2O}$ (without considering polymer chain ends): C, 71.23; H, 5.57. Found: C, 71.68; H, 6.27. Poly**5′**: ^{1}H NMR (400 MHz, $\mathrm{CDCl_3}$, δ): 5.1–5.5 (1nH, H–C═C in cholesteryl), 4.2–4.9 (1nH, $-$OCHH), 2.8–3.9 (1nH, main chain CH), 0.5–2.8 (other Hs in cholesteryl). Anal. Calcd for $\mathrm{C_{29}H_{46}O_2 \cdot 0.8H_2O}$ (without considering polymer chain ends): C, 78.97; H, 10.88. Found: C, 78.49; H, 10.45. Copolymer of *n*-HDA **3** and BnDA **2**: ^{1}H NMR (400 MHz, $\mathrm{CDCl_3}$, δ): 6.9–7.5 (Ph–*H*), 4.4–5.4 ($-\mathrm{O}C\mathrm{H_2}$Ph), 2.8–4.2 ($-\mathrm{OCH_2}-$ from *n*-HDA and main chain CH), 0.9–1.8 ($-[C\mathrm{H_2}]_4\mathrm{CH_3}$), 0.7–0.9 ($-\mathrm{CH_3}$). The composition of the copolymer was calculated based on the signal intensities of the resonances at 4.4–5.4 ($-\mathrm{O}C\mathrm{H_2}$Ph) and 2.8–4.2 ppm ($-\mathrm{OCH_2}-$ from *n*-HDA and main chain CH). Copolymer of EDA **1** and ChDA **5**: ^{1}H NMR (400 MHz, $\mathrm{CDCl_3}$, δ): 5.2–5.5 (H–C═C in cholesteryl), 3.8–4.8 ($-$OCH in cholesteryl and $-\mathrm{OCH_2}$ from EDA), 2.7–3.8 (main chain CH), 0.5–2.7 (other Hs in cholesteryl and from EDA). The composition of the copolymer was calculated based on the signal intensities of the resonances at 5.2–5.5 (H–C═C in cholesteryl) and 3.8–4.8 ppm ($-$OCH in cholesteryl and $-\mathrm{OCH_2}$ from EDA).

ASSOCIATED CONTENT

Supporting Information. ^{1}H NMR spectra for poly**4′**, poly**6′**, poly**5′**, and a copolymer from EDA and **5**. This material is available free of charge via the Internet at http://pubs.acs.org.

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REFERENCES

(1) Jellema, E.; Jongerius, A. L.; Reek, J. N. H.; de Bruin, B. *Chem. Soc. Rev.* **2010**, *39*, 1706–1723 and references cited therein.

(2) Ihara, E. *Adv. Polym. Sci.* **2010**, *231*, 191–231 and references cited therein.

(3) Luo, J.; Shea, K. J. *Acc. Chem. Res.* **2010**, *43*, 1420–1433 and references cited therein.

(4) 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.

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

(6) Jellema, E.; Jongerius, A. L.; Walters, A. J. C.; Smits, J. M. M.; Reek, J. N. H.; de Bruin, B. *Organometallics* **2010**, *29*, 2823–2826.

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

(8) Ihara, E.; Ishiguro, Y.; Yoshida, N.; Hiraren, T.; Itoh, T.; Inoue, K. *Macromolecules* **2009**, *42*, 8608–8610.

(9) Toma, T.; Shimokawa, J.; Fukuyama, T. *Org. Lett.* **2007**, *9*, 3195–3197.

(10) House, H. O.; Blankley, C. J. *J. Org. Chem.* **1968**, *33*, 53–60.

(11) Franssen, N. M. G.; Reek, J. N. H.; de Bruin, B. *Polym. Chem.* **2011**, *2*, 422–431.

(12) Liquid crystallinity has been observed for analogous cholesteryl-containing vinyl polymers. For examples: (a) Friedzon, Y. S.; Boiko, N. I.; Shibaev, V. P.; Platé, N. A. *Eur. Polym. J.* **1986**, *22*, 13–16. (b) Tsai, M. L.; Chen, S. H. *Macromolecules* **1990**, *23*, 1908–1911. (c) Hamley, I. W.; Castelletto, V.; Parras, P.; Lu, Z. B.; Imrie, C. T.; Itoh, T. *Soft Matter* **2005**, *1*, 355–363.

(13) Searle, N. E. In *Organic Synthesis Collection*; Rabjohn, N., Ed.; John Wiley and Sons: New York, 1963; Vol. 4, pp 424—426.

(14) Yakelis, N. A.; Bergman, R. G. *Organometallics* **2005**, *24*, 3579–3581.

(15) Hodgson, D.; Angrish, D. *Chem.—Eur. J.* **2007**, *13*, 3470–3479.

(16) Fukushima, K.; Lu, Y.-Q.; Ibata, T. *Bull. Chem. Soc. Jpn.* **1996**, *69*, 3289–3295.